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GAS CHROMATOGRAPHY

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Edited by

M. VAN SWAAY

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FOREWORD

IN KEEPING with the tradition established by previous Symposia the Fourth International Gas Chromatography Symposium was held on the Continent. The Fachgruppe Analytische Chemie of the Gesellschaft Deutscher Chemiker co-operated with the Gas Chromatography Discussion Group of the Hydrocarbon Research Group under the auspices of the Institute of Petroleum for the organization of this Symposium, which was held in Germany. Under the honorary chairmanship of Professor Dr G. Hesse an Organizing Committee was set up, with the following members:

Professor Dr G. Hesse (Honorary Chairman)
Mr C. S. G. Phillips, Dr H. Kienitz } (Chairmen)
Dr W. Fritsche (Secretary)
Dr M. van Swaay (Editor)
Professor Dr Ir A. I. M. Keulemans
Dr R. P. W. Scott

More than 60 authors responded to the invitations published in appropriate journals, and submitted abstracts of papers; a selection committee represented by Mr E. R. Adlard, Dr E. Bayer, Dr G. Bergmann, Dr J. F. K. Huber, Dr R. Kaiser and Dr B. T. Whitham succeeded in reaching unanimous decisions on the selection of the 27 papers presented. These papers were divided into three categories, namely: Theory, Apparatus and Technique, and Applications.

In order to satisfy the demand for free discussion, the Organizing Committee decided to include three Panel Discussions on topics of general interest. In addition, participants were encouraged to indicate any topics they would like to discuss, so that informal meetings could be organized for groups of people with similar interests.

The Symposium was attended by over 700 participants from 21 countries. The regular sessions, as well as the Panel Discussions and the informal discussions, were well attended; some of the informal gatherings drew such a large audience that the Organizing Committee invited persons to act as chairmen.

Participants to the Symposium enjoyed the hospitality of the City of Hamburg; the meetings were held in the Auditorium Maximum of Hamburg State University, which provided unique accommodation for the scientific meetings, as well as for the exhibition of commercial gas chromatographic equipment held in connection with the Symposium.

Participants and their guests were invited to a Banquet on Friday, June 15th, and there was an informal gathering on the evening of Tuesday, June 12th. The Local Committee, consisting of Dir. Dr A. Eckhardt, Professor Dr K. Heyns, Professor Dr E. Jantzen and Dr H. Oertel, had arranged a number of excursions to local industries, as well as a social programme including sight-seeing tours in Hamburg, an opera performance, and boat trips on the Elbe.

Although all authors were informed that their papers would be printed in English, some manuscripts were submitted in German. The co-operation of the Netherlands State Mines, Shell Thornton Research Centre and Dr M. M. Wirth, who assisted with the translations, is gratefully acknowledged.

The use of the facilities of Eindhoven Technical University has been invaluable and was highly appreciated.

The Organizing Committee is much indebted to those German Industries which helped to strengthen the financial basis of the Symposium by their generous gifts.

Finally, the Organizing Committee wish to thank Messrs Butterworths for their co-operation in the production of the preprints and the final proceedings.

C. S. G. PHILLIPS
H. KIENITZ
M. VAN SWAAY

BEGRÜSSUNGSANSPRACHE I

FIRST OPENING ADDRESS

Dr H. KIENITZ

MEINE DAMEN UND HERREN! Ich habe die große Ehre, das 4. Internationale Gaschromatographische Symposium zu eröffnen, das von der Gas Chromatography Discussion Group, einer Sektion des Institute of Petroleum, London, und der Fachgruppe 'Analytische Chemie' in der Gesellschaft Deutscher Chemiker veranstaltet wird. Das Symposium ist zugleich die 41. Veranstaltung der Europäischen Föderation für Chemie-Ingenieurwesen.

Fast 700 Teilnehmer aus über 20 Ländern, von denen viele eine weite Anreise hatten — einige kamen sogar von Übersee —, sind der Einladung der Gesellschaft Deutscher Chemiker gefolgt. Sie alle darf ich auf das herzlichste willkommen heißen und ihnen anregende und schöne Tage hier in Hamburg wünschen.

Ich begrüße die Ehrengäste der Eröffnungssitzung unseres Symposiums, unter denen dem Vertreter des Hohen Senates der Freien und Hansestadt Hamburg, Herrn Senator Dr. Drexelius, sowie dem Rektor der Universität, Se. Magnifizenz Professor Dr. Sieverts, meine besonderen Grüße gelten. Herrn Professor Dr. Sieverts darf ich an dieser Stelle im Namen der Teilnehmer besonders herzlich danken, daß wir in dem schönen und modernen Auditorium Maximum tagen dürfen.

Eine besondere Freude ist es für mich, auch die Herren Plenarvortragenden, Herrn Professor Dr. Richard Kuhn aus Heidelberg, Herrn Dr. Martin aus London und Herrn Professor Dr. Kiselev aus Moskau, auf das herzlichste zu begrüßen. Sie werden uns in den anschließenden Vorträgen einen Überblick über die Entwicklung und die Grundlagen der chromatographischen Trennmethoden unter besonderer Berücksichtigung der Gaschromatographie geben. Wir danken ihnen, daß sie sich bereit erklärt haben, die Plenarvorträge des Symposiums zu übernehmen.

Schließlich darf ich noch ein herzliches Begrüßungswort an alle Damen richten, die mit nach Hamburg gekommen sind. Wir glauben, Sie werden sich sicherlich in der schönen und lebhaften Stadt wohlfühlen und angenehme Tage hier verleben. Für Sie haben wir ein Programm mit Besichtigungen von Hamburg, Ausflügen in die Umgebung und einer Fahrt nach Helgoland zusammengestellt, das manchen Ihrer Ehegatten vielleicht dazu verleiten könnte, ausnahmsweise den einen oder anderen Vortrag oder die eine oder andere Diskussion zu versäumen.

Meine Damen und Herren! Nun möchte ich allen denen meinen persönlichen Dank aussprechen, die zum Gelingen des Symposiums beigetragen haben. Der Ortsausschuß mit den Herren Professor Heyns, Professor Jantzen, Direktor Eckardt und Dr. Oertel war zusammen mit Herrn Dr. Fritsche von der Gesellschaft Deutscher Chemiker bemüht, daß unsere Tagung einen guten Verlauf nimmt und daß Sie sich während dieser Zeit in Hamburg wohlfühlen.

Der Wissenschaftliche Ausschuß hatte die schwere Aufgabe, das Vortragsprogramm zusammenzustellen. Von den mehr als 60 Anmeldungen zu Vorträgen, die bis November vergangenen Jahres eingegangen waren, konnte der zeitlichen Beschränkung wegen nur etwa die Hälfte angenommen werden. Ich denke, der Wissenschaftliche Ausschuß hat alle die Vorträge sorgfältig ausgewählt, die die bedeutendsten Fortschritte der Grundlagen, der Methodik und der experimentellen Technik auf dem Gebiet der Gaschromatographie aufweisen. Die Mitglieder des Wissenschaftlichen Ausschusses mögen dafür herzlichen Dank entgegennehmen; besonders aber muß ich unter ihnen Herrn Dr. van Swaay hervorheben, der für die Veröffentlichung der Preprints sorgte. Ohne seine mühevolle Arbeit wäre der erfolgreiche Ablauf unseres Symposiums weit weniger sichergestellt.

Meinen ganz besonderen Dank möchte ich schließlich der Gas Chromatography Discussion Group abstatten, die der Einladung der Fachgruppe 'Analytische Chemie' in der Gesellschaft Deutscher Chemiker entsprochen hat, das 4. Gaschromatographische Symposium in Deutschland abzuhalten. Wir sind darüber sehr erfreut und hoffen, daß wir das Vertrauen, das uns von unseren englischen Kollegen gegeben wurde, nicht enttäuschen werden.

Herzlichen Dank möchte ich auch an dieser Stelle Herrn Professor Keulemans sagen, der den Vorschlag der deutschen Analytiker wärmstens bei unseren englischen Kollegen unterstützte, der aber leider wegen einer plötzlichen Erkrankung nicht unter uns weilen kann.

Die Stadt Hamburg haben wir als Tagungsort gewählt, weil wir damit nicht nur einer Tradition der Symposien treu geblieben sind, eine Hafenstadt als Tagungsort zu wählen; vielmehr glauben wir, daß der weltoffene und internationale Charakter einer Stadt wie Hamburg mit seinem Hafen und seiner lebhaften und bedeutenden Industrie am ehesten dem Geist internationaler Symposien entsprechen dürfte. Hier in den Räumen der Universität werden unsere Gedanken mehr auf die wissenschaftlichen Grundlagen; durch die Industrie Hamburgs, die rege Anteilnahme an unserem Symposium zeigte, mehr auf die Anwendungen der Gaschromatographie, dieses neuesten, äußerst lebendigen und immer bedeutungsvolleren Zweiges der analytischen Arbeitsmethoden, gelenkt.

Gerade hier in Hamburg konnten wir aber auch erschreckend eindrucksvoll erleben, wie machtlos und klein alle wissenschaftlichen Erkenntnisse und Fortschritte vor Gewalten sein können, wie sie im Februar dieses Jahres über die Nordseeküste hereingebrochen sind. Den Flutwellen der See konnten die Deiche an vielen Stellen nicht mehr Widerstand leisten, und bis Hamburg kamen sie überraschend und mit elementarer Gewalt landeinwärts. Sie forderten viele Menschenleben als Opfer, und vielen nahmen sie ihr Heim und ihre Habe.

Ich werte es als ein besonderes Zeichen der Freundschaft und des Mitgefühls unserer englischen Kollegen, als die Gesellschaft Deutscher Chemiker bald nach der Katastrophe die Nachricht erhielt, die Gas Chromatography Discussion Group wolle durch eine Geldspende die Not mit abwenden helfen. Wir schlossen uns dem Gedanken der englischen Freunde an und haben dem Roten Kreuz eine gemeinsame Spende übergeben.

Ich kann die Eröffnungsansprache des 4. Gaschromatographischen Symposiums nicht abschließen, ohne des 10. Jahrestages der Gaschromato-

graphie zu gedenken. Vor zehn Jahren haben Dr. Martin und Dr. James, die beide hier in Hamburg unter uns weilen, auf dem Internationalen Kongreß für Analytische Chemie in Oxford die 'Gas-Liquid Partition Chromatography' das erste Mal als bedeutsame und entwicklungsfähige analytische Methode für flüchtige Substanzen vorgestellt. Im 'Analyst' wurden ihre Arbeiten veröffentlicht; und auf die fast gleichzeitig erschienenen Arbeiten im 'Biochemical Journal', in denen über die Trennung von Fettsäuren und Aminen berichtet wurde, folgte in den zehn Jahren seit diesen ersten Veröffentlichungen die ungeheure Zahl von mehr als 5 000 Arbeiten, die sich sowohl mit den Grundlagen der Gaschromatographie befassen, als auch auf breitester Ebene analytische Möglichkeiten für die reine und angewandte Forschung, wie auch für die Industrie aufzeigen. Wohl selten hat eine analytische Methode solch große und allgemeine Bedeutung in so kurzer Zeit erlangt wie gerade die Gaschromatographie. Unser Symposium soll Ihnen in Vorträgen und Diskussionen die neuesten Entwicklungen gaschromatographischer Geräte aufzeigen und die neuesten Erkenntnisse und Fortschritte vermitteln.

Wir danken den ausstellenden Firmen für das Interesse an unserem Symposium, wie auch ganz besonders einer Anzahl deutscher Firmen für ihre finanzielle Hilfe.

Mögen die Tage hier in Hamburg für Sie fachlich anregend und ergiebig sein, und möge unser gesellschaftliches Programm Ihnen Freude bereiten. In der heutigen, politisch oft sehr bewegten Zeit ist der Erfolg des Symposiums über die wissenschaftlichen Belange hinaus besonders dann gegeben, wenn nicht nur fachliche Diskussionen, sondern auch persönliche Freundschaften uns über die Grenzen der Nationen zusammenführen.

BEGRÜSSUNGSANSPRACHE II

SECOND OPENING ADDRESS

Senator Dr W. DREXELIUS

MAGNIFIZENZ! MEINE DAMEN UND HERREN! Ich bin Ihnen dankbar, daß Ihre Tradition diese Symposien in Hafenstädte legt und daß die Freie und Hansestadt Hamburg die Ehre hat, Ihre Tagung — man sagt — in ihren Mauern zu beherbergen, obgleich wir seit über 100 Jahren keine Stadtmauern mehr haben.

Sie tagen in einer Hafenstadt, die als solche auch eine Stadt der Kaufleute ist — was Sie alle wahrscheinlich wissen —, die aber auch — und das werden viele von Ihnen vielleicht nicht wissen — die größte Industriestadt der Bundesrepublik Deutschland ist und schon deswegen an Ihren Forschungen ein unmittelbares, auch wirtschaftliches Interesse hat.

Sie tagen in einer Stadt und einer Universität, die beide verschiedenen Alters sind: eine alte Stadt und eine sehr junge Universität. Diese Universität ist nur wenig älter als 40 Jahre, unter den deutschen Universitäten also ein sehr junges Mitglied. Trotzdem ist sie inzwischen die drittgrößte deutsche Universität und steht im Begriffe, in dieser großen Stadt eine Rolle zu spielen.

Trotzdem ist das Hauptmerkmal der Stadt, in der Sie tagen, nicht, daß sie eine Universitätsstadt ist, sondern ihr Hauptmerkmal ist, daß sie eine große, beinahe eine 2-Millionen-Stadt ist, die von ihrem Hafen, von ihrem Handel und nicht zuletzt von ihrer Industrie lebt, die sehr bewegt lebt und die in sehr lebhaften Beziehungen zu auswärtigen Ländern steht. In dieser Stadt ist man sich dessen sehr bewußt, daß es andere Länder gibt. Jeder Bürger dieser Stadt weiß, daß sein Leben davon abhängt, daß gute Beziehungen zu anderen — und zu möglichst vielen anderen — Ländern bestehen. Daher werden Sie in dieser Stadt insoweit eine gewisse Weltaufgeschlossenheit finden.

Wenn Sie in diesen Tagen Gelegenheit finden sollten, mit ihr in Berührung zu kommen, werden Sie aber auch den Gegenzug finden und feststellen, daß sie oft eine kleine Stadt ist, eine Stadt mit sehr kleinbürgerlichen und sogar kleinstädtischen Zügen, die sich beinahe nicht damit vertragen, daß ihre Einwohner in einer — wie gesagt — 2-Millionen-Stadt leben. Sie leben in einem der drei Stadtstaaten; Bremen ist der andere und Berlin notgedrungen der dritte. Aber Bremen und Hamburg sind die beiden in deutscher Geschichte überkommenen Stadtstaaten, für manche von Ihnen vielleicht unverständlich, weil Sie aus Ländern kommen, die keine Bundesstaaten sind und die es daher nicht kennen, daß unter der Ebene des Gesamtstaates noch einmal staatliche Aufgaben selbständig wahrgenommen werden, verbunden mit dem eifersüchtig bewahrten Ehrgeiz, sie auch wirklich selbständig wahrzunehmen.

Wie gesagt, in der Bundesrepublik Deutschland ist Hamburg ein Staat, einer der Mitgliedstaaten, der viele seiner Aufgaben — unter anderem die Aufgaben kultureller Art — selbständig als eigene Aufgaben wahrnimmt.

Ich hoffe, Sie sehen auch etwas von diesem staatsrechtlichen Kuriosum, das es sonst nirgends mehr auf der Welt gibt, das aber — wie Sie wissen — in der griechischen und auch in der mittelalterlichen italienischen Geschichte eine große Rolle gespielt hat.

Magnifizenz! Sie und ich sind die beiden einzigen, die nur sehr lose wissen, wovon hier die Rede sein wird. Aber wir beide sind ja wenigstens von derselben Fakultät, so daß wir uns vor Beginn der Tagung leise darüber unterhalten konnten, wie wenig man doch als Außenstehender bei wissenschaftlichen Kongressen von den eigentlichen Problemen noch wissen kann. Es ist das Glück, vielleicht aber auch das Schicksal heutiger Wissenschaft, daß der Rektor der Universität und der für die Wissenschaft zuständige Landesminister — in Hamburg Senator — von dem, was Sie hier tun, nur noch — wie gesagt — andeutungsweise wissen können und nicht mehr verstehen, um welche Probleme Sie sich hier im einzelnen kümmern.

Sie leben, sagte ich, in einer weltaufgeschlossenen, in einer liberalen Stadt. Auch in diesem Sinne sind wir liberal. So wünsche ich Ihrer Tagung einen vollen wissenschaftlichen, menschlichen und vielleicht auch praktischen Erfolg.

BEGRÜSSUNGSANSPRACHE III

THIRD OPENING ADDRESS

Se Magnifizenz Professor Dr R. SIEVERTS

HERR SENATOR! HERR PRÄSIDENT! MEINE DAMEN UND HERREN! Es ist mir eine große Ehre und Freude, Sie im Namen der Universität Hamburg begrüßen zu dürfen. Ich bin sicher, im Namen aller meiner Kollegen zu sprechen, wenn ich Ihnen unsere große Befriedigung ausdrücke, daß Sie Ihren Kongreß nach Hamburg verlegt haben.

Herr Senator Dr Drexelius hat Ihnen eben gesagt, daß wir eine der jüngsten Universitäten in der Bundesrepublik sind, aber — man kann fast sagen, leider — inzwischen zur drittgrößten Universität der Bundesrepublik geworden sind; eine Entwicklung, die übrigens erst nach dem Krieg eingesetzt hat und noch nicht zum Stillstand gekommen ist. Wir haben in diesem Semester die Zahl von 16 000 Studenten erreicht, und Sie können sich vorstellen, was für Probleme das unserer Universität aufgibt, die vor dem Kriege nur etwa 3 000 bis 4 000 Studenten hatte.

Sie tagen hier im Zentrum unserer neuen Universitätsstadt, die Sie rings um dieses Haus entstehen sehen. Es ist ungefähr ein Drittel des auf mehrere Jahre angelegten Bauprogramms. Sie ersehen daraus, daß man bei dem Neubau der Universität Hamburg nicht den Weg des Campus draußen vor der Stadt eingeschlagen hat, sondern daß man hier den Versuch macht, den Neubau der Universität mitten im Zentrum der Stadt durchzuführen und sie damit eng mit der Stadt zu verbinden.

Als die Universität gegründet wurde, war ihre Gründung innerhalb der Stadt außerordentlich umstritten. Besonders die Kreise der Wirtschaft waren sehr skeptisch, ob nach Hamburg, dieser Handels- und Industriestadt, wirklich eine Universität passe. Nun, um diese Frage ist es völlig still geworden, und auch ich kann von seiten der Universität bestätigen, daß wir immer stärker in diese Stadt hineingewachsen sind und gerade mit den Kreisen, die uns anfänglich sehr skeptisch gegenüberstanden, inzwischen einen sehr engen menschlichen und sachlichen Kontakt gefunden haben.

In dem Neubau der Universität spielt auch das sogenannte Chemiezentrum eine große Rolle. Gerade die chemischen Institute hier in Hamburg waren viel zu klein geworden. Es waren Institute, die schon vor der Gründung der Universität als 'Chemische Staats Institute' bestanden, wie überhaupt die Gründung dieser Universität im wesentlichen auf den vorhandenen wissenschaftlichen Staatsinstituten beruhte und dadurch sehr erleichtert wurde.

Ich nehme an, daß der eine oder andere von Ihnen ein Interesse daran hat zu sehen, wie dieses Chemiezentrum geplant ist. Sie finden im Vorraum — im Erdgeschoß — ein Modell dieses neuen Chemiezentrums und auch Pläne ausgestellt, die zeigen, wie es weiter ausgeführt werden soll. Außerdem werden meine Kollegen von den chemischen Disziplinen gern bereit sein, diejenigen, die besonders daran interessiert sind, auch einmal in zehn Minuten

von hier aus zu der Baustelle zu führen, wo Sie dann die neuen Bauten in Wirklichkeit sehen können. Wir hoffen, daß schon im nächsten Jahr das Institut für Organische Chemie und für Biochemie bezogen werden kann und daß die anderen Institute in den anschließenden Jahren dann sehr rasch folgen werden.

Ich wünsche Ihnen für Ihre Tagung auch seitens der Universität einen recht guten Verlauf. Wir hoffen, daß Sie am Ende Hamburg mit guten Erinnerungen verlassen werden.

FIRST OPENING LECTURE

Professor Dr R. KUHN

ZUR ENTWICKLUNG VON TRENNUNGSVERFAHREN

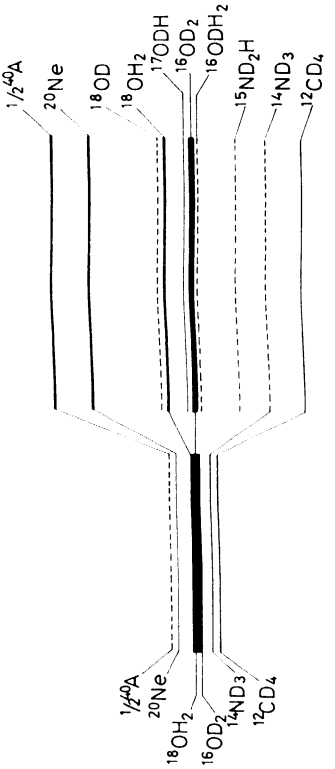
JEDES VERFAHREN zur Trennung von Gemischen chemischer Stoffe durchläuft im Zuge seiner Entwicklung drei verschiedene, meist zeitlich aufeinanderfolgende Stadien. Zunächst kommt es nur darauf an, irgendwie ein solches Gemisch in seine Komponenten zu zerlegen, um die physikalischen und chemischen Eigenschaften der reinen Komponenten kennen zu lernen. In einem zweiten Stadium — dem der analytischen Chemie — kommt es schon darauf an, derartige Trennungen auch möglichst rasch und genau, mit möglichst wenig apparativem und arbeitsmäßigem Aufwand durchzuführen. Im dritten Stadium, das sich mitunter anschließt, tritt dann das Problem auf, derartige Gemische präparativ in größerem Maßstab aufzutrennen — damit kommen wir bis in die Bereiche der Chemie-Ingenieurtechnik. In all diesen Fällen — das Folgende gilt für die Gebiete der Astronomie, Physik, Chemie und Biologie gleichermaßen — ist das Auflösungsvermögen, die Trennschärfe, von erstrangiger Bedeutung. Das ließe sich historisch an zahllosen Beispielen belegen. Es wäre wohl auch ein lohnendes Objekt für diejenigen, die sich in die Geschichte der Naturwissenschaften und der Technik vertiefen wollen. Denken Sie an die Entwicklung des Fernrohrs, die es ermöglicht hat, Sterne als Doppelsterne zu erkennen; an den Fortschritt vom Lichtmikroskop zum Elektronenmikroskop; an die Trennungsverfahren für seltene Erden, für Isotope und vieles andere — immer wieder kommt es entscheidend darauf an, das Auflösungsvermögen, die Trennschärfe, weiter zu steigern.

Von den zahlreichen Beispielen, die man hier anführen könnte, sei eines hervorgehoben, das zur Gaschromatographie insofern in Beziehung steht, als gerade massenspektroskopische Verfahren heute im Zusammenwirken mit der gaschromatographischen Analyse von Kohlenwasserstoffgemischen und anderen wichtig geworden sind.

Figur 1 zeigt die Fortschritte der Massenspektrographie, die am Max-Planck-Institut für Chemie von Herrn Professor J. Mattauch mit seinen Mitarbeitern in den Jahren 1938 bis 1959 erzielt worden sind. Man erkennt u. a. die Masse von Neon, des Radikals ^{18}OD und von $^{18}OH_2$. Im landläufigen Sinne haben alle diese Teilchen die Masse 20; auch $^{14}ND_3$, das Ammoniakmolekül mit drei schweren Wasserstoffatomen. Man sieht, wie im Laufe der Jahre die Trennschärfe immer weiter gesteigert werden konnte.

Wir wollen nun zur Frage übergehen, mit welcher Schärfe sich organische Substanzen trennen lassen. Die Lehrbücher der organischen Chemie beginnen mit den Paraffinen. Bei solchen Kohlenwasserstoffen mit 7, 8, 9, 10 und 11 C-Atomen beträgt die Zahl von Isomeriemöglichkeiten 9, 18, 35, 75 und 159. Aber wie weit geht die Trennschärfe der heute bekannten Methoden? Könnten wir zum Beispiel noch ein Gemisch aller 159 Undecane mit 11 C-Atomen in die einzelnen Komponenten auftrennen? Bei 20 C-Atomen beträgt die Zahl der Isomeren bereits 366 319!

Wer diese Zahlen betrachtet, könnte leicht extrapolierend sagen, daß es hoffnungslos sein wird, Gemische von Kohlenwasserstoffen, die 40 C-Atome enthalten, in einzelne Komponenten zerlegen zu wollen. Und doch ist gerade an Gemischen von Kohlenwasserstoffen mit 40 C-Atomen erstmals chromatographisch-präparativ eine Trennung durchgeführt worden, die Trennung von α-, β- und γ-Carotin. Wieso war das möglich? Es beruht



Figur 1. Massenspektren im Bereich $M/e \approx 20$
Oben: R. Bieri, F. Everling u. J. Mattauch (1954)
Unten: J. Mattauch u. A. Bönisch (1938)

darauf, daß die Carotine mit 40 C-Atomen nicht Paraffine sondern ungesättigte Kohlenwasserstoffe sind und daß durch den Eintritt von Doppelbindungen — besonders von konjugierten Doppelbindungen — nicht nur die Farbigkeit der Moleküle bedingt wird, sondern überdies die Adsorptionseigenschaften und die Verteilungskoeffizienten in entscheidender Weise bestimmt werden.

Tabelle 1 zeigt die Ergebnisse der Trennung von α-, β- und γ-Carotin, wie sie vor 30 Jahren an unserem Institut durchgeführt wurde.

Die Bedeutung von Doppelbindungen — besonders konjugierter Doppelbindungen — kann nicht genügend betont werden. Das Wort Chromatographie bedeutete ursprünglich, daß es sich um die Trennung farbiger

Tabelle 1. Die isomeren Carotine $C_{40}H_{56}$
(R. Kuhn, E. Lederer u. H. Brockmann)

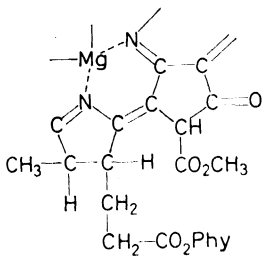
	Schmp.	λ_{max} *in* CS_2	$[\alpha]_{643}$
α-Carotin	187–188°	509 477	+385°
β-Carotin	181–182°	520 485	0°
γ-Carotin	177–178°	534 496	0°

Adsorbierbarkeit: $\alpha < \beta < \gamma$

Substanzen handelte. Heute hat es diese sprachliche und ursprüngliche Bedeutung schon längst verloren. Wenn dieses Symposium ein solches für Gaschromatographie ist, so darf man vielleicht am Rande bemerken, daß kaum von der Trennung wirklich farbiger Substanzen die Rede sein wird.

Es gibt Erscheinungen, die schon bei der ersten Trennung von α-, β- und γ-Carotin an Aluminiumoxydsäulen auffielen. Z. B. die Reihenfolge der Adsorbierbarkeit. α-Carotin, dessen Absorptionsbande die kürzestwellige ist, wird schwächer adsorbiert als β-Carotin, und β-Carotin schwächer als γ-Carotin, das die längstwellige Absorptionsbande unter den drei Isomeren besitzt.

Daß die von M. Tswett erstmals beschriebenen chromatographischen Methoden erst spät in die Praxis der organischen Chemie eingedrungen sind, hängt mit einem — wenn ich so sagen darf — Mißgeschick zusammen, das

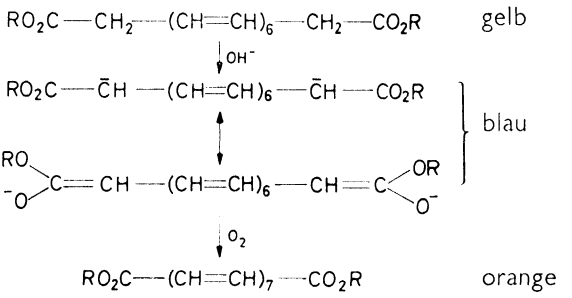


bei der Trennung von Chlorophyll a und Chlorophyll b im Spiel war. Die Entwicklung der chromatographischen Methoden ist schon oft historisch dargestellt worden, aber in diesem Punkte möchte ich einiges hinzufügen, was mir R. Willstätter überliefert hat.

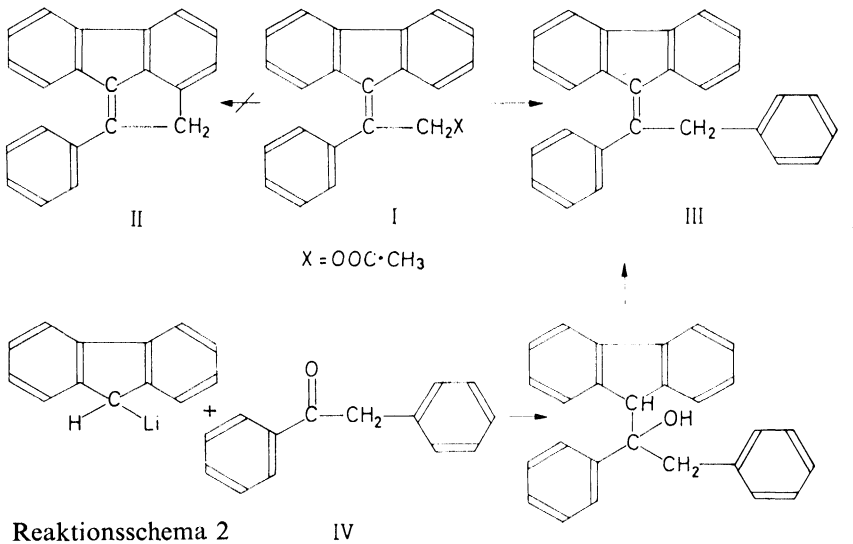
Tswett hatte die Trennung der beiden grünen Blattpigmente, Chlorophyll a und Chlorophyll b, erzieltdurch Adsorption an Säulen, die mit Aluminiumoxyd, Calciumoxyd, Magnesiumoxyd, Kieselsäure u. a. beschickt waren. R. Willstätter und A. Stoll haben diese Versuche wiederholt, sind aber zu dem Ergebnis gekommen, daß es die Chromatographie nicht erlaubt, intaktes Chlorophyll a und Chlorophyll b zu gewinnen, und zwar aus folgendem Grund: Lösungen von nativem Chlorophyll, die grün gefärbt sind, geben auf Zusatz von etwas Alkali eine tief braune Färbung, die bei einigem Stehenlassen wieder in Grün übergeht. Die Bildung der 'braunen Phase' ist ein Zeichen des intakten Chlorophylls. Wenn man nach Tswett Chlorophyll a und b trennte, so trat die 'braune Phase' nicht mehr auf; das Chlorophyll war — wie man sagte — allomerisiert.

Tswett hatte etwa zehn verschiedene Adsorbentien zur Trennung von Chlorophyll a und b beschrieben, doch hatte man nur sechs oder sieben davon bei der Nacharbeitung geprüft. In jedem dieser Fälle gab das Chlorophyll die braune Phase nicht mehr. Unter den Adsorbentien von Tswett befand

Reaktionsschema 1



sich aber überdies auch Rohrzucker. An diesem findet keine 'Allomerisierung' statt, was erst 1932 von A. Winterstein in unserem Institut festgestellt wurde. An Rohrzucker kann man — das ist heute ein Gattermann-Beispiel im Praktikum — Chlorophyll a und b einwandfrei trennen. Die Allomerisierung ist in Wirklichkeit eine Dehydrierung (J. B. Conant), eine Autoxydation, an welcher der isozyklische Ring des Chlorophylls beteiligt ist. Man



Reaktionsschema 2 IV

hätte das schon vor 50 Jahren entdecken können, wenn man die Chromatographie unter extrem sauerstoff-freien Bedingungen durchgeführt hätte.

Das Reaktionsschema 1 zeigt ein einfacheres Modell für derartige Dehydrierungen: ein Dihydro-polyen von gelber Farbe, das mit Hydroxylionen — entsprechend der Bildung der braunen Phase des Chlorophylls — ein blaues Anion liefert, dessen zwei Ladungen am Kohlenstoff oder Sauerstoff geschrieben werden können. Wenn Sauerstoff hinzukommt, schlägt die Farbe von

Blau nach Orange um (Dehydrierung; Bildung des durchkonjugierten Systems). Auch derartige Veränderungen erfolgen an Adsorbentien überaus leicht. Bedenken, wie sie Willstätter wegen der Möglichkeit von Veränderungen organischer Substanzen beim Adsorptionsprozeß hatte, sind nicht generell beseitigt. Durch Adsorption kann die Reaktivität in unerwarteter Weise gesteigert werden. In unserem Institut hat vor kurzem U. Breyer ein eindrucksvolles weiteres Beispiel hierfür gefunden (Reaktionsschema 2).

Die Absicht war, an Verbindungen vom Typ I durch Abspaltung von HX einen Ringschluß zu II zu erzielen. Dies hat sich nicht durchführen lassen. Wurde I mit Eisessig-Schwefelsäure gekocht — um den Ringschluß zu erzwingen — und anschließend an Aluminiumoxyd in Benzollösung chromatographiert, dann reagierte das Allyl-System von I mit dem Benzol schon bei gewöhnlicher Temperatur nach Art einer Friedel-Crafts-Reaktion. Es handelt sich um eine Allylierung von Benzol an einer Aluminiumoxydsäule. Daß III die angegebene Konstitution besitzt, ist durch eine unabhängige Synthese aus Desoxybenzoin (IV) bewiesen worden.

Unter den energischen Bedingungen des Kochens mit Eisessig-Schwefelsäure bleibt also I unverändert. Wenn man es aber über gewisse Sorten von Aluminiumoxyd schickt, so erfolgt schon bei Raumtemperatur Kernkondensation mit Benzol und Anisol. Wir treffen bei chromatographischen Prozessen auf oft unerwartete Veränderungen der Moleküle.

Die Gaschromatographie ist an die Voraussetzung gebunden, daß sich die zu untersuchenden Substanzen unzersetzt verflüchtigen lassen. Für denjenigen, der auf dem Gebiet hochmolekularer Naturstoffe arbeitet, ist diese Voraussetzung nicht gegeben. Doch sollen einige Beispiele zeigen, wie weit gaschromatographische Methoden im Laufe der letzten Zeit auch bei der Konstitutionsaufklärung komplizierter Naturstoffe Anwendung in unserem Institut gefunden haben.

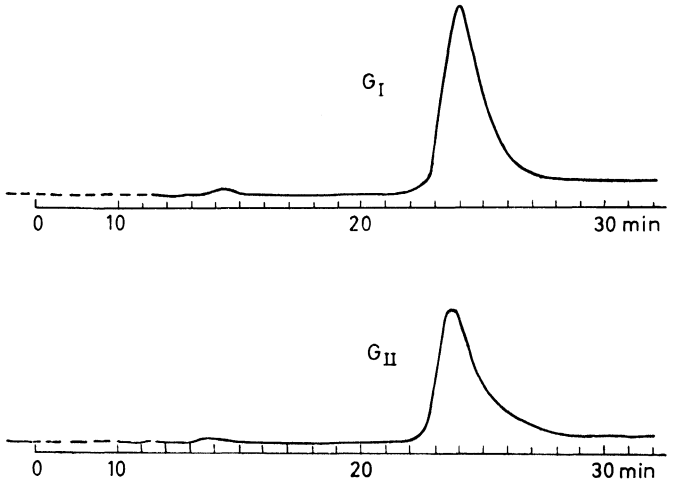
Es handelt sich um Versuche von H. Egge an Substanzen aus menschlichem Gehirn und Rinderhirn, deren Molekulargewichte zwischen 1 500 und 2 500 liegen, insbesondere um die Gruppe der Ganglioside, deren einzelne Vertreter die Bezeichnungen G_I, G_{II}, G_{III} und G_{IV} erhalten haben.

Tabelle 2. Analyse der Bausteine (in Molen pro Mol Gangliosid)

	G_I	G_{II}	G_{III}	G_{IV}
Fettsäure (Stearinsäure)	1	1	1	1
Sphingosin	1	1	1	1
Glucose	1	1	1	1
Galaktose	2	2	2	2
N-Acetyl-galaktosamin	1	1	1	1
Lactaminsäure (NANA)	1	2	2	3

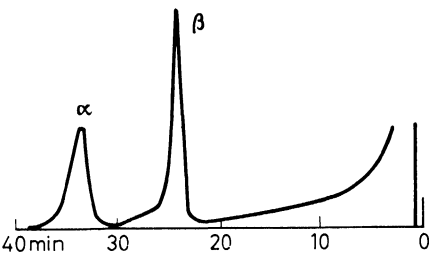
Jede dieser Substanzen (*Tabelle 2*) enthält 1 Mol Fettsäure, 1 Mol Sphingosin (eine N-haltige Base), 1 Mol Glucose, 2 Mol Galaktose, 1 Mol N-Acetylgalaktosamin und 1–3 Mol einer Ketosäure mit 9 C-Atomen (Sialinsäure). Die Lösung des Problems, die Verknüpfungsweise dieser Bausteine zu ermitteln, ist unter anderem auch auf gaschromatographischem Wege in Kombination mit anderen Methoden versucht worden. Ich will hier nur einige der gaschromatographischen Ergebnisse vorführen.

Fettsäuren, bzw. deren Methylester, lassen sich bekanntlich leicht und genau auf Homogenität im Gaschromatographen untersuchen. Es hat sich herausgestellt, daß in den kristallin erhaltenen Gangliosiden vor allem Stearinsäure gebunden vorliegt (*Figur 2*).



Figur 2. Gaschromatogramme der Fettsäure-methylester aus den Gangliosiden G_I und G_{II}
Kolonne: 3 m Silicon-Hochvakuumfett/Na-capronat, betrieben bei 230°C mit Wasserstoff als Trägergas.

Zucker kann man nicht als solche gaschromatographieren. Es ist üblich, zunächst zu permethylieren und dann mit methanolischem Chlorwasserstoff zu spalten, so daß flüchtige und unzersetzt destillierbare Methylglykoside mehrfach methylierter Hexosen, Hexosamine usw. auftreten.

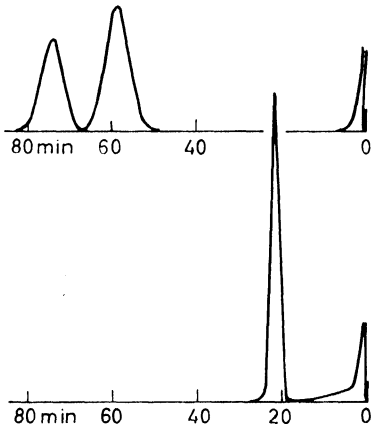


Figur 3. Gaschromatogramm von α- und β-Pentamethylglucose
Kolonne: 2 m × 4.6 mm, 20% Butandiol-bernsteinsäure-polyester auf Celite;
Temperatur: 200°C;
Trägergas: 100 Nml He/min. (2 atü).

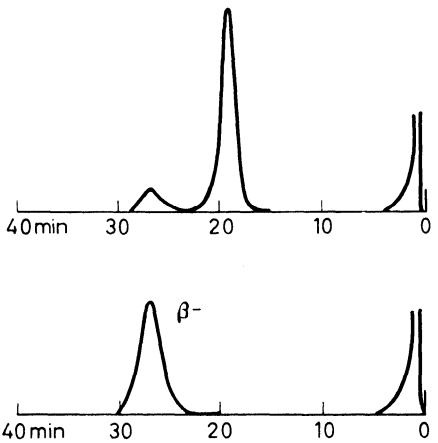
Figur 3 zeigt eine gaschromatographische Trennung von α- und β-Pentamethylglucose bei 200° an Butandiolbernsteinsäurepolyester und Celite. Bei reduzierenden Zuckern entstehen immer α- und β-Verbindungen nebeneinander. In der Figur ist die α-Verbindung langsamer als die β-Verbindung.

Das ist aber keine allgemeine Regel, sondern bei einzelnen Zuckern und Aminozuckern verschieden.

Gute Trennungsmöglichkeiten bestehen auch noch für Disaccharide (*Figur 4*). Saccharose gibt als Octamethylverbindung nur einen einzigen Peak; die



Figur 4. Gaschromatogramme von Octamethyllactose (oben) und Octamethylsaccharose (unten)
Kolonne: 1 m × 4.6 mm, 10% Butandiol-bernsteinsäure-polyester auf Kieselgurr;
Temperatur: 226°C;
Trägergas: 80 Nml He/min. (2 atü).

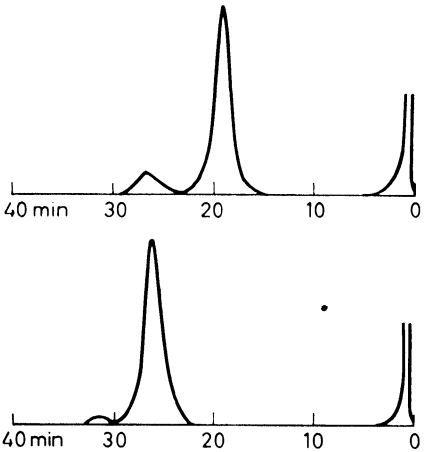


Figur 5. Gaschromatogramme von α- und β-Tetramethyl-N-acetyl-glucosamin
Kolonne und Bedingungen: siehe Figur 4

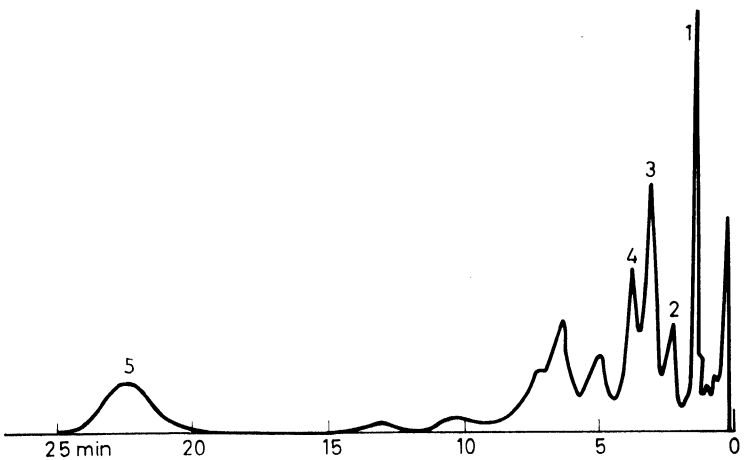
reduzierende Lactose aber einen Doppel-Peak (α- und β-Form der Octamethylverbindung).

Bei den Trisacchariden kommt man an die Grenze der Möglichkeiten, Permethylverbindungen noch unzersetzt zu verflüchtigen.

Für Aminozucker fand H. Egge, daß sich α- und β-Formen (Beispiel: α- und β-Tetramethyl-N-acetyl-glucosamin, *Figur 5*; mit einem üblichen Perkin-Elmer- oder Rubarth-Gerät schön trennen lassen; hierbei handelt es



Figur 6. Gaschromatogramme von α-Tetramethyl-N-acetyl-glucosamin (oben) und α-Tetramethyl-N-acetyl-galaktosamin (unten)
Kolonne und Bedingungen: siehe Abb. 4



Figur 7. Gaschromatogramme von Pentamethylgalaktose (1), 2,3,6-Trimethyl-β-methylglucosid (2), Stearinsäure-methylester (3), 2,3,6-Trimethyl-α-methyl-glucosid (4) und α-1,4,6,-Trimethyl-N-acetyl-galaktosamin (5)
Kolonne: siehe Abb. 4;
Trägergas: 80 Nml He/min. (2 atü).

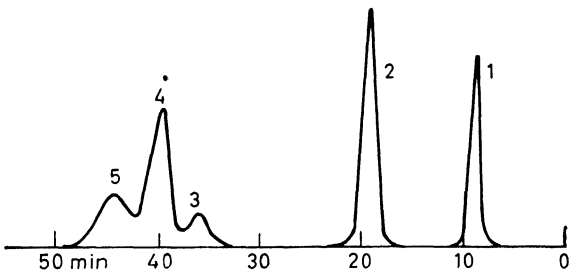
sich um Epimere, die sich durch die sterische Anordnung am C-Atom 1 unterscheiden.

Figur 6 zeigt einen Vergleich von N-Acetyl-glucosamin- und N-Acetyl-galaktosamin-Derivaten, die sich am C-Atom 3 sterisch unterscheiden.

Die Analyse eines Gemisches, wie man es nach Methylierung und Methanolyse eines Gangliosids erhielt, ist in *Figur 7* dargestellt.

Figur 8 zeigt, daß mitunter chemische Veränderungen der erwarteten Spaltstücke eintreten. Peak 1 hat sich z. B. als Pyrrol-α-carbonsäuremethylester erwiesen, eine Substanz, die mit p-Dimethylamino-benzaldehyd Purpurfärbung gibt. Das ist kein ursprünglicher Baustein. Der Ester 1 entsteht vielmehr aus den Ketosäuren mit 9 C-Atomen (Sialinsäuren) im Laufe der Methylierung.

Die Gaschromatographie hat nicht zuletzt bei Arbeiten auf diesem Gebiet eine Rolle für die Reinheitsprüfung von Substanzen gespielt und damit die Entwicklung anderweitiger präparativer Methoden wesentlich gefördert, zum



Figur 8. Gaschromatographischer Nachweis von bei der Methylierung entstandenem Pyrrolcarbonsäure-methylester
Kolonne: 3 m × 6 mm, 20% permethylierte Hydroxyäthylcellulose auf Chromosorb W;
Temperatur: 205°C;
Trägergas: 105 Nml H_2/min.
1: Pyrrol-α-carbonsäure-methylester
2: Pentamethylgalaktose
3: 2,3,6-Trimethyl-β-methylglucosid
4: 2,4,6-Trimethyl-β-methylgalaktosid
5: 2,3,6-Trimethyl-α-methylglucosid und 2,4,6-Trimethyl-α-methylgalaktosid

Beispiel diejenige von Methylierungsverfahren. Sehr schwierig zu methylieren war z. B. Meso-Inosit. Nur nach wiederholten Methylierungen gab er in kleinen Mengen die Hexamethylverbindung (daneben verschiedene Tetra- und Pentamethylverbindungen). Durch Anwendung von Dimethylsulfat und Bariumhydroxyd in einem Gemisch von Dimethylformamid und von Dimethylsulfoxyd gelang es H. Trischmann, den Meso-Inosit in einer Stufe glatt zu permethylieren und den Hexamethyläther kristallisiert — Schmelzpunkt 18°C — zu gewinnen. Dann ist er auch gaschromatographisch einheitlich, und die Kontrolle im Dünnschicht-Chromatogramm bestätigt dies.

Alle Aussagen, die man bei Versuchen zur Konstitutionsermittlung so komplizierter Naturstoffe mit Hilfe der Gaschromatographie erhält, sind davon abhängig, wieweit zum Beispiel die Methylierung wirklich alle freien OH-Gruppen erfaßt hat. Die Gaschromatographie ist parallel mit Dünnschichtchromatographie und mit anderen Methoden durchgeführt worden; aber nicht nur für das Analytische, sondern auch für das Präparative hat sie viele Anregungen und neue Hinweise gegeben.

SECOND OPENING LECTURE

Dr A. J. P. MARTIN

FUTURE POSSIBILITIES IN MICRO-ANALYSIS

THE GAS CHROMATOGRAPHY Discussion Group held its last informal symposium at the National Chemical Laboratory at Teddington, and we were addressed by the Director of the Laboratory, Professor Anderson, who surprised us—and delighted me—by suggesting that we should consider whether the time had not come to bring the Group to an end. He made the excellent point that a society devoted to a technique is of value only while the technique is advancing. An increase in its applications in a new field is really no justification for continuing meetings on a technique. However, on this criterion I have little doubt that we can justify our existence at present and for some time to come, and indeed there is one particular direction in which I feel we can work for many years, which, perhaps surprisingly, lies in advances in mechanical manipulation. This advancement is in the direction of decreasing the scale of our operations, and doing everything with smaller quantities.

The processes of chemistry are seldom much influenced by the scale on which they are carried out, and appropriate changes can be made for this difference in scale. I feel that one has only to look through a microscope at a bacterium, and to remember the thousands of substances which it synthesises, to be convinced of this.

The scale on which we normally work is dictated by the size of our hands, or the size that we thus prefer to make our apparatus. There are indeed a few cases, such as the determination of extremely small absorption constants for radiation, where many grams or kilograms of material are required, but these are few and far between.

If we learn the techniques of manipulating very small quantities, we can pursue the study of chemistry, using quantities 10^6 or 10^{12} times smaller than we habitually do.

Let us consider what are the advantages of working on a small scale. Even where materials are not limited there are usually advantages in speed. Any process where diffusion is normally rate-limiting will gain in speed on a small scale, and thus many purification processes will be quicker. Isothermal conditions are easily obtained and temperatures can be very rapidly altered. Certain processes will indeed be very slow, for instance the initiation of crystallization with substances which are difficult to crystallize. Crystallization as an initial method of purification may, therefore, have to be abandoned when one works on a very small scale, although it should still be useful when greater purity is reached. However, the most obvious advantage is to those whose material is limited for financial or other reasons. I started my scientific life as a biochemist, and biochemists are chronically short of materials, nature being so much cleverer than we are in the use of small quantities.

The relevance of this discussion on the use of small quantities to a meeting

about gas chromatography lies in the fact that in gas-, and indeed in all forms of chromatography, we have an ideal method of dealing with small quantities. One can expect the process to work as well or better on 1,000 mol. as on 10^{24} mol. Not only can we separate small quantities, we can also detect them. We already have several methods of measuring quantities of about 10^{-9} g; a paper at this symposium deals with just such a case.

So far, we have not really tried to detect minimal quantities. The most sensitive methods employed are ionization methods. As yet, they have concerned ionization in gases; but in many cases ionization by electrolytic processes would be possible, with total ionization of the substances of interest.

Let us see what quantities are involved. Assume for the sake of argument that we are dealing with substances with a molecular weight of 200. 200 g will thus require 100,000 C for reduction or oxidation. 10^{-12} g will therefore require 5.10^{-10} C, or a current, say, of 10^{-11} A for 50 seconds. With existing amplifying gear, which one can buy off the shelf, one can measure currents of, say, 10^{-13} A without any difficulty over such periods of time. Even with low ionization efficiency we should be able to do accurate work with 10^{-9} g.

Mass spectroscopy is, of course, an ionization method. You count the ions. Its sensitivity is essentially of the same order as that of the other ionization methods used in chromatography. With the conventional mass spectrometer one has to obtain a collimated beam, so the yield will be less; with the time-of-flight instrument the sensitivity should be of the same order.

It is perhaps a little surprising that absorption spectrographic methods are quite a lot less sensitive, at least in the infra-red region, where the limit seems to be about 10^{-6} or 10^{-7} g. In the visible and ultra-violet range, where individual photons can be counted, the quantities involved can perhaps be reduced, possibly 10 or 100 times. If we could make and manipulate the apparatus there is no theoretical difficulty in the long wave length region of X-rays in making elementary analyses on quantities of 10^{-9} g or less, and indeed Engstrom did this for microscope sections—even if not very accurately—some fifteen years ago. X-ray crystal structure methods have also been used for crystals weighing less than 10^{-8} g. Olga Kennard at the National Institute for Medical Research used a crystal of tri-iodothyronine some $10 \times 5 \times 100$ μ long, which is equivalent to a volume of $5{\cdot}10^{-9}$ ml; with this crystal she was able to establish its structure.

The labqur involved in a full structure analysis is still, even in this age of computers, formidable. It does, however, provide the structural formula as part of the crystallographic data. If only the cell dimensions are required a certain identification can be provided, for those substances for which data exist, with less than a day's work. If apparatus were improved a crystal of 1,000 mol. in each direction should suffice, weighing less than 10^{-12} g. It seems to me quite probable that in time X-ray crystallographic methods may come to be the preferred method of identification of materials which have been separated chromatographically. If this method comes into general use, then obviously the library of information on the crystal structures of cell dimensions of various crystals will soon become enormous, and it may well be that most of the substances which people are interested in can be identified merely by the cell dimensions. The chemist has normally no method of

handling amounts of substances of even 10^{-6} g. The preferred method, after all, of putting one μg of substance on to a capillary column at the present time is to put on a mg and by a divider throw the rest of it away. This is done because we have no proper apparatus for weighing out the required μg and putting it on to a column. We come back again, in fact, to the problem of the size of our hands.

To return to this problem of the size of our hands: if ants were endowed with our intelligence they would have no trouble either in handling material in amounts of this order or in building and operating a balance to weigh it. The balance does not have to differ in any essential respect from those we use at present; it just has to be smaller. Probably the only trouble encountered will be Brownian movement, which at room temperature corresponds to a mean energy of about one-fortieth of an eV or $4 \cdot 10^{-21}$ J or $4 \cdot 10^{-14}$ erg. If the stiffness of the balance is such that the pointer, or whatever one uses, will move one μ for 10^{-12} g the root mean square of the Brownian movement will be 0·6 μ. It should thus be possible to weigh accurately at room temperature a mass of 10^{-9} g. If the temperature were much lower, say a few degrees absolute, 10^{-11} g could perhaps be weighed accurately. This suggests that the ideal detector for gas chromatography might consist of a minute balance, carrying a plane or cylinder loaded with an adsorbent on its surface over which the gas from the capillary had to flow, the flow being so arranged as not to disturb the balance. The balance must, of course, be at the same temperature as the gas issuing from the column to avoid convection troubles. The heat of adsorption would normally be negligible. If the clearance between the leaf and the walls were of the same order as the diameter of the capillary column, the diameter of the leaf, I believe, would need to be only some 20 to 25 times that of the column in order to ensure complete absorption. This detector would give the total mass of condensable material as it left the column, and would have to be furnished with the appropriate continuous recording gear. The record furnished would, in my opinion, be ideal for the analyst. The weight of each component would be shown as the height of a step and no calibration factors would be required. The ease and certainty with which a material balance could be drawn for the analysis would, I am convinced, lead to improved standards of work.

If fraction cutting were required, it would be necessary to stop the chromatogram flow and replace the leaf with a new one. The required fraction could then be evaporated from the leaf and condensed in the cold capillary tube, appropriately cooled and evacuated vessels being provided for this purpose.

It seems unlikely that there will be difficulty about any of the unit operations of chemistry: solution, crystallization, filtration, distillation, centrifugation, etc., on a very small scale. Gravity will become very unimportant, and surface tension will dominate the movement of liquids. Hence, relatively high pressures will be required to move liquids. High pressures will also be required to move liquids in and out of burettes through the fine holes in the tips; fine holes being required in order to reduce diffusion to a tolerable level. However, given an appropriate apparatus and the ability to make movements as desired without breaking anything, I foresee no special difficulties in 'Pico Chemistry' as such. The difficulty lies in making the appropriate movements and apparatus.

This problem of micro-manipulation has fascinated me for the past few years. I believe I now see how it should be tackled; in fact, it is not intrinsically difficult. Indeed, the solution should be obvious from what I have said before: we must make small hands. It is a matter for argument as to how faithful a reproduction we should attempt. Obviously, what we make will be a very crude affair compared to a real hand, particularly in its sensory aspects, but I think that probably in addition to the three degrees of freedom of translation and the three degrees of rotation it should have five or ten degrees of freedom in fingers for gripping. The fingers should also have devices for measurement of the pressures which they exert. It is probably unnecessary for the forces exerted by the arm itself to be recorded, those of the fingers should be enough. Though a complicated and elaborate machine, such a hand would not be very difficult to construct, if a modest ratio of reduction—say eight or ten to one—could be accepted. These hands would be driven from gloves into which one fitted one's hands, and the movements of similar parts would be strictly proportional. The force-measuring gear would amplify the forces by the square of the reduction ratio, and one should therefore be able to feel when one had got hold of something and what its shape was. Note that the 'muscular' and the 'sensory' parts would be entirely separate in nature and in function, as with our own hands. I believe that this would be far simpler than trying to combine force and distance in one type of function.

There are, of course, a very large number of ways in which such a machine could be constructed, but I believe a mechanical system for the movement and a pneumatic system for the sensory part would be the easiest and the most useful.

I should like to digress here to say that this conception of micro-manipulation differs widely from that of previous micro-manipulators. Although we have been able for some 300 years to see things under a microscope, the only tools presently available for use under the microscope are those essentially belonging to the stone age: a spear and a battle-axe. These have three or four degrees of freedom. Of course, these can be made with much more than the 10:1 reduction I am proposing, and it would not be possible at the present time to construct a machine such as I suggest with 100:1 reduction. It would be necessary with the first few pairs of hands with the 10:1 reduction to construct a small world; in particular a small workshop complete with all the hand and machine tool types which exist on the normal scale. When such an adequate workshop has been built, it will be possible to construct a 100th-scale hand, and to build a 100th-scale world: the first manipulator directly operating the second. I believe that very little change of design will be required in changing the scale. It would be possible to make most of the one-tenth scale world without employing the micro-manipulators at all, but the whole object of the operation would be to learn how to use the manipulators, to work through the small hands. Working through two or more stages should not be appreciably different from working through one. At the 100th-scale we should already be able to make things which could be made in no other way.

It is interesting to consider the properties of the small world. The mass of the machine, of course, goes down as the cube of the scale of reduction.

If the speed of rotation or frequency of reciprocation increases linearly as the scale decreases, the stresses in the materials will be identical with those of the larger machines. To keep everything in step, the viscosity of all liquids and gases would also have to be reduced on the same scale, which is not possible of course, and this might limit the actual speeds which could be used. Temperature differences from processes not involving viscosity will be inversely proportional to size. Wear is an interesting problem, because it will be proportionately faster, but considering, say, an automatic lathe, the work will be produced at a rate one hundred times faster and the wear will also be one hundred times faster, which will permit the same number of pieces to be produced before the machine is worn out. One's tools may last only an hour or two, but they should perhaps be able to produce a few million pieces in that time.

The problems to be faced due to the grain structure of metals and corrosion are difficult to estimate at the present time, and may make it impossible to use many materials. However, as the size of the apparatus goes down the cost of the raw materials involved rapidly becomes negligible. If the chemist wants to use platinum and diamonds for his reaction vessels there is no reason why he should not do so. He may find that as the scale is reduced glass is not quite so unreactive as he normally considers it, as the ratio of surface to volume increases.

If we possessed such a workshop we could make all the apparatus the chemist requires at the 100th-scale, thus using quantities of material 10^6 times less than is conventional; in most branches of chemistry we should suffer no particular difficulty from this change of scale.

It seems to me probable that we can go down some four or five stages of 10 before finding that the finite size of atoms begins to make difficulties. Down to this stage I believe we shall find that everything is extremely similar to operations on the present scale, except that at the one-tenth scale we shall have become noticeably short-sighted and have to keep changing our focus in order to find out what we are doing. On the 100th-scale we become extremely short-sighted and begin to feel rather blind using visible light, because we shall have difficulty in seeing any detail of surface finish, and so on; below this scale it will be necessary to use the electron microscope to see what we are doing. There seems to be no real reason why this should introduce special difficulties, unless leakage of gas from our pneumatic system is troublesome.

The appetite of the chemist to work on a small scale will grow as it becomes more possible. He will be able to analyse and experiment on single cells. There is obviously an almost limitless field in making and using apparatus for measuring various physical properties on small objects. How much further can we go? If we assume that we have learned to work blind by feel only, I believe that we can carry the process of making our manipulators to the limit where the ends of our fingers consist of single atoms. We will have fingers with a single atom of tungsten or diamond at the end. No doubt we shall have to learn many new techniques when individual atoms start to matter. I see no present reason to believe that it is impossible to devise such techniques. If it is possible to make such manipulators, there seems to be no reason why we cannot work with our 'micro-feeler' to feel the shape of

individual molecules. A micro-feeler of this kind should have powers altogether greater than the electron microscope. The electron microscope at present uses very energetic electrons with many thousand eV energy. This energy is greatly in excess of that required to disrupt molecules. For instance, the energy required to separate the two atoms of an oxygen molecule is about 8 eV. Even allowing for advances in electron microscopes it seems improbable that it will ever be possible to reduce the energy to a level that will not produce serious disturbance in the object being looked at, and indeed it seems certain to make it evaporate if it does not disrupt it altogether. On the other hand, the disturbance to be dealt with in a mechanical feeling system would seem to be only Brownian movement. In any case, at temperatures within a few degrees of absolute zero, such disturbances should be quite negligible, permitting the measurement of even the forces needed to distort the molecule. I am far from saying that I know how to make such an instrument or how to measure the forces which might be of the order of, say, 10^{-6} dyn. I have a fancy that a pneumatic method will still be the best, measuring the position of a spring which partially closes an opening through which helium would stream, the rate of flow then giving the required information. As far as I can see, this system would not add to the disturbance of the whole at all; the disturbances would still be those corresponding to the energy of a molecule at the temperature of the system. Electrical methods might indeed be possible; I have not yet attempted to estimate the usefulness of electrical methods at this scale.

I imagine, therefore, two hands with at least six fingers in all, with which it would be possible to pick up individual molecules and pull off any other molecules adhering with Van der Waals forces; then holding the molecule with one hand one could pull the atoms through the fingers of the other like a string of beads. They would no doubt be clumsy fingers, but it should still be possible to identify the nature of the atom and its bonding after a little practice with substances of known structure.

Unless I have made some elementary mistake in my reasoning—and that is not impossible—it must be possible for a machine appropriately constructed to work in this way. If, in fact, it is possible I would expect that within, say, 30 years, we shall have technicians sitting on a mountain consisting of a single frozen cell, painstakingly taking it to pieces, sometimes breaking covalent bonds in the structural material to get at more interesting pieces—such as the inside of a protein molecule—and then following the chain along, examining each side chain and working out in the course of an hour a structure that at present it takes many men years to unravel.

Further, such an instrument should make possible a detailed three-dimensional picture of a frozen cell, perhaps still a life's work even with computer aids and mechanical automated movement.

During the past few weeks I have read a lecture given by Dr Feynman of the California Institute of Technology, who has put forward views very similar to mine for work on a small scale, and has suggested that single molecules can be synthesized by pressing the atoms together. Reading this has helped me raise the courage to make public these somewhat wild speculations. If we could make this micro-feeler it would transform the subject of biochemistry in a few years and have a profound influence on many

subjects. Chromatography would still be required for quantitative work and for concentration of molecules which were rare, but the micro-feeler would take over all the work of identification.

Finally, I would just say that we do not know what we can do until we try.

Discussion

D. Roberts (*prepared contribution presented in the Saturday morning session*): I think we were all very impressed with Dr Martin's suggestion that we needed a sub-micro world in which to work, in order to obtain the ultimate from gas–liquid chromatography or gas–solid chromatography. I began to think about this during the week, and it came to me that our German hosts are themselves masters at micro-manipulation and the production of small instruments. Lo and behold: here in Hamburg I found what Dr Martin said he wanted for his first stage: almost a factor of ten reduction in the size of instruments. I should like to take the opportunity of presenting to Dr Martin what I have found, and if he would come forward I think he might find these very useful. I hope, Dr Martin, that you find these come up to scratch. (Presents a pair of back scratchers.)

A. J. P. Martin: Die Fachgruppe Analytische Chemie der Gesellschaft Deutscher Chemiker versteht es, daß ich, wenn ich mein Programm durchführen will, dies nicht auf gewöhnliche Art mache. Und so hat sie mir zwei ganz praktische Geschenke mitgegeben.

Einmal dieses Paar von kleinen Händen, und zweitens ein Buch: 'Der Stein der Weisen'. Doch gleichzeitig hat sie mir eine Warnung von Goethe aus Faust mitgegeben. Ich will es Ihnen vorlesen: 'Wenn Sie den Stein der Weisen hätten, der Weise mangelte dem Stein.'

THIRD OPENING LECTURE

Professor Dr A. V. KISELEV

THE IMPORTANCE OF THE SOLID SURFACE IN PARTITION, ADSORPTION AND CAPILLARY GAS CHROMATOGRAPHY

THE SURFACE heterogeneity of common 'active' adsorbents is the main obstacle to their application in gas chromatography. However, the properties of many adsorbents, such as silica gels and porous glasses, can be greatly improved by geometrical modification of their structure and chemical modification of their surface. Uniform wide-pore silica gels on to which a chemically inert and thermally stable modifying layer is grafted show practically no chemisorption or catalytic activity of the structural solid, and adsorption is greatly reduced. Such modified silica gels are very convenient as supports, not only for liquid immobile films (gas–liquid chromatography), but also for highly dispersed solids with homogeneous surfaces, such as thermal carbon blacks graphitized at 3,000°C (gas–solid chromatography). Geometrical and chemical surface modifications also improve capillary columns. The preparation and improvement of adsorbents with sufficiently homogeneous and weakly but selectively adsorbing surfaces, as well as of the corresponding supports and capillaries with geometrically and chemically modified surfaces, in combination with the purely geometrical action of molecular sieves, is one of the most important physico-chemical problems of gas chromatography.

Introduction

Conventional 'active' adsorbents and catalysts are fine-pored bodies having an immense and geometrically and chemically very heterogeneous surface area. That is why such adsorbents have not found very wide use in gas chromatography. Large-sized molecules and molecules with large dipole and quadrupole moments or π-electron bonds cannot be separated satisfactorily on such adsorbents. The relative rate of emergence of various concentrations of such compounds, for which the adsorption isotherms are sharply concave towards the pressure axis, is not constant; and the chromatographic bands are greatly drawn out.

After Martin and James[1] suggested such a useful gas–liquid version of chromatography ten years ago, the gas–solid version receded into the background, owing to the great heterogeneity of the surfaces of 'active' adsorbents in comparison with the ideally smooth liquid surfaces. However, some limitations of the gas–liquid version soon became apparent: these were related to a certain 'activity' of the solid supports and to the difficulty of working at high temperatures. At temperatures of 300–500° liquids begin to break down on the aluminosilicate surfaces; their vapours and decomposition products spoil the detector background; and finally, the molecules of the sample penetrating the liquid layer undergo catalytic transformation when they reach the surface of the support. In addition, strong adsorption of many substances impairs separation at lower temperatures as well.

Thus the extension of gas chromatography to strongly adsorbing substances and to high temperatures requires the use of more stable supports and more stable immobile phases than liquids can provide. All this makes it necessary to devote serious attention to the quality of the adsorbents and capillary column walls used in gas chromatography.

Geometric Modification of Xerogels

Let us first consider the geometrical modification of adsorbents and supports. The geometrical heterogeneity is due to their fine pores, and therefore the latter must be greatly widened. This problem is easily solved for xerogels,

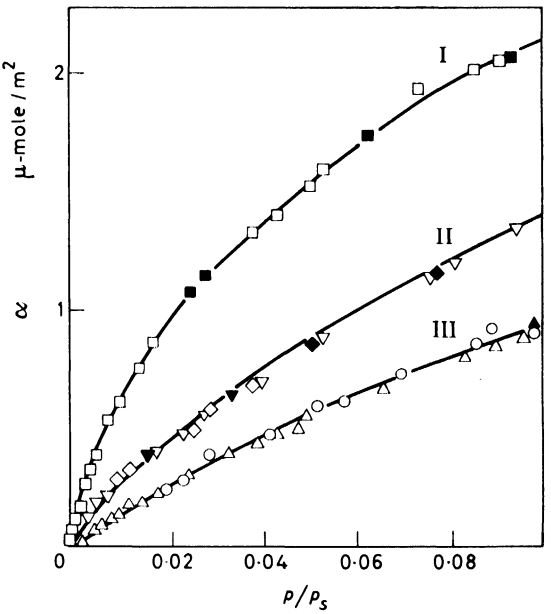


Figure 1. Adsorption isotherms for n-pentane on quartz and on silica gels with different pore diameters
Curve I: silica gel, pore diameter 25 Å
Curve II: silica gels, pore diameters 36 and 38 Å
Curve III: silica gel, pore diameter 100 Å, and quartz

e.g. silica gels. The silica gel skeleton consists of intergrown silica globules which are not very large (usually less than 100 Å), heterogeneous, and not ideally packed[2]. Therefore, the pores, i.e. the clearances between the globules, are also very small. The energy of the dispersion forces at the points of contact between the globules is large, particularly for large molecules adsorbed on material consisting of a dense packing of small globules[3]. Naturally, as the pores become narrower the adsorption isotherms become more pronouncedly distorted. This can be seen in *Figure 1*, which shows the initial parts of the adsorption isotherms of n-pentane on quartz and silica gels of different porosity. The most concave isotherm was obtained for the

specimen with the finest pores[4]. Narrowing of the silica gel pores greatly increases the heat of adsorption of hydrocarbons, especially n-alkanes with large numbers of carbon atoms[3]. Narrowing of the silica gel pores has a much less pronounced effect on the adsorption of small molecules, such as nitrogen[5] and methanol[6]. The effect is especially small for water[7], which is adsorbed mainly by virtue of hydrogen bonding. In these cases the differential heat of adsorption also drops rapidly with increasing coverage, owing chiefly to the chemical heterogeneity of the silica surface and to the irregular location of the hydroxyl groups[8].

First of all we attempted to reduce the geometrical heterogeneity of silica gels. Hydrothermal treatment of silica gels causes growth of their globules,

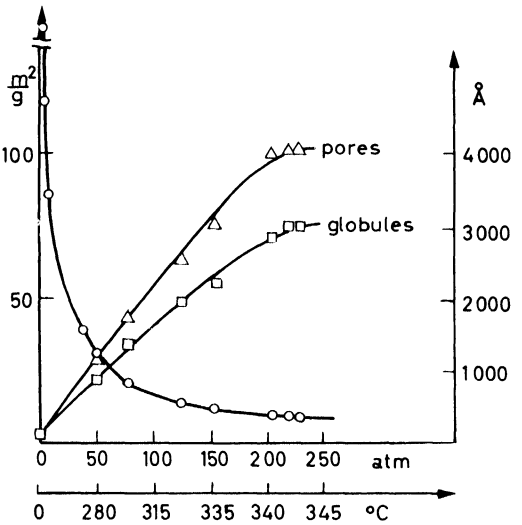


Figure 2. Structural characteristics of silica gels as a function of the conditions of steam treatment
△ Average diameter of pores
□ Average diameter of globules
○ Surface area (m^2/g)

and therefore pronounced widening of their pores[9,10,11]. *Figure 2* illustrates the effect of the conditions of steam treatment on the structural characteristics of the silica gel. Making use of this curve and proceeding from an ordinary silica gel, e.g. with a specific surface area about 300 m^2/g and with a pore diameter of 100 Å, we can obtain a specimen with any desired smaller surface area and larger pore diameter. In this way very large pores and globules can be obtained, up to 5,000 Å in size, which can be very clearly seen under the electron microscope. In this case the geometrical heterogeneity at the points of globule contact is of no substantial significance. Such silica gels can be employed directly for chromatographic separation of large molecules with symmetrical electron shells, e.g. alkanes and cyclanes. The choice of specific surface area and pore size obviously depends on the properties of the molecules to be separated. However, it can be seen from

Figure 3, that, whereas alkanes and cyclanes emerge in rather symmetrical peaks, the peak of benzene lags greatly and has a large tail[12]. The π-electron density of the benzene molecule is high and the molecule is sensitive not only

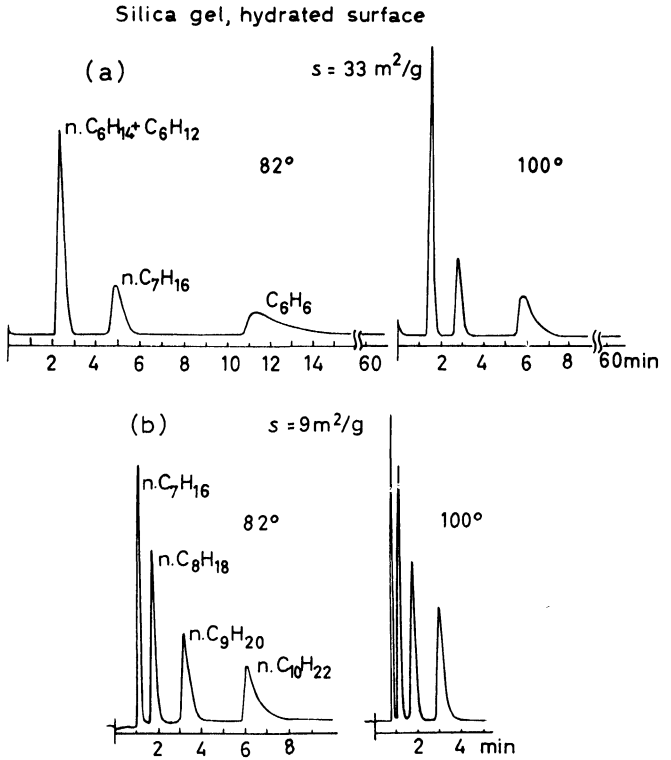


Figure 3. Chromatograms of various hydrocarbons on two silica gels modified by steam treatment

A. silica gel treated with steam at 850°C for 24 h; surface area 33 m^2/g. The sample contained acetone, which could not be eluted from this column

B. silica gel modified by steam treatment in an autoclave; surface area 9 m^2/g

Column length 1 m, inside diameter 6 mm; flow rate at column inlet 45 ml nitrogen per minute

to geometrical heterogeneity, but to hydration of the silica surface as well. The molecules of acetone and ether, which are capable of forming hydrogen bonds with the hydroxyl groups on the silica surface, emerge very slowly from such a column under the conditions of the test. The high energy of interaction between these compounds and the hydroxyl groups of the silica surface may be deduced from the value of the heat of adsorption and the different sensitivity to dehydration of the surface[13,14], as well as from the changes in the infra-red spectrum of the silica surface caused by their adsorption[8,15]. It is evident from *Figure 4* that the adsorption of hexane produces only an insignificant shift of the stretching frequency of the OD

hydroxyl groups on a deuterated surface. When benzene and, especially, ether are adsorbed, the shift of this stretching frequency is much greater. These data are consistent with the considerable effect of the degree of hydration on the heat of adsorption of benzene and ether[13,14,16-18], and with the

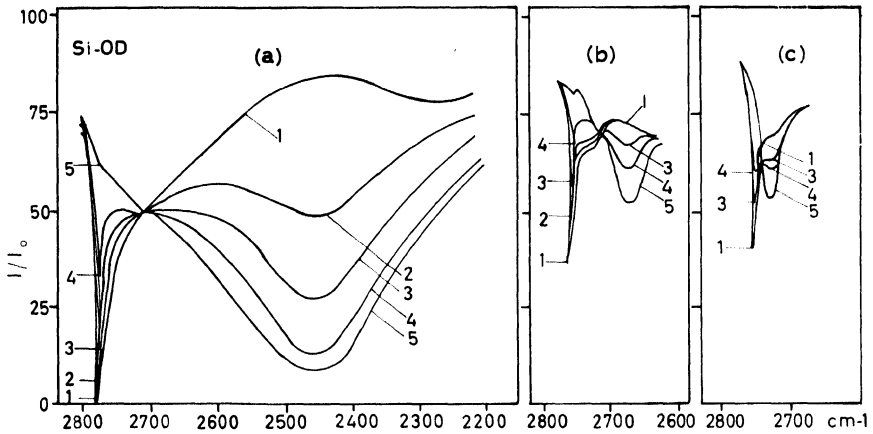


Figure 4. Infra-red spectra of deuterated silica
A 1: after three hours under vacuum at 400°C
2: with 0·4 monolayer of adsorbed diethyl ether
3: with 0·7 monolayer of adsorbed diethyl ether
4: with 0·8 monolayer of adsorbed diethyl ether
5: with 1·1 monolayer of adsorbed diethyl ether
B 1: after 6 h under vacuum at 200°C
2: with 0·1 monolayer of adsorbed benzene
3: with 0·5 monolayer of adsorbed benzene
4: with 1·0 monolayer of adsorbed benzene
5: after condensation of benzene in the capillaries
C 1 to *C* 5: similar to *B*, but for adsorption of n-hexane

fact that their retention time is much greater than that of saturated hydrocarbons with the same number of carbon atoms. We therefore have to undertake the chemical modification of silica surfaces.

Chemical Modification of Silica Surfaces

The chemical activity and heterogeneity of a silica surface can be reduced by substitution of more inert groups for the hydroxyls. As the modified adsorbents and supports are to be used at high temperatures, the silico-organic groups to be grafted to the silica surface must have a high thermal and chemical stability. The reaction between the hydrated silica surface and trimethylchlorosilane results in a layer of trimethylsilyl groups chemically grafted to the surface, which is stable up to 350 or 400°C, as shown by Janak by means of thermo-analysis[9] and infra-red studies[19,*]. This layer keeps the molecules of the adsorbate away from the silica proper[9,22,23], so that

* White and Cowan[20] grafted a layer of large organic cations on to montmorillonite by means of ion exchange[21]. However, such a layer is not so stable as a layer of silico-organic compounds.

the adsorptive forces are considerably weakened[9,13,14,22]. Owing to steric effects small gaps remain between the chemisorbed trimethylsilyl groups which cannot be filled with new trimethylsilyl groups. At the resulting sites with unmasked hydroxyl groups only small molecules can be adsorbed. Convincing proof of this can be obtained from e.g. an infra-red study of the exchange reaction between D_2O and surface hydroxyl groups[8]. Other chlorosilanes used by us for the modification of silica gels produced results similar to those obtained by Purnell and co-workers[45], who used hexamethyldisilazane to modify Sil-O-Cel. In all these cases it is important to make the modifying layers as dense as possible.

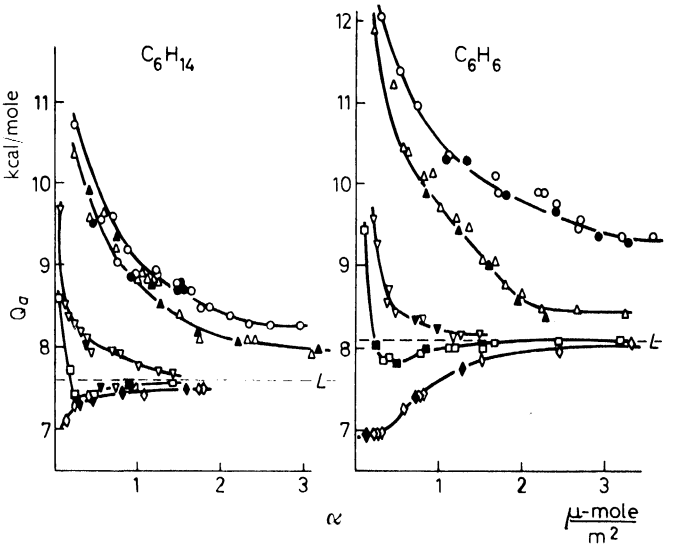


Figure 5. Differential heats of adsorption for n-hexane on silica gels with surfaces partly modified by grafting of trimethylsilyl groups

○ unmodified surface
△ 60 per cent trimethylsilyl coverage
▽ 86 per cent trimethylsilyl coverage
□ 90 per cent trimethylsilyl coverage
◇ *ca* 100 per cent trimethylsilyl coverage

Figure 5 shows how the differential heats of adsorption of benzene and n-hexane depend on the coverage of silicas with hydrated surfaces and with surfaces coated to various degrees with trimethylsilyl groups[23]. The hydrated surface of the initial silica specimen is very heterogeneous both geometrically and chemically; this causes a sharply decreasing heat of adsorption, the value of which is much greater than the heat of condensation. Though at 60 per cent coverage of the surface with trimethylsilyl groups the heat of adsorption is somewhat lower, the surface is not improved very much because a large heterogeneous surface area on the silica proper still remains available for adsorption. Only when the surface concentration of the chemically grafted Me_3-Si groups becomes close to 100 per cent, i.e. when all the residual silanol hydroxyls are already well screened by adjacent

trimethylsilyl groups, the heat of adsorption of the large benzene and hexane molecules becomes practically independent of the surface coverage; it is now lower than the heat of condensation. We thus approach an ideally homogeneous, weakly adsorbing surface. Although the adsorption isotherms of benzene vapour on the hydrated surface of the initial specimen and on the surface of insufficiently modified material are pronouncedly concave to the pressure axis (*Figure 6*), only little adsorption occurs on the most completely modified specimen, and the isotherms are practically linear in their initial

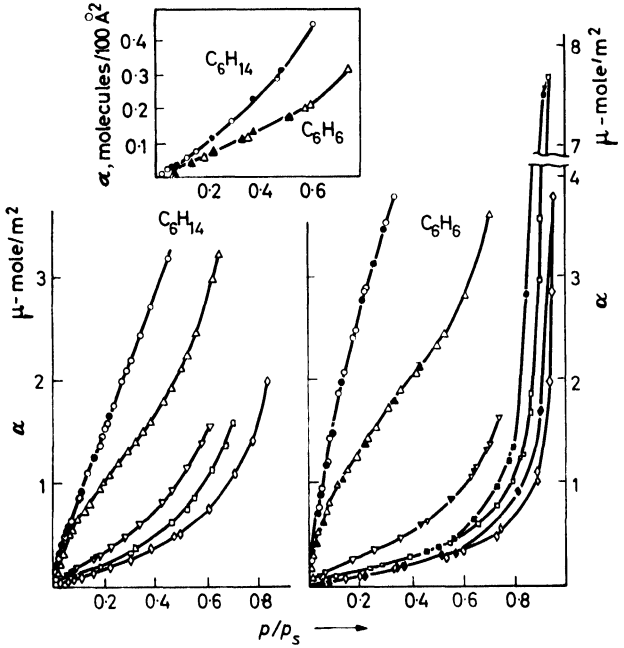


Figure 6. Adsorption isotherms for the same systems as those of *Figure 5*. Insert: initial part of isotherms on the fully modified adsorbent

parts. Benzene and n-hexane have now changed places, as the interaction of the π-electron bonds of benzene with the silanol hydroxyls[16,17] has been eliminated.

In *Figure 7* the heats of adsorption and the surface concentration of various adsorbates are plotted as a function of the surface coverage and of the relative vapour pressure for an adsorbent before modification and after coating with the maximum density of trimethylsilyl groups[14,23]. A sharp decrease in the heat of adsorption to values below the heat of condensation is observed for all sufficiently large molecules (relative to the trimethylsilyl group): namely benzene, n-hexane and carbon tetrachloride. Only the small molecules of methanol and especially water, which can penetrate into the gaps between the trimethylsilyl groups and interact strongly with the residual silanol hydroxyls, show a smaller change in adsorption, and the heat of adsorption of water remains larger than its heat of condensation. These results

show that such a chemically modified layer is sufficiently dense for work with large molecules.

Of course, this leads to a loss of selectivity of the adsorption properties of the surface. Therefore such geometrically and chemically modified silica gels can be employed in gas chromatography: first, as chemically inert material with very weak and non-selective adsorptive properties, to support

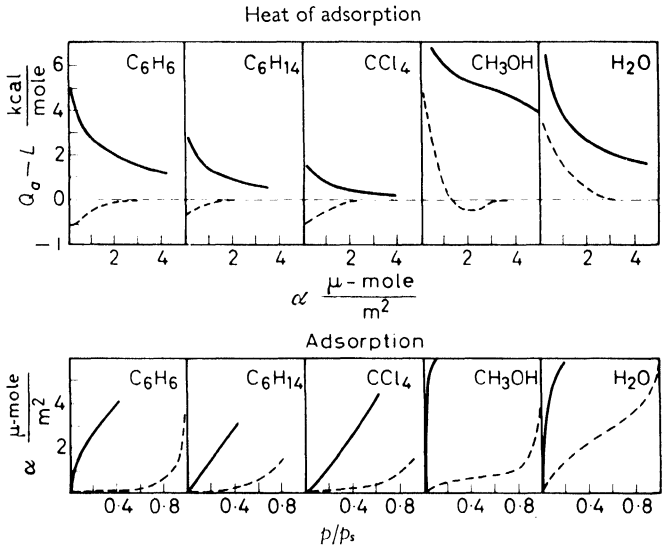


Figure 7. Heats of adsorption (top) and adsorption isotherms at 20°C (bottom) for various compounds on silica gels with hydrated surface (—) and with trimethylsilyl-covered surface (---). The horizontal dotted line indicates the heat of condensation

other immobile phases (liquid or solid); and secondly, as non-specific weak adsorbents for the separation at comparatively low temperatures of compounds which differ sufficiently in the potentials of their dispersion forces. Such compounds may be members of homologous series of hydrocarbons and their derivatives of normal and branched structure, and other high-boiling substances differing mainly in the number of their atoms and groups which contact the surface.

Applications

Figure 8 shows a number of chromatograms obtained on geometrically and chemically modified silica gels. The chemical modification not only causes benzene to emerge practically together with hexane, but even acetone is eluted rapidly from such a column. The lower chromatogram in *Figure 8* shows good separation of n-alkanes (up to decane) even at very low temperature (30°C).

Silica gel modified with methylsilyl groups possesses a non-polar surface. To screen the silica, and at the same time to make a modifying layer selective,

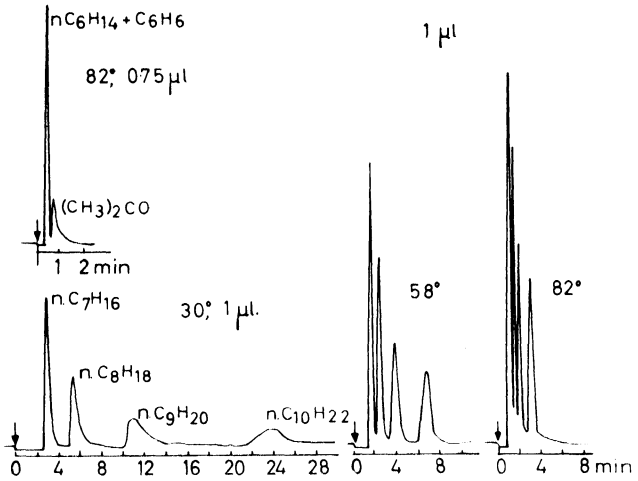


Figure 8. Chromatograms of various compounds on silica gel (23 m^2/g) coated with trimethylsilyl groups. Experimental conditions similar to those of *Figure 3*

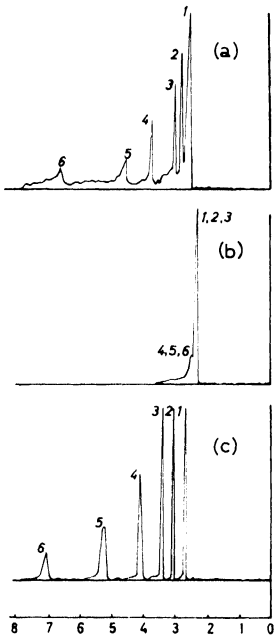


Figure 9. Chromatograms of various compounds on glass capillary columns
A: unmodified glass surface, coated with silicone oil; *B*: glass surface modified with trimethylchlorosilane; *C*: same surface as *B*, coated with silicone oil
1: acetone; 2: n-hexane; 3: benzene; 4: n-heptane; 5: toluene; 6: n-octane

we graft chlorosilanes with different functional groups (—OH, —COOH, —CH=CH_2, etc.) on to the silica surface.

Various methods of chemical modification with chlorosilanes[12] and hexamethyldisilazane all produce rather similar results. Such silica gels with small and very weakly adsorbing surface areas can be successfully employed as inert supports for various immobile phases, particularly liquids. Such chemical surface modification is important for packed as well as capillary columns.

Chromatograms of a mixture of several vapours, obtained on glass capillaries before and after modification of their surfaces[24], are shown in *Figure 9*. The upper chromatogram was obtained with a non-modified capillary coated with a silicone oil film. The resulting peaks were very diffuse. The glass capillary whose surface was modified with trimethylsilyl groups released all components practically simultaneously with the carrier gas, which indicates that the modifying layer was inert. After application of a film of silicone oil to such a modified capillary, excellent separation was obtained, all the components emerging as distinct symmetrical peaks, so that this case can be regarded as an ideal example of gas–liquid chromatography.

Thus, the geometrical and chemical modification described has been found especially useful and convenient for purposes of gas–liquid chromatography, as well as directly for gas-adsorption chromatography of high-boiling substances.

Use of Highly Dispersed Solids as Immobile Phases

Let us now consider the application of highly dispersed solids as immobile phases in gas chromatography. In the course of the past ten or fifteen years dispersed solids have been obtained with sufficiently homogeneous chemical and geometrical surface structure. Carbon blacks graphitized at 3,000°, especially thermal carbon blacks, are non-polar dispersed solids with very homogeneous surfaces[9,13,14,25–29]. Particles of graphitized thermal and furnace carbon blacks with specific surface areas ranging from 6–60 m^2/g consist of separate polyhedrons with basal graphite faces[28,30]; they are very homogeneous and non-selective adsorbents[13,14,29,31]. These carbon blacks can be introduced into the pores of the modified supports described above to serve as immobile phase, because adsorption on the support is negligibly small compared with the adsorption on the carbon black[9,32]. Formerly, carbon blacks were employed in gas chromatography in the non-graphitized form, with squalane added as binder[33]. The introduction of fine powders into the large support pores is not difficult and has already been accomplished by Cremer[34] for the determination of the specific surface area of ordinary (non-graphitized) carbon blacks by gas chromatographic methods.

Whereas adsorption on the heterogeneous surface of non-graphitized carbon blacks causes a decrease in the heat of adsorption, with graphitized carbon blacks the region of heterogeneity is much narrower and the heat of adsorption increases with surface coverage. This increase continues up to the transition to predominant adsorption in the second layer, whereupon the heat of adsorption drops off sharply to values close to the heat of condensation[14,29,35].

The increase of the heat of adsorption with coverage in the first adsorption layer on the homogeneous surface of graphitized carbon black is due to the energy of mutual attraction between the adsorbed molecules (adsorbate-adsorbate-interactions), which must be added to the energy of adsorbent-adsorbate interaction. On heterogeneous surfaces this attraction term is camouflaged by a drop in the energy of adsorbent-adsorbate interaction[14, 36]. Consistent with the change of slope in the curve for the heat of adsorption (from drop to rise), the shape of the adsorption isotherms of the corresponding substances also changes from concave to convex (to the pressure axis) at small surface coverage. *Figure 10* shows the initial parts of the adsorption isotherms for n-hexane on channel black calcined at 2,800° (large residual heterogeneity; isotherm concave to the pressure axis) and on thermal carbon black calcined at 3,100° (small residual heterogeneity; isotherm convex to the pressure axis[14]). The results obtained with different samples in

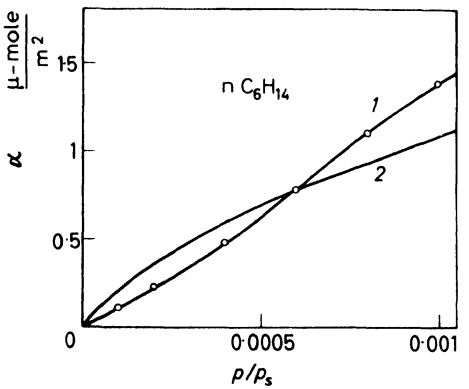


Figure 10. Adsorption isotherms for n-hexane on carbon blacks
1: MT-1 thermal carbon black, calcined at 3,100°C
2: Spheron-6 channel black, calcined at 2,800°C

various countries coincide if they are referred to unit surface area[14, 30, 36]; this means that the adsorption properties of such carbon blacks are already practically unaffected by the heterogeneity and are physico-chemical constants depending only on the nature of the adsorbate-basal graphite face system. Secondly, it was found that in the great majority of cases the heat of adsorption increases with increasing surface coverage, and the initial parts of the isotherms are convex rather than concave to the pressure axis[14, 31, 36]. Therefore, a little residual heterogeneity is admissible because the isotherm still remains practically linear (surface heterogeneity makes the isotherm concave to the pressure axis, while adsorbate-adsorbate attraction makes it convex).

Carbon blacks were introduced in about 20 per cent amounts into the large pores of modified silica gel supports, as suggested by Cremer. After filling with graphitized carbon black the support was placed in a chromatographic column.

In *Figure 11* the differential heat of adsorption, determined by calorimetry[9,29,31], is plotted as a function of surface coverage for graphitized thermal carbon black.

The adsorption values and the shape of the isotherms shown in *Figure 12* change in accordance with the order of the values for the heat of adsorption and with the sharp increase of the heats of adsorption with increasing surface coverage which is observed for acetone and n-hexane. The adsorption of acetone is much smaller than that of benzene, which in turn is smaller than

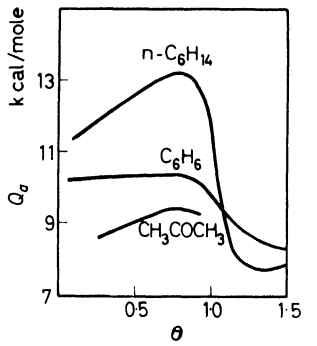


Figure 11. Differential heats of adsorption as a function of surface coverage on thermal carbon black calcined at 3,000°C

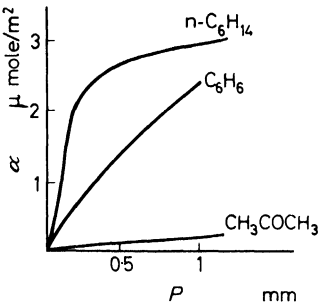


Figure 12. Initial part of isotherms at 20°C for n-hexane (convex to pressure axis), benzene (concave) and acetone (convex), on thermal carbon black calcined at 3,000°C

the adsorption of n-hexane; the adsorption isotherms of acetone and n-hexane are convex to the pressure axis in their initial parts, and that of benzene, concave. Accordingly, the first to emerge on the chromatograms (*Figure 13*) is acetone, followed by benzene and lastly n-hexane.

The acetone peak has a large tail, owing to the insufficient density of the modifying layer on the silica gel support employed. But in the case of the large molecules of benzene and n-hexane the shape of the peaks corresponds to that of the adsorption isotherms on carbon black: the benzene peak has a sharp front and a drawn-out tail, and the n-hexane peak (convex isotherm) has a drawn-out front and sharp rear.

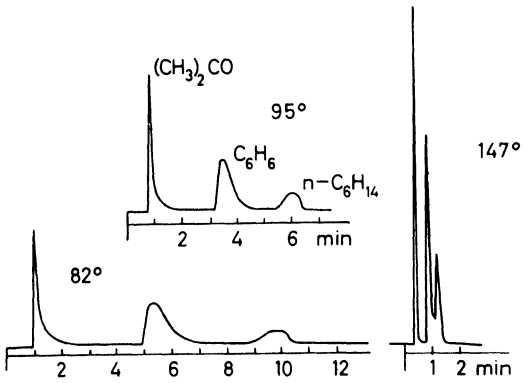


Figure 13. Chromatograms of acetone, benzene and hexane on graphitized thermal carbon black supported in the pores of trimethylsilyl-covered silica gel (s = 23 m²/g). Experimental conditions similar to those of *Figure 3*

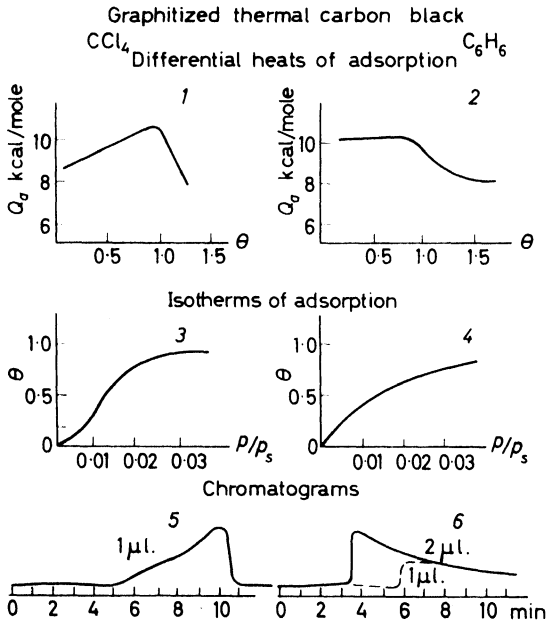


Figure 14. Differential heats of adsorption for carbon tetrachloride (1) and benzene (2) as a function of the surface coverage on thermal carbon black. (3) and (4) are the corresponding isotherms; and (5) and (6) are chromatograms, obtained with the adsorbent supported on modified silica gel. Experimental conditions of the chromatogram similar to those of *Figure 3*

Figure 14 shows the very striking picture of the adsorption and chromatographic characteristics of two typical cases—carbon tetrachloride and benzene on graphitized thermal carbon black. The heat of adsorption of carbon tetrachloride increases with surface coverage; therefore the adsorption isotherm is at first convex to the pressure axis, and then becomes concave. The heat of the adsorption of benzene, owing to the peculiarities of the structure of its molecule, does not change with surface coverage; and accordingly the adsorption isotherm of benzene is concave to the pressure axis. This difference in the shape of the adsorption isotherm leads to the pronounced difference in the shape of chromatographic peaks. In the case of carbon tetrachloride the front is drawn out and the rear sharp, but with benzene the front is sharp and the rear drawn out. These results are in agreement with the theory of ideal nonlinear chromatography and fill the gap apparently existing in gas–solid chromatography till now: when the isotherm begins convex to the pressure axis the chromatographic peak has a diffuse front and a sharp rear.

Graphitized carbon blacks can substitute non-polar liquids. In addition, other thermally stable crystals with homogeneous surfaces could also be employed as immobile phases. By the use of various polar adsorbents with homogeneous surfaces, adsorption columns with a great variety of properties can be obtained for operation at any high temperature desired. The results of our adsorption studies show that by altering the surface chemistry of solids we can change their adsorptive capacities up to several hundredfold[9,37]. Of course, we must try to obtain crystalline adsorbents with homogeneous surfaces in a granulated form, so as to be able to use them in a chromatographic column without the need for any support. This would make things much more simple and would extend the range of operating temperatures still further.

Porous Glasses and Porous Crystals

Porous glasses are of very great interest for gas chromatography as adsorbents and supports, and as materials for porous capillary columns. Their structure can easily be controlled by the choice of the chemical composition of the starting material and the conditions of heat treatment and leaching.

Thus we can prepare porous glasses with uniform pore sizes ranging from molecular dimensions to 1,000 Å, but also glasses with a peculiar bidisperse structure, in which pores of various types with greatly different size predominate[38]. A glass with small pores for adsorption and large pores which serve as transport channels will be particularly favourable for gas chromatographic purposes.

A glass containing 7 mole per cent Na_2O, 23 mole per cent B_2O_3 and 70 mole per cent SiO_2 was heat-treated and ground, and the 0·25–0·5 mm fraction was treated with 3N HCl at 50°C, washed with water and dried in air at 250°C. A test mixture containing methane, ethane and ethylene was then separated on a column packed with the material thus prepared[40]. Methane and ethane have a comparatively homogeneous structure (σ-bonds only) and adsorption is due mainly to universal dispersion interactions with the adsorbent. The electron density in the ethylene molecule is less uniform

(π-bonds); the molecule therefore also interacts with the hydroxyl groups on the glass surface[13,39]. *Figure 15* shows that even at 80°C the three components of the test mixture could be separated on the porous glass column. In contrast, ethane could not be separated from ethylene on ordinary silica gel at 50°C.

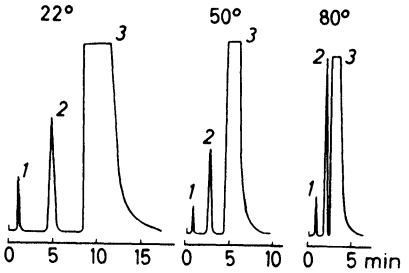


Figure 15. Chromatograms of 0·015 per cent methane (1) and 0·1 per cent ethane (2) in ethylene (3) on porous glass. Column length 2 m; sample size 0·2 ml; carrier gas 33 ml hydrogen/min

Another interesting possibility is the formation of a film of porous glass on the inner surface of a glass capillary to be used in the capillary version of gas adsorption chromatography. A capillary 0·5 mm in diameter and 10 m long was drawn from a tube of sodium borosilicate glass of the composition indicated above. After heat treatment the inner surface was etched with

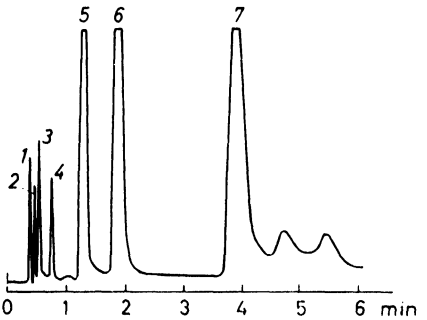


Figure 16. Chromatograms of methane (1), ethane (2), ethylene (3), propane (4), propylene (5), n-butane (6) and iso-butylene (7) on a glass capillary with a 0·1 mm porous glass film, at 25°C. Column length 10 m, inside diameter 0·5 mm; sample size 0·05 ml; carrier gas 3·5 ml nitrogen/min

0·1N HCl at 25°C for 5 min and washed with water. The thickness of the resulting porous film, measured with a microscope on fractures of the capillary, was about 0·1 mm. The resulting capillary column was dried in a stream of nitrogen at 150°C; *Figure 16* shows the separation of a mixture of hydrocarbon gases at 25°C.

This example of capillary adsorption chromatography[9,40] indicates that

comparatively short columns may be effective if the surface of their walls is prepared by formation or application of a thin porous coating with favourable geometrical, chemical and adsorptive properties.

Porous zeolite crystals[41] are usually employed as molecular sieves only, i.e. use is made of the fact that the channels of the porous crystals have a size close to that of the molecules being separated. However, for molecules capable of penetrating inside the channels, the chemical factor (the nature of the adsorbate-adsorbent system) stands out in full measure.

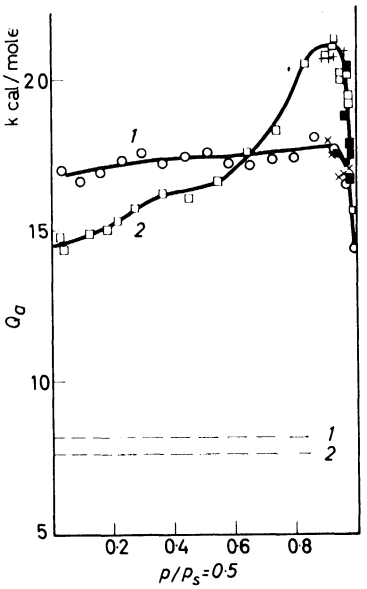


Figure 17. Differential heats of adsorption for benzene (1) and n-hexane (2) on 13 X porous crystals

○ and □: our calorimetric data[42]
+: isosteric heats by Barrer, Bultitude and Sutherland[44]
Dotted lines indicate heats of condensation

The walls of the zeolite channels consist of silicon-oxygen and aluminium-oxygen tetrahedrons, the latter carrying a negative charge which is compensated by cations projecting inside the cavity. The electrostatic field surrounding these cations results in a strong adsorption of dipole and quadrupole molecules, as well as of molecules having π-electron bonds (aromatic and unsaturated hydrocarbons). It is evident from *Figure 17* that in the case of 13 X porous crystals, whose openings are accessible both to n-hexane and to benzene, the heat of adsorption at small coverage is much higher for benzene than for n-hexane[42]. Therefore, porous crystals may be employed to separate mixtures not only in the function of molecular sieves, but as chemically specific adsorbents.

Of very great interest in this respect is the adsorption of n-pentane and diethyl ether, the molecules of which are geometrically similar, so that they

fit equally well in the pores of 5A zeolite[43] (*Figure 18*). However, the heat of adsorption of polar molecules in the zeolite channels is much larger, owing to the interaction with the electrostatic field. In contrast the heats of adsorption on a non-polar adsorbent, such as graphitized carbon black, are comparable, because the dipole moment in the ether molecule does not

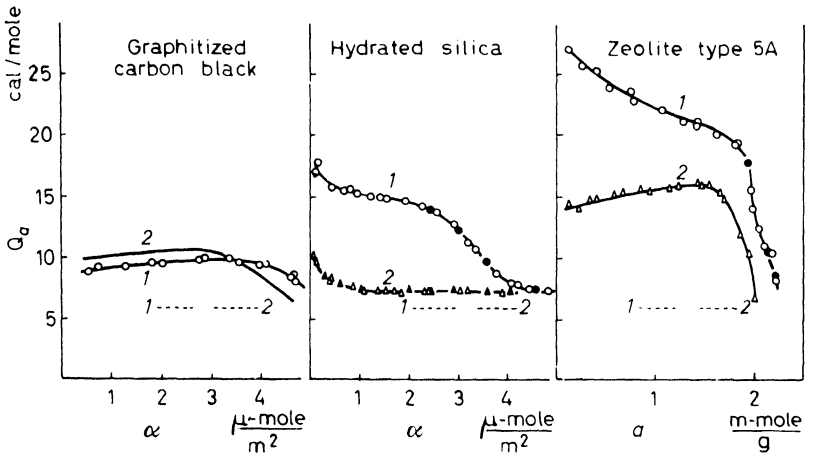


Figure 18. Heats of adsorption for diethyl ether (1) and n-pentane (2) on various adsorbents. Dotted lines indicate heats of condensation

manifest itself to any significant extent. It can be seen from *Figure 18* that the heat of adsorption in zeolite channels is almost twice as large for ether as for pentane. This is a striking example of the possibility of employing zeolites for the separation of molecules on the basis of their electronic structure, rather than their geometric dimensions. Further examples of the study of heats of adsorption by zeolites are given in the paper by Shcherbakova (page 18).

Conclusion

The ways of modifying solids (adsorbents, inert supports, capillary column walls) for gas chromatography discussed in this lecture show that, in addition to improvement of chromatographic equipment, such as we have seen in the exhibition in this building, and to improvement of immobile liquids, the important task for the further progress of gas chromatography is the improvement of the solid bodies used therein. Such solid bodies are primarily uniformly porous adsorbents with surfaces modified by both inert and active groups; secondly, inert porous supports for liquid and solid phases; thirdly, dispersed solids with homogeneous non-polar and polar surfaces to be used as, e.g., immobile solid phases, either supported in the pores of inert carriers for use at high temperatures, or without any support; and, fourthly, capillaries with geometrically and chemically prepared walls for optimum operation in gas–liquid and gas–solid chromatography.

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SECTION I

THEORY

Chairmen:

G. HESSE

A. T. JAMES

PANEL DISCUSSION

LARGE-SCALE GAS CHROMATOGRAPHY

Chairman: F. H. HUYTEN

1

NON-EQUILIBRIUM THEORY OF CAPILLARY COLUMNS AND THE EFFECT OF INTERFACIAL RESISTANCE ON COLUMN EFFICIENCY

M. A. KHAN

Shell Research Ltd., Thornton Research Centre, Chester, Great Britain

A non-equilibrium theory of capillary columns is presented. This, unlike other theories, is free from the restriction of dynamic equilibrium at any point within the column, and thus it offers a more realistic picture of the chromatographic process, which constitutes a flow system.

The theory is based on simple laws of linear kinetics. The mathematical treatment is direct and unified. The simultaneous solution of the fundamental partial differential equations is sought by the technique of Laplace transformation, without resort to the concept of a moving axis applied hitherto. To simplify the procedure, the results are interpreted in terms of the Laplace-transformed concentrations (of the effluent) rather than the concentrations themselves.

Expressions for the retention time and HETP are derived, and it emerges directly from the analysis that the contributions of all the disturbing factors to HETP are additive. The expression for HETP shows how the interfacial resistance, arising from the non-attainment of equilibrium at the gas–liquid interface, affects the column efficiency. For the particular case of interfacial equilibrium, the expression for HETP reduces to exactly the same form as that first derived by Golay.

The accommodation coefficient of a given component is taken as equal to the free angle ratio, and an expression is theoretically developed which permits the calculation of the absorption rate constant. Finally, the theory is applied to the acetone-chloroform system, for which the requisite data are readily available in the literature. Numerical calculations show how, for this system, HETP is mainly determined by interfacial resistance.

WHEN a solute is injected into a solvent flowing slowly through a narrow tube, it spreads out under the combined influence of molecular diffusion and convection. This complex phenomenon was first analysed by Taylor[1] in 1953. He showed that, in spite of the variation of velocity over the tube cross-section, the solute distributes itself symmetrically about a point which moves with the mean speed of flow. About three years later, Aris[2] gave a more rigorous analysis of the same problem. He not only removed the restrictions which Taylor imposed on his analysis, but his treatment is also more general, i.e. it is not restricted to any particular flow profile or to any particular geometry of the tube cross-section.

Golay[3] extended Taylor's method to circular and rectangular tubes, the walls of which are coated with a thin layer of stationary phase. Not long after Golay had presented his theory of capillary columns at the Amsterdam Gas Chromatography Symposium in 1958, Aris[4] published his work 'On the dispersion of a solute by diffusion, convection and exchange between the

phases'. Aris's treatment is a slight generalization of Golay's results in so far as a practical column is concerned.

Golay's theory of capillary columns has laid the ground work for a great many applications in chromatography and has been the subject of active study. However, it is based on the postulate of interfacial equilibrium, which implies that if concentration on the liquid-phase side of the interface is specified, the concentration at the gas-phase side of the interface would be the same as if the two phases had been in contact with each other for an indefinitely long period of time. Owing to the continuous flow of the carrier gas, it is highly unlikely that the molecules which have once escaped from the surface would strike the same spot again. This obviously presents conceptual difficulties regarding the nature and application of dynamic equilibrium within the column. A natural consequence of the assumption of interfacial equilibrium is that once the diffusing molecules strike the interface they enter the solution without any resistance. Discrepancies between the calculated and observed rates of gas absorption[5,6,7], experiments on the diffusion of a third component across the interface between two liquids which are free from any contamination[8,9], and the fall in efficiency of liquid–liquid extraction on addition of certain surface active agents[10,11] all demonstrate the presence of resistance to mass-transfer at the interface. Nevertheless there are indications in the literature[12,13] that interfacial resistance (IR) is not an important factor. In spite of the apparent contradictory nature of the data, the role of IR cannot be overlooked. In fact, in certain cases, IR might be a rate-controlling step. Hence it is not always safe to assume equilibrium conditions at the interface, as has hitherto been done.

Dynamic behaviour of capillary columns

Consider a circular capillary having a uniform area of cross-section. Let the wall of the capillary be wetted with a thin even film of a stationary liquid. Imagine a stream of an inert gas, insoluble in the liquid phase, passing continuously through the tube. Introduce a solute sample into the column in the form of a pulse of constant concentration (C_0) over the injection period ϵ. Mathematically speaking:

$$\text{For } x = 0 \qquad \left\{\begin{array}{lll} C_g^* = C_0 & \text{when} & 0 < t \leqslant \epsilon \\ C_g^* = 0 & \text{when} & t > \epsilon \end{array}\right\} \tag{1}$$

The combined effect of radial and longitudinal diffusion, and convection in the mobile phase is governed by the equation:

$$D_g\left(\frac{\partial^2 C_g}{\partial r^2}+\frac{1}{r}\frac{\partial C_g}{\partial r}+\frac{\partial^2 C_g}{\partial x^2}\right)-2u^*\left(1-\frac{r^2}{r_0^2}\right)\frac{\partial C_g}{\partial x}-\frac{\partial C_g}{\partial t}=0 \tag{1a}$$

By making a material balance on a section of differential length dx, we may write the equation for the combined effect of convection, diffusion and exchange of solute between the two phases:

$$D_g\frac{\partial^2 C_g^*}{\partial x^2}-\frac{4u^*}{r_0^2}\int_0^{r_0}\frac{\partial C_g}{\partial x}\left(1-\frac{r^2}{r_0^2}\right)r\mathrm{d}r-\frac{\partial C_g^*}{\partial t}-\frac{F_l}{F_g}\frac{\partial C_l^*}{\partial t}=0 \tag{2}$$

The equation for transverse diffusion in the stationary phase may be expressed as:

$$D_l \frac{\partial^2 C_l}{\partial z^2} = \frac{\partial C_l}{\partial t} \tag{3}$$

The net transfer of solute across the interface (into the liquid phase) at any given instant at any point of the tube is given by:

$$F_l \frac{\partial C_l^*}{\partial t} = k_a \Gamma (C_g)_i - k_d \Gamma (C_l)_i \tag{4}$$

Taking the Laplace transform with respect to t of eqns (3) and (4) and putting $F_l = \Gamma d_f$, we obtain for an initially empty column:

$$D_l \frac{\partial^2 \bar{C}_l}{\partial z^2} - s\bar{C}_l = 0 \tag{5}$$

and

$$s d_f \overline{C_l^*} - k_a (\bar{C}_g)_i + k_d (\bar{C}_l)_i = 0 \tag{6}$$

Evaluation of $(\bar{C}_g)_i$

Let

$$C_g = C_g^* + \Delta C_g \tag{7}$$

so that

$$\int_0^{r_0} \Delta C_g r \, dr \equiv 0 \tag{8}$$

In order to evaluate ΔC_g, representing small radial variations in C_g, let us introduce the approximation already used by Golay:

$$\Delta C_g \leqslant C_g^* \tag{9}$$

Making use of this approximation and combining (1a) and (2), we have:

$$\frac{\partial^2}{\partial r^2}(\Delta C_g) + \frac{1}{r}\frac{\partial}{\partial r}(\Delta C_g) - \frac{u^*}{D_g}\left(1 - 2\frac{r^2}{r_0^2}\right)\frac{\partial C_g^*}{\partial x} + \frac{F_l}{D_g F_g}\cdot\frac{\partial C_l^*}{\partial t} = 0 \tag{10}$$

Solving for ΔC_g under the condition that ΔC_g remains finite at $r=0$, making use of relation (8), and finally putting $\Delta C_g = C_g - C_g^*$, we obtain:

$$C_g = C_g^* + \frac{u^*}{D_g}\left(\frac{r^2}{4} - \frac{r^4}{8r_0^2} - \frac{r_0^2}{12}\right)\frac{\partial C_g^*}{\partial x} - \frac{1}{D_g}\frac{F_l}{F_g}\left(\frac{r^2}{4} - \frac{r_0^2}{8}\right)\frac{\partial C_l^*}{\partial t} \tag{11}$$

At $r = r_0$, we have:

$$(C_g)_i = C_g^* + \frac{u^* r_0^2}{24 D_g}\frac{\partial C_g^*}{\partial x} - \frac{r_0^2}{8 D_g}\frac{F_l}{F_g}\frac{\partial C_l^*}{\partial t} \tag{12}$$

Or, on taking the Laplace transform of all the members with respect to t, we have:

$$(\bar{C}_g)_i = \overline{C_g^*} + \frac{u^* r_0^2}{24 D_g}\frac{d\overline{C_g^*}}{dx} - \frac{r_0^2}{8 D_g}\frac{F_l}{F_g} s\overline{C_l^*} \tag{13}$$

Also, substituting the value of $(\bar{C}_g)_i$ in eqn (6), we get:

$$s\,\mathrm{d}_f\overline{C_l^*} - k_a\left(\overline{C_g^*} + \frac{u^* r_0^2}{24 D_g}\frac{\mathrm{d}\overline{C_g^*}}{\mathrm{d}x} - \frac{r_0^2 F_l}{8 D_g F_g}\cdot s\overline{C_l^*}\right) + k_d(\bar{C}_l)_i = 0 \qquad (14)$$

Evaluation of $(\bar{C}_l)_i$

Taking the Laplace transform of eqn (5) with respect to x:

$$D_l\frac{\mathrm{d}^2\bar{\bar{C}}_l}{\mathrm{d}z^2} - s\bar{\bar{C}}_l = 0 \qquad (15)$$

The boundary conditions for this equation are:

$$\begin{cases} \bar{\bar{C}}_l = (\bar{C}_l)_i & \text{for } z = 0 \qquad (15a) \\ \dfrac{\mathrm{d}\bar{\bar{C}}_l}{\mathrm{d}z} = 0 & \text{for } z = d_f \qquad (15b) \end{cases}$$

The boundary condition (15b) expresses the fact that the wall of the tube is impermeable to the diffusing molecules.

The solution of (15) for the above boundary conditions, when expressed in $\bar{C}_l$, is given by:

$$\bar{C}_l = \{\cosh[(s/D_l)^{\frac{1}{2}}\cdot z] - \tanh[(s/D_l)^{\frac{1}{2}}\cdot d_f]\cdot\sinh[(s/D_l)^{\frac{1}{2}}\cdot z]\}(\bar{C}_l)_i \qquad (16)$$

Since $C_l^* = \dfrac{1}{d_f}\displaystyle\int_0^{d_f} C_l\,\mathrm{d}z$, the above eqn leads to:

$$(\bar{C}_l)_i = d_f(s/D_l)^{\frac{1}{2}}\coth[(s/D_l)^{\frac{1}{2}}\cdot d_f]\overline{C^*} \qquad (17)$$

Substituting the value of $(\bar{C}_l)_i$ in equation (14) gives:

$$\overline{C_l^*} = \frac{k_a}{k_d}\left\{s\left[\frac{d_f}{k_d} + \frac{r_0^2}{8D_g}\cdot\frac{F_l k_a}{F_g k_d}\right] + (s/D_l)^{\frac{1}{2}} d_f\cdot\coth[(s/D_l)^{\frac{1}{2}}\cdot d_f]\right\}^{-1} \times\left(\overline{C_g^*} + \frac{u^* r_0^2}{24 D_g}\frac{\mathrm{d}\overline{C_g^*}}{\mathrm{d}x}\right) \qquad (18)$$

Solution of eqn (2)

Differentiating eqn (11) with respect to x, we get:

$$\frac{\partial C_g}{\partial x} = \frac{\partial C_g^*}{\partial x} + \frac{u^*}{D_g}\left(\frac{r^2}{4} - \frac{r^4}{8r_0^2} - \frac{r_0^2}{12}\right)\frac{\partial^2 C_g^*}{\partial x^2} - \frac{F_l}{D_g F_g}\left(\frac{r^2}{4} - \frac{r_0^2}{8}\right)\frac{\partial^2 C_l^*}{\partial x\partial t} \qquad (19)$$

Hence

$$\frac{4u^*}{r_0^2}\int_0^{r_0}\left(1 - \frac{r^2}{r_0^2}\right)\frac{\partial C_g}{\partial x}\,r\,\mathrm{d}r = u^*\frac{\partial C_g^*}{\partial x} - \frac{(u^* r_0)^2}{48 D_g}\frac{\partial^2 C_g^*}{\partial x^2} + \frac{u^* r_0^2}{24 D_g}\frac{F_l}{F_g}\frac{\partial^2 C_l^*}{\partial x\partial t} \qquad (20)$$

Making this substitution in eqn (2):

$$\left(D_g + \frac{u^{*2} r_0^2}{48 D_g}\right)\frac{\partial^2 C_g^*}{\partial x^2} - u^*\frac{\partial C_g^*}{\partial x} - \frac{\partial C_g^*}{\partial t} - \frac{F_l}{F_g}\left(\frac{\partial C_l^*}{\partial t} + \frac{u^* r_0^2}{24 D_g}\frac{\partial^2 C_l^*}{\partial x\partial t}\right) = 0 \qquad (21)$$

Taking the Laplace transform with respect to t and further assuming that the order of integration and differentiation can be interchanged, we obtain:

$$\left(D_g+\frac{u^{*2}r_0^2}{48D_g}\right)\frac{d^2\overline{C_g^*}}{dx^2}-u^*\frac{d\overline{C_g^*}}{dx}-\frac{F_l}{F_g}s\left(\overline{C_l^*}+\frac{u^*r_0^2}{24D_g}\frac{d\overline{C_l^*}}{dx}\right)-s\overline{C_g^*}=0 \quad (22)$$

Substituting the value of $\overline{C_l^*}$ from eqn (18), the above equation may be cast in the form:

$$A\frac{d^2\overline{C_g^*}}{dx^2}-\frac{d\overline{C_g^*}}{dx}-B\,\overline{C_g^*}=0 \quad (23)$$

where

$$A=(u^*\theta)^{-1}\left[2\frac{F_lk_a}{F_gk_d}r_0^2+\left(D_g+\frac{u^{*2}r_0^2}{48D_g}\right)\left(\frac{F_lk_a}{F_gk_d}\cdot\frac{r_0^2}{D_g}+24\psi\right)\right] \quad (23a)$$

$$B=(u^*\theta)^{-1}\left[3\frac{F_lk_a}{F_gk_d}\left(8+\frac{r_0^2}{D_g}s\right)+24s\psi\right] \quad (23b)$$

$$\theta=5\frac{F_lk_a}{F_gk_d}\cdot\frac{r_0^2}{D_g}+24\psi \quad (23c)$$

and

$$\psi=\frac{d_f}{k_d}+\frac{d_f}{(sD_l)^{\frac{1}{2}}}\coth\left[(s/D_l)^{\frac{1}{2}}\cdot d_f\right] \quad (23d)$$

Taking the Laplace transform with respect to t of eqn (1) we have:

$$\text{(i)}\ \overline{C_g^*}=\frac{C_0}{s}(1-e^{-\epsilon s}) \quad \text{when} \quad x=0$$

Also, C_g^* remains finite for any column length. We therefore have:

$$\text{(ii)}\ \overline{C_g^*} \text{ remains finite when } x\to\infty$$

Eqn (23) is a second order linear differential equation with constant coefficients. The required solution, obeying the above boundary conditions (i) and (ii), for $x=L$, is given by:

$$\frac{\overline{C_g^*}}{\epsilon C_0}=\left(1-\frac{\epsilon s}{2!}+\frac{\epsilon^2s^2}{3!}+\cdots\right)\exp\left\{\frac{L}{2A}\left[1-(1+4AB)^{\frac{1}{2}}\right]\right\} \quad (24)$$

Differentiating with respect to s and taking limits of the first and second derivatives for $s\to 0$, we have:

$$\lim_{s\to0}\frac{d}{ds}\left(\frac{\overline{C_g^*}}{\epsilon C_0}\right)=-\frac{\epsilon}{2}-\frac{L}{u^*}\left(1+\frac{F_lk_a}{F_gk_d}\right)$$

$$=-\frac{\epsilon}{2}-\frac{L}{u^*}\left(1+K\frac{F_l}{F_g}\right)=-\frac{\epsilon}{2}-\frac{L}{u^*}(1+k') \quad (25)$$

$$\lim_{s\to0}\frac{d^2}{ds^2}\left(\frac{\overline{C_g^*}}{\epsilon C_0}\right)=\frac{\epsilon^2}{12}+\left\{\frac{\epsilon}{2}+\frac{L}{u^*}(1+k')\right\}^2+\frac{2L}{u^*}\frac{k'}{k_d}d_f+\frac{2}{3}\frac{L}{u^*}k'\frac{d_f^2}{D_l}$$

$$+\frac{L}{u^{*2}}(1+k')^2\left\{\frac{2D_g}{u^*}+\frac{1+6k'+11k'^2}{24(1+k')^2}\frac{u^*r_0^2}{D_g}\right\} \quad (26)$$

It has been shown by van der Laan[14] that

$$\lim_{s\to 0} \frac{\mathrm{d}}{\mathrm{d}s}\left(\frac{\overline{C_g^*}}{\epsilon C_0}\right) = -t_R \tag{27}$$

$$\lim_{s\to 0} \frac{\mathrm{d}^2}{\mathrm{d}s^2}\left(\frac{\overline{C_g^*}}{\epsilon C_0}\right) = \sigma_t^2 + t_R^2 \tag{28}$$

Comparison of eqns (25) and (27) gives the retention time.

$$t_R = \frac{1}{2}\epsilon + \frac{L}{u^*}(1+k') \tag{29}$$

Again, comparing eqns (26) and (28) and dividing both sides by $t_r^2 = \{L(1+k')/u^*\}^2$, we obtain:

$$\frac{\sigma_t^2}{t_r^2} = \frac{1}{12}\frac{\epsilon^2}{t_r^2} + \frac{1}{L}\left[\frac{2D_g}{u^*} + \frac{1+6k'+11k'^2}{24(1+k')^2}\cdot\frac{u^* r_0^2}{D_g}\right] + 2\frac{u^*}{L}\frac{k'}{(1+k')^2}\frac{d_f}{k_d} + \frac{2}{3}\frac{u^*}{L}\frac{k'}{(1+k')^2}\frac{d_f^2}{D_l} \tag{30}$$

It can be shown from the plate theory that the absolute variance is given by

$$\frac{\sigma_v^2}{V_r^2} = \frac{1}{12}\frac{V_0^2}{V_r^2} + \frac{1}{n} \tag{31}$$

Comparing eqn (30) with eqn (31), recalling that $L/n = H$, we finally obtain:

$$H = \underbrace{\frac{2D_g}{u^*}}_{(1)} + \overbrace{\frac{1+6k'+11k'^2}{24(1+k')^2}\cdot\frac{u^* r_0^2}{D_g}}^{\text{Gas Phase Resistance}}_{(2)} + \overbrace{2\frac{k'}{(1+k')^2}\cdot\frac{d_f}{k_d}u^*}^{\text{Interfacial Resistance}}_{(3)} + \overbrace{\frac{2}{3}\frac{k'}{(1+k')^2}\frac{d_f^2}{D_l}\cdot u^*}^{\text{Liquid Phase Resistance}}_{(4)} \tag{32}$$

Terms (1), (2) and (4) are the ones already derived by Golay; whereas the inclusion of term (3) was first suggested by the author[15]. The present treatment removes the restriction of interfacial equilibrium which Golay imposed on his analysis. That the removal of this restriction should have some physical meaning is seen by the appearance of an additional resistance to mass transfer at the interface. Also, the present study demonstrates the validity of the principle of additivity of variances first applied by Klinkenberg and Sjenitzer[16] to chromatographic processes. The effects of longitudinal and radial diffusion in the mobile phase, and of transverse diffusion in the liquid phase, on column efficiency have already been investigated in some detail[17,18]. Here we shall critically examine the role played by interfacial resistance, giving the theoretical basis of the rate constant k_a (or k_d).

Theoretical prediction of interfacial resistance

According to the kinetic theory of gases, the number of moles, G, of substance 1 striking unit area of a liquid surface in unit time is given by the well-known Knudsen[19] equation:

$$G = p_1(2\pi M_1 RT)^{-\frac{1}{2}} \tag{33}$$

If every collision with the surface results in condensation, G should represent the rate of condensation (absorption) of the vapour of substance 1 per unit surface area. However, for various reasons, all the collisions with the surface may not lead to condensation and hence the rate of condensation, G', should be represented as:

$$G' = \alpha \cdot p_1 (2\pi M_1 RT)^{-\frac{1}{2}} = \alpha \left(\frac{RT}{2\pi M_1}\right)^{\frac{1}{2}} C_{g_1} \tag{34}$$

According to the notation used in the preceding pages:

$$G' = k_a C_{g_1} \tag{35}$$

Hence

$$k_a = \alpha \left(\frac{RT}{2\pi M_1}\right)^{\frac{1}{2}} = 0{\cdot}399\alpha \left(\frac{RT}{M_1}\right)^{\frac{1}{2}} \tag{36}$$

In connection with his investigations on the condensation and reflection of molecules, Knudsen[20] measured the accommodation coefficient of mercury vapour on the surface of pure liquid mercury. His experiments showed that α was unity, so he concluded that every collision with the mercury surface led to condensation. This, however, leaves open the question whether the accommodation coefficient is unity when the underlying liquid surface consists of complex molecules.

Using the molecular effusion technique, Wyllie[21] studied the condensation of glycerol vapour on its own surface, and found a value of 10^{-2} for α. From the data of Higbie[22] on the absorption of carbon dioxide in water, Danckwerts[23] calculated the value of α to be 4×10^{-6}. Emmert and Pigford[5] give a value of $3{\cdot}7 \times 10^{-8}$ for α calculated from the experiments of Peaceman[24] on the solubility of oxygen in water. When α has a value of 10^{-4} or less, the IR, as we shall see later, becomes the rate-controlling step in the exchange of solute between the two phases.

Evaluation of the absorption rate constant k_a

It is clear from eqns (33) and (34) that α is the ratio between the observed and calculated rates of condensation. It may be taken to represent the probability of a molecule (hitting the surface) being caught by the surface. Statistical theories have been advanced which express α in terms of physical constants of the substances involved.

Wyllie[21] was the first to identify the accommodation coefficient with the free angle ratio: i.e.

$$\alpha = \delta = j_{l_1} j_{g_1}{}^{-1} \tag{37}$$

From the work of Hirschfelder and co-workers[25] it can be shown that for a binary liquid mixture:

$$j_{l_1} j_{g_1}{}^{-1} = \frac{x_1 kT}{p_1 v_{fm}} \exp\left\{\frac{\Delta_s H_1}{RT} - \frac{n_1 + n_2}{v_{fm}} \frac{\partial v_{f_m}}{\partial n_1}\right\} \tag{38}$$

Combining eqns (36), (37) and (38), we have:

$$k_a = 0{\cdot}399(M_1)^{-\frac{1}{2}} \cdot \frac{(RT)^{\frac{3}{2}}}{\gamma_1 p_1{}^0 V_{fm}} \exp\left\{\frac{\Delta_s H_1}{RT} - \frac{n_1+n_2}{v_{fm}} \frac{\partial v_{f_m}}{\partial n_1}\right\} \tag{39}$$

According to Eyring[26] the free volume of a pure liquid can be expressed as:

$$V_f = \lambda^3(V^{\frac{1}{3}} - 0{\cdot}7816\, b^{\frac{1}{3}})^3 \tag{40}$$

If λ is assumed to remain sensibly constant over the range of concentrations studied, the total free volume of a binary liquid mixture containing n_1 molecules of component 1 and n_2 molecules of component 2 may be expressed by:

$$V^{\frac{1}{3}}{}_{f_m} = \lambda[V^{\frac{1}{3}}{}_m - 0{\cdot}7816(b_1 - b_1 X_2 + b_2 X_2)^{\frac{1}{3}}] \tag{41}$$

On differentiating with respect to X_2, making use of the thermodynamic relation

$$\bar{V}_1 = V_m - X_2 \frac{\partial V_m}{\partial X_2} \text{ so that } \frac{X_2}{V_m}\frac{\partial V_m}{\partial X_2} = 1 - \frac{\bar{V}_1}{V_m}$$

we obtain:

$$\frac{n_1+n_2}{v_{fm}} \frac{\partial v_{f_m}}{\partial n_1} = -\lambda\left[\left(1-\frac{\bar{V}_1}{V_m}\right)\left(\frac{V_m}{V_{fm}}\right)^{\frac{1}{3}} - 0{\cdot}7816\, X_2 (b_m{}^2 V_{f_m})^{-\frac{1}{3}}(b_2 - b_1)\right] \tag{42}$$

Making this substitution in eqn (39) and letting $X_2 \to 1$, we have for infinitely dilute solutions:

$$k_a = \frac{0{\cdot}399(RT)^{\frac{3}{2}}}{\sqrt{M_1}\gamma_1 p_1{}^0 V_{f_2}} \exp\left[\frac{\overset{\infty}{\Delta_s H_1}}{RT} + \lambda\left\{\left(1-\frac{\overset{\infty}{\bar{V}_1}}{V_2}\right)\left(\frac{V_2}{V_{f_2}}\right)^{\frac{1}{3}} - 0{\cdot}7816\left(\frac{b_2}{V_{f_2}}\right)^{\frac{1}{3}}\frac{b_2-b_1}{b_2}\right\}\right] \tag{43}$$

Using the statistical thermodynamic relationship between pressure and partition function for the free volume model of liquids consistent with eqns (38) and (42), we obtain:

$$\left(P + \frac{a}{V^2}\right) = RT \frac{\partial \ln V_f}{\partial V} \tag{44}$$

The molar free volume of a liquid in which the molecules remain in a face-centred cubic arrangement is given by (*loc. cit.*)

$$V_f = 9(V^{\frac{1}{3}} - 0{\cdot}7163\, b^{\frac{1}{3}})^3 \tag{45}$$

Combining eqn (44) with eqn (40), and eqn (44) with eqn (45) we have:

$$\left(P + \frac{a}{V^2}\right)(V - 0{\cdot}7816\, V^{\frac{1}{3}} b^{\frac{1}{3}}) = RT \tag{46}$$

and

$$\left(P + \frac{a}{V^2}\right)(V - 0{\cdot}7163\, V^{\frac{1}{3}} b^{\frac{1}{3}}) = RT \tag{47}$$

By combination of eqn (47) (valid for dense liquids) with the Happel–Majumdar equation of state (valid for moderately concentrated gases), Eyring and co-workers[26] obtain:

$$\left(P+\frac{a}{V^2}\right) = RT\left[1+\left(\frac{b}{V}\right)+0{\cdot}625\left(\frac{b}{V}\right)^2+0{\cdot}2869\left(\frac{b}{V}\right)^3+0{\cdot}1928\left(\frac{b}{V}\right)^4\right] \quad (48)$$

Provided the experimental values of a, and P, V and T are given, b can be determined. Obviously, the value of b appearing in eqn (46) would be $(0{\cdot}7163/0{\cdot}7816)^3$ times the value of b derived from the Happel–Majumdar–Eyring (HME) equation given in eqn (48).

The precise determination of λ is possible only if b and V_f are accurately known. There are various ways of determining V_f, but we shall prefer the one given by Kincaid and Eyring[27].

Our primary aim is to apply eqn (43) to systems which are of direct interest in gas–liquid chromatography, i.e. systems in which the solvent is practically non-volatile. Unfortunately, the physical constants required by eqn (43) are not available for such systems.

The scope of gas–liquid chromatography is, however, not restricted to non-volatile solvents. The application of the technique has been usefully extended to systems in which both the solute and the solvent are volatile[28]. Hofstee, Kwantes and Rijnders[29] have shown that gas–liquid chromatography can even be applied to determine the activity coefficients of solutes which are less volatile than the solvents.

We shall, for the present, apply eqn (43) to determine the absorption rate constant of acetone (component 1) in chloroform (component 2) and thence calculate the interfacial resistance for this system.

The acetone–chloroform system

There is no special reason for selecting this system except that thermodynamically it is a classical system for which the necessary physical constants and the relevant thermodynamic functions are either directly available or can be calculated from existing data. We shall study the system at 25°C and at normal atmospheric pressure.

Analysing the calorimetric data by Schmidt[30] on the heat of mixing of acetone–chloroform mixtures at 287·2°K, we find that these data can be represented by the quadratic expression:

$$\frac{\Delta_m H}{X_1 X_2} = 2165-467{\cdot}7(X_1-X_2)-391{\cdot}7(X_1-X_2)^2, \text{ giving } \Delta\bar{H}_1^{\infty} = -2.24 \text{ kcal}$$

Taking 7·73 kcal as the molar heat of vaporization of acetone[31], we get:

$$\Delta_s H_1 = -(7{\cdot}73+2{\cdot}24) = -9{\cdot}97 \text{ kcal}$$

The vapour pressure data of Zawidzki[32] and those of Rosanoff and Easley[33] show that acetone–chloroform mixtures approximately obey the van Laar theory. Taking $\Delta W = -569$ cal, as calculated from Zawidzki's data[31], we have:

$$\log \gamma_1^{\infty} = -\frac{569}{2{\cdot}303\times 1{\cdot}987\times 298{\cdot}2} \quad \therefore \gamma_1^{\infty} = 0{\cdot}38$$

Taking $a_1 = 17{\cdot}90$ atm l.^{2} mole^{-2} as the cohesive constant[34]; $P_c = 46{\cdot}6$ atm; $T_c = 508{\cdot}7°$K; $V_c = 212{\cdot}7$ cm^3 as the critical constants[35] for acetone, and then making these substitutions in the HME equation, we obtain:

$$(b_1)\text{HME} = 157{\cdot}2 \text{ cm}^3 \text{ mole}^{-1}, \text{ so that } b_1 = 157{\cdot}2\left(\frac{0{\cdot}7163}{0{\cdot}7816}\right)^3 = 121 \text{ cm}^3 \text{ mole}^{-1}.$$

Similarly for chloroform: $b_2 = 154{\cdot}9$ cm^3 mole^{-1}.

With 0·286 cm^3 as the molar free volume of chloroform, calculated from the Kincaid–Eyring relation, eqn (40) leads to:

$$\lambda = (0{\cdot}286)^{\frac{1}{3}}\{(80{\cdot}69)^{\frac{1}{3}} - 0{\cdot}7816(154{\cdot}9)^{\frac{1}{3}}\}^{-1} = 5{\cdot}36$$

Using 226·5 mm (Hg) as the vapour pressure of acetone at 298·2°K and substituting the values of the various factors calculated above, we find that:

$$\frac{0{\cdot}399}{\sqrt{M_1 \gamma_1 V_{f_2}}} \cdot \frac{(RT)^{\frac{1}{3}}}{p_1^{\,0}} = 6{\cdot}223 \times 10^9 \text{ cm sec}^{-1}$$

$$\frac{\Delta_s H_1}{RT} = -\frac{9{\cdot}97 \times 10^3}{1{\cdot}987 \times 298{\cdot}2} = -16{\cdot}83$$

Taking 72·74 cm^3 as the value of $\overset{\infty}{V}_1$ for acetone[31], we have:

$$\lambda\left[\left(1 - \frac{\overset{\infty}{V}_1}{V_2}\right)\left(\frac{V_2}{V_{f_2}}\right)^{\frac{1}{3}} - 0{\cdot}7816\left(\frac{b_2}{V_{f_2}}\right)^{\frac{1}{3}}\frac{b_2 - b_1}{b_2}\right] = -4{\cdot}02$$

Hence

$$k_a = 6{\cdot}223 \times 10^9 \exp(-16{\cdot}83 - 4{\cdot}02) = 5{\cdot}48 \text{ cm sec}^{-1}$$

Absolute values of three resistances

We can now calculate, for the acetone–chloroform system, the values of the individual coefficients representing the three mass transfer resistances.

Using the formula, $K_1 = \dfrac{\rho_2 RT}{M_2 \gamma_1 \overset{\infty}{p}_1}$, we find that at 25°C the partition coefficient K_1 is equal to $2{\cdot}68 \times 10^3$.

Let us now consider a typical capillary column for which

$$r_0 = 0{\cdot}02 \text{ cm}; \; d_f = 0{\cdot}2\ \mu = 2 \times 10^{-5} \text{ cm}; \; \frac{F_l}{F_g} = 2 \times 10^{-3}$$

so that $k' = (2 \times 10^{-3}) \times (2{\cdot}68 \times 10^3) = 5{\cdot}36$.

(i) *Gas-phase resistance* (c_g). We know that $k_d = k_a/K \therefore k_d = \dfrac{5{\cdot}48}{2{\cdot}68 \times 10^3} = 2{\cdot}04 \times 10^{-3}$ cm sec^{-1}.

Norman and Hu[36] give a value of 0·0944 cm^2 sec^{-1} at 292°K for the diffusivity of acetone in air. According to Arnold[37], the diffusivity D_g at 298·2°K can be calculated as 0·0983 cm^2 sec^{-1}.

Substituting the above values we have:

$$c_g = \frac{1+6k'+11k'^2}{24(1+k')^2} \cdot \frac{r_0^2}{D_g}$$

$$= \frac{1+6\times 5{\cdot}36+11\times(5{\cdot}36)^2}{24(1+5{\cdot}36)^2} \times \frac{(0{\cdot}02)^2}{0{\cdot}0983} = 14{\cdot}64\times 10^{-4} \text{ sec}$$

(ii) *Interfacial resistance* (c_i). Using the above values, we calculate:

$$c_i = 2\,\frac{k'}{(1+k')^2} \cdot \frac{d_f}{k_d} = 2\times \frac{5{\cdot}36}{(1+5{\cdot}36)^2} \cdot \frac{2\times 10^{-5}}{2{\cdot}04\times 10^{-3}} = 2{\cdot}60\times 10^{-3} \text{ sec}$$

(iii) *Liquid-phase resistance* (c_l). Examining the experimental values of diffusivities for different systems tabulated by Johnson and Babb[38], we find that at 288·2°K the diffusivity of acetone in chloroform for a very dilute solution is $2{\cdot}36\times 10^{-5}$ cm^2 sec^{-1}. Making use of the relation established by Wilke and Chang[39], we calculate the diffusivity at 298·2°K as $2{\cdot}68\times 10^{-5}$ cm^2 sec^{-1}.

The liquid-phase resistance is, therefore, given by:

$$c_l = \frac{2}{3}\,\frac{k'}{(1+k')^2} \cdot \frac{d_f^2}{D_l} = \frac{2}{3} \cdot \frac{5{\cdot}36}{(1+5{\cdot}36)^2} \cdot \frac{(2\times 10^{-5})^2}{2{\cdot}68\times 10^{-5}} = 1{\cdot}32\times 10^{-6} \text{ sec}$$

Remembering that $2D_g = 2\times 0{\cdot}0983 = 19{\cdot}66\times 10^{-2}$ cm^2 sec^{-1}, we can express the height (H) equivalent to a theoretical plate, as:

$$H = 19{\cdot}66\times 10^{-2}(u^*)^{-1} + 14{\cdot}64\times 10^{-4}u^* + 2{\cdot}60\times 10^{-3}u^* + 1{\cdot}32\times 10^{-6}u^*$$

Using a linear velocity of 20 cm/sec, we have:

$$H \approx \overbrace{0{\cdot}1 \text{ mm}}^{\text{Axial diffusion}} + \overbrace{0{\cdot}29 \text{ mm}}^{\text{Radial diffusion}} + \overbrace{0{\cdot}52 \text{ mm}}^{\text{Interfacial resistance}} + \overbrace{0{\cdot}0003 \text{ mm}}^{\text{Transverse liquid diffusion}}$$

It is clear from the above that for the acetone–chloroform system the HETP, under the conditions stated, is mainly determined by the interfacial resistance. Although interfacial resistance may not play such a dominant role in other systems, it is certainly not always justifiable to assume equilibrium conditions at the interface and to neglect altogether the effect of IR on HETP.

The author is thankful to Dr P. T. Davies for checking the mathematics, and to Miss E. Elliott for her assistance in some of the calculations.

List of symbols

A, B functions depending on s but not on x and r

C concentration (mole cm^{-3})

C^* concentration averaged over the tube cross-section

$\bar{C}$ $= \int_0^\infty e^{-st}\, C\, dt$ (Laplace transform of C with respect to t)

C $= \int_0^\infty e^{-qx}\, \bar{C}\, dx$ (Laplace transform of $\bar{C}$ with respect to x)

D diffusivity of solute ($cm^2\ sec^{-1}$)
F fractional volume
G rate of evaporation per unit surface area (mole $cm^{-2}\ sec^{-1}$)
H height equivalent to a theoretical plate (cm)
$\Delta_m H$ molar heat of mixing (cal $mole^{-1}$)
$\Delta \bar{H}_1$ partial molar heat of mixing for component 1 (cal $mole^{-1}$)
$\Delta_s H_1$ molar heat of solution of component 1 (cal $mole^{-1}$)
K distribution ratio $= \dfrac{\text{moles of solute in unit vol. of liquid phase}}{\text{moles of solute in unit vol. of gas phase}}$
L column length (cm)
L_e latent heat of evaporation (cal $mole^{-1}$)
M molar weight
N total number of molecules in a system
N_0 Avogadro's number
P pressure
R gas constant
T temperature in degrees Kelvin (°K)
ΔW molar interchange energy (cal $mole^{-1}$)
V volume (cm^3)
V_R, V_r retention volumes corresponding to retention times t_R and t_r respectively
X mole fraction in the liquid phase
a cohesive constant (atm $l.^2\ mole^{-2}$)
b = four times the volume occupied by N_0 molecules
c mass transfer resistance (sec)
d incompressible diameter of a molecule (cm)
d_f film thickness (cm)
j molecular rotational partition function
$k' = K\dfrac{F_1}{F_g}$ = capacity ratio
k_a absorption rate constant ($cm\ sec^{-1}$)
k_d desorption rate constant ($cm\ sec^{-1}$)
m molecular weight
n number of molecules
p pressure
q Laplace parameter with respect to x (cm^{-1})
r distance from the tube centre (cm)
r_0 radius of the tube (cm)
s Laplace parameter with respect to t (sec^{-1})
t time (sec)
t_R retention time for finite sample size (sec)
t_r retention time representing the distance between the point of injection and the centroid of the band when the peak is sharp
u velocity of the carrier gas ($cm\ sec^{-1}$)
v molecular volume (cm^3)
x distance measured from the column entrance (cm)
z coordinate perpendicular to the liquid film
Γ surface area per unit column volume (cm^{-1})

α = actual rate of absorption / calculated rate of absorption

γ activity coefficient

δ free angle ratio = rotational partition function of the molecule in the liquid phase / rotational partition function of the molecule in the gas phase

ϵ injection time corresponding to sample volume V_0

λ packing factor describing the arrangement of molecules within the liquid

ρ density (g cm^{-3})

ψ, θ functions depending on s

σ_t, σ_v standard deviations, expressed in time and volume units respectively

Subscripts

c at the critical point

f free volume

g, i, l gas phase, interface and liquid phase respectively

1, 2 solute and solvent respectively

m mixture

Superscripts

∞ at infinite dilution

0 pure substance

$\bar{}$ a partial molar thermodynamic quantity

$*$ average over tube cross-section

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DISCUSSION

A. J. P. Martin: Can you tell me what value of the accommodation coefficient your case with acetone corresponds to?

M. A. Khan: I could not give you the exact figure. It is lower than 10^{-4}.

A. J. P. Martin: The whole procedure of calculating this seems to me to smack rather of black magic. You have taken a number of factors which do not seem to be related and calculated this accommodation coefficient. I am surprised that one can do this calculation at all using only bulk properties. Is there not some special surface factor which should be involved, something affecting the surface only?

M. A. Khan: The difficulty is, that if you introduce certain surface factors, then how are you going to determine them?

A. J. P. Martin: How is it possible to avoid considering surface factors?

M. A. Khan: As I have shown, the treatment is based on transition state theory. You have partition functions of the molecule in the gas and liquid phases, and that for the 'activated complex' with the surface. What you do is, that you evaluate these partition functions and then find out the respective chemical potentials. On equating the chemical potential of the activated complex to those in the gas and liquid phases, you obtain the expression I have derived. This procedure indirectly takes account of the surface factors. Did I understand you correctly?

A. J. P. Martin: I think so, but I am not sure that I understand you.

G. Dijkstra: I have a question on equation 26 (p. 7). The k_a has disappeared; the k_d is still there. I do not see how one of those factors, the absorption rate constant, can disappear on differentiation while the other one remains.

M. A. Khan: That is very simple. If you have a reaction, chemical or physical, going on, you can interpret it in terms of two rate constants, the ratio of which is

the equilibrium constant. You can put $(k')^2$ above and k_a below if you want to, but you can equally well have k' only, if you put k_d below.

A. Goldup: I would not dare to ask Dr Khan a question about his mathematics. At the Edinburgh Symposium, Desty and I presented a paper in which we investigated a number of operating parameters of the coated capillary column, and we found that the agreement between theory and experiment was very poor indeed. I wonder whether Dr Khan would like to comment on whether interfacial resistance in a completely hydrocarbon system might account for this discrepancy.

M. A. Khan: I remember this question being raised at the last Symposium at Edinburgh. Dr Scott has been doing some work on heptane in dinonyl phthalate. His results show that there is no interfacial resistance, or at least, if there is any, it is very small. As I said at the end of the presentation it is not essential that each and every system should show interfacial resistance. It is only experiment which will prove whether it is important or not. Coming to theoretical predictions on your hydrocarbons, where you are using squalane as stationary phase, the trouble is that for the evaluation of k_a you need the free volume of the solvent, which is squalane, and the heat of solution of the solute. If you have these constants, then obviously you could proceed to calculate k_a. Once the absorption rate constant is known, then from column parameters it is possible to determine the interfacial resistance. However, the main difficulty lies in the fact that at the moment there is no figure available for the free volume of squalane.

A. Goldup: No accommodation coefficients have been measured in hydrocarbon systems?

M. A. Khan: Not to my knowledge.

A. Goldup: The second part of my question really concerns terms (2) and (4) (p. 8). If you take a capillary coated with a given film thickness, a constant stationary phase and a constant solute, and you work out the term for resistance to mass transfer in the gas and liquid phases, you get certain values. If you now increase the film thickness—in other words all you are doing to the equation is to increase k'—you find that the term for resistance to mass transfer in the gas phase increases, and so does the term for resistance to mass transfer in the liquid phase. I am rather surprised that both should increase. I should rather have expected that the resistance to mass transfer in the gas phase would either stay constant or decrease. Could either Dr Khan or Dr Golay answer this point?

G. Schay: I should like only to remark that interfacial resistance is not the only factor which causes non-equilibrium, for in principle in every sort of column, capillary or packed, when any peak is travelling there must be non-equilibrium. There are two peaks travelling together, one in the stationary phase and one in the moving phase, and the one in the stationary phase must be left behind that in the moving phase; for otherwise there is no driving force for the mass transfer between the two phases, nor for sorption or desorption. Thus naturally the interfacial resistance may increase this lag, but it is only one factor which may increase it.

M. A. Khan: Do you not think that this has something to do with the time of contact between the two phases? Would you get any absorption if the mobile phase moves through the column at a speed approaching infinity?

G. Schay: No, none.

Chairman: I am afraid that the discussion time is now over.

2

STUDY OF PHYSICO-CHEMICAL ADSORPTION CHARACTERISTICS BY GAS CHROMATOGRAPHIC METHODS

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Gas chromatography is a convenient technique for rapid comparison of specific surface areas of chemically similar large-pore adsorbents and of finely powdered solids supported in the pores of an inert carrier.

Comparison of heats of adsorption obtained from gas chromatographic data with results of direct calorimetric measurements on the same adsorbent indicates that an estimate of these values, and of their dependence on the nature of adsorbent and adsorbate, can be rapidly obtained by gas chromatographic methods.

THE PRINCIPAL physico-chemical characteristics of an adsorbent may be divided into two categories:

1. the structural properties, such as specific surface area and porosity, which are largely independent of the properties of the adsorbate;
2. the chemical properties, such as adsorption energy, adsorption isotherms, etc., which are determined by the nature of the adsorbent–adsorbate system.

Values of all these parameters are usually determined by adsorption tests under static conditions. However, adsorption measurements and particularly calorimetric determinations of differential heats of adsorption, which require complex apparatus sensitive to fluctuations in ambient conditions, are often tedious and time-consuming. Lately much attention has been devoted to chromatographic investigation of adsorption isotherms[1,2]. In a number of papers it is shown that under certain conditions gas chromatography can be used for rapid determination of adsorption isotherms; the agreement with isotherms measured under static conditions is satisfactory. Determination of heats of adsorption from gas chromatographic data has received much less attention[3,4,5], because gas chromatography laboratories normally do not possess calorimeters by means of which the heats of adsorption could be measured directly for comparison.

As the logarithm of retention time or retention volume is proportional to the standard free energy of adsorption (or solution), the heat of adsorption can easily be computed from chromatographic data by means of an equation of the type of the van't Hoff isochore:

$$Q = 4{\cdot}575 \frac{T_1 T_2}{T_2 - T_1} \log \frac{V_1}{V_2} \qquad (1)$$

where T_1 and T_2 are absolute temperatures, and V_1 and V_2 the corresponding retention volumes. When the isotherm is linear Q is independent of concentration. Generally Q depends on surface coverage; for comparison with calorimetric data an approximate value for this parameter must therefore be determined from the chromatogram.

As calorimetric investigations of adsorption heats are performed in our laboratory, we undertook a study with the object of comparing the results of gas chromatographic and calorimetric studies of this important physico-chemical characteristic of adsorption systems. Chromatograms were obtained for various vapours on modified adsorbents and on finely powdered solids supported on large-pore carriers with weakly adsorbing surfaces.

In the opening lecture by Professor Kiselev (page xxxiv) and in previous publications from this laboratory[6,7,8] it has been pointed out that geometrically and chemically modified adsorbents, having a weakly adsorbing surface, low surface area and homogeneous wide-pore globular structure, can be employed in gas–solid chromatography, both directly and as support for finely powdered solids.

Experimental

Ordinary silica gels were geometrically modified by treatment with steam at elevated temperature under various conditions; subsequent chemical modification was achieved by treatment with trimethylchlorosilane and dimethyldichlorosilane. Samples with especially wide pores and low surface area were also used as supports for the determination of the specific surface area

Table 1. Structural characteristics of geometrically modified silica gels

Sample	*Steam treatment*			*Surface area*, m^2/g		*Pore volume* ml/g	*Globule diameter* Å	*Pore diameter* Å
	Atm	°C	Hours	BET *krypton*	*chromatogram*			
A	185	350	2	15	15*	0·93	1,800	2,500
B	90	300	2	23	22–26	1·01	1,200	1,800
D	220	350	2	9	9	0·92	3,000	4,100
E	175	340	6	45	40–42	1·01	600	900
F	180	340	18	8	6–10	1·01	3,400	5,050
G		310	10 min	37	32–33	0·95	750	1,050
H	200	355	1	13	11–14	0·90	2,100	2,800
I	190	350	2	11	10–12	0·87	2,500	3,200
Unmodified				280	330	1·01	95	125

* Taken as reference standard

of fine carbon black powders, as first suggested by Cremer[9]. The carbon black was introduced into the wide pores of a silica gel acting as inert support. Adsorption on the surface of the support should be small compared to adsorption on the powder.

Table 1 gives conditions of treatment and structural characteristics for the modified silica gels employed by us. Specific surface areas were determined

by BET method with krypton at 78°K. With sample *A* as reference standard the specific surface areas of the other samples with closely related structural and chemical character were determined[9] from chromatograms of n-butane, n-hexane and benzene.

Chemical modification was effected by interaction of the hydroxyl groups of the silica gel surface with trimethylchlorosilane and with dimethyldichlorosilane[7,8].

Samples *A*, *B* and *D* were chemically modified and used as supports for carbon blacks. (Acetone, hexane and benzene are eluted rapidly and almost simultaneously from these supports.) The carbon black was introduced into the support by shaking of the materials for 8 hours in an evacuated ampoule. Remaining loose carbon black was removed with an air stream and by sieving.

Table 2. Characteristics of carbon blacks supported on modified silica gel supports

Sample			*Surface area of carbon black*, m^2/g	
Carbon black graphitized at 3,000°C	*Support*	*Carbon black content*, wt %	BET	*Chromatogram*
Thermal *T*1	*A*-Si $(CH_3)_3$	18	29	30
Thermal *T*1	*B*-Si $(CH_3)_3$	23	29	29*
Thermal *T*1	*D*-Si$(CH_3)_3$	24	29	25
Thermal MT	*D*-Si$(CH_3)_3$	25	7	6
Vulkan 3	*D*-Si$(CH_3)_3$	25	70	70
Channel	*B*-Si$(CH_3)_3$	20	85	95
Acetylene	*D*-Si$(CH_3)_3$	9	90	73

* Taken as reference standard

Data for two types of carbon black on modified silica gel supports are summarized in *Table 2*. Benzene and toluene were used in the BET measurements[10,11]; acetone, benzene and n-hexane were used for the chromatograms. The gas chromatographic results agree well with the adsorption data, regardless of the choice of support.

On all adsorbents chromatograms of normal C_6–C_{10} hydrocarbons, as well as acetone, benzene and cyclohexane, were obtained at various temperatures (*Figures 1* and *2*), and the influence of modification of adsorbent on separating power was studied. A 'Griffin and George' chromatograph was used for the experiments. The column was a glass tube of 6 mm i.d., filled with adsorbent over a length of 89 mm. A constant flow of 45 ml nitrogen per minute (at room temperature) was maintained at the column entrance, at a pressure between 749 and 729 mm Hg absolute. Pressure drop across the column varied between 70 and 130 mm, depending on experimental conditions. Filling of the silica gels with carbon blacks resulted in good separations and changed the order of elution: acetone emerged first, followed by cyclohexane, benzene, n-hexane and n-heptane (*Figure 1*), as expected from the dispersion interaction energies of these substances with carbon black[12].

Heats of adsorption were determined as the slopes of curves of log retention time versus reciprocal absolute temperature, at surface coverage of about

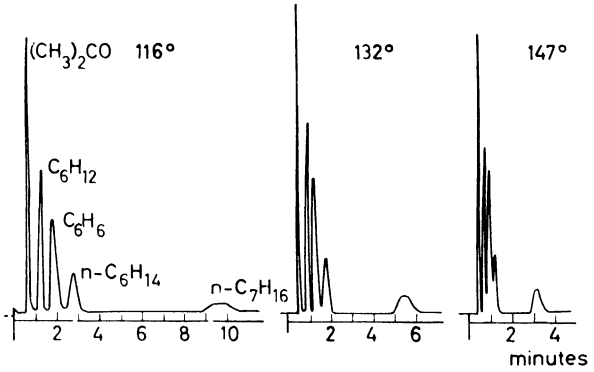


Figure 1. Chromatograms of a mixture of acetone, cyclohexane, benzene, n-hexane and n-heptane on *T*1 thermal carbon black supported on silica gel *B* modified with trimethylchlorosilane

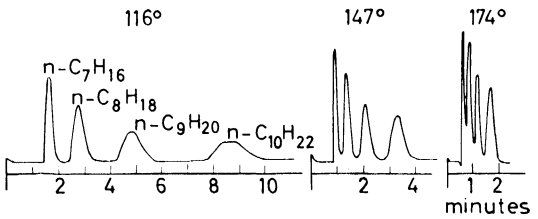


Figure 2. Chromatograms of a mixture of n-heptane, n-octane, n-nonane and n-decane on silica gel *C* modified with dimethyldichlorosilane

0·01 to 0·1. Curves of log retention time versus reciprocal absolute temperature are given in *Figure 3* for five aliphatic hydrocarbons, benzene and acetone, eluted from adsorbent (*C*) modified with dimethyldichlorosilane. The heat of adsorption for acetone is rather large, owing to residual surface heterogeneity, to which the polar acetone molecule is sensitive. Contrary to the elution peaks of the hydrocarbons, the acetone peak has a sharp front, even though the compound is the first to emerge.

In *Figure 4* the heats of adsorption on three adsorbents are plotted as function of carbon number. The heats of adsorption increase linearly with increasing number of carbon atoms, as expected for adsorption of molecules with their long axis oriented along the surface. The heat of adsorption for any compound is greater on the dimethyldichlorosilane-treated surface than on the trimethylchlorosilane-treated adsorbent. This is probably due to the fact that the polydimethylsiloxane film is denser than the film of separate trimethylsilyl groups, so that the hydrocarbon molecules can interact with a larger number of methyl groups of the polydimethylsiloxane layer without coming in contact with the silica surface. The heats of adsorption on the carbon blacks are considerably greater, in accordance with the higher energy of the adsorption forces.

Figure 4 also shows clearly that values of chromatographically determined heats of adsorption for n-alkanes are in good agreement with data obtained by direct calorimetry at 20°C and for surface coverage approaching zero [10, 13].

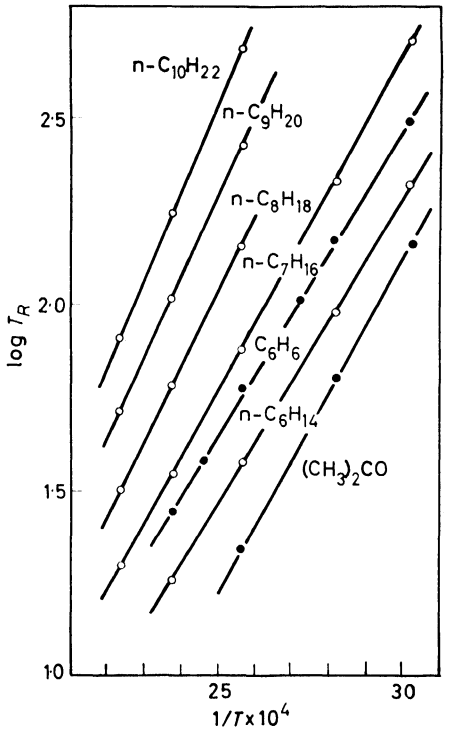


Figure 3. Log retention time versus reciprocal absolute temperature for normal hydrocarbons from C_6H_{14} to $C_{10}H_{22}$, benzene and acetone on silica gel *C* modified with dimethyldichlorosilane

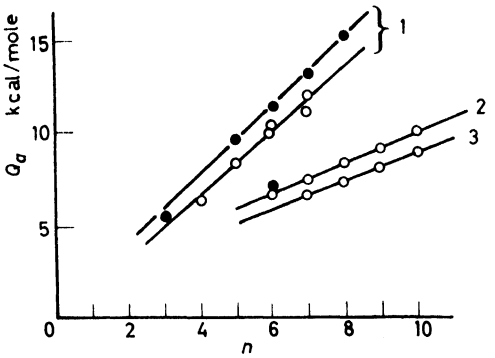


Figure 4. Heat of adsorption as a function of number of carbon atoms for n-alkanes. ●, calorimetric data; ○, chromatographic data. Curve 1: adsorbent graphitized carbon blacks. Curve 2: adsorbent silica gel *C*, modified with dimethyldichlorosilane. Curve 3: adsorbent silica gel *B*, modified with trimethylchlorosilane

Table 3 shows that agreement between the two methods is also satisfactory for benzene adsorption. Thus the gas chromatographic method, although not replacing detailed calorimetric investigation, allows us to obtain a quick

Table 3. Heats of adsorption of benzene on various adsorbents

Adsorbent	*Heat of adsorption*, kcal/mole	
	Calorimetric, at 20°C	*Gas chromatographic, 30 to* 150°C
Modified aerosil[14]	7·0	—
Modified silica gel *C*	—	6·6
Graphitized thermal carbon black	10·3	—
Idem, supported on *A*-$Si(CH_3)_3$	—	9·1
Idem, supported on *B*-$Si(CH_3)_3$	—	9·1
Idem, supported on *D*-$Si(CH_3)_3$	—	9·1

estimate of heats of adsorption. In some cases the values of Q determined chromatographically are slightly lower than the calorimetric values. This is due to the fact that the gas chromatographic data are obtained at surface coverage $\Theta < 0{\cdot}1$, which corresponds to the range of initial heterogeneity, for which the calorimetric method gives higher Q values. It is precisely in this range that the differences in operating conditions for chromatographic and calorimetric experiments play a great part: under vacuum the surface is free of adsorbed substances, whereas in the column the most active centres of the surface may be occupied by adsorbed molecules. Therefore chromatographic heats should be compared with calorimetric heats obtained by extrapolation to $\Theta = 0$.

We have also made estimates of the heats of adsorption from chromatograms of certain lower hydrocarbons (C_1 to C_4) on Linde 5A molecular sieve and on a similar material prepared in the USSR. A glass column of 4 mm i.d. was packed with the adsorbent over a length of 40 cm, and connected to a heat of combustion detector.

Air was used as carrier gas, at a flow of 80 ml/min, measured at room temperature at the column exit. Methane was eluted with a carrier gas flow of 40 or 30 ml/min. Column temperature was controlled to $\pm 0{\cdot}2$–$0{\cdot}3$°C between 20 and 300°C in an aluminium thermostat.

Figure 5 shows a plot of log retention time versus reciprocal absolute temperature for one of the zeolite adsorbents; in *Figure 6* heats of adsorption are plotted as a function of the number of carbon atoms of the adsorbate. Greene and Pust[3] have reported a value of 4,000 cal/mole for the heat of adsorption of methane on Linde 5A sieve, obtained from chromatographic data; this value closely agrees with our results.

The heat of adsorption of pentane on a crystalline zeolite powder of 5A type has been determined at 20°C by direct calorimetry[15]. It is evident from *Figure 6* that for this case of adsorption in very fine pores chromatographic data are in good agreement with calorimetric data, particularly if the small decrease in heat of adsorption with increasing temperature is taken into account. For n-alkanes the heat of adsorption increases linearly with the

number of carbon atoms in the molecule. For C_2 hydrocarbons the heat of adsorption increases from ethane to ethylene, in accordance with the additional interaction energy of the π-electron bonds of ethylene with ions on the surface of the pores in the zeolites.

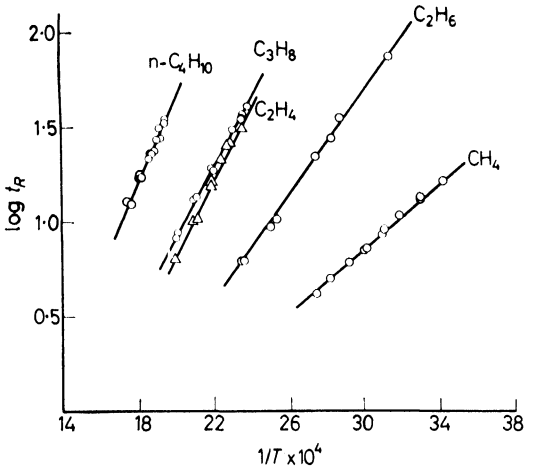


Figure 5. Log retention time versus reciprocal absolute temperature for some light hydrocarbons on Linde 5A zeolite

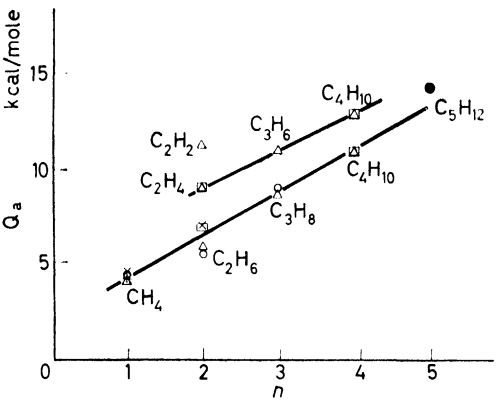


Figure 6. Heat of adsorption as a function of number of carbon atoms for some light hydrocarbons on zeolite adsorbents. △ Linde 5A zeolite. □ and ○ Zeolites manufactured in the USSR. + Reported by Green and Pust[3]. × Isosteric heats on faujasite at low loading (Barrer[16]). ● Value obtained by direct calorimetry at 20°C[15]

The authors thank Professor A. V. Kiselev for his advice on this work.

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DISCUSSION

F. Sjenitzer (*prepared contribution*): I should like to ask something about a sentence on page 21, which runs: 'Contrary to the elution peaks of the hydrocarbons, the acetone peak has a sharp front, even though the compound is the first to emerge.' I find it very difficult to understand this sentence. Would you be so kind as to explain to me what you mean precisely by the words 'even though'? I just don't understand this.

K. D. Shcherbakova: The heat of adsorption of acetone on a surface covered with trimethylchlorosilane groups is much greater than the heat of adsorption of other substances. We ran the chromatograms on a surface covered with dimethyldichlorosilane; and from these chromatograms, which were run at a number of different temperatures, we calculated the heat of adsorption of acetone.

F. Sjenitzer: But you say in the sentence that the acetone peak has a sharp front. Is that connected, then, with the heat of adsorption, as you say?

K. D. Shcherbakova: I think not.

3

NONLINEAR IDEAL CHROMATOGRAPHY AND THE POTENTIALITIES OF LINEAR GAS–SOLID CHROMATOGRAPHY

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A comparison is made between gas–solid and gas–liquid chromatography with respect to the potential separating efficiency. A theory, based on the concept of mass balance, is used to describe the main features of linear as well as nonlinear chromatography; it can also serve as a basis for the development of suitable adsorbents.

The validity of the theory is demonstrated by experimental verification of a procedure for the determination of adsorption isotherms from gas chromatographic data. Under appropriate conditions the rapid and experimentally simple procedure gives satisfactory results.

A brief report is given on the development of efficient columns with solid stationary phases.

ALTHOUGH adsorption chromatography has been used for the separation of gases and vapours before the advent of gas–liquid chromatography, the phenomenal growth of gas chromatography in recent years must be ascribed to the ease with which reproducibility and high separation efficiency can be attained in gas–liquid chromatography. The two techniques may be compared by reference to two important parameters:

(1) slope of the distribution* isotherm;
(2) mass transport velocity.

In practice good separations may be obtained if the slopes of the distribution isotherms have suitable constant values up to sufficiently high concentration, and when the mass transfer coefficient is large. Under such conditions elution bands are narrow, which permits separation of similar components in reasonable time and at concentrations in the eluate which allow easy detection.

The mass transport parameter should have a more favourable value in GSC because there is no contribution from exchange resistance in the liquid. Conversely, the slope and linearity of the distribution isotherm up to high concentrations are generally superior in GLC.

In principle the above-mentioned conditions for good separating power can also be attained in GSC. This can be realized in practice by the use of

* The term distribution is used here in the general sense to describe the partition of material among the phases of a multi-phase system; accordingly a distribution isotherm may refer to solution as well as adsorption equilibria.

solids with suitable surfaces and operation at sufficiently high temperature (chemical reaction of the sample imposes an upper limit on the temperature). Use of sensitive detectors simplifies the task, as only a small portion of the isotherm near the origin need then be linear.

The need for GSC arises because of two limitations of GLC. For low-boiling compounds suitable slopes of the distribution isotherms are not easily realized, and for high-boiling compounds the volatility of the stationary phase imposes an upper limit on the operating temperature.

Only adequate knowledge of the relationship between the shape of the chromatographic curve and the properties and operating parameters of the separating system can serve as a basis for the preparation of suitable adsorbents and the choice of favourable operating conditions. If this relationship can be quantitatively expressed adsorption data are accessible via easy and rapid chromatographic measurements.

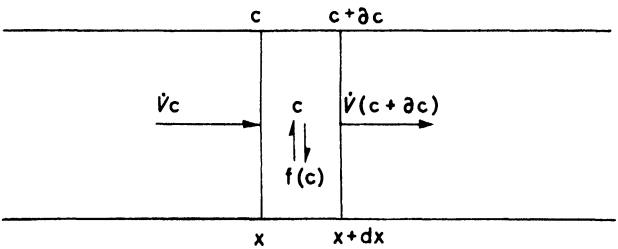


Figure 1. Schematic representation of basic transport mechanisms under conditions of 'ideal' chromatography

Theory

The transport of a sample through a chromatographic column can be described in two ways:

(a) statistical treatment of the behaviour of individual molecules (in view of the mathematical difficulties involved, only limited success may be expected with this approach);
(b) treatment of the macroscopic properties of the materials concerned (this approach is based on the mass balance in a thin segment of the column perpendicular to its axis).

We propose to follow the latter approach. In order to obtain useful results, we must make a number of simplifying assumptions. We will treat the case of one-dimensional transport of a sample of a single component by an inert fluid carrier through a column containing stationary sorption material, and derive an expression relating the concentration of the sample in the effluent to the volume of carrier fluid which has passed through the column since injection of the sample.

In *Figure 1* the mechanisms responsible for the transport of a component are indicated schematically. A number of assumptions have been made:

(1) A segment of the column containing a given amount of stationary phase also contains a volume of moving phase which is invariant with time and with position of the segment.
(2) The temperature of the column is constant and uniform along its length.
(3) The volume velocity of the carrier fluid, averaged over any cross section of the column, is constant.
(4) The volume velocity of the moving phase is equal to the volume velocity of the carrier fluid.
(5) All axial transport is due to convection.
(6) Equilibrium is maintained at all times within any cross section.

The assumptions correspond to ideal conditions for separation; the term ideal chromatography is used to indicate operation under these conditions.

According to Wilson[1] the mass balance equation for the sample content $(\partial n/\partial x)_t \, dx$ contained in a segment of length dx along the column can now be written:

$$\dot{V}\left(\frac{\partial c}{\partial x}\right)_t dx = -\left[\frac{\partial}{\partial t}\left(\frac{\partial n}{\partial x}\right)_t dx\right]_x \tag{1}$$

where $\dot{V}$ is the volume velocity of the moving phase and c is the concentration of the sample in the moving phase.

From the work of de Vault[2] and Weiss[3] it follows that the fraction of the total change of sample content corresponding to the change in the moving phase is equal to $1/1+(m/V_D)f'(c)$, in which V_D is the volume of the moving phase in the column (the dead volume), m is the amount of stationary phase and $f'(c)$ is the first derivative of the distribution isotherm. Eqn (1) may now be written:

$$\dot{V}\left(\frac{\partial c}{\partial x}\right)_t dx = -\left[1+\frac{m}{V_D}f'(c)\right]\left(\frac{\partial c}{\partial t}\right)_x q dx \tag{2}$$

from which it follows that

$$\frac{\dot{x}}{1+(m/V_D)f'(c)} = -\left(\frac{\partial c}{\partial t}\right)_x \Big/ \left(\frac{\partial c}{\partial x}\right)_t \tag{3}$$

The average linear velocity of the fluid through the cross sectional area q occupied by the moving phase is represented by $\dot{x}$.

By equating the total differential dc to zero:

$$dc = \left(\frac{\partial c}{\partial x}\right)_t dx + \left(\frac{\partial c}{\partial t}\right)_x dt = 0$$

we obtain an expression for the velocity of a particular sample concentration in the mobile phase:

$$\left(\frac{dx}{dt}\right)_c = u(c) = -\left(\frac{\partial c}{\partial t}\right)_x \Big/ \left(\frac{\partial c}{\partial x}\right)_t \tag{4}$$

From eqns (3) and (4) it follows that

$$u(c) = \frac{\dot{x}}{1+(m/V_D)f'(c)} \tag{5}$$

When linear velocities vary along the column, values averaged over the length of the column may be used:

$$\bar{u}(c) = \frac{\bar{\dot{x}}}{1+(m/V_D)f'(c)} \tag{6}$$

At the end of the column $L/\bar{u}(c) = t_r(c)$ and $t_r(c)\bar{\dot{V}} = V_r(c)$ so that

$$V_r(c) = mf'(c) + V_D \tag{7}$$

where $t_r(c)$ and $V_r(c)$ are residence volumes and residence times of concentrations, and L is the length of the column. The concentration profile of a sample at the column exit can be easily described if it is assumed that the concentration profile at the column entrance has virtually perpendicular sides. (This implies that all sample concentrations are introduced simultaneously.) The elution curve is then described by the inverse function of eqn (7):

$$c = \varphi(V_r) \tag{8}$$

Obviously the integral $\int c\, \mathrm{d}V_r$ must be equal to the size of the injected sample.

A comparison of results predicted by eqn (7) with experimental data will reveal the influence of factors ignored in the derivation, i.e. the non-ideality in any particular case. For this purpose the function $V_r(c)$ must be computed from the shape of the chromatographic peak[4].

A peak of a differential chromatogram may be described by means of the following equations:

$$A = \int_0^\infty \delta \, \mathrm{d}\lambda$$

$$\mathrm{d}\lambda = \dot{\lambda} \cdot \mathrm{d}t$$

$$\mathrm{d}t = \frac{\mathrm{d}V'}{\dot{V}'}$$

$$\delta = S\frac{\mathrm{d}n'}{\mathrm{d}V'}$$

in which δ and λ are the coordinates of the chromatogram, $\dot{V}'$ is the volume velocity in the detector, and A is the area under the chromatographic peak. The sensivity of detection S may be expressed as

$$S = \frac{A\dot{V}'}{\dot{\lambda}n} \tag{9}$$

where n is the amount of sample injected. The parameters $\dot{V}'$, S, and $\dot{\lambda}$ are assumed to be constant.

By means of the transformations $c = \delta/S$ and $V_r = (\lambda_r/\dot{\lambda})\bar{\dot{V}}$ the desired curve $V_r(c)$ can be graphically constructed from the chromatogram. The parameter λ_r represents the distance on the chromatogram from the point of injection. Thus the adsorption isotherm may be determined from the shape of the chromatographic peak of a substance, and vice versa.

Assumption (4), which is not valid at high sample concentrations, may be eliminated if the influence of sample concentration is taken into account[5,6], although the added complication is normally not justified in gas chromatographic calculations. Experience has shown that the above theory adequately describes the major features obtained under normal gas chromatographic conditions.

An accurate description of all aspects of the chromatographic process can only be given if the effects neglected here are included in the treatment.

Chromatographic determination of adsorption data

All methods for the determination of adsorption data must eventually lead to a determination of the adsorption isotherm, from which further parameters such as surface area, heat and entropy of adsorption, etc. may be calculated in the normal manner. Frontal analysis as well as elution techniques have been used for the chromatographic determination of adsorption isotherms of gases. Some techniques yield point values[7,8,9]; with other procedures larger or smaller segments of the isotherm may be determined in one experiment. The latter procedures will now be dealt with in greater detail.

Glueckauf[10] was the first to derive an adsorption isotherm from liquid chromatographic data, by means of a relationship equivalent to eqn (7). Gas chromatographic techniques were first used by Wicke[5], by Cremer[11,12] and by Gregg[13], for the determination of adsorption isotherms of gases, heats of adsorption, and adsorption isotherms of vapours, respectively. Both Wicke[5] and Gregg[13] based their calculations on the assumption that the amount of adsorbate in the moving phase is negligible in comparison with the amount adsorbed on the stationary phase. Although this assumption is justified for strong adsorption and large solid–gas phase ratio, it is not generally valid. In addition the experimental technique was somewhat cumbersome, as sample introduction involved the maintenance of a given sample concentration in the carrier gas until the entire column had reached equilibrium with this sample gas. Lastly non-ideality and means to reduce its effects were not discussed. These three aspects are the subject of the following discussion.

From the treatment given above it follows that under ideal conditions chromatographic data are related to a thermodynamic function:

$$\frac{V_r(c) - V_D}{m} = f'(c) \tag{10}$$

Values of the first derivative of the adsorption isotherm are equal to the so-called specific retention volumes of corresponding points on the diffuse edge of an asymmetric concentration peak. The integral $f(c)$, i.e. the actual adsorption isotherm, can be graphically obtained according to eqn (10) from the chromatographic peak:

$$\int_0^c f'(c)\,\mathrm{d}c = f(c) = \frac{\bar{V}}{\lambda m S}\int_0^{\delta} \lambda_n(\delta)\,\mathrm{d}\delta \tag{11}$$

Here $\lambda_n(\delta) = \lambda_r(\delta) - \lambda_D$ denotes the distance from the centre of the inert gas peak of a point at height δ on the diffuse edge of the chromatographic peak. No simplifying assumption of virtually complete adsorption of the sample,

as mentioned above, has been made here. Glueckauf[10] arrives at an expression equivalent to eqn (11) by a more complicated process involving partial integration.

The procedure described above for the calculation of adsorption isotherms from chromatograms involves only simple handling of easily accessible experimental data. Normal elution techniques may be utilized, and only one sample of known size need be introduced in a correspondingly small volume into the column. Near-ideal conditions may be realized if the slopes of the diffuse edge of the chromatographic peak are made sufficiently small, e.g. by the use of long columns. It may be noted here that in linear chromatography the theory is always valid for the peak maximum, since at that point the concentration gradient is zero and ideal conditions are attained.

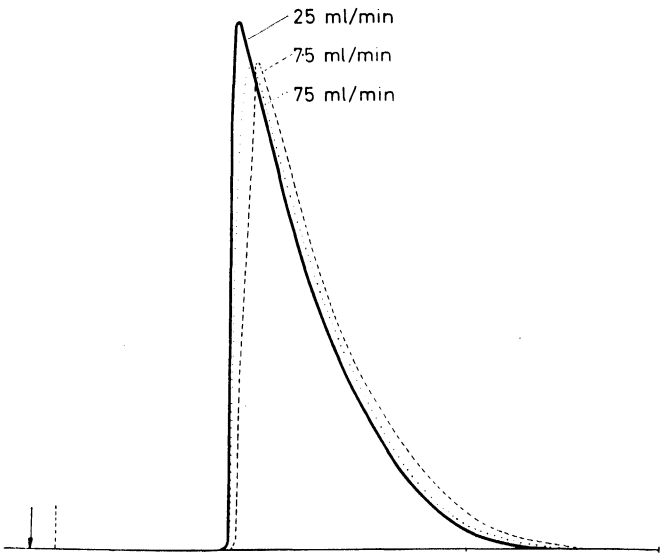


Figure 2. Influence of carrier gas velocity on the desorption edge of a chromatographic peak, for elution of ethylene from active charcoal at 101°C

The procedure was experimentally verified for a number of systems with concave adsorption isotherms and at temperatures ensuring weak adsorption. Here the necessity to account for the sample content of the mobile phase will be clearly apparent. It will be shown how the remaining operating parameters can be chosen so that deviations from ideality may be neglected.

As an example, results will be given for the system active charcoal–ethylene at 100°C. *Figure 2* shows the influence of flow velocity. As expected, kinetic effects, and associated non-ideality, reach a minimum at a particular flow velocity, in complete analogy with the well-known behaviour in linear chromatography. Although the flow velocity only slightly affects the position of the desorption edge, it should preferably be chosen near the optimum value.

Figure 3 shows the influence of sample size. The diffuse edges of the peaks coincide only approximately, although the theory of ideal chromatography predicts exact coincidence. Neither is the theoretically predicted perpendicular front observed in practice. Nevertheless discrepancies for the values used in the calculation of adsorption isotherms are only small.

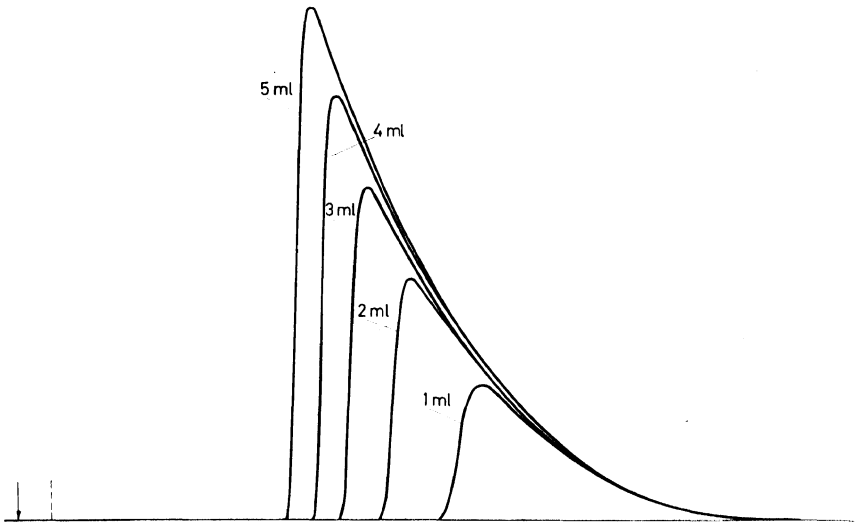


Figure 3. Influence of sample size on the desorption edge of a chromatographic peak, for elution of ethylene from active charcoal at 101°C

In *Figure 4* two adsorption isotherms (2) are reproduced, together with the chromatograms (1) from which they were constructed. Agreement with the isotherm obtained by static measurements is satisfactory for the curve derived from the long-column experiment, but use of the shorter column resulted in slightly greater discrepancies, as might be expected.

The usefulness of this method for determination of adsorption isotherms for the measurement of surface areas of solids has also been tested. Specific surface areas of active charcoals and silica gels were calculated from nitrogen isotherms at −196°C by means of the BET equation. Our values agreed well with those obtained with classical volumetric equipment.

Linear gas–solid chromatography

With linear chromatography the width of the elution peaks depends only on the magnitude of the secondary effects, which can be made small, and good separating power can be achieved. Linearity in GSC can be attained with commonly used adsorbents if the operating temperature is considerably higher than the boiling point of the adsorbed sample. Cremer has separated gases in this manner[11,12].

A second technique involves preloading of the adsorbent surface with

liquids, as has been done by Eggertsen[14], Halasz[15] and others. The technique is an intermediate between GSC and GLC.

Thirdly adsorbents with suitable surface characteristics may be prepared. Scott[16,17] and Kiselev[18] have successfully used this approach. We are presently investigating the preparation of suitable adsorbents by thermal treatment of silica gels. Preliminary results justify the hope that this will prove to be a practical approach to the preparation of adsorbents for use in gas chromatography.

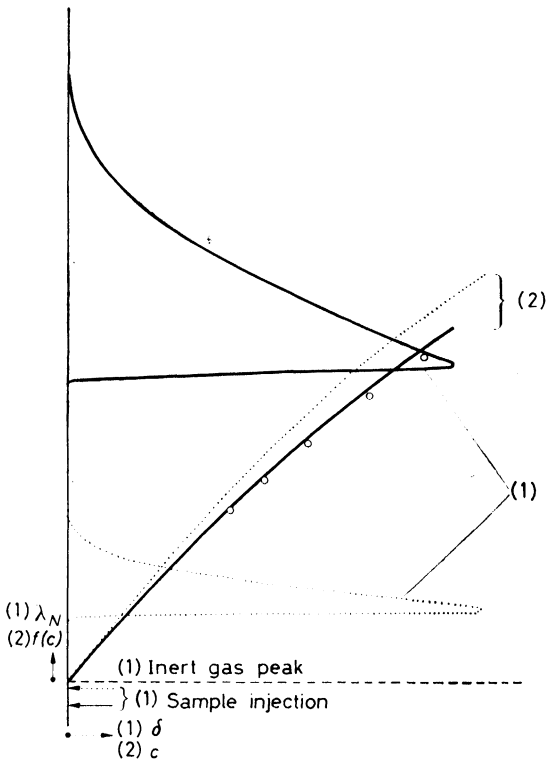


Figure 4. Adsorption isotherms for ethylene on active charcoal at 101°C, and chromatographic peaks from which the isotherms were constructed. Solid curves: 1 m column, packed with 6·91 g active charcoal. Dotted curves: 30 cm column, packed with 1·60 g active charcoal. Circles: point data from static measurements

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DISCUSSION

Author's Additional Comments

The preparation of efficient packing material for GSC columns by thermal treatment of silica gel has proved to be successful.

The chromatogram shown in *Figure 5* was obtained with a column packed with the 160–170 μ fraction of a material produced by heat treatment of silica gel at

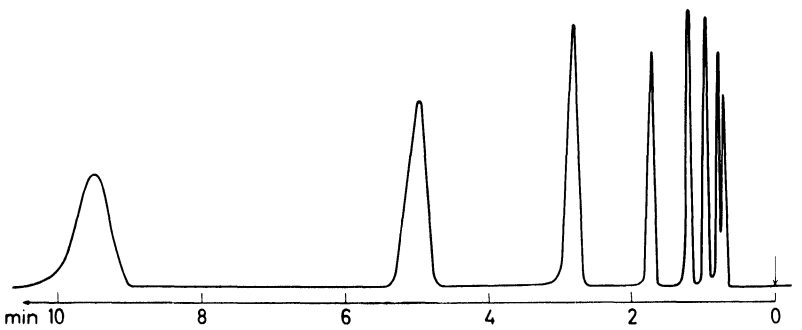


Figure 5. Chromatogram of the n-alkanes from C_5 to C_{12}, obtained at 150°C with thermally modified silica gel

950°C for 15 hours. The peaks are practically symmetrical; the separating efficiency of this GSC column is comparable to that of a good packed GLC column and the permeability is satisfactory.

Figure 6 gives the HETP for this column as a function of the average gas velocity, as determined with a test sample. The steep rise of the curve at high velocities is quite remarkable; it will be interesting to investigate which processes are responsible for the transfer resistance and therefore determine the mass transfer velocity.

The data obtained so far should be regarded as preliminary results, and attempts to optimize packed GSC columns with respect to resolution and permeability are expected to lead to improvements. Sufficient knowledge of the properties of solid surfaces appears to be an essential prerequisite in this work. We are presently working on the characterization of the surfaces of thermally modified silica gels

with respect to their dimensions, topography and adsorption properties towards various classes of compounds.

From a gas chromatographic viewpoint the stability and catalytic activity of the surface merits special attention. These problems are also being investigated.

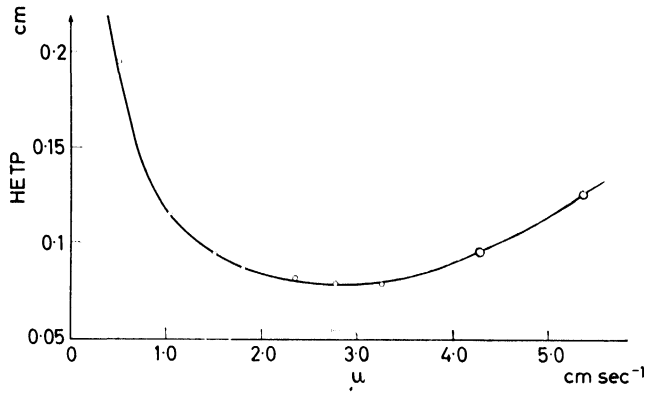


Figure 6. The HETP as function of the linear gas velocity for n-heptane at 100°C on thermally modified silica gel

4

LINEAR GAS–SOLID CHROMATOGRAPHY

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The conditions giving rise to the symmetrical elution of hydrocarbons from columns packed with aluminas modified with sodium hydroxide at column temperatures below the boiling points of the hydrocarbons have been investigated.

The original alumina surface must be completely covered with modifier. The energy of adsorption then has a minimum value which is little affected by further additions of modifier. Heats and standard entropies of adsorption were determined for n-heptane, iso-octane (2,2,4-trimethyl pentane), cyclohexane and benzene on two modified aluminas, as well as on solid benzophenone deposited on Celite. With all these materials linear behaviour was observed.

Measured heats of adsorption have the same numerical magnitude as the latent heats of vaporization of the adsorbates. Although entropies of adsorption indicate ideal two-dimensional gas behaviour, the deactivation process for alumina is compatible with the B.E.T. (Brunauer, Emmett and Teller) theory of multilayer adsorption, which is based on a localized site model.

SYMMETRICAL elution peaks indicative of a linear distribution isotherm (for the partial pressures existing in gas chromatographic columns) can be obtained from most active solid packings if the columns are operated at temperatures considerably higher than the boiling point of the adsorbate.

Linear behaviour at temperatures below the boiling point of the eluted component has been observed with column packings consisting of alumina modified with sodium hydroxide; this material has been used to separate n-alkanes up to C_{45} (b.p. n-C_{45}, 350°C at 1 mm[1]) at a column temperature of 425°C[2]. Similar behaviour has also been observed in this laboratory with columns packed with crystalline organic compounds deposited on Celite.

In the following a report is given of a preliminary investigation of conditions leading to such linear elution of some low-boiling hydrocarbons.

Experimental

Modification of alumina

Low surface area alumina[a] (for gas chromatography, having a surface area between 100 and 125 $m^2\,g^{-1}$) is heated overnight at 400°C to reduce the water content. An appropriate amount of sodium hydroxide is dissolved in a predetermined volume of water sufficient to wet completely the alumina when the solution is subsequently added and mixed. The added water is then removed by further heating at 400°C and the resulting material is sieved. The initial removal of water serves to make the alumina receptive to the volume of water required to dissolve all the sodium hydroxide necessary when 40 weight per cent additions are made.

Benzophenone deposited on Celite

The required weight of benzophenone is dissolved in acetone and mixed with Celite which has been pre-heated at 150°C. The acetone is removed at a temperature above the melting point of the benzophenone.

Retention volume data

All retention volumes were obtained with $\frac{1}{4}$-in. o.d. coiled copper columns of sufficient length to give a minimum measured retention volume of 200 ml. The column was mounted in a water bath controlled to $\pm 0{\cdot}1$°C. The carrier gas was preheated in a 10 ft. length of tubing placed in the same thermostat. Nitrogen was used as carrier gas; retention volumes were corrected for dead volume (retention for hydrogen, measured with flame thermojunction detector) and pressure drop across the column to give the net retention volume.

Nomenclature

V_g net retention volume per gramme of liquid phase, converted to the volume at 0°C.

U_G net retention volume per gramme of active solid packing at the column temperature.

U_A net retention volume per square metre of active solid surface at the column temperature.

Alumina modified with sodium hydroxide

Of the numerous modified adsorbents reported in the literature, the system alumina plus sodium hydroxide appeared to be the most suitable for this study: after heat treatment of the wholly inorganic material at 400°C for some 16 hours, it could be assumed that partition effects would be negligible.

Effect of sodium hydroxide addition on surface area, retention volume and peak symmetry

The effect of sodium hydroxide addition on the surface areas of two aluminas is shown in *Figure 1*. In *Figure 2* the retention volumes per square metre of

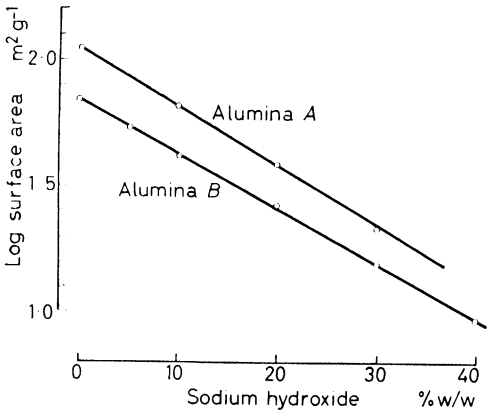


Figure 1. Effect of sodium hydroxide addition on B.E.T.-nitrogen surface areas of alumina

surface U_A (obtained with flame thermojunction detector) for n-pentane at 293°K are plotted against weight per cent sodium hydroxide added to alumina A. The U_A values, which are essentially relative measures of the free energy of adsorption for n-pentane, fall off rapidly with the first additions, and remain fairly constant for all additions greater than 10 weight per cent, even though the surface area decreases continuously (*Figure 1*).

Figure 2 also shows the changes in polarity of the surface with sodium hydroxide additions (measured in terms of retention of butadiene relative to n-pentane). A minimum value is observed at almost exactly the coverage at which constant adsorption energy is attained. It has previously been reported that alumina modified with water shows a point of minimum polarity at monolayer coverage[3] and it would appear that all of the original alumina surface has to be modified with sodium hydroxide before constant adsorption energy is obtained. In the following, such aluminas are referred to as fully modified.

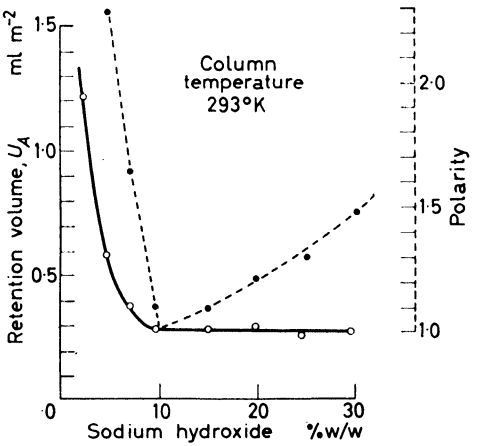


Figure 2. Effect of sodium hydroxide addition on retention volume for n-pentane (———) and on polarity of surface as reflected by ratio of retentions for butadiene and n-pentane (– – – – –)

It was found that the degree of symmetry of the elution peaks for n-pentane followed the same pattern as the adsorption energy: peaks from the original alumina were extremely asymmetric (sharp fronts and long tails); they improved markedly with increasing amounts of sodium hydroxide added and became acceptably symmetrical with the fully modified aluminas.

Linearity and temperature dependence of the behaviour of some hydrocarbons on two fully modified aluminas

Retention volumes (U_G) for n-heptane, iso-octane, cyclohexane and benzene on two fully modified aluminas are plotted against reciprocal temperature in *Figures 3* and *4*. The results at all four temperatures (303, 318, 333 and 348°K) were found to be independent of sample size over the thousand-fold range investigated (sample sizes consistent with the sensitivities of both flame thermojunction and flame ionization detectors). The isotherms are therefore

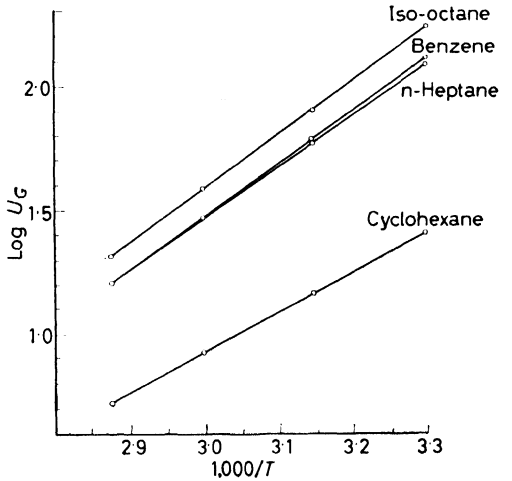


Figure 3. Retention characteristics for alumina modified by addition of 20% w/w sodium hydroxide (surface area 38 m^2 g^{-1})

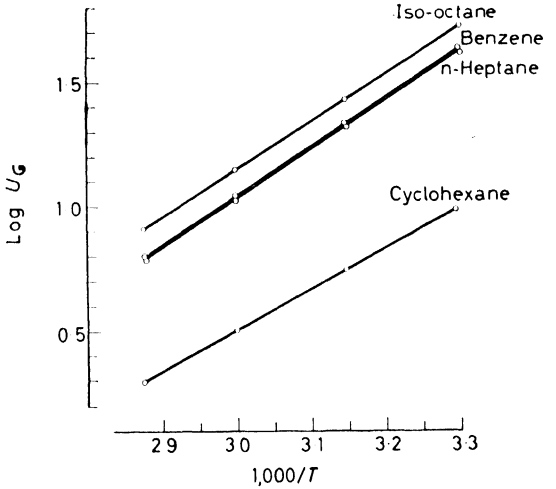


Figure 4. Retention characteristics for alumina modified by addition of 40% w/w sodium hydroxide (surface area 14·5 m^2 g^{-1})

linear and heats of adsorption are independent of sample size for the partial pressures normally used in gas chromatography. Heats of adsorption were calculated from the temperature dependence of the retention volumes; they are listed in *Table 1.*

Benzophenone deposited on Celite

Symmetrical elution peaks can be obtained with columns packed with crystals of aromatic compounds. (Benzophenone, diphenyl and diphenylamine have been used.) As these materials have low surface areas, the compounds were

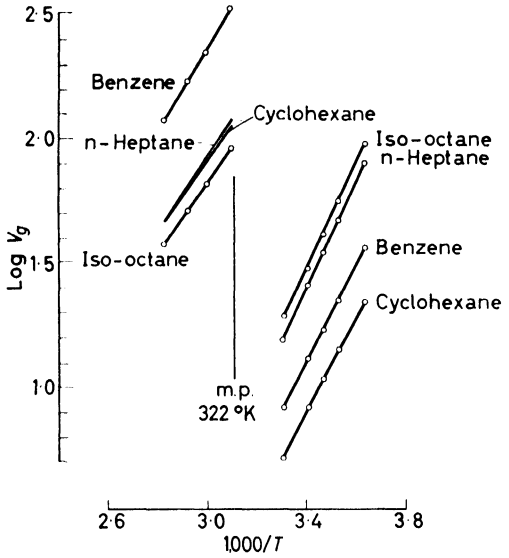


Figure 5. Retention characteristics for benzophenone on Celite

deposited in the liquid state on to Celite, a procedure which, apart from increasing surface area, also makes it possible to compare partition and adsorption effects.

Figure 5 shows the retention volumes (V_g) for n-heptane, iso-octane,

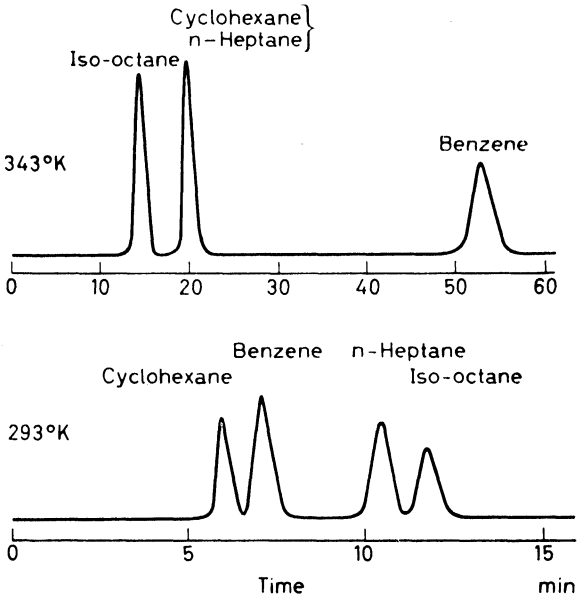


Figure 6. Partition (343°K) and adsorption (293°K) chromatograms for benzophenone on Celite

cyclohexane and benzene, plotted against reciprocal absolute temperature, for a column packed with benzophenone (m.p. 322°K) on Celite (10:90 w/w). At column temperatures above the melting point, the elution order obtained is characteristic of partition in an aromatic solvent.

At the solidification temperature, retention volumes decrease to extremely low values over a temperature drop of about 2 degrees. With further decrease in temperature, adsorption occurs, accompanied by rearrangement of elution order. The same V_g values were obtained (at any given temperature), irrespective of whether the temperature was changed from above the melting point downwards or from below the melting point upwards. A partition chromatogram at 343°K and its adsorption counterpart at 293°K are shown in *Figure 6*.

The elution order cyclohexane, benzene, n-heptane and iso-octane observed with the solid benzophenone on Celite was also obtained from columns packed with benzophenone crystals; this order differs from that obtained from the fully modified alumina columns only in the position of the benzene peak. Here also retention volumes and heats of adsorption (*Table 1*) were found to be independent of sample size.

Table 1

Adsorbate	*Heat of vaporization* ΔH_v *at* 298°K (kcal mole^{-1})	*Differential heats of adsorption* $-\Delta\bar{H}$ (kcal mole^{-1})		
		Alumina + 40% NaOH 318°K	*Alumina* + 20% NaOH 318°K	*Benzophenone on Celite* 278°K
n-Heptane	8·72	9·0	9·5	9·1
Iso-octane	8·38	8·8	9·7	9·2
Cyclohexane	7·88	7·3	7·4	8·0
Benzene	8·08	9·0	9·7	8·3

Entropies of adsorption

Determination of the entropy change occurring when a molecule is adsorbed at a surface can provide valuable data for the formulation of the adsorption model most appropriate to a given adsorption system[4]. Entropies of adsorption were obtained from the experimental results by means of the thermodynamic relationship

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

When 1 mole of a gas is transferred from a three-dimensional standard pressure p_0 (conventionally chosen as 1 atmosphere) to a 'standard adsorbed state', the change in free energy ΔG_0 is given by

$$\Delta G_0 = RT \ln \frac{p}{p_0} \tag{2}$$

where p is the pressure (in atmospheres) of the gas in equilibrium with the adsorbate in the standard adsorbed state.

For our calculation we adopted the standard adsorbed state previously

An indication of the possible heterogeneity of the fully modified aluminas is given by the decrease in heats of adsorption caused by the increase of sodium hydroxide addition from 20 to 40 per cent. However, the fact that all measured heats of adsorption have the same numerical magnitude as the respective latent heats of vaporization of the adsorbates constitutes a significant aspect of the results presented here on adsorption according to Henry's law at temperatures below the boiling point of the adsorbates (*Table 1*). Heats of adsorption at 318°K for n-heptane on alumina modified with only 10 per cent sodium hydroxide (only just covering the original alumina surface) were $-9{\cdot}9$ and $-10{\cdot}7$ kcal mole^{-1} respectively, when sample sizes consistent with the sensitivities of the flame thermojunction and flame ionization detectors were employed. Retention volumes with the latter detector were approximately one third greater than with the former. From this it follows that the process of modification involves the deactivation of sites or areas having high affinity for the adsorbate, for which Henry's law would only be obeyed at higher column temperature.

If this behaviour is general we should not expect Henry's law to be obeyed if the heat of adsorption has a value considerably greater than the heat of vaporization, even when the heat of adsorption is independent of surface concentration.

In this respect it may be significant that, although linear behaviour is observed for the fully modified aluminas up to quite high surface concentrations, Kemball was unable to observe linear behaviour even at the lowest surface concentrations used in his experiments for adsorptions on mercury, where the heats for n-heptane and benzene were independent of concentration but had values of $-13{\cdot}4$ and $-16{\cdot}4$ kcal mole^{-1} respectively at 310°K. Everett[7] has shown theoretically that ideal two-dimensional gas behaviour should be characterized by a differential heat of adsorption independent of surface concentration and a differential entropy of adsorption varying linearly with the logarithm of the surface concentration. In practice, for adsorption at temperatures below the boiling point of the adsorbates, it would appear that if the heat of adsorption is much greater than the heat of vaporization, the entropy term is more likely to be consistent with either a non-ideal gas model or a localized site model. It should also be noted that isotherm behaviour dependent on the heat of adsorption is embodied in the B.E.T. multilayer theory which is based on a localized adsorption model. This aspect has been discussed in a previous publication[9].

Surface areas available to hydrocarbons on low surface area active solids

The accuracy of the 'standard entropy loss' data given in *Table 2* is determined in part by the validity of the assumption that the total surface areas of the active solids, as determined by B.E.T. low-temperature nitrogen adsorption, are wholly available to the hydrocarbon molecules.

Direct determination of the surface areas by means of the hydrocarbons themselves is complicated by uncertainty regarding their configuration on the surface. Reported values for the area occupied by an adsorbed n-heptane molecule range from $33{\cdot}3 \times 10^{-16}$ cm^2 at 323°K on mercury to $59{\cdot}4 \times 10^{-16}$ cm^2 at 297°K on carbon[10]. An area of $47{\cdot}0 \times 10^{-16}$ cm^2 has been calculated for a freely rotating adsorbed n-heptane molecule[11].

Nevertheless as a limiting case we determined four isotherms (303, 318, 333 and 348°K) for n-heptane on the original alumina (B.E.T.-nitrogen surface 114 $m^2 g^{-1}$), using the procedure described by Gregg and Stock[12]. The isotherms are reproduced in *Figure 7*. Both the 303 and 318°K isotherms were within the pressure range in which the B.E.T. equation may be applied and gave estimates of 59 mg n-heptane to cover 1 g of alumina. If the total area of 114 $m^2 g^{-1}$ were available, this would correspond to $32{\cdot}1 \times 10^{-16}$ cm^2 per molecule. If any appreciable area was not available to the hydrocarbon, the actual area occupied would be smaller than this, approaching a value corresponding to adsorption of the molecules in an almost vertical position. It

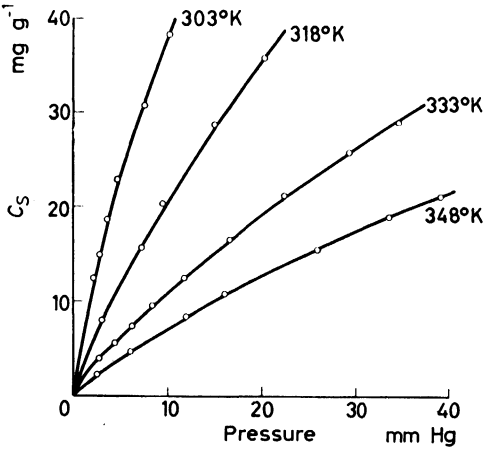


Figure 7. Adsorption isotherms for n-heptane on alumina (surface area 114 $m^2 g^{-1}$)

was therefore assumed that the nitrogen areas of the materials for which the thermodynamic data were calculated can be used as a reasonable estimate of the areas available to the hydrocarbons, particularly as these areas were considerably smaller and therefore probably corresponded to a 'smoother' surface than that of the original alumina.

Thanks are due to the management of Lobitos Oilfields Ltd for permission to publish this paper and also to D. A. Rowell and Miss N. F. Lewis for assistance with some of the experimental work.

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DISCUSSION

Author's Additional Comments

In the first publication[2] describing the modification of alumina with inorganic compounds to give column packings yielding symmetrical elution peaks for hydrocarbons, a brief comparison of the effects of several modifiers was made. This comparison indicated that sodium hydroxide was probably the most efficient from the point of view of reducing retention times and column temperatures.

Other modifiers can, however, be used to advantage, as shown by work now being carried out in collaboration with Mr C. S. G. Phillips at the Inorganic Chemistry Laboratories at Oxford.*

Table 3. Retentions for some hydrocarbons relative to n-heptane at 373°K

Modifier	*Cyclohexane*	iso-*Octane*	*Heptene*-1	*Benzene*
NaOH	0·36	1·21	1·34	1·05
NaCl	0·28	1·28	1·80	1·97
NaBr	0·27	1·32	2·00	3·00
NaI	0·30	1·37	2·31	3·90

Table 3 gives the retentions of some hydrocarbons relative to n-heptane on an alumina modified separately with sodium hydroxide and the sodium halides. Whereas the relative retentions for iso-octane and cyclohexane have values independent of the modifier, the ratios for heptene-1 increase, and those for benzene increase markedly on changing from hydroxide through chloride and bromide to iodide. The relative temperature dependencies are such that the benzene–n-heptane retention ratio for the sodium iodide-treated material can be increased to about 7:1 by lowering the column temperature to 323°K. Thus by suitable choice of modifier and column temperature any desired aromatic/aliphatic hydrocarbon retention ratio can be selected over quite a wide range.

The somewhat lengthy retentions characterizing these columns can to some extent be reduced by sintering the alumina at about 800°C before the modifier is added. Without doubt the most effective way of using these materials would be in the packed capillary columns described earlier, which were further discussed by Halasz at this Symposium (page 33).

Specific interactions between the adsorbate and the cation of the modifier can also be obtained. With cuprous chloride deposited on alumina, alkenes can be retarded to such an extent that the retention ratio of propene to propane is of the order of 500:1 at 373°K.

* Thanks are due to Messrs Lobitos Oilfields Limited for their support of this work and to Messrs W. G. Pye and Co. Ltd, for the loan of a Pye Argon Chromatograph and Thermal Conductivity Unit.

Reference has been made in the paper to the dependence of the shape of the elution peak on the relative values of the heats of adsorption and vaporization. *Figure 8* shows isotherms for cyclohexane and benzene at 303°K on a sodium hydroxide-modified alumina. These were determined with the assistance of Dr Stock by means of the McBain balance at the Liverpool College of Technology. They conform to the expected pattern: the curve for cyclohexane, which has a heat of adsorption slightly lower numerically than its heat of vaporization, is convex to the pressure axis. For both cyclohexane and benzene on this type of column, acceptably symmetrical peaks are obtained with any type of detector having average sensitivity, provided the column temperature is not lower than about 305°K. *Figure 9* shows the elution peaks (superimposed to the same retention volume scale) obtained for sample sizes consistent with the sensitivities of the Pye argon and thermal

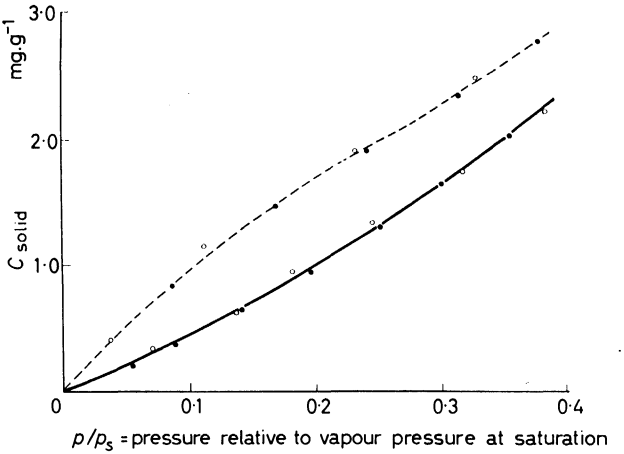


Figure 8. Adsorption isotherms on alumina modified by addition of 40 per cent w/w NaOH, determined by means of McBain quartz spring balance at 303°K

—— Cyclohexane ○ Adsorption
----- Benzene ● Desorption

conductivity detectors at 291°K. The same behaviour is obtained with the other hydrocarbon types, but their elution peaks at low column temperatures and large sample sizes have sharp fronts and diffuse tails.

With cadmium iodide as the modifying agent, heats of adsorption for all hydrocarbon types are considerably larger and it has been found that with this packing, even at column temperatures only just below the boiling point of the adsorbate, symmetrical elution peaks can only be obtained with the highly sensitive detector. *Figure 10* illustrates this feature for cyclohexane at 338°K. The asymmetry this time is reversed (as compared with *Figure 9*) owing to the heat of adsorption being numerically greater than the heat of vaporization.

The results just described show that modification of alumina with various inorganic compounds provides surfaces yielding different interactions and behaviours even for hydrocarbons; these we believe will facilitate the study of the adsorption process, particularly as it applies to gas chromatography. It is of interest to note that Jentzsch and Hövermann (page 204) show curves similar to *Figure 10* for varying sample sizes with gas–liquid capillary columns and remark on the temperature dependence of the asymmetry.

The similarity of the relative retentions of hydrocarbons reported in the paper for packings as widely divergent as alumina modified with sodium hydroxide and benzophenone on Celite suggested that there might be very little variation in selectivity between different gas–solid systems giving rise to symmetrical elution peaks.

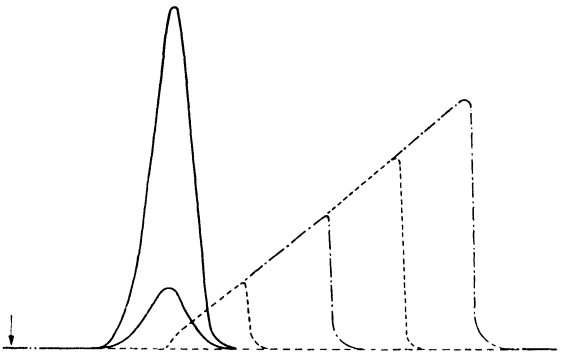


Figure 9. Peak shapes for elution of cyclohexane from alumina modified with NaOH, at 291°K. Sample sizes consistent with sensitivity of argon detector (——) and katharometer detector (------ and -·-·-·-)

The more recent results reported here show that a very wide range of selectivity can be obtained and, even though the heat of adsorption is much greater than the heat of vaporization, symmetrical elutions can be obtained by the use of an extremely sensitive detector. This suggests that the surfaces of these materials have no

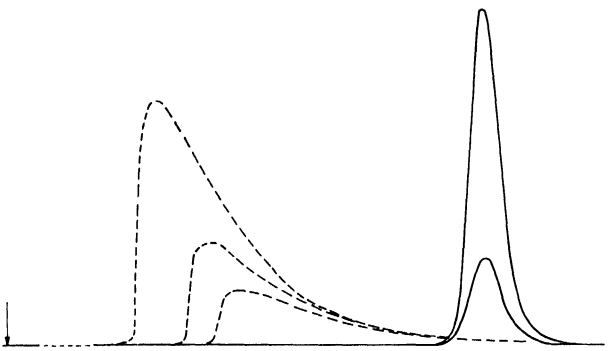


Figure 10. Peak shapes for elution of cyclohexane from alumina modified with Cd I_2, at 338°K. Sample sizes consistent with sensitivity of argon detector (——) and katharometer detector (-----)

residual heterogeneity. The apparent disadvantage of the extreme temperature dependence of the isotherm shape may well be turned to good use. By operating at low column temperatures and high sample concentrations we can obtain a range of tailor-made materials for preparative scale separations by means of displacement techniques. We propose to investigate these and other aspects in the near future.

General Discussion

E. Cremer: A part of the paper by Huber and Keulemans is a continuation of a thesis written by Dr Huber in Innsbruck a few years ago. However, the work presented here is an improvement and an extension of the thoughts expressed at that time. In the thesis, the retention volume was still used in the expression for the first derivative of the adsorption isotherms, as was also done by Wicke, although a consideration of the equilibrium conditions would dictate the use of the net retention volume. The cause of the discrepancy was the fact that in the mass balance equation the sample content of the gas phase was neglected.

The authors have also been able to produce further experimental evidence that the isotherms derived from the break-through curve agree with those determined by static measurements. The problem treated in the thesis, concerning the correction for diffusion, was not further discussed here.

In the meantime, we have also used this method in Innsbruck to determine a few adsorption isotherms. Another co-worker, H. F. Huber, has measured the adsorption of benzene and hexane on various alumina and silica catalysts at

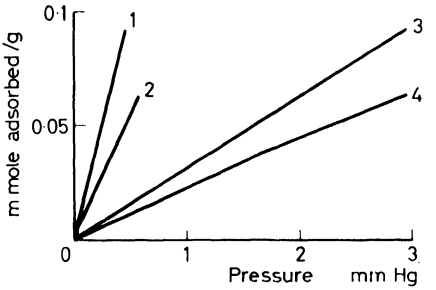


Figure 11. Adsorption isotherms for ortho- and para-hydrogen on molecular sieves 13X, as determined by E. Bechtold

1. o-H_2 at 77°K
2. p-H_2 at 77°K
3. o-H_2 at 90°K
4. p-H_2 at 90°K

temperatures between 370 and 500°C[14]. The determination of isotherms by static measurements would have been very difficult under these conditions.

A number of isotherms, determined by my co-worker Bechtold for adsorption of ortho- and para-hydrogen on molecular sieves at different temperatures, are reproduced in *Figure 11*. The figure clearly shows the important differences in adsorption behaviour which allow a good separation of the isomers.

The method is also very suitable for use with aggressive materials. Thus we have determined isotherms for Cl_2 and HCl. *Figure 12* gives isotherms for HCl on glass. The data could be closely represented by a Langmuir isotherm, and we were able to determine the surface area of glass powders by extrapolation to saturation[15].

E. Bechtold: In order to determine adsorption isotherms by the method described by Dr Huber, we have attempted to reduce and correct for the effects which affect the shape of the diffuse edge of the peak in addition to the sorption. The main effects to be considered here are the slow attainment of sorption equilibrium and the diffusion in the gas phase. If a gas velocity significantly below the velocity for minimum HETP is chosen, the influence of slow equilibration can generally be neglected.

The broadening of a band by diffusion becomes slower as the slope and curvature of the flanks decrease. The experiments can be made in such a manner that the slope of the diffuse edge is already small at the entrance of the column. The

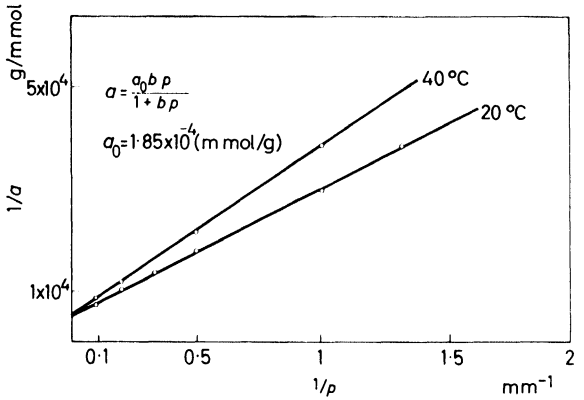


Figure 12. Adsorption isotherms for HCl on glass spheres (diameter *ca.* 0·1 mm). Geometrical surface area 203 cm^2/g; surface area determined from isotherm 210 cm^2/g

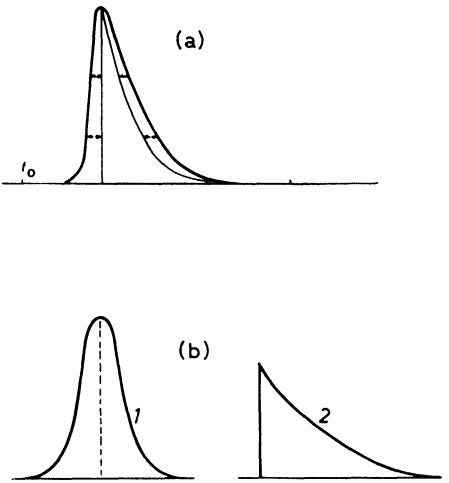


Figure 13. Graphical correction for the influence of diffusion on the tail edge of a band
A: schematic diagram, showing how the correction is applied
B: limiting cases, for which the correction is exact:
1 fully symmetric peak (linear isotherm)
2 fully asymmetric peak (sharply curved isotherm; negligible diffusion)

influence of diffusion on the retention volumes is then significantly smaller than when the sample is introduced with a steep concentration profile; in addition the effect can be calculated to a good approximation. The profile must be recorded at the column entrance and exit.

In order to avoid the calculations and the somewhat complicated experimental work we have attempted to make approximate corrections by graphical methods for the effect of diffusion with normal elution bands. For this correction a line is drawn through the peak maximum and perpendicular to the base line, and for each concentration the distance between the vertical and the forefront is subtracted from the tail edge (*Figure 13*). This correction is exact for the extreme cases: symmetrical bands and bands with a perpendicular front. For other cases the limit of error may be estimated. The specific retention volumes obtained in this way are less influenced by experimental parameters such as column length, flow rate and size of sample pulse, than the uncorrected values.

P. Fejes and A. Pethó (*prepared contribution, presented by P. Fejes*): Recently, attempts at integration of the system of partial differential equations describing the gas chromatographic process could be successfully concluded for the boundary conditions normally imposed for the frontal method. The calculations were based on the following basic assumptions:

(1) The gas velocity changes along the column, owing to sorption.

(2) Normal gas diffusion occurs in the space between the particles of the support.

(3) Sorption in the pores of the support proceeds at a finite rate.

(The last effect is taken into account by equations *A* and *B* in the treatment by E. Glueckauf[16].)

The solution, referred to the gas front, can conveniently be written as follows:

$$\left(\frac{dx}{d\tau}\right)_L = k\lambda_1 x + k\lambda_2 x^2 + k\lambda_3 x^3 + \cdots \qquad (1)$$

in which

x (cm^3/cm^3) = concentration,
τ (sec) = time,
L (cm) = column length,
k (sec^{-1}) = velocity constant of diffusion in the pores, and
$\lambda_1, \lambda_2, \lambda_3$ = concentration-independent constants, the values of which are known functions of the experimental parameters only.

A limiting case for low initial concentrations has practical significance in elution chromatography:

$$\frac{{x_0}^2}{4\left(\frac{dx}{d\tau}\right)_{L,\ x/x_0 \approx 0{\cdot}5}} = \frac{\bar{D}}{qu^2} + \frac{1}{k} \qquad (2)$$

where

x_0 (cm^3/cm^3) = initial concentration
$\bar{D}$ (cm^2/sec) = normal gas diffusion constant under experimental conditions,
q = a parameter with a value proportional to the slope of the sorption isotherm,
$u\left(=\frac{c_0}{1+q}\right)$ (cm/sec) = linear velocity of the front, and
c_0 (cm/sec) = linear velocity of the carrier gas.

Figure 14 is a graphic representation of eqn. 1 for a series of measurements on sorption of n-butane. The sorbent consisted of 15 per cent w/w squalane supported on Thermolit (similar to Firebrick 22). The temperature was 20°C for all measurements; changes in front velocity were effected by corresponding changes in the carrier gas flow.

In *Figure 15* the same data are plotted after transformation according to eqn. 2. From the slope a value of 0·18 cm^2/sec may be calculated for D; from the intercept, a value of $k = 0{\cdot}38$ sec^{-1} is obtained for the transport velocity constant.

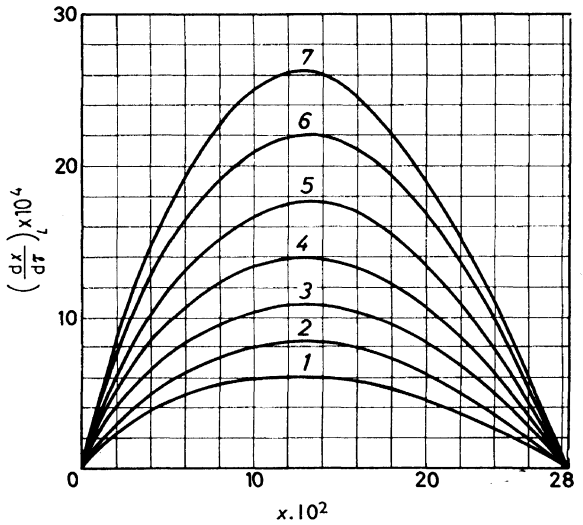


Figure 14. Sorption of n-butane by 15 per cent w/w squalane on Thermolit. Front curves, plotted according to eqn. 1. Temperature 20°C; $q = 6{\cdot}59$

Curve	u
1	$2{\cdot}83 \times 10^{-2}$
2	3·48
3	4·11
4	4·88
5	5·64
6	6·34
7	7·25

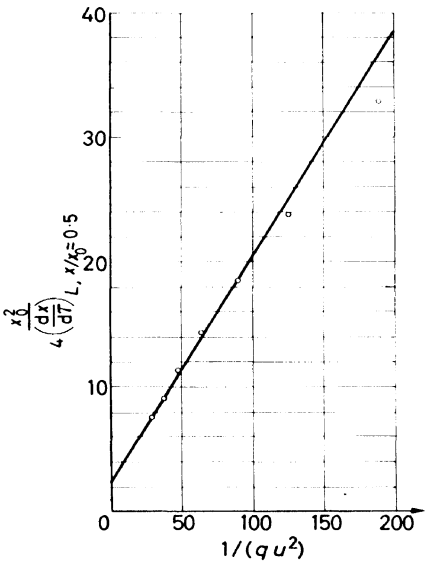


Figure 15. Experimental data of *Figure 14* plotted according to eqn. 2
$k = 0{\cdot}38$ sec $^{-1}$ (Glueckauf, eqn. *B*)
$D = 0{\cdot}18$ cm^2 sec^{-1}

On the basis of similar measurements the following conclusions may be drawn:
(1) For linear front velocities, u, between $3{\cdot}5 \times 10^{-2}$ and 10^{-1} cm/sec the approximations A and B by Glueckauf for the transport velocity in the case of linear sorption isotherms can be used with sufficient accuracy.
(2) At higher carrier gas velocities deviations occur, resulting in an apparent increase of the velocity constant. This experimental fact is also often observed in elution chromatography[17]. Contrary to the observations by Glueckauf we found that the semi-empirical linear velocity equation loses its validity also when the isotherms are curved, as should be expected particularly in adsorption chromatography.
(3) For the investigation of the efficiency of coated supports we believe that the frontal method, with the evaluation developed here, is equally suitable as the normal HETP representation.

R. L. Martin (*prepared contribution, presented by J. C. Winters*): At the 1960 Edinburgh meeting, I discussed the work of Dr R. L. Martin of our American Oil Company research laboratories. He showed that solute adsorption at the liquid–gas interface markedly affects elution orders and retention volumes in gas chromatography. That work was published a year later[18]. Today, I should like to share with you a pre-publication look at independent confirmation and extension of the theory.

Our first paper showed that the exact contributions to retention volume from adsorption at the liquid surface and from solution in the liquid could be calculated according to eqn. 1:

$$V_R^{\circ} = kV_L + k_a A_L \tag{1}$$

The first part ($V_R^{\circ} = kV_L$) is the original James and Martin equation for retention volume. The second part ($k_a A_L$) accounts for the contribution from adsorption at the liquid–gas interface: k_a is called the adsorption coefficient and A_L is the area of the liquid surface.

Figure 16 shows the relative contribution to retention volume of solubility and adsorption at 1–25 per cent by weight of polar liquid phase. At lower coating percentage almost all of the retention is due to adsorption.

Although most people accepted the conclusions of this initial publication, there were those who did not. Therefore, after the first publication, we measured adsorption by an independent method that would corroborate the measurements made by gas chromatography and verify the original postulate of adsorption at the liquid surface in gas chromatography. A second object was to develop equations for the calculation of solute concentrations at liquid surfaces from the gas chromatographic measurements. Both goals were attained. The Gibbs adsorption equation is utilized in the corroborating method for measuring solute adsorption. Eqn. 2 is a common form of the Gibbs equation for dilute solutions:

$$\Gamma = -\frac{x}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}x} \tag{2}$$

Here, x is the mole fraction of solute in the bulk liquid, R is the gas constant, T is temperature, $\mathrm{d}\gamma/\mathrm{d}x$ is the rate of change of liquid surface tension with solute concentration, and Γ is the excess of solute at the surface, in mol/cm^2, over that which would be taken up by a surfaceless solvent. In order to compare adsorption data obtained by means of the Gibbs equation with gas chromatographic data, we developed an equation for gas chromatography that also allows calculation of Γ, the number of moles of solute adsorbed per square centimeter of surface.

Eqn. 3 is the expression utilized in the determination of adsorption data by means of gas chromatography; the derivation will not be given here.

$$\Gamma = \frac{k_a}{k}.x.M_L \tag{3}$$

Γ is the moles of solute per cm^2 of liquid surface in excess of the amount that would be dissolved by a surfaceless solvent; k_a and k are, respectively, the adsorption and partition coefficients, both of which are evaluated from gas chromatographic data; and M_L is the number of moles of liquid phase per ml of liquid. This equation

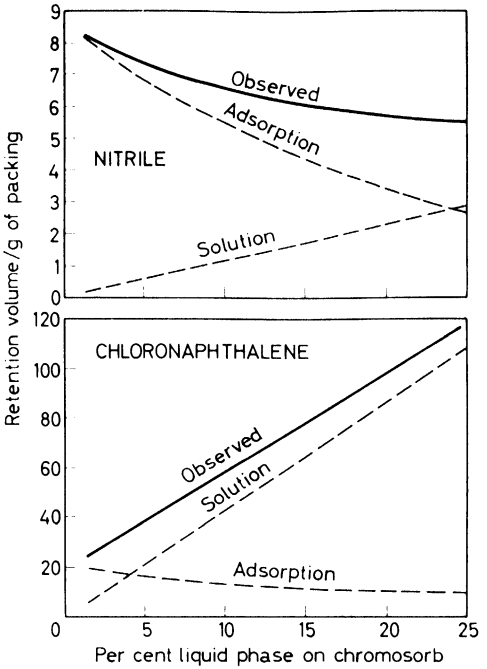


Figure 16. Contributions to retention volumes for 2,2,4-trimethylpentane

permits evaluation of the number of moles of solute adsorbed per square centimeter of liquid surface under static conditions. Adsorption data obtained via the Gibbs equation and by gas chromatography can thus be compared. Conditions imposed on the equation by the derivation are that the solute approach infinite dilution and be in equilibrium with the liquid.

The validity of the new equation and the Gibbs equation was tested for thirteen solutes with 1-chloronaphthalene as the solvent. To determine adsorption with the Gibbs equation, we measured the decrease in surface tension of chloronaphthalene with a du Noüy tensiometer for 0·0100 mole fraction of added solute. At this concentration measurable surface tension decreases could be recorded; but the range of solute concentrations in which the Gibbs equation is valid was not exceeded. *Table 4* contains data for 6 solutes, obtained by the two methods.

Data by the two methods check quite closely. The agreement, although not perfect, is remarkable in view of the several assumptions and approximations made and the error present in the measurement of the decrease of surface tensions as

Table 4. Adsorption of various solutes on the surface of 1-chloronaphthalene. Mole fraction of the solute 0·0100

Solute	*Surface concentration, mole/cm² of liquid surface,* $\times 10^{-11}$	
	Gibbs	*Gas chromatography*
3-Methylpentane	5·7	6·8
2,2,4-Trimethylpentane	9·3	10·1
Methylcyclopentane	2·8	3·7
Cyclohexene	2·4	2·5
1-Hexene	4·9	5·8
Benzene	2·4	2·6

well as k and k_a. An error of about 10 per cent is probably involved in the determination of the decrease of surface tension.

Although the gas chromatographic values are higher for all solutes, the strong correlation between the two methods is evident from *Figure 17*. The deviation of

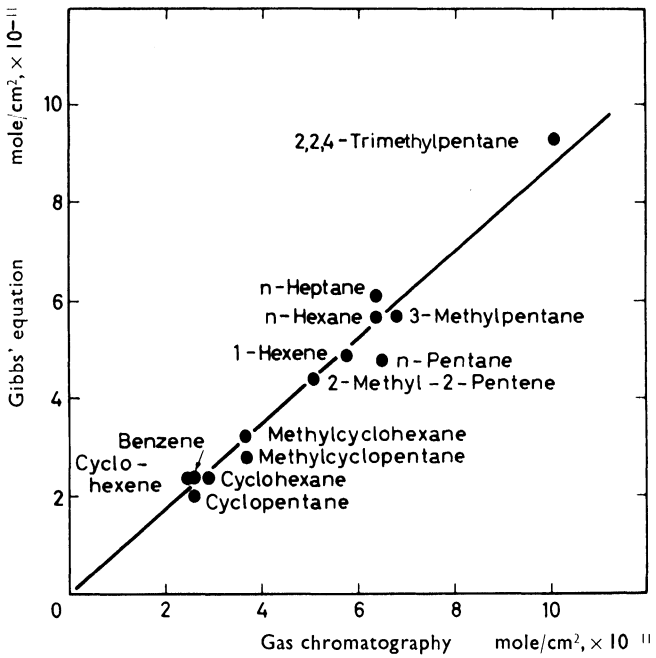


Figure 17. Adsorption on 1-chloronaphthalene of some hydrocarbon solutes at 0·0100 mole fraction, determined from gas chromatographic data and by means of the Gibbs equation

points from the line is about equal to the uncertainty in the measurement of the decrease of surface tension.

In conclusion, the close agreement between adsorption data obtained by means of the new equation and the Gibbs equation is further confirmation of our original

postulate of adsorption at the liquid–gas interface in gas chromatography. Conversely, the gas chromatographic measurements are an excellent verification of the Gibbs equation, which no one doubts, but which has been difficult to confirm experimentally.

Gas chromatography provides a new means for measuring the concentration of solutes at liquid surfaces. Small differences between solute concentrations in the bulk liquid and at the surface can be determined by this means; however, the partition and adsorption coefficients, k and k_a, must be evaluated from gas chromatographic measurements before the calculations can be made. Interesting physicochemical studies of adsorption of volatile solutes on non-volatile liquids, previously difficult or impossible, should be possible by this new approach.

E. R. Adlard: This afternoon we have had several papers on various aspects of gas–solid chromatography, and a good proportion pertained to adsorption isotherms and the separation of substances such as benzene and n-hexane. This is very interesting, but it is somewhat academic if one works in a laboratory in which anything under about C_{30} is rather low-boiling stuff.

Some time ago C. G. Scott published a note in *Nature* on the gas–solid separation of some high-boiling hydrocarbons. I think they were in about the C_{30}–C_{40} region, and he was using—no doubt he will be able to correct me here if necessary —temperatures somewhere around 450°C. This is very unattractive from the point of view of practical separations. I noticed that Dr Huber in his Paper had managed to get quite symmetrical peaks up to normal C_{12} at 150°, and I wonder if either Mr Scott or Dr Huber, or both, would like to comment on the possibilities of extending gas–solid chromatography to the separation of really high-boiling mixtures.

J. F. K. Huber: We have just started to chromatograph stationary phases, e.g. dinonyl phthalate and squalane, at a temperature of 300–400°C, and we are working on paraffin mixtures with a melting point of 50°C. We have also done dieldrin, which has a melting point of 150°C; but I haven't reported on this, because the work is not finished yet. I am quite sure, however, that linear isotherms and linear chromatography can be obtained with high-boiling materials; but the decomposition by catalytic activity at higher temperatures sets a limit there. We hope to try a few substances which are very easily decomposed, to study this effect.

I think the limitations will not be set by the nonlinearity of the isotherms, but by the onset of catalytic activity.

G. W. A. Rijnders: The first remark I wish to make is also on behalf of Mr Huyten, who has carried out the experiments.

GSC is suggested as a tool for the separation of high-boiling compounds. In our laboratory we have investigated this application for higher-boiling hydrocarbons, but the results were not very promising. In the experiments we used alumina, chromatographic grade, and also samples in which the active centres were poisoned by various amounts of NaOH. The main cause of the disappointing results was the decomposition of the hydrocarbon, which started at 350–400° for aliphatic compounds. The separation we got there was comparable with the separation you can obtain with GLC at a temperature of about 100° lower. The alkali used for the de-activation of the surface proved to have an accelerating effect on the decomposition.

I have another question for Mr Scott. In *Table 2* on page 43, he gives a comparison between the experimental entropy of adsorption and the values calculated under the assumption that in the adsorption process one degree of freedom, the translation entropy in the direction perpendicular to the surface, is lost. If I understand correctly, the decrease in entropy is attributed to the loss of one degree of freedom. Is it not more plausible that this degree of freedom is only partly lost and that a

certain amount of vibrational entropy perpendicular to the surface is left, while the rest of the decrease of entropy during adsorption must be ascribed to the decrease of rotational entropy and perhaps to the translational entropy along the surface?

C. G. Scott: I entirely agree with your last remark. In choosing a reference state we had to pick a purely ideal state. We could not make any assumptions as to the amount of vibration or other factors. We just had to assume for a purely reference state that these did not exist, although without doubt they must.

The other point concerned the suitability and the application of alumina to the high hydrocarbons. Again, in our experience, about 425°C was the absolute maximum temperature at which one could operate a column without decomposing the sample, not actually on the column but even during injection, as far as hydrocarbons go.

Concerning the other point, about reducing the column operating temperatures, which is really what we are after, I mentioned in my own presentation, that one of the difficulties of these columns is the high retention time. You can offset this by sintering the alumina to reduce the surface area, but you can only do this to a limited extent. If you attempt to sinter the alumina by taking it up to 900 or 950° it is transformed from the gamma to the alpha form, and I am afraid this has a shocking effect on column performance. In fact, I did this only last week and got about 20 plates per foot. As soon as you really try to sinter it, even though you are not decreasing the surface area by a terrific amount, you do in fact lose your column performance, which is probably due to the mixed type of material which you started with. This, I think, is possibly where Mr Heine's technique of packed capillary columns may be helpful to produce low retentions, which will allow you to use lower column temperatures.

G. Schomburg: In connection with the question by Mr Adlard, I should like to ask Dr Huber what is the behaviour of polar materials in GSC columns. For high-temperature chromatography it is pretty important if one can chromatograph polar substances; we are not always dealing with saturated hydrocarbons!

J. F. K. Huber: This is a question I have expected. So far, we have only looked at homologous alcohols. As I have said, we intend to investigate a whole set of homologous series.

In general, the alcohol isotherms can be made linear. Of course, alcohols start loosing water at temperatures much lower than those we can use when we are dealing with hydrocarbons. For the separation of higher alcohols—and those are the only ones I can comment on now—one should not be too optimistic.

J. Janak: In connection with the discussion on the modification of solids and the measurement of column characteristics I wish to point out some results obtained by a colleague and myself in the investigation of some support materials. It always had to be accepted that the value for the average film thickness in the van Deemter equation has a real meaning, but, in fact, there is a lack of information about the actual value and about the structure of this film. Owing to the good disperson ability of the electron microscope in the micron range we have been able to make some micrographs.

Figure 18 is a photomicrograph of the German support material Sterchamol, with a specific surface area of about 6 m^2/g. It may be seen that this support material consists of globules with a diameter of 0·1–0·2 μ. These globules form space-linked chains with free interspaces up to a few microns. From the agglomerate of 5 globules indicated by the white circle, we can see that the globules have an inner porous structure with pores of up to 0·05 μ. If we accept this structure as being typical, we can easily establish that the globules account for up to 95 per cent of the surface area and less than 5 per cent of the free volume.

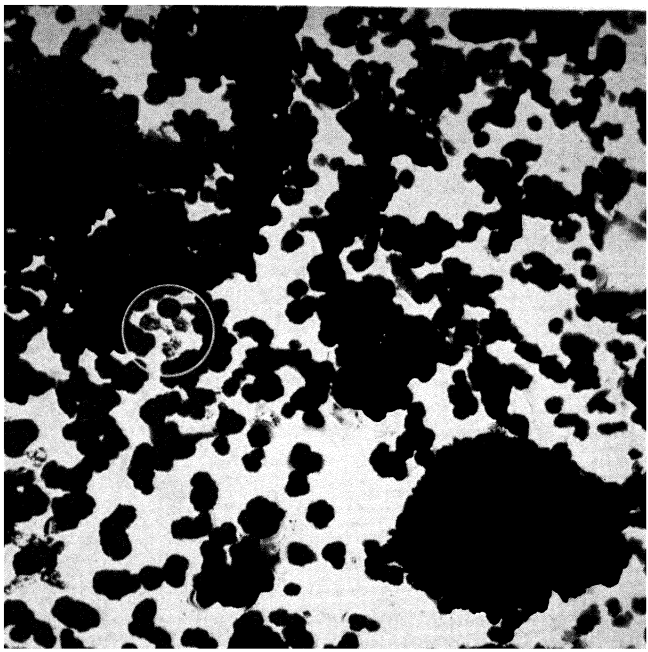


Figure 18. Electron micrograph of Sterchamol, showing structure and distribution of globules

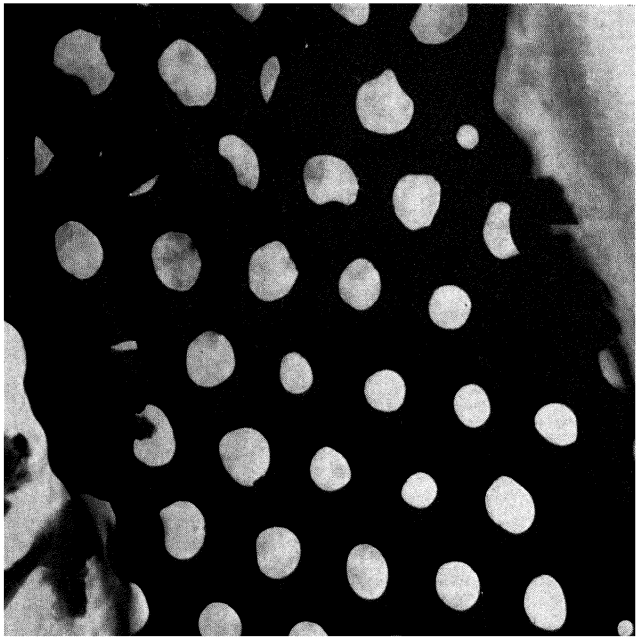


Figure 19. Electron micrograph of Celite, showing structure of a globule

In the same way we have made a photograph of Celite (*Figure 19*). Unfortunately there is a lack of data about the distribution of pores; we only know that the average surface area is of the order of 1–2 m^2/g. The figure shows a typical Celite structure; the material contains mainly pores of two sizes: 0·2–0·5 μ and 2–5 μ. It may be shown that droplets are formed when the support is loaded with more than 2 per cent stationary phase.

We can see that in all these cases we are not allowed to say that the stationary phase has the form of a film of uniform structure.

E. Cremer: I was very impressed with the large amount of work Dr Shcherbakova has done on the calculation of adsorption energies, and I was especially impressed also with the wonderful symmetric peaks she showed us, so that she could use the maximum in her calculations.

We did some measurements in 1947, but although we used the peak maximum, the peaks were very asymmetric; therefore the data were not exact. If you want to get exact data for heterogeneous materials which give rise to large tails, I think you would have to calculate the isotherms from the tailing of the peak, as described by Dr Huber; then you can use the isosteric values of the isotherm to find the adsorption energy. This perhaps would not be necessary for the material you showed us, but if you are testing materials normally used in chromatography or adsorption, you should always test whether the isotherm is curved and whether you can really use the peak maximum. Then you would have to calculate the isotherm from the shape of the tail of the peak.

K. D. Shcherbakova: We set ourselves the task of treating solids, so that they would have a homogeneous surface. Then we got these symmetric peaks. The question is related to the remark by Dr Sjenitzer, which was not completely cleared then. Dr Sjenitzer asked why the acetylene peaks were asymmetric. This is caused by the inhomogeneity of the surface. If we let the hydroxyl groups of the surface react with $(CH_3)_3SiCl$, a few hydroxyl groups always remain on the surface. When small polar molecules are then adsorbed, they can interact with these remaining hydroxyl groups, and we obtain asymmetric peaks. This means that the surface is not uniform yet. When the surface is completely uniform, i.e. when it is covered with a polymer layer, the peaks become symmetrical. For these peaks we have compared our results with calorimetric data, as was correctly stated by Professor Cremer.

When the peaks are not symmetric we must, of course, use the method described by Dr Huber before we can compare the results.

L. Rohrschneider: In his paper, Mr Scott gives an explanation for the different entropies of adsorption on materials treated with different amounts of NaOH. He states that at low NaOH coverage the field of the alumina still extends through the NaOH layer.

In his *Figure 2* (page 38) we see, however, that the adsorption of butadiene reaches a minimum at 20 per cent loading, so that there the field of the alumina does not extend beyond the NaOH layer. Is there an explanation for this phenomenon?

E. E. Wegner: I think I know what Dr Rohrschneider means. Dr Scott pointed out some years ago that alumina can be covered with water, that water would be a fine stationary phase on alumina, and that the polarity passes through a minimum when a monolayer of water is adsorbed on the alumina. Dr Halasz found similar effects with some other polar liquids, such as oxydipropionitrile and ethylene glycol. With higher amounts of polar liquid the polarity increases again, and I think this is the same effect as that observed here with solid NaOH.

C. G. Scott: The inference drawn from the effect of the amount of modifier on the entropy losses is strengthened by the fact that the heats of adsorption given in

Table 1 (page 41) decrease when the amount of added NaOH is increased from 20 to 40 per cent. The anomalous behaviour of butadiene (and other alkenes) has also been observed on alumina modified with water[3] and with polar organic liquids[19], and this must be ascribed to a cause more subtle than just thickness of modifier. The determination of heats and entropies of adsorption for several alkenes on a range of modified aluminas might throw light on this problem.

D. H. Desty: I should like to describe briefly some results which I got from a few experiments with uncoated stainless steel capillaries some months ago, and to ask for comments on them. The capillary concerned is a 100-ft. length of type 316 stainless steel, 17 per cent Cr, 13 per cent Ni and about 2½ per cent Mo.

This capillary was prepared by the manufacturers in a way in which they guaranteed that it was uncontaminated by organic materials, and it had rather an unusual surface with a dense, matt texture. I understand that the final cleaning process involved some etching with nitric acid.

Table 5. Relative retentions (n-hexane = 1·00) of some hydrocarbons on an uncoated capillary of stainless steel, type 316. Column dimensions: length 100 ft.; inside diameter 0·010 in.

n-Pentane	0·22
n-Hexane	1·00
n-Heptane	4·6
n-Octane	19·1
2,2-Dimethyl butane	0·43
3-Methyl pentane	0·65
2,4-Dimethyl pentane	1·8
2,2,4-Trimethyl pentane	5·0
Cyclo-pentane	0·16
Methyl cyclo-pentane	0·59
Cyclo-hexane	0·59
Methyl cyclo-hexane	2·3
Benzene	9·7

At the top of *Table 5* we have a series of normal paraffins and a separation factor for these, for adjacent members of homologous series, of about 4·6. The striking thing is the very low retention for cyclopentane and cyclohexane; in fact cyclohexane emerges before normal hexane, as has been shown with the graphitized carbon blacks on page 20. However, what I cannot understand is why benzene is so strongly adsorbed in this situation. The peaks are quite reasonably symmetrical for the saturated hydrocarbons. In fact, the column performs nearly as efficiently for the lower-boiling compounds as it would do if it were coated reasonably well. The benzene peak is strongly tailed, and perhaps some of the authors could comment on these results.

A. V. Kiselev: We don't work with steel surfaces, but I should like to comment on the problem of thermal stability.

The way I see the problem, the solid surface is very inhomogeneous, and we have to modify it; this would apply to the walls of metal columns as well as the surface of porous supports and glass capillary walls.

Dr Shcherbakova has already told us (page 18) that the first step should be to change the polar surface to a non-polar one. With silicates we can follow this process by measuring the deuterium exchange reaction with the remaining OH groups by means of infra-red spectroscopy. Because of steric hindrance, complete coverage with individual groups is not possible, but we can screen the complete SiO_2 surface by grafting a polymer film on to the surface. This film is prepared with chlorosilanes, and has a high thermal stability. An infra-red study of the

C—H vibration frequencies showed that no changes occur up to a temperature of about 350°C, as was also observed in DTA studies by Janak. Thus this film may be regarded as stable up to 300, possibly 340°C.

A second problem concerns the selectivity. We now have a non-polar film containing only σ-bonds, and benzene is adsorbed less strongly than hexane. Now we can try to insert polar groups such as OH, COOH, NH_2, $CH{=}CH_2$, etc., in the film, but the problem here is that they should be inserted in a regular pattern; otherwise sites with a high density of polar groups will occur, and we will get tailing peaks.

Such a film would be very useful in gas chromatography; it would be selective, and it would have a low vapour pressure, because the whole film is retained by chemical bonds.

The thermal stability is not so good, however, but from the advances made in the field of inorganic polymers I believe that we may be able to cover a solid with a layer with better thermal stability.

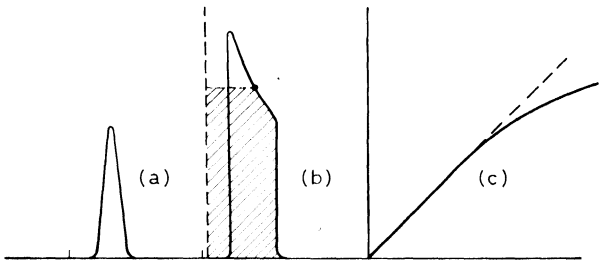


Figure 20. Chromatographic peaks for two sample sizes (*A* and *B*), and the corresponding sorption isotherm (*C*)

I believe similar methods could also be used for metal capillary walls. We could, e.g., prepare a metal-organic compound on the surface. In this context I may remind you that with the usual glass capillaries we get diffuse peaks, because the oil film appears as a reticulated film when we look at it through a microscope. After chemical modification of the glass surface we find a very uniform film, and we get narrow peaks. Thus if we modify the walls of a metal capillary, e.g. by forming an oxide or a metal-organic layer, we might also succeed in applying a uniform thin film, and thereby improve the corresponding term in the van Deemter equation. This may be an interesting direction in which to do further research.

I believe we may state four problems in gas chromatography:

(*1*) Improvement of equipment, such as detectors, etc.
(*2*) Liquid phases.
(*3*) Preparation of supports and solids with the proper surface characteristics.
(*4*) Properties of the gas phase, as shown by Mr Khan (page 3).

All four should be considered in future research. When I talk about solids I don't mean to advocate a change in gas–liquid chromatography, but an improvement of support and an extension of gas–solid chromatography for use at high temperatures. If we can cover the surface with a film that is stable at 400°C, we can use the solid modified with this film as a support for highly dispersed solids, such as carbon black, which can serve as solid immobile phases at very high temperatures.

I have one question for Dr Huber. When we chromatograph CCl_4 on graphitized carbon black we get a series of peaks, the shape of which depends on

the size of the sample, as illustrated in *Figure 20*. How should one integrate such peaks to determine the isotherms?

J. F. K. Huber: For the calculation of an isotherm by the method described in our paper the most diffuse edge of the peak should always be used as the integration boundary. When the rear edge of the peak has the smallest slope, then the tail should be used in the integration, and the isotherm will be concave to the pressure axis, as shown in *Figure 4* on page 33. Conversely, when the peak has a diffuse front, this should be used in the calculation, and the isotherm will be convex to the pressure axis. When a part of a peak has a diffuse front, while the other part is more diffuse on the rear edge, the calculation has to be split into two parts, as was already done by Glueckauf.

In *Figure 20* the calculation of one point of the isotherm is schematically illustrated, together with the shape of the complete isotherm.

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PANEL DISCUSSION

LARGE-SCALE GAS CHROMATOGRAPHY

Chairman: F. H. HUYTEN

Panel: E. KOVATS and R. P. W. SCOTT

Report by: R. KAISER

Under the chairmanship of Dr F. H. Huyten a large number of participants gathered for a discussion of the problems of large-scale chromatography, which was opened by brief introductions by Dr E. Kovats and Dr R. P. W. Scott.

In his introduction Dr Kovats made a distinction between two applications of large-scale chromatography: purification of a compound, and separation of a mixture. He briefly sketched how these goals can be attained in a batch process by judicious trapping and recycling of appropriate fractions of the eluate.

The batch process may be subdivided into three parts: sample introduction, separation in the column, and recovery of the pure compounds from the gas emerging from the column. Samples may be introduced by rapid evaporation in a strongly overheated inlet system; they may be brought on to the column as a gas from a special vaporizing chamber; or the sample may be slowly injected at strongly reduced carrier gas velocity via an injection system held at the column temperature.

Three approaches have been proposed for the separation of large quantities: preparation of columns of large diameter, use of thin columns connected in parallel, and batch-wise chromatography with a relatively thin column. For general purposes batch-wise operation with columns of 2–5 cm diameter seems to be a profitable compromise.

For the recovery of products from the eluate a number of techniques have again been suggested; a general problem seems to be the formation of fog, which may be trapped only with difficulty. Dr Kovats suggested that rotating cold traps might best be used for high-boiling substances (b.p. > 120°C), and that strongly-cooled thin-walled vessels would be suitable for low-boiling components.

The discontinuous nature of the normal gas chromatographic technique has often been felt as a disadvantage, particularly for large-scale separations. Dr Scott in his talk dwelt mainly on a continuous process used by various workers in Germany, England and the U.S., which is based on the movement of the 'stationary' phase in a direction opposite that of the carrier gas. Although a technique involving the movement of the column packing does not strictly conform to the present definition of gas chromatography, a comparison between continuous and discontinuous processes is of particular interest in work on a preparative scale; and some of the data obtained by Dr Scott will be presented here.

Different parts of the column developed by Dr Scott could be maintained at different temperatures, which allowed the utilization of thermal effects for the separation. Thus Dr Scott was able to isolate benzene from a feed containing 90 per cent benzene by a non-isothermal continuous process with a yield of 94 per cent. The product has a melting point of 5·494°C and was produced at a rate of 3 g/h. The partitioning phase was polyethylene glycol benzoate on 6/30 mesh ordinary firebrick; aromatics were separated from aliphatics on a 6-ft. column 2 in. in diameter, and the benzene was subsequently separated from higher-boiling aromatics in a second column with the same packing. The need for two columns for the isolation of any one component is a general disadvantage of the continuous

process. Experiments with bands of support dyed with red ink showed that mixing of the moving support is not serious even in columns of 2 in. diameter.

Continuous processes were further discussed in more detail in connection with the paper by H. Schulz (page 225).

The remaining time of the Panel Discussion was largely devoted to the three aspects mentioned by Dr Kovats, namely the preparation and evaluation of columns of high capacity, the introduction of the sample, and its recovery from the eluate.

The goal of preparative gas chromatography is the economic and rapid separation of large amounts of material into products of high purity. This goal can only be achieved with columns having both a high capacity and a good separating power. From the discussion it became apparent that general agreement has not yet been reached on a set of criteria for the evaluation of the capacity of a preparative column. A decision would have to be made with what component pair and under what conditions the measurements should be made. For purposes of comparison with other separation processes, Mr K. J. Sakodynski suggested the use of the specific capacity, which is defined as the number of grams which can be separated per unit of column cross section. From comments by this speaker and by Dr H. Schulz and Dr G. Schomburg it may be inferred that this definition can only be used when the relative retention of the component pair and the degree of separation per unit column length are also included. According to Dr Schulz the capacity of a column for a mixture with relative retention of 3 may be some 100 times larger than the capacity for a sample with relative retention of 1·1, for comparable purity of the products. Mr Sakodynski reached the conclusion that the capacity of good preparative columns would be about one order of magnitude smaller than that of a distillation column, but he mentioned that according to E. Bayer the two processes might even be comparable.

The preparation of columns with a high capacity, but without sacrifice in efficiency, is still an unsolved problem. Although the capacity increases with the square of the column diameter, the separation efficiency decreases with increasing cross section, so that an upper limit is set on the diameter which is economically justified. Where this limit lies has yet to be determined.

In the preparation of suitable columns the packing technique may well play an important role. Ing. G. L. Guillemin summarized the main aspects of a forthcoming publication concerning the packing of a column by fluidization and settling of the coated support. Columns can be rapidly and reproducibly prepared in this way, and the resulting packing has good stability. A column of 1 m length and 60 mm diameter packed with 20 per cent silicone oil DC 200 on 30–40 mesh Chromosorb has a separating efficiency of 320 plates for n-hexane. A further advantage of the technique is that the packing can be aged by the use of heated fluidizing gas.

Dr Schomburg remarked that by increasing the length of a column one can also increase the sample size that can be handled. This, however, does not necessarily improve the overall process; for more time is involved in one cycle, and the cost of the packing may become very high. As a solution for the latter problem Mr Sakodynski proposed a scheme whereby two columns are used in a recycling process, so that effectively a column of unlimited length is available for the separation (*Figure 1*).

Dr Kovats suggested that in general the use of two columns would be advisable for purification, as well as for the separation of mixtures. A column filled with a non-polar phase, followed by a polar column, would be most suitable. In this context Professor G. Hesse mentioned an interesting example of preparative gas chromatography, which is utilized in his laboratory for the preparation of pure ozone. An oxygen stream containing ozone is led over silica gel at -78°C.

Oxygen is not retained by the adsorbent at this temperature, but ozone and nitrogen oxides are strongly bound. Upon heating, very pure ozone may be eluted with helium or nitrogen, and the nitrogen oxides can subsequently be washed out at a higher temperature.

The second aspect discussed was the introduction of the sample, and here the opinions of various speakers diverged widely. The method of sample introduction strongly depends on the properties of the sample. Thermally stable materials can be injected in liquid or solid form and brought on to the column as a gas by rapid evaporation in a relatively hot vaporizing chamber. D. H. Desty and G. R. Primavesi noted that a sample introduction system should eventually result in a solution of the sample in the liquid of the first plate, and that any method involving

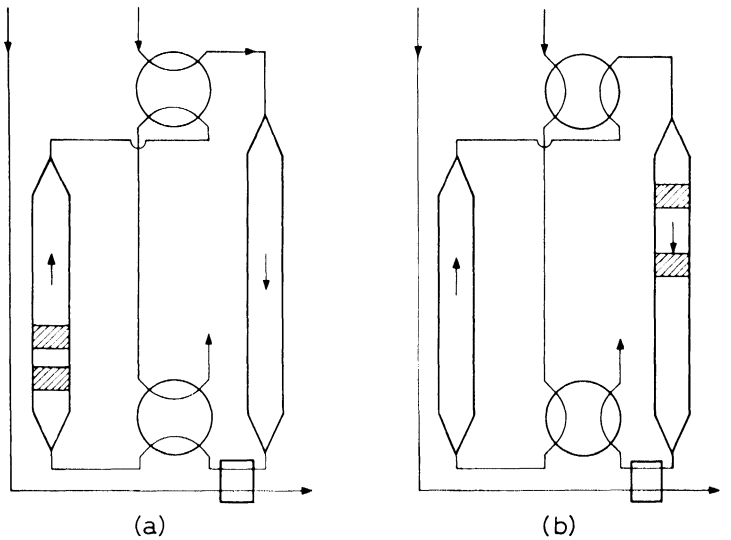


Figure 1. Switching arrangement described by K. J. Sakodynski for repeated percolation of a sample through two columns. By appropriate switching between (*A*) and (*B*) the sample can be made to run through a system resembling a column of unlimited length

vaporization and recondensation would appear to be somewhat awkward in this respect. However, Dr Kovats remarked that the required even distribution of a liquid sample over the first plate might prove to be very difficult.

Mr S. J. Hawkes commented on the problem of injecting highly sensitive essential oils, which he had tried to solve by stopping the flow of carrier gas for, e.g., one minute and allowing the injected sample to vaporize at the column temperature. According to Dr Kovats it would then be better to allow a small stream of carrier gas to bleed in via a capillary, to avoid back diffusion of the sample into colder regions of the equipment (*Figure 2*).

Lastly the discussion was opened to the methods for quantitative recovery of products from the eluate. Among those who defended the desirability of avoiding fog formation, J. Pypker claimed that he had been able to achieve virtually 100 per cent trapping efficiency by directing the hot gas stream directly on to a very cold surface. Presumably the high efficiency was due to the fact that the hot laminar gas stream had no opportunity to mix with colder gas, so that fog formation could not occur.

In contrast with this, Mr K. D. Kilburn said that in his experience simple traps designed to avoid fog formation tended to clog easily. He described a trap of 2 ml capacity, which consists of a 50 cm-long tapered tube wound into a spiral, with a bell-shaped enlargement at the end. About 80 per cent of the sample condenses on the walls of the tube, and the remaining 20 per cent is trapped as a fog by an asbestos filter (Cambridge Filter Co., U.S.A.) mounted in the bell shape. The trap can be used at flow rates of up to 1½ l nitrogen per minute.

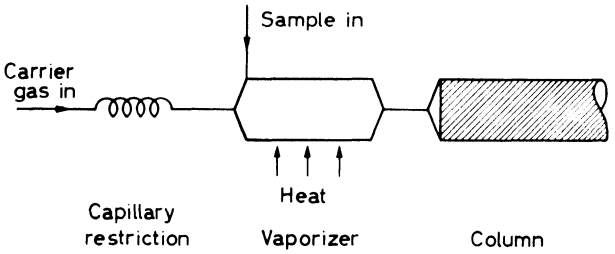


Figure 2. Sample inlet system described by E. Kovats for introduction of heat-sensitive materials by slow evaporation at reduced carrier gas flow

The situation regarding trapping systems may be effectively summarized by the remark of Dr Kovats: that traps of a few different types would be adequate for most problems occurring in normal practice; but that for specific applications special traps could be designed with optimum characteristics for the problem at hand. Thus quantitative recovery can be guaranteed by the use of traps filled with suitable absorbents, and special traps may be constructed to fit directly into, e.g., an infra-red spectrometer for subsequent identification of a compound by its infra-red spectrum.

In closing the discussion, Dr F. H. Huyten summarized the present position of large-scale chromatography: No decision can yet be reached on the relative merits of the different methods for increasing the capacity of gas chromatographic processes. Nevertheless there is reason for optimism that the capacity may be increased in comparison with other methods, such as distillation. The main difficulties seem to concern the introduction of the sample and the recovery of the products. Much work still remains to be done in this area.

5

THE EFFECT OF CARRIER GAS AND COLUMN PRESSURE ON SOLUTE RETENTION

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The variations of solute retention with choice of carrier gas and mean absolute column pressure have been examined for a number of hydrocarbons and are accounted for by changes in the gas phase imperfections. An equation has been derived relating the k' factor to the mean absolute column pressure and the second virial coefficient, B_{12}.

For a given hydrocarbon solute, retention with different carrier gases decreases in the order helium, hydrogen, nitrogen, argon, oxygen, carbon monoxide and carbon dioxide, at a constant mean absolute column pressure and temperature, and for a particular stationary phase. It is also shown that solute retention decreases with increasing mean absolute column pressure; the magnitude of the effect depends on the carrier gas and is greatest for carbon dioxide. Both effects are to some extent dependent on the structure of the hydrocarbon in the gas phase and give rise to small changes in separation factors. These are most pronounced for benzene/paraffin and naphthene/paraffin separations and can be employed to advantage when difficult separations are encountered.

The significance of these results with regard to definition of the specific retention volume is mentioned.

IT HAS hitherto been assumed that interactions occurring between solute and carrier gas molecules in the gas phase are negligibly small; these have consequently been neglected except where serious attempts have been made to determine accurately activity coefficients at infinite dilution[1,2]. In a recent paper[3] it was observed that the degree of separation of close-boiling pairs of hydrocarbons in the gasoline fraction of a crude petroleum could be significantly altered by the use of hydrogen instead of nitrogen as carrier gas. It was found that the variations in resolution could only be accounted for by changes in the solute–carrier gas interactions. Subsequently it was shown[4] that for a number of solute–carrier gas systems a linear relationship exists between log k', where k' is defined as the ratio of the liquid phase capacity to the gas phase capacity (i.e. the solute retention), and the second virial coefficient B_{12}. It was also pointed out that solute retention should vary with the mean absolute column pressure. Such observations have already been made by Scott[5]. This effect should be most marked in solute–carrier gas systems where B_{12} is large.

In this paper these two effects are examined for the C_5–C_7 paraffins, cyclopentane, methylcyclopentane, cyclohexane and benzene, with the carrier gases hydrogen, helium, nitrogen, argon, oxygen, carbon monoxide and

carbon dioxide, at a constant temperature of 25°C and with mean absolute column pressures between 2 and 5 atm.

Experimental

The apparatus used for the investigation was similar to that described in a previous paper[6], comprising a flame ionization detector and a vapour divider device for sample introduction. The carrier gas was purified by passing through a trap containing activated molecular sieve (Linde type 5A) at ambient temperature; the column inlet pressure was maintained constant with a Negretti and Zambra precision pressure regulator. The column consisted of 300 ft. of glass capillary, 0·006 in. i.d., coated, as previously described[6], with squalane from a 20 per cent v/v solution in carbon tetrachloride. The average film thickness of squalane deposited on the column was about 0·13 μ. The temperature of the column was maintained at 25·0 ± 0·01°C (Colora Ultrathermostat, type NB). The recording system was similar to that already described[6]; it comprised a vibrating reed electrometer (Vibron, model 33B^a) and a potentiometric recorder (Sunvic, type RSP2). Vapour samples of approximately 0·5 ml, consisting of blends of methane, C_5–C_7 paraffins, cyclopentane, methylcyclopentane, cyclohexane and benzene were introduced through a rubber septum with a 1 ml syringe and split by the vapour divider to 150–200:1. The sample size of each component estimated from peak area measurements and based on a detector response factor of 5×10^{-3} coulomb/g for n-heptane[7], was about 4×10^{-10} g. At all times, symmetrical elution peaks were obtained and the column had an efficiency of about 250,000 plates for n-heptane ($k' \sim 5$). The k' factor (the ratio of the retention time of the peak maximum of the solute, measured from the peak maximum of methane, to that of methane, measured from the start) was determined for each hydrocarbon with all of the carrier gases employed. Poiseuille flow was assumed, and the mean absolute column pressure $\bar{P}$ was calculated from the formula,

$$\bar{P} = \frac{2}{3} P_o \left[\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \right]$$

where P_i = inlet pressure

P_o = outlet pressure (1 atm in all experiments)

The repeatability of the determination of the k' factor was better than ± 0·3 per cent, and with n-hexane as a standard, relative retention volumes could be calculated with a repeatability of about ± 0·10 per cent.

Theoretical

The partition coefficient, K, is defined as

$$K = \frac{\text{amount of solute per unit volume in the liquid phase}}{\text{amount of solute per unit volume in the gas phase}}$$

If n_2^l = number of moles of solute in the liquid phase
n_2^g = number of moles of solute in the gas phase
V^l = volume of the liquid phase
and V^g = volume of the gas phase

$$K = \frac{n_2^l}{n_2^g} \cdot \frac{V^g}{V^l}$$

or

$$K = \frac{x}{y} \cdot \frac{n^l + n_2^l}{V^l} \cdot \frac{V^g}{n^g + n_2^g} \tag{1}$$

where x and y are the mole fractions of the solute in the liquid and gas phase respectively; n^l and n^g are the number of moles of stationary phase and carrier gas.

The activity coefficient, γ_2, of the solute in a liquid mixture at a concentration x is given by

$$\gamma_2 = \frac{p_2^g}{p_2^0} \cdot \frac{1}{x}$$

where p_2^g is the partial pressure and p_2^0 the vapour pressure of the pure solute. More correctly,

$$\gamma_2 = \frac{p_2^{g^*}}{p_2^{0^*}} \cdot \frac{1}{x} \tag{2}$$

Where $p_2^{g^*}$ and $p_2^{0^*}$ are the corresponding fugacities, related to p_2^g and p_2^0 respectively by the equations[8],

$$\ln p_2^{0^*} = \ln p_2^0 + \frac{B_{22} p_2^0}{RT} \tag{3}$$

and

$$\ln p_2^{g^*} = \ln p_2^g + \frac{\bar{P}}{RT}[B_{22} - (1-y)^2(B_{11} - 2B_{12} + B_{22})] \tag{4}$$

B_{11} and B_{22} are the second virial coefficients of the carrier gas and pure solute respectively, at T°K.

The second virial coefficient B_{12}, which characterizes the interactions between unlike molecules, is given by the expression relating B_{11} and B_{22} to the second virial coefficient of a gaseous mixture B_m[9];

$$B_m = y^2 B_{22} + 2y(1-y)B_{12} + (1-y)^2 B_{11}$$

From eqns (1), (2), (3) and (4) and with $p_2^g = y\bar{P}$,

$$\ln \gamma_2 = \ln \left[\frac{n^l + n_2^l}{KV^l} \cdot \frac{V^g}{n^g + n_2^g} \right] + \ln \bar{P} + \frac{\bar{P}}{RT}[B_{22} - (1-y)^2(B_{11} - 2B_{12} + B_{22})] - \ln p_2^0 - \frac{B_{22} p_2^0}{RT} \tag{5}$$

but $$\frac{V^g}{n^g+n_2{}^g} = \frac{RT}{\bar{P}} + y^2B_{22} + 2y(1-y)B_{12} + (1-y)^2B_{11} \quad (6)$$

$$\therefore \quad \ln \gamma_2 = \ln \left\{ \frac{n^l+n_2{}^l}{KV^l} \cdot \left[\frac{RT}{\bar{P}} + y^2B_{22} + 2y(1-y)B_{12} + (1-y)^2B_{11} \right] \right\}$$

$$+ \ln \bar{P} + \frac{\bar{P}}{RT}[B_{22} - (1-y)^2(B_{11} - 2B_{12} + B_{22})] - \ln p_2{}^0 - \frac{B_{22}p_2{}^0}{RT} \quad (7)$$

At infinite dilution y and $n_2{}^l \to 0$ and $\gamma_2 \to \gamma_2{}^\infty$, so that by rearranging eqn (7) and expanding $\ln \left[1 + \frac{B_{11}\bar{P}}{RT}\right]$, neglecting all but first order terms, we obtain:

$$\ln \gamma_2{}^\infty = \ln \frac{n^lRT}{KV^lp_2{}^0} + \frac{2B_{12}}{RT} \cdot \bar{P} - \frac{B_{22}p_2{}^0}{RT} \quad (8)$$

Fugacity varies with pressure P, however, according to the expression

$$\left(\frac{\partial \ln p_2{}^*}{\partial p} \right) = \frac{v_2}{RT}$$

where v_2 = partial molar volume of the solute.

Integration gives:

$$\ln p_2{}^*(0) = \ln p_2{}^*(P) - \frac{Pv_2}{RT}$$

For the pure solute vapour,

$$\ln p_2{}^{0*}(0) = \ln p_2{}^{0*}(p_2{}^0) - \frac{p_2{}^0v_2{}^0}{RT}$$

where $v_2{}^0$ = molar volume of the solute at T°K; the compressibility of the liquid is neglected.

For the solute at pressure $\bar{P}$,

$$\ln p_2{}^{g*}(0) = \ln p_2{}^{g*}(\bar{P}) - \frac{\bar{P}v_2}{RT}$$

Since the solutions are very dilute, $v_2{}^0 = v_2$; after correction of the fugacities to a standard pressure eqn (8) then becomes:

$$\ln \gamma_2{}^\infty = \ln \frac{n^lRT}{KV^lp_2{}^0} + \frac{\bar{P}}{RT}(2B_{12} - v_2{}^0) - \frac{p_2{}^0}{RT}(B_{22} - v_2{}^0) \quad (9)$$

With $\frac{V^g}{n^g+n_2{}^g} = \frac{RT}{\bar{P}}$, which implies ideality in the gas phase, instead of eqn (6), Everett and Stoddart's equation[2] is obtained:

$$\ln \gamma_2{}^\infty = \ln \gamma_p{}^\infty + \frac{\bar{P}}{RT}(2B_{12} - B_{11} - v_2{}^0) - \frac{p_2{}^0}{RT}(B_{22} - v_2{}^0)$$

Eqn (9) can be rearranged:

$$\ln K = \ln \frac{n^l RT}{V^l \gamma_2^{\infty} p_2^0} + \frac{\bar{P}}{RT}(2B_{12} - v_2^0) - \frac{p_2^0}{RT}(B_{22} - v_2^0) \qquad (10)$$

At constant temperature and for the same solute (first and last terms on the RHS constant) K will be determined by the average column pressure and by the choice of carrier gas.

The k' factor is a more readily measurable quantity in gas chromatography than the partition coefficient, particularly where capillary columns are involved. The two are related by the expression

$$k' = \frac{V_N}{Vg} = \frac{KV^l}{Vg}$$

V_N is the net retention volume[10], so that at constant temperature, for the same solute, column and stationary phase

$$\log k' = A + \frac{\bar{P}}{2{\cdot}303RT}(2B_{12} - v_2^0) \qquad (11)$$

where A is a constant.

Eqn (11) shows that for a particular solute and carrier gas ($2B_{12} - v_2^0$ constant) $\log k'$ should be a linear function of the mean absolute column pressure; or, for a particular solute (v_2^0 constant) at constant pressure, $\log k'$ should be linearly related to B_{12}. Certain assumptions are implied in the definition of B_{12}, namely that the intermolecular forces between different molecules and between similar molecules are mainly London dispersive forces, and that the molecules have spherical symmetry. Nevertheless the simple model serves as a useful guide to the interpretation of the results. Owing to the lack of published experimental data for B_{12} it is not possible to verify eqn (11) directly. However, if it is assumed that the carrier gas and hydrocarbon mixtures conform to the principle of corresponding states, an approximate value of B_{12} can be calculated from the universal reduced equation of state[11]. Guggenheim and McGlashan[11] have shown that the latter is represented closely over a wide temperature range for pure substances and mixtures by an empirical formula of the type recommended by Beattie and Bridgeman[12]:

$$\frac{B}{V^*} = 0{\cdot}461 - 1{\cdot}158\left(\frac{T^*}{T}\right) - 0{\cdot}503\left(\frac{T^*}{T}\right)^3$$

where V^* and T^* are the critical (or characteristic[11]) volume and temperature respectively. The critical or characteristic constants of mixtures, V_{12}^*, T_{12}^*, are obtained by application of the combining rules,

$$T_{12}^* = (T_1^* \cdot T_2^*)^{1/2}$$

and

$$(V_{12}^*)^{1/3} = \tfrac{1}{2}[(V_1^*)^{1/3} + (V_2^*)^{1/3}]$$

which are again only valid if the interactions are of the London type and the molecules behave as spheres. *Table 1* shows values of B_{11}, B_{22} and B_{12} calculated from the Beattie and Bridgeman formula.

Table 1. Calculated second virial coefficients for pure hydrocarbons, carrier gases and their mixtures at 25°C

(cm^3 $mole^{-1}$)

Hydrocarbon	B_{22}	B_{12}						
		Helium	*Hydrogen*	*Nitrogen*	*Carbon monoxide*	*Argon*	*Oxygen*	*Carbon dioxide*
Isopentane	−979	+28	−20	−132	−142	−150	−154	−367
n-Pentane	−1033	+28	−21	−135	−146	−157	−158	−377
2,2-Dimethylbutane	−1318	+30	−26	−155	−167	−178	−182	−431
Cyclopentane	−1056	+24	−23	−133	−144	−153	−157	−373
2,3-Dimethylbutane	−1382	+30	−27	−158	−170	−181	−185	−441
2-Methylpentane	−1398	+30	−27	−160	−172	−183	−187	−444
3-Methylpentane	−1442	+30	−28	−162	−175	−186	−190	−452
n-Hexane	−1468	+30	−28	−164	−176	−188	−193	−456
Methylcyclopentane	−1426	+27	−29	−158	−171	−182	−185	−439
2,2-Dimethylpentane	−1713	+32	−32	−178	−192	−205	−210	−495
2,4-Dimethylpentane	−1777	+33	−33	−182	−197	−210	−215	−507
Benzene	−1326	+22	−28	−149	−161	−170	−174	−415
2,2,3-Trimethylbutane	−1753	+31	−33	−180	−194	−207	−211	−498
3,3-Dimethylpentane	−1798	+31	−33	−182	−196	−210	−214	−506
Cyclohexane	−1510	+25	−30	−162	−175	−185	−189	−451
2-Methylhexane	−1905	+32	−35	−189	−204	−218	−222	−525
2,3-Dimethylpentane	−1855	+31	−34	−185	−200	−213	−217	−514
3-Methylhexane	−1889	+32	−34	−188	−203	−216	−221	−521
3-Ethylpentane	−1930	+32	−35	−189	−204	−218	−223	−526
n-Heptane	−1968	+32	−35	−192	−207	−222	−226	−534
B_{11} for pure carrier gas		+15	+15	−8	−12	−14	−16	−124

Discussion

Values of k' for a number of carrier gases and mean absolute column pressures are shown in *Table 2*. At constant pressure the k' factor for a particular hydrocarbon decreases with choice of carrier gas in the order helium, hydrogen, nitrogen, argon, oxygen, carbon monoxide and carbon dioxide. The k' factors for carbon dioxide are about 7 per cent lower than those for helium at the same column pressure of 2·883 atm, and about 12 per cent lower at 4·384 atm. Typical results are shown in *Figure 1*, representing a plot of log k' versus B_{12} at 2·883 atm for cyclopentane, 2,3-dimethylbutane and 2-methylpentane. The theoretical slope, $10{\cdot}2 \times 10^{-5}$ mole cm^{-3}, has been drawn through the points for helium. Carbon monoxide and particularly carbon dioxide show greater deviations for all three hydrocarbons.

The effect of increasing the mean absolute column pressure on solute retention is shown for a typical case in *Figure 2*. Plots of log k' against $\bar{P}$ are found to be approximately linear, except for helium, where k' remains constant within experimental error over the pressure range studied. The slopes, which increase from hydrogen to carbon dioxide, may be extrapolated to the same point at $\bar{P}=0$, in accord with theory. From this extrapolated value of log k', the activity coefficient, γ_2^{∞}, may be readily calculated without the need to correct for carrier gas–solute interactions. B_{12} coefficients may be

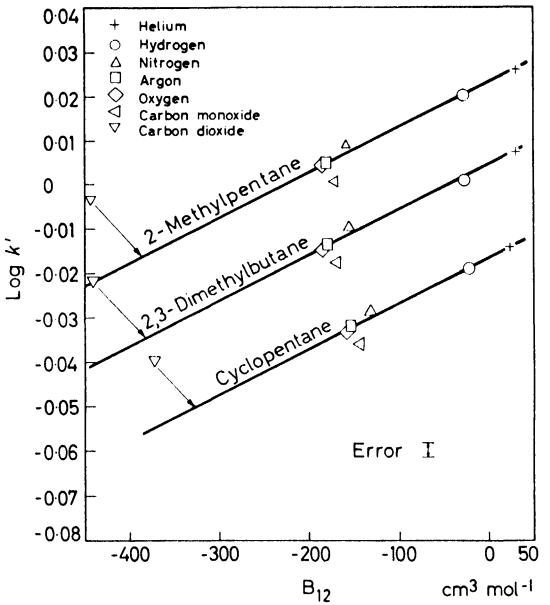


Figure 1. Log k' versus B_{12} at 2·883 atm for cyclopentane, 2,3-dimethylbutane and 2-methylpentane

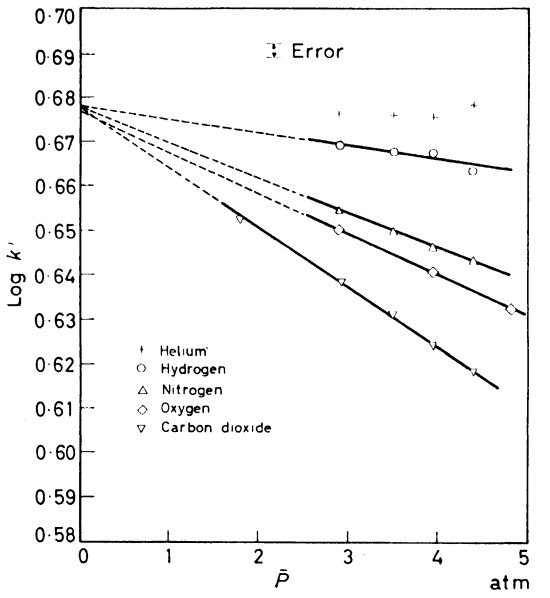


Figure 2. Log k' versus $\bar{P}$ for *n*-heptane

Table 2. The k' factor for different mean absolute column pressure and carrier gases at 25°C

Hydrocarbon	*Helium*				*Hydrogen*				*Nitrogen*			
	2·883 atm	3·497 atm	3·940 atm	4·384 atm	2·883 atm	3·497 atm	3·940 atm	4·384 atm	2·883 atm	3·497 atm	3·940 atm	4·384 atm
Isopentane	0·348	0·350	0·350	0·350	0·345	0·345	0·343	0·339	0·339	0·334	0·333	0·331
n-Pentane	0·474	0·475	0·475	0·475	0 468	0·467	0·465	0·463	0·457	0·453	0·451	0·451
2,2-Dimethylbutane	0·712	0·713	0·713	0·715	0·703	0·706	0·704	0·699	0·688	0·679	0·676	0·672
Cyclopentane	0·968	0·969	0·969	0·972	0·958	0·957	0·955	0·948	0·937	0·928	0·923	0·921
2,3-Dimethylbutane	1·017	1·016	1·016	1·019	1·002	1·001	0·998	0·992	0·977	0·967	0·961	0·957
2-Methylpentane	1·062	1·062	1·063	1·065	1·048	1·045	1·042	1·037	1·021	1·008	1·003	0·999
3-Methylpentane	1·246	1·245	1·247	1·248	1·229	1·229	1·223	1·217	1·197	1·183	1·178	1·170
n-Hexane	1·516	1·515	1·518	1·520	1·494	1·492	1·490	1·480	1·454	1·439	1·430	1·421
Methylcyclopentane	1·981	1·979	1·982	1·986	1·954	1·950	1·947	1·934	1·907	1·890	1·879	1·866
2,2-Dimethylpentane	2·005	2·002	2·006	2·010	1·973	1·968	1·967	1·952	1·916	1·890	1·879	1·866
2,4-Dimethylpentane	2·120	2·118	2·121	2·125	2·089	2·080	2·078	2·066	2·026	2·003	1·988	1·976
Benzene	2·139	2·138	2·141	2·145	2·109	2·102	2·102	1·090	2·061	2·041	2·029	2·021
2,2,3-Trimethylbutane	2·291	2·288	2·292	2·297	2·257	2·249	2·246	2·232	2·190	2·165	2·153	2·138
3,3-Dimethylpentane	2·856	2·854	2·860	2·863	2·814	2·803	2·801	2·785	2·729	2·698	2·680	2·663
Cyclohexane	2·887	2·883	2·889	2·894	2·847	2·839	2·837	2·820	2·773	2·746	2·729	2·714
2-Methylhexane	3·238	3·236	3·239	3·246	3·186	3·175	3·170	3·148	3·085	3·050	3·028	3·006
2,3-Dimethylpentane	3·356	3·353	3·358	3·365	3·305	3·293	3·290	3·263	3·202	3·167	3·145	3·122
3-Methylhexane	3·585	3·582	3·587	3·595	3·530	3·517	3·513	3·489	3·417	3·380	3·353	3·329
3-Ethylpentane	3·981	3·979	3·984	3·994	3·921	3·905	3·904	3·871	3·798	3·755	3·726	3·697
n-Heptane	4·746	4·744	4·736	4·764	4·671	4·655	4·651	4·611	4·517	4·468	4·432	4·397
Average linear gas velocity (cm. sec^{-1})	7·90	10·07	11·64	13·32	17·50	22·22	25·79	29·20	8·68	11·23	12·98	14·78

Table 2 (continued)

Hydrocarbon	*Oxygen*			*Carbon monoxide*	*Argon*	*Carbon dioxide*				
	2·883 atm	3·940 atm	4·830 atm	2·883 atm	2·883 atm	1·772 atm	2·883 atm	3·497 atm	3·940 atm	4·384 atm
Isopentane	0·334	0·329	0·325	0·332	0·335	0·337	0·330	0·328	0·324	0·322
n-Pentane	0·454	0·447	0·439	0·451	0·455	0·456	0·447	0·443	0·440	0·436
2,2-Dimethylbutane	0·680	0·668	0·658	0·676	0·681	0·685	0·670	0·663	0·656	0·652
Cyclopentane	0·926	0·913	0·899	0·920	0·929	0·931	0·913	0·904	0·895	0·886
2,3-Dimethylbutane	0·966	0·950	0·934	0·960	0·969	0·973	0·961	0·941	0·931	0·920
2-Methylpentane	1·010	0·992	0·974	1·002	1·012	1·016	0·992	0·980	0·969	0·960
3-Methylpentane	1·183	1·163	1·142	1·175	1·187	1·191	1·162	1·147	1·135	1·124
n-Hexane	1·438	1·412	1·388	1·427	1·441	1·447	1·410	1·392	1·375	1·359
Methylcyclopentane	1·883	—	—	—	—	1·892	—	1·827	1·804	1·783
2,2-Dimethylpentane	1·893	—	—	—	—	1·906	—	1·827	1·804	1·783
2,4-Dimethylpentane	2·001	1·963	1·925	1·988	2·007	2·014	1·960	1·934	1·907	1·884
Benzene	2·038	2·007	1·975	2·022	2·046	2·037	1·985	1·962	1·937	1·916
2,2,3-Trimethylbutane	2·166	2·126	2·087	2·151	2·173	2·180	2·123	2·094	2·069	2·043
3,3-Dimethylpentane	2·698	2·648	2·598	2·679	2·707	2·713	2·641	2·603	2·566	2·534
Cyclohexane	2·742	2·696	2·651	2·722	2·751	2·751	2·683	2·649	2·615	2·583
2-Methylhexane	3·047	2·990	2·932	3·028	3·059	3·066	2·979	2·934	2·891	2·853
2,3-Dimethylpentane	3·163	3·105	3·046	3·143	3·176	3·184	3·094	3·047	3·003	2·963
3-Methylhexane	3·374	3·311	3·249	3·354	3·388	3·396	3·296	3·247	3·199	3·155
3-Ethylpentane	3·749	3·680	3·609	3·726	3·766	3·772	3·662	3·605	3·551	3·502
n-Heptane	4·465	4·374	4·290	4·433	4·473	4·487	4·350	4·279	4·211	4·152
Average linear gas velocity (cm. sec^{-1})	7·51	11·13	14·24	8·67	6·89	4·92	10·36	13·29	15·35	17·52

evaluated from the slopes of these plots and *Table 3* shows that, except for carbon dioxide, these agree with the calculated values as well as may be expected.

Table 3. Experimental B_{12} coefficients ($cm^3\ mole^{-1}$)

Hydrocarbon	*Hydrogen*	*Nitrogen*	*Oxygen*	*Carbon dioxide*
Isopentane	+26	−105	−125	−163
n-Pentane	+7	−105	−152	−173
2,2-Dimethylbutane	+26	−105	−145	−168
Cyclopentane	+5	−91	−152	−197
2,3-Dimethylbutane	+9	−112	−153	−203
2-Methylpentane	−7	−127	−155	−206
3-Methylpentane	+3	−117	−163	−211
n-Hexane	0	−128	−163	−233
Methylcyclopentane	−12	−128	—	−234
2,2-Dimethylpentane	−14	−133	—	−245
2,4-Dimethylpentane	−5	−130	−165	−249
Benzene	−13	−117	−157	−251
2,2,3-Trimethylbutane	−6	−123	−160	−222
3,3-Dimethylpentane	−12	−131	−166	−242
Cyclohexane	−18	−120	−163	−236
2-Methylhexane	−35	−135	−175	−272
2,3-Dimethylpentane	−6	−133	−167	−264
3-Methylhexane	−32	−136	−180	−276
3-Ethylpentane	−36	−144	−176	−292
n-Heptane	−36	−154	−183	−294

The variations in solute retention not only depend on carrier gas and column pressure, but also to some extent on the structure of the hydrocarbon. The decrease in k' with choice of carrier gas and pressure may be expressed relative to helium, since helium/hydrocarbon systems represent the closest approach to ideality. From a consideration of the decrease in solute retention, $-\Delta \log k'$, with choice of carrier gas, at constant pressure (*Table 4*), three features become apparent. The value of $-\Delta \log k'$ increases with increasing molecular weight of the solute; the change being approximately linear for normal and 2-methyl paraffins, the only paraffins for which more than two homologues were examined. Secondly, the value of $-\Delta \log k'$ for the C_6 and C_7 paraffins decreases with the extent of branching, the spread being much greater in carbon dioxide. Thirdly, the values of $-\Delta \log k'$ for cyclopentane, methylcyclopentane, cyclohexane and benzene are much smaller than for the paraffins with similar retentions. These results are in satisfactory agreement with the order predicted from the calculated B_{12} coefficients. However, both benzene and cyclohexane have relatively larger $-\Delta \log k'$ values in carbon dioxide than in any other gas, with the exception of hydrogen. Little can be said about the magnitude of this structural effect at this stage, since only three naphthenes and one aromatic hydrocarbon have been examined.

Since the retentions of hydrocarbons in helium are almost independent of pressure, the values of $-\Delta \log k'$ in *Table 4* provide an indication of the slope of the pressure versus $-\Delta \log k'$ plots (cf. *Figure 2*) and may be used to assess the relative effect of pressure on solute retention for the remaining carrier

Table 4. Decrease of solute retention, $-\Delta \log k'$, for different carrier gases at 2·883 atm and 25°C

Hydrocarbon	*Mean* log k' *for helium*	$-\Delta \log k'$ *Hydrogen*	$-\Delta \log k'$ *Nitrogen*	$-\Delta \log k'$ *Argon*	$-\Delta \log k'$ *Oxygen*	$-\Delta \log k'$ *Carbon monoxide*	$-\Delta \log k'$ *Carbon dioxide*
Isopentane	−0·4566	0·0053	0·0136	0·0188	0·0193	0 0222	0·0245
n-Pentane	−0·3235	0·0063	0·0162	0·0187	0·0191	0·0220	0·0262
2,2-Dimethylbutane	−0·1467	0·0066	0·0159	0·0202	0·0219	0·0236	0·0271
Cyclopentane	−0·0135	0·0054	0·0149	0·0187	0·0198	0·0226	0·0262
2,3-Dimethylbutane	0·0072	0·0064	0·0172	0·0209	0·0221	0·0251	0·0291
2-Methylpentane	0·0265	0 0062	0·0175	0·0214	0·0222	0·0257	0·0300
3-Methylpentane	0·0958	0·0063	0 0177	0·0213	0·0228	0·0257	0·0305
n-Hexane	0·1810	0·0066	0·0184	0·0223	0·0233	0·0266	0·0318
Methylcyclopentane	0·2971	0·0062	0·0167	—	0·0222	—	—
2,2-Dimethylpentane	0·3023	0·0071	0·0200	—	0·0251	—	—
2,4-Dimethylpentane	0·3265	0·0065	0·0198	0·0240	0·0253	0·0280	0·0342
Benzene	0·3306	0·0066	0·0165	0·0197	0·0214	0·0248	0·0328
2,2,3-Trimethylbutane	0·3602	0·0066	0·0198	0·0231	0·0245	0·0276	0·0333
3,3-Dimethylpentane	0·4560	0·0067	0·0200	0·0235	0·0249	0·0280	0·0342
Cyclohexane	0·4606	0·0062	0·0176	0·0211	0·0225	0·0257	0·0320
2-Methylhexane	0·5105	0·0073	0·0212	0·0249	0·0266	0·0294	0·0364
2,3-Dimethylpentane	0·5260	0·0069	0·0208	0·0241	0·0259	0·0287	0·0354
3-Methylhexane	0·5548	0·0070	0·0211	0·0249	0·0267	0·0293	0·0368
3-Ethylpentane	0·6004	0·0070	0·0209	0·0245	0·0265	0·0292	0·0367
n-Heptane	0·6765	0·0071	0·0216	0·0259	0·0267	0·0298	0·0380

gases. In the pressure range studied higher pressures increase the magnitude of the gas phase interactions equally for all hydrocarbon/carrier gas systems and no specific effects have been observed.

Although the results have so far been discussed exclusively in terms of carrier gas–solute interactions there are at least two other effects which could contribute to differences in retention for different carrier gases. If surface adsorption contributes significantly to the solute retention, the use of high molecular weight gases or particularly polar gases will tend to reduce this contribution and thus make the absolute retention smaller. Under the conditions used, however, it seems likely that the effect is negligible, except for the carbon dioxide/benzene system, where it could form a large part of the observed retention reduction.

Secondly, solubility of the carrier gas in the stationary phase could conceivably change to some extent the solvent character of the latter. This again should be negligible under the prevailing conditions. The solubility of carbon dioxide in squalane, at 25°C and 1 atm pressure, even on an ideal basis, must be less than 0·1 mole per cent; it seems extremely unlikely that this small concentration could produce more than a very small fraction of the observed changes in retention. With more polar or easily condensable gases both these effects will be aggravated, and interpretation of results may well become more difficult.

From a chromatographic viewpoint the relative changes in solute retention are most important, and the effects of carrier gas and column pressure on various separations are shown in *Tables 5a* and *5b*. The most pronounced changes occur for 2,3-dimethylbutane/cyclopentane, 2,2-dimethylpentane/methylcyclopentane, cyclohexane/3,3-dimethylpentane and benzene/2,4-dimethylpentane. The separation factor of benzene/2,4-dimethylpentane in carbon dioxide is particularly small in comparison with the behaviour in nitrogen, argon, oxygen and carbon monoxide at the same pressure.

Although the change in separation factor may be small, the number of theoretical plates, n, required to achieve a given separation x, which is given by the equation[3],

$$n = \left[\frac{4x}{\alpha - 1}\left(1 + \frac{1}{k'}\right)\right]^2$$

may be considerably altered, since n is inversely proportional to $(\alpha - 1)^2$. Thus, the number of plates required to separate benzene and 2,4-dimethylpentane by four standard deviations in helium and argon at 2·883 atm is 429,000 and 99,700 respectively; i.e. more than a four-fold decrease. The number of plates required to separate cyclohexane and 3,3-dimethylpentane in carbon dioxide at an average column pressure of 1·772 atm is 177,400, compared to 86,300 plates at 4·384 atm; i.e. the separation may be effected in less time (at the higher pressure) and in addition the number of plates may be halved.

The effect of a change of carrier gas and/or column pressure as an additional aid to peak identification is attractive; the technique is relatively simple and may be applied to advantage in addition to variation of stationary phase and column temperature where difficult separations are encountered, as with the higher molecular weight petroleum fractions.

Table 5a. Separation factors in different carrier gases at 2·883 atm and 25°C

Separation	*Helium*	*Hydrogen*	*Nitrogen*	*Argon*	*Oxygen*	*Carbon monoxide*	*Carbon dioxide*
2,3-Dimethylbutane/cyclopentane	1·050	1·046	1·043	1·043	1·043	1·042	1·041
2-Methylpentane/2,3-dimethylbutane	1·044	1·045	1·044	1·043	1·044	1·044	1·042
2,2-Dimethylpentane/methylcyclopentane	1·011	1·009	1·004	—	1·005	—	—
n-Hexane/2,2-dimethylbutane	2·130	2·125	2·113	2·117	2·116	2·115	2·104
Benzene/2,4-dimethylpentane	1·009	1·009	1·017	1·019	1·018	1·018	1·012
Cyclohexane/3,3-dimethylpentane	1·010	1·011	1·015	1·016	1·016	1·016	1·015
2,3-Dimethylpentane/2-methylhexane	1·036	1·037	1·037	1·037	1·037	1·038	1·038
n-Heptane/2,2-dimethylpentane	2·366	2·368	2·356	—	2·357	—	—

Table 5b. The effect of pressure on separation factors for carbon dioxide at 25°C

Separation	1·772 atm	2·883 atm	3·497 atm	3·940 atm	4·384 atm
2,3-Dimethylbutane/cyclopentane	1·045	1·041	1·040	1·039	1·038
2-Methylpentane/2,3-dimethylbutane	1·043	1·042	1·042	1·041	1·042
2,2-Dimethylpentane/methylcyclopentane	1·007	—	1·000	1·000	1·000
n-Hexane/2,2-dimethylbutane	2·108	2·104	2·101	2·098	2·085
Benzene/2,4-dimethylpentane	1·011	1·012	1·014	1·015	1·016
Cyclohexane/3,3-dimethylpentane	1·013	1·015	1·017	1·018	1·019
2,3-Dimethylpentane/2-methylhexane	1·037	1·038	1·038	1·038	1·038
n-Heptane/2,2-dimethylpentane	2·353	—	2·340	2·332	2·326

Because of the variation of solute retention with the carrier gas and mean absolute column pressure, it is suggested that these be stated when specific or relative retention data are reported in the future. It would seem best at a later stage, when more data have been accumulated, to consider a redefinition of the specific retention volume in terms of zero column pressure, in order that it remain independent of carrier gas–solute interactions.

Conclusion

The potentialities of employing gas phase interactions as an additional aid to peak separation and identification are considerable, particularly if extended to the use of polar substances, such as water vapour and ammonia, as carrier gases. Interesting possibilities exist in the analysis of complex mixtures, such as are encountered in the higher molecular weight petroleum fractions, especially in conjunction with use of high efficiency capillary columns.

In addition the method has promise for study of the interesting specific aspects of intermolecular forces in the gas phase, provided the precision of the results can be improved and the contribution of other effects, such as adsorption and solubility of the carrier gas, can be distinguished.

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DISCUSSION

F. Sjenitzer (*prepared contribution*): I should like to make two points on this very beautiful paper. The first point refers to *Table 3* on page 76. This does not contain experimental values of B_{12} coefficients for helium, carbon monoxide or argon. Is there perhaps a special reason for not including these data?

The second point concerns the first five lines on page 80. Here it is suggested that the carrier gas used and the mean absolute column pressure be stated when relative retention data are reported in the future. I have also seen in *Table 2*, on page 74, that helium seems to be the ideal carrier gas, because for this gas the k' factor is independent of pressure and seems to be identical with the k' value at zero pressure for the other gases. Therefore, I should like to suggest that in the future helium at some convenient pressure be used as a standard carrier gas for the measurement of relative retention data.

W. T. Swanton: The B_{12} coefficients for argon and carbon monoxide are not included, because the variation of k' with pressure was not measured for these gases. I don't believe that calculated B_{12} coefficients will really be markedly different from those for oxygen. It is only for academic interest that we have included the B_{12} coefficients. With our experimental error we cannot calculate second virial coefficients to better than ± 30 cc/mole. The results for helium are within the experimental error, and therefore we cannot say what the B_{12} coefficients will be.

With regard to the second point, about relative data being obtained with helium as the carrier gas: I do not think this is necessary. All I am asking is that in the future perhaps we can have an indication of the column pressure, so that we can correlate results from different sources. If possible, it would be interesting to get a series of relative data in the same carrier gas for a series of pressures, so that we could extrapolate to zero column pressure.

S. K. Bawa (*prepared contribution*): It has been shown by Desty, Goldup, Luckhurst and Swanton that the solute retention of hydrocarbons is influenced by the mean absolute column pressure and by the choice of carrier gas.

We have measured the effect of a change of pressure for methyl oleate, a polar molecule of high molecular weight; the results confirm the findings of the above workers.

Figure 3 shows how the solute retention decreases with increasing mean absolute column pressure. The stationary phase was polyethylene glycol adipate; the column was operated at 145°C with argon as carrier gas.

The effect of a change of carrier gas has also been investigated for the retention of toluene by the same stationary phase. These results also confirm Desty's findings; they are reproduced in *Figure 4*.

W. T. Swanton: It is very comforting to hear from Dr Bawa additional confirmation of our work. I think that the figure showing the variation of solute retention with argon pressure probably answers Dr Sjenitzer's question to some extent.

S. J. Hawkes: I was interested in the final suggestion, that we should always give the pressure and the nature of the carrier gas when recording retention times. Would I be right in supposing that, to be of any value, these experiments should be conducted at two pressures at least, so that one can extrapolate the data?

W. T. Swanton: Yes, I think that, when relative retention data are given, it would probably be useful to have at least two or three pressures, so that one can extrapolate to zero column pressure. With packed columns the variation of solute

retention with pressure is probably not so very marked. Here the most important factor is control of column temperature. This is probably a much more important thing than the pressure variation; but if we can control column temperature to $\pm 0{\cdot}5^{\circ}C$, I think these pressure variations become more significant.

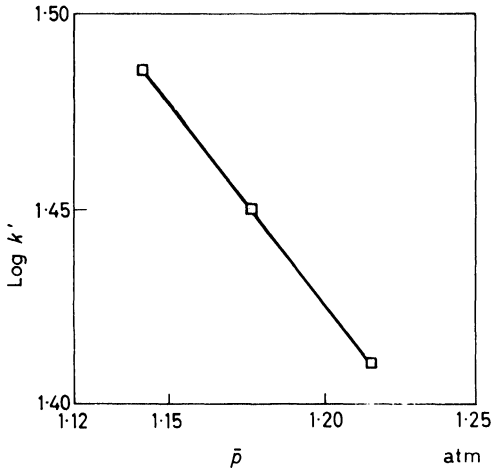


Figure 3. The effect of column pressure on solute retention. Solute methyl oleate; stationary phase polyethylene glycol adipate; carrier gas argon; operating temperature 145°C

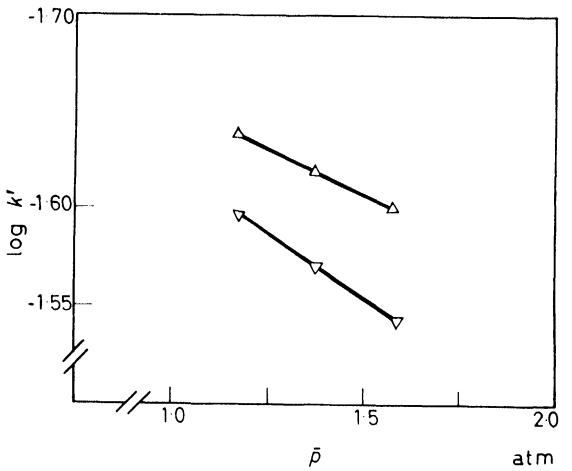


Figure 4. The effect of carrier gas on solute retention. Solute toluene; stationary phase polyethylene glycol adipate
△ nitrogen carrier gas; ▽ carbon dioxide carrier gas

J. H. Knox: I wonder to what extent some of these results may be explained by the carrier gas dissolving in the liquid phase; and in particular, can this account for the discrepancy between the calculated and experimental values of B_{12} with carbon dioxide?

W. T. Swanton: This is certainly a point which must be ironed out. You have two additional effects creeping in here which we have not really examined yet in great detail. One is, of course, residual adsorption on the glass capillary; and the other—as Dr Knox has suggested—is the solubility of the carbon dioxide or other carrier gases in the stationary phase. On an ideal basis I think the solubility of carbon dioxide in squalane works out to be about 0·1 mole per cent. I therefore believe that this will have a negligible effect on the solute retention, but this is a point which has to be ironed out.

D. H. Desty: Just to put this thing of retention volumes in perspective: to people using conventional packed columns, as Mr Swanton suggested, this effect is scarcely relevant at the normal precision level with which relative retention volumes are measured. At the precision level of 1–2 per cent the effects are not significant at all, so that it is only when one measures relative retention volumes to a few tenths of a per cent that the statement of the carrier gas and mean column pressure is really relevant. In the statement of specific retention data it seems to me that this effect may be much more critical, because the absolute size of the effect is quite large (*ca.* 5 per cent).

6

THE APPLICATION OF CAPILLARY COLUMNS IN THE STUDY OF THE THERMODYNAMIC BEHAVIOUR OF ETHANOL AND CARBON TETRACHLORIDE IN DINONYL PHTHALATE

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The apparatus and the procedure for the determination of specific retention volumes by means of capillary columns are described. As a test of the validity and accuracy of the data derived from these columns the specific retention volumes of benzene in dinonyl phthalate at various temperatures have been compared with the results obtained from conventional packed columns.

The retention volumes of a non-polar solute, carbon tetrachloride, and of a polar solute, ethanol, in dinonyl phthalate have been determined; from the data the activity coefficients of these solutes at infinite dilution were evaluated. The determinations, by means of capillary columns, have been carried out at temperatures between 20 and 45°C in order that the heat and entropy contributions to non-ideal behaviour of the two systems could be apportioned. Ancillary experimental data for the partial molar volumes of carbon tetrachloride and ethanol in dinonyl phthalate are provided. The results are used to explain the solute-solvent behaviour in the light of the modern statistical theories of infinitely dilute binary solutions involving molecules of widely different sizes.

THE IMPORTANCE of specific retention volumes for identification and for the thermodynamic study of solutions has been discussed in a number of papers[1–7]. It has been shown that specific retention volumes can be determined with a precision of about ± 1 per cent when packed columns are used. The increasing use of capillary columns has raised the question whether retention volumes obtained from these columns are the same as those from packed columns. Some preliminary investigations on this point have already been reported[8]. The accurate data available from packed columns for the system benzene/dinonyl phthalate[5] have now made it possible to compare retention volumes from both types of column.

In some respects capillary columns are experimentally more convenient to use for the determination of retention volumes, and in view of this an investigation has been carried out into their application in the prediction of the thermodynamic properties of solutions.

Experimental

Retention volumes were measured with apparatus which is largely standard equipment for capillary GLC, modified to allow better control and measurement of temperature and gas flow rate. The dinonyl phthalate used was a pure sample prepared for the earlier work with packed columns.

The results reported from packed columns in the present work were obtained with an apparatus which, except for the detector employed, was similar to that previously described[5].

Columns

The capillary columns consisted of 60 ft. lengths of stainless steel tubing[a], 0·010 in. i.d. Before coating they were washed with redistilled <40°C petroleum spirit and blown dry with pure nitrogen.

Coating was carried out with 2 ml of a 20 per cent v/v solution of dinonyl phthalate in redistilled <40°C petroleum spirit in the manner described by Scott[9].

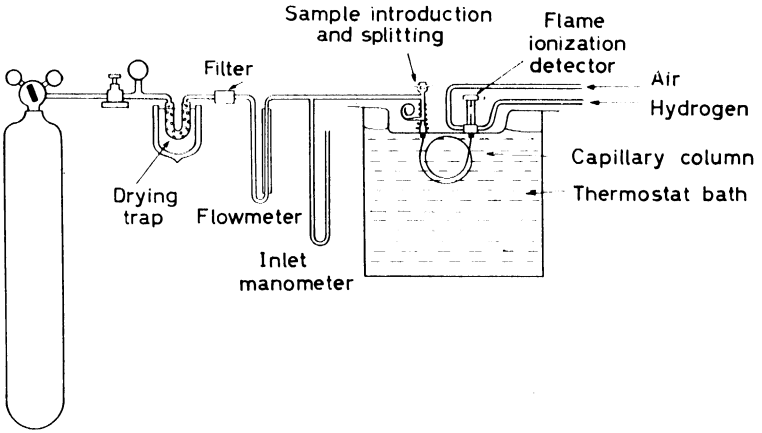


Figure 1. Flow system

Attempts to determine the amount of liquid phase in the column by weighing before and after coating were not very successful, since the column was too heavy to be weighed on a micro balance. The most satisfactory way to determine the weight of liquid phase was by washing it out of the column, at the end of the experiments, with 1 ml portions of <40°C redistilled petroleum spirit. These portions were added until there was no further increase in the weight of a small collecting vessel after the evaporation of the solvent in a slow stream of pure nitrogen at room temperature.

Temperature control and measurement

The capillary column was immersed in a large water bath controlled to ±0·02°C. The bath temperatures were measured with N.P.L. certificated mercury-in-glass thermometers calibrated to 0·02°C.

The flow system

The flow system is shown in *Figure 1*. The nitrogen carrier gas was taken from a cylinder via a standard reducing valve to a precision pressure control valve[b]. This valve was used to set and control the inlet pressure to give the required flow rate. From the control valve the gas passed through a drying tube containing 5A molecular sieve and silica gel immersed in liquid air, a

sintered stainless steel filter, and a flowmeter[c], which served to indicate the approximate total gas flow rate. Finally the gas passed into the column inlet and sample splitter. A mercury manometer was connected to the column inlet to measure the gas inlet pressure. The sample introduction

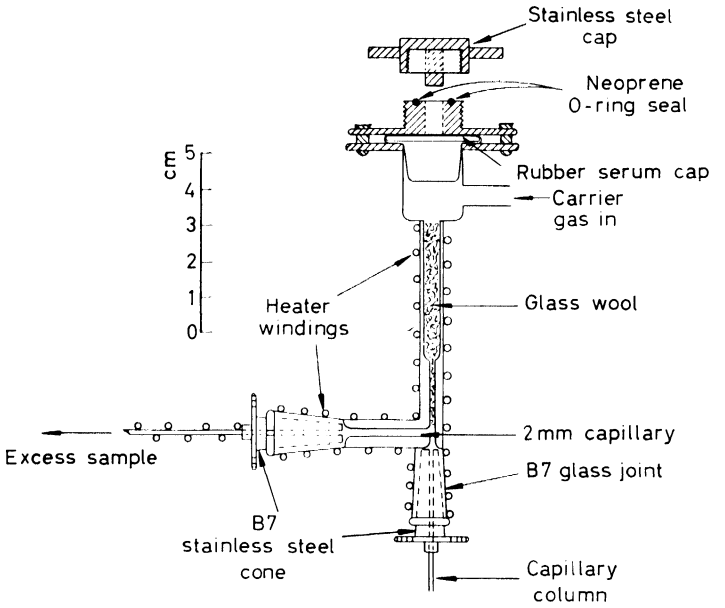


Figure 2. Sample introduction system for use with capillary columns

unit, constructed of glass, is shown in *Figure 2*. The inlet end of the capillary was fitted with a stainless steel B7 cone. The outlet was attached to the base of a flame ionization detector by means of a miniature compression union.

Flow measurement

The carrier gas flow was obtained from Poiseuille's equation:

$$V = \frac{\pi r^4}{16\eta l} \cdot \frac{p_i^2 - p_o^2}{p_o} \qquad (1)$$

A calibration graph of V versus $(p_i^2 - p_o^2)/p_o$ was obtained for each of the column temperatures used. These determinations were carried out by collection over water of a measured volume of carrier gas at different inlet pressures.

Sample addition and sample size

The samples were added to the column in the form of vapour by means of a hypodermic syringe through a rubber serum cap (*Figure 2*). The sample introduction point was kept warm to avoid condensation of vapour. At the bottom of the sample introduction head, the gas stream was split in the ratio of 180:1.

A small amount of methane added with each sample gave an indication of the gas residence time of the apparatus. The size of the sample actually entering the capillary column did not exceed 0·5 μg.

Detector

The flame ionization detector is shown in *Figure 3*. The gas from the column passes through the centre needle into the flame. The hydrogen for the flame passes through the annular space between the inner and outer needles and

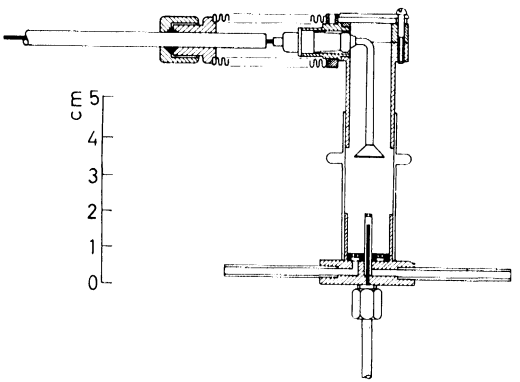


Figure 3. Flame ionization detector

the air supply enters the combustion chamber through a diffuser in the base. The outer needle is made of platinum/iridium alloy and the collector electrode of platinum gauze. The rest of the metal parts of the detector proper are of stainless steel. The insulator is a ceramic lead-in seal (KLG type No. CS308/4).

The detector was used in conjunction with a Vibron amplifier type 56A[d] and a 5 mV, $\frac{1}{4}$ sec Honeywell Brown recorder. A similar detector unit was used with the packed columns.

The flame ionization detector was very satisfactory for the work described. It does, however, suffer from the limitation that it does not respond to permanent gases, which can make it difficult to determine the gas residence time in the apparatus. Although methane was satisfactory for this purpose in our work, it might not be so for low column temperatures, or for other stationary liquids, or for the measurement of small retention times.

Retention volume measurements

Retention times were measured with a stop watch, from the peak maximum of methane to the peak maximum of the substance under study. Inlet pressure and barometric pressure were measured immediately before injection of the sample and the flow rate was read from the calibration graph.

The retention volumes were calculated[5], and corrected for the pressure gradient[10] in the usual way.

Results

(a) *Retention volumes.* The retention volumes of benzene in DNP-coated capillary columns were determined at 48 and 56°C. The results are shown in *Table 1*, together with values obtained from packed columns.

Table 1. Retention volumes of benzene in DNP obtained with capillary and packed columns

t°C	*Capillary column* 1 (6·58 mg DNP) V_g^t	*Capillary column* 2 (10·33 mg DNP) V_g^t	*Packed columns*[5] V_g^t
48·8	346·0 346·0 } *345·9* 345·8	345·9 346·5 } *346·6* 346·7	*350·3*
56·6	—	266·0 265·9 } *265·8* 265·5	*269·2*

The repeatability of the retention volumes determined with capillary columns is about ± 1 per cent, which is similar to results from packed columns, and there is good agreement between the two sets of data. Retention data for carbon tetrachloride/DNP and ethanol/DNP were also obtained with packed columns and compared with those from capillary columns. The packed column retention volumes were determined relative to benzene. *Table 2* gives the values obtained on packed and capillary columns for carbon tetrachloride.

Table 2. Retention volumes of carbon tetrachloride in DNP obtained with capillary and packed columns

Temperature °C	*Capillary column* V_g^t ml/g*	*Packed column* V_g^t ml/g†
23·0	744·8	747·0
34·7	460·6	462·0
49·3	272·8	276·0
56·4	216·9	218·7
64·4	170·5	170·7
76·0	123·9	122·3
81·0	109·0	106·8
96·5	75·8	72·2

* Calculated from the Antoine equation given on page 89.
† Average of at least five determinations at each temperature, and calculated by means of the Antoine equation for benzene given in reference 5.

The agreement between the two sets of data in *Table 2* is very good. A similar table is not given for ethanol, since the repeatability of the results on packed columns was found to be very poor. This may probably be ascribed to adsorption on the untreated Celite solid support, as the peaks were badly tailed and the retention time was considerably affected by sample size.

The retention data obtained from the capillary columns for carbon tetrachloride and ethanol in dinonyl phthalate over the range 20–45°C are given in *Tables 3* and *4*. The following expressions were obtained to fit these data:

Carbon tetrachloride

$$\log V_g = \frac{765{\cdot}158}{t+170{\cdot}45} - 1{\cdot}11830 \qquad (2a)$$

Ethanol

$$\log V_g = \frac{3008{\cdot}86}{t+358{\cdot}14} - 5{\cdot}49841 \qquad (2b)$$

where V_g is the specific retention volume, i.e. the retention volume per gramme of stationary phase, at 0°C and average column pressure.

Table 3. Retention volumes and activity coefficients of carbon tetrachloride in dinonyl phthalate

Temperature °C	*Retention volume* V_g^t ml/g	*True activity coefficient* $^{\infty}\gamma_1$
20·02	855·7 853·9 856·0 856·1 851·1 — *854·6*	*0·558*
25·00	678·5 678·8 676·9 — *678·1*	*0·572*
30·00	555·5 555·9 553·6 551·6 551·6 — *553·6*	*0·574*
34·99	454·4 455·9 455·5 — *455·3*	*0·577*
39·98	384·6 385·3 378·5 385·1 378·7 — *382·4*	*0·572*
44·97	313·0 314·2 314·2 313·5 314·1 — *313·8*	*0·585*

Our measurements confirm that accurate retention data can be obtained with stainless steel capillary columns and show that these columns have some marked advantages over packed columns for this type of work. In particular, they give more reliable results for polar compounds and an easier control of temperature and flow rate. Their main disadvantage is the difficulty of the accurate determination of the small quantity of liquid phase (about 10 mg).

Table 4. Retention volumes and activity coefficients of ethanol in dinonyl phthalate

Temperature °C	*Retention volume* V_g^t ml/g	*True activity coefficient* $\overset{\infty}{\gamma_1}$
20·01	309·0, 311·2, 309·7, 310·6, 307·3 } *309·6*	*3·049*
24·99	246·8, 245·0, 247·4 } *246·4*	*2·937*
30·01	197·8, 198·8, 198·3, 197·4 } *198·1*	*2·812*
35·00	159·8, 160·3, 160·1 } *160·1*	*2·713*
39·98	134·4, 134·3, 134·1, 134·3, 134·1 } *134·2*	*2·546*
44·98	106·7, 106·2, 107·0, 106·6, 106·2 } *106·5*	*2·545*

The following expression, obtained by the method of least squares, represents the temperature variation of $\overset{\infty}{\gamma_1}$ for ethanol to within $\pm 0{\cdot}004$

$$\log \overset{\infty}{\gamma_1} = \frac{295{\cdot}4382}{T} - 0{\cdot}5240 \qquad (3)$$

(b) *Volume changes on mixing.* The densities, ρ, of the solutions of CCl_4 in DNP and C_2H_5OH in DNP were measured at 20°C as a function of the concentrations (c_1) of the solutes. It was found that ρ varied linearly with c_1 over the range 5 to 50 mole per cent with respect to the solutes. The following linear equations best describe the experimental data obtained:

$$\left.\begin{aligned} CCl_4\text{–DNP} &: \rho = 0{\cdot}3924\, c_1 + 0{\cdot}9700 \\ C_2H_5OH\text{–DNP} &: \rho = -0{\cdot}2232\, c_1 + 0{\cdot}9700 \end{aligned}\right\} (\pm 0{\cdot}0002)$$

where c_1 is the concentration of CCl_4 or C_2H_5OH in DNP in g/ml. This shows that mixing does not cause a change in volume.

(c) *Calculation of activity coefficients.* The Raoult law deviation factor $\overset{\infty}{\Gamma}$ was calculated from:

$$\overset{\infty}{\Gamma} = \frac{RT}{Mp_1^{\circ}V_g^t}$$

The values of $\overset{\infty}{\Gamma}$ calculated from the expression given above are based on the assumptions that (i) the gas phase behaves ideally and (ii) the standard state of activity corresponds to the unmixed (pure) liquid component at the column temperature, but under its own vapour pressure. The deviation from the perfect gas law may be appreciable, and a correction must therefore be applied accordingly. Moreover, it is customary in the thermodynamic study of solutions to define the standard state of activity as that of the pure substance at the ambient temperature and pressure. These corrections were made with the help of the expression[7]:

$$\overset{\infty}{\gamma}_1 = \overset{\infty}{\Gamma}_1 \cdot \exp\left\{\frac{p^*}{RT}(2B_{12} - B_{22} - \bar{V}_1) - \frac{p_1^\circ}{RT}(B_{11} - V_1^\circ)\right\} \tag{4}$$

where B_{11} and B_{22} are the second virial coefficients for the solute vapour and the carrier gas respectively. The cross coefficient B_{12} results from the binary collisions between solute and carrier gas molecules.

Since the partial molar volumes are independent of composition, we may take $\bar{V}_j = V_j^\circ$. Hence the above relation may be re-written in the form:

$$\log \overset{\infty}{\gamma}_1 = \log \overset{\infty}{\Gamma}_1 + \frac{p^*}{2{\cdot}303\ RT}(2B_{12} - B_{22} - V_1^\circ) - \frac{p_1^\circ}{2{\cdot}303\ RT}(B_{11} - V_1^\circ) \tag{5}$$

(d) B_{11} (*carbon tetrachloride*). The second virial coefficients of CCl_4 were calculated from the expression[11]:

$$B_{11} = -71{\cdot}4 - \frac{13{\cdot}25}{T^2} \times 10^7 \tag{6}$$

(e) B_{11} (*ethanol*). No experimental data on the second virial coefficients of ethanol vapour between 20 and 40°C could be found in the literature. By means of the Clapeyron–Clausius equation the saturated vapour volumes were calculated from the heats of vaporization[12] and the vapour pressure data[13] available for ethanol within this temperature range. The values of B_{11}were then obtained as the difference between RT/p_1° and the corresponding values of the saturated vapour volume. The following expression, obtained by the method of least squares, describes the values to within ± 1·5 per cent.

$$B_{11} = -1534 - 7{\cdot}0883 \times 10^{-7} \exp(6328/T) \tag{7}$$

(f) B_{22} (*nitrogen*). The second virial coefficients of N_2 were calculated from the constants of the Beattie–Bridgeman equation of state[14]

$$B_{22} = 50{\cdot}46 - \frac{1344{\cdot}5}{0{\cdot}08206\ T} - \frac{4{\cdot}20 \times 10^7}{T^3} \tag{8}$$

(g) B_{12} (*carbon tetrachloride–nitrogen*). These were calculated from the critical constants of carbon tetrachloride and nitrogen[15] after the method suggested by Guggenheim and McGlashan[16].

(h) B_{12} (*ethanol–nitrogen*). The values of B_{12} used in this paper were calculated by the method of Scatchard and Ticknor[17].

The fully corrected activity coefficients for the various temperatures are given in *Tables 3* and *4*.

Theoretical

Provided the contributions of the internal and external degrees of freedom to the complete partition function can be regarded as independent, the Helmholtz free energies of pure liquids (1) and (2) and of a mixture containing N_1 molecules of liquid (1) and N_2 molecules of liquid (2) can be expressed as[18]

$$\mathscr{F} = -N_j kT \ln \phi_j^\circ - kT \ln Q_j^\circ \quad (j = 1, 2) \tag{9a}$$

and

$$\mathscr{F}^M = -N_1 kT \ln \phi_j - N_2 kT \ln \phi_2 - kT \ln Q^M \tag{9b}$$

where

where ϕ = the product of $(2\pi mkT/h^2)^{3/2}$ and the partition function for all the internal degrees of freedom.
Q = the configurational partition function.

If it is further assumed that the internal degrees of freedom remain practically unchanged during the mixing process, the change in the Helmholtz free energy on mixing the two liquids is given by:

$$\Delta\mathscr{F}^M = \mathscr{F}^M - (\mathscr{F}_1^\circ + \mathscr{F}_2^\circ) = -kT(\ln Q^M - \ln Q_1^\circ - \ln Q_2^\circ)$$

$$= -kT \ln \frac{Q^M}{Q_1^\circ Q_2^\circ} \tag{10}$$

the configurational partition functions being defined as:

$$Q_j^\circ = \frac{1}{N_j!} \int \cdots \int e^{-(U_j^\circ/kT)} (d\tau_j)^{Nj} \quad (j = 1, 2) \tag{11a}$$

and

$$Q^M = \frac{1}{N_1! N_2!} \int \cdots \int e^{-(U/kt)} (d\tau_1)^{N_1} \cdot (d\tau_2)^{N_2} \tag{11b}$$

The main difficulty of statistical mechanics in the prediction of the equilibrium properties of liquids and solutions is inherent in the evaluation of Q_j° and Q^M. The literature contains a number of rather arbitrary schemes for the evaluation of these functions, from which equilibrium properties of liquids may be approximately predicted. In the absence of any rigorous theory we shall assume[19]

$$Q_j^\circ = \frac{(N_j v_j^\circ)^{N_j}}{N_j!} \exp\left(-\frac{N_j w_j^\circ}{kT}\right) \quad (j = 1, 2) \tag{12a}$$

and

$$Q^M = \frac{\{N_1 \bar{v}_1 + N_2 \bar{v}_2\}^{(N_1+N_2)}}{N_1! \times N_2!} \exp\left[-\frac{1}{kT}\left(N_1 w_1^\circ + N_2 w_2^\circ + \frac{N_1 N_2 (\bar{v}_1 \bar{v}_2)^{\frac{1}{2}}}{N_1 \bar{v}_1 + N_2 \bar{v}_2} \cdot \Delta w\right)\right] \tag{12b}$$

Since the systems in question do not show any volume changes when the two components are mixed, the partial molecular volumes can be replaced by the

molecular volumes of pure liquids, i.e. $\bar{v}_j = v_j^\circ$. Also, it follows that for such systems $\Delta\mathscr{F}^M = \Delta\mathscr{G}^M$. Substituting (12a) and (12b) in (10) we get:

$$\Delta\mathscr{G}^M = N_1 kT \ln \frac{N_1 v_1^\circ}{N_1 v_1^\circ + N_2 v_2^\circ} + N_2 kT \ln \frac{N_2 v_2^\circ}{N_1 v_1^\circ + N_2 v_2^\circ} + \frac{N_1 N_2 (v_1^\circ v_2^\circ)^{\frac{1}{2}}}{N_1 v_1^\circ + N_2 v_2^\circ} \Delta w \tag{13}$$

For an ideal solution ($v_1^\circ = v_2^\circ$ and $\Delta w = 0$) the above equation reduces to:

$$\Delta\mathscr{G}_{id}{}^M = N_1 kT \ln \frac{N_1}{N_1 + N_2} + N_2 kT \ln \frac{N_2}{N_1 + N_2} \tag{14}$$

Subtracting (14) from (13) and denoting $\Delta\mathscr{G}^M - \Delta\mathscr{G}_{id}{}^M = \Delta_e\mathscr{G}$, we have:

$$\Delta_e\mathscr{G} = N_1 kT \ln \frac{(N_1 + N_2) v_1^\circ}{N_1 v_1^\circ + N_2 v_2^\circ} + N_2 kT \ln \frac{(N_1 + N_2) v_2^\circ}{N_1 v_1^\circ + N_2 v_2^\circ} + \frac{N_1 N_2 (v_1^\circ v_2^\circ)^{\frac{1}{2}}}{N_1 v_1^\circ + N_2 v_2^\circ} \Delta w \tag{15}$$

Differentiating with respect to N_1 and letting $N_1/N_2 \to 0$, we get:

$$\frac{\partial}{\partial N_1} (\Delta_e\mathscr{G})_{N_1/N_2 \to 0} = \Delta_e \overline{g_1}^\infty = \ln \frac{v_1^\circ}{v_2^\circ} + \left(1 - \frac{v_1^\circ}{v_2^\circ}\right) + \left(\frac{v_1^\circ}{v_2^\circ}\right)^{\frac{1}{2}} \frac{\Delta w}{kT} \tag{16}$$

Making use of the well-known relationship between excess chemical potential and activity coefficient and finally expressing the results in partial molar rather than partial molecular quantities, we obtain:

$$\ln \gamma_1^\infty = \ln \frac{V_1^\circ}{V_2^\circ} + \left(1 - \frac{V_1^\circ}{V_2^\circ}\right) + \left(\frac{V_1^\circ}{V_2^\circ}\right)^{\frac{1}{2}} \frac{\Delta W}{RT} \tag{17}$$

Recalling that $\mathscr{G} = \mathscr{F} + \mathscr{P}\mathscr{V}$, and using the Gibbs–Helmholtz equation, which relates functions $\mathscr{H}$ and $\mathscr{G}$, we derive the following expression for the partial molar (excess) heat of mixing of component 1 at infinite dilution:

$$\Delta_e \overline{H_1}^\infty = \left(\frac{V_1^\circ}{V_2^\circ}\right)^{\frac{1}{2}} \left[\Delta W - \frac{T}{2}(\alpha_1 - \alpha_2)\Delta W - T\frac{\mathrm{d}}{\mathrm{d}T}(\Delta W)\right] - RT^2\left(1 - \frac{V_1^\circ}{V_2^\circ}\right)(\alpha_1 - \alpha_2) \tag{18}$$

Finally, we may use the Gibbs relation $G = H - TS$, and write for the partial molar excess entropy of component 1:

$$\Delta_e \overline{S_1}^\infty = \overbrace{-R\left[\ln \frac{V_1^\circ}{V_2^\circ} + \left(1 - \frac{V_1^\circ}{V_2^\circ}\right)\right]}^{\text{geometrical part}} \overbrace{- RT(\alpha_1 - \alpha_2)\left(1 - \frac{V_1^\circ}{V_2^\circ}\right)}^{\text{geometrical + expansion part}}$$

$$\overbrace{- \left(\frac{V_1^\circ}{V_2^\circ}\right)^{\frac{1}{2}} \left[\tfrac{1}{2}(\alpha_1 - \alpha_2)\Delta W + \frac{\mathrm{d}W}{\mathrm{d}T}\right]}^{\text{geometrical + expansion + energetical part}} \tag{19}$$

For a detailed application of the above theory to the systems CCl_4/DNP and C_2H_5OH/DNP, a knowledge of activity coefficients alone is not sufficient. For a quantitative confirmation of the theory the heats of mixing for these systems must be known from an independent source such as calorimetry. We propose to confine the present considerations to the evaluation of the excess thermodynamic functions and to explain the solution behaviour in the light of these functions.

Discussion

(a) *The partial molar excess functions*

It is clear from (17) that the contributions to $\overset{\infty}{\gamma}_1$ arise from geometric and energetic effects. The geometric contribution is due purely to the difference in the molecular volumes of the two components and is independent of their nature. The energetic contribution stems from the interactions and the relative orientations between molecules. The latter contribution does not appear independent of the molecular volumes and it is therefore not possible to give its actual value. When

$$[(v_2^\circ/v_1^\circ)^{\frac{1}{3}} - (v_1^\circ/v_2^\circ)^{\frac{1}{3}}] \gg \Delta w/kT$$

the non-ideality of the system is determined by the relative volumes of the two species. *Tables 5* and *6* give the values of

$$[(v_2^\circ/v_1^\circ)^{\frac{1}{3}} - (v_1^\circ/v_2^\circ)^{\frac{1}{3}}]/(\Delta w/kT)$$

and also the values of γ_1 for CCl_4 for the geometrical effect when $\Delta w = 0$. It can be seen that for CCl_4, the main contribution to $\overset{\infty}{\gamma}_1$ comes from the size effect, whereas for ethanol this effect is relatively small.

The data in *Table 4* show that the activity coefficient of ethanol varies about 17 per cent over the temperature range studied. As the activity coefficients decrease with rise in temperature, heat must be absorbed during the mixing process, i.e. the partial molar heat of mixing of ethanol in DNP is positive. The graph of $\log \overset{\infty}{\gamma}_1$ against $1/T$ is a straight line, indicating that $\Delta_e\overset{\infty}{H}_1$ is independent of temperature. The value of $\Delta_e\overset{\infty}{H}_1$, calculated as the product of the slope of the line (determined by the least square fit) by R, is given in *Table 6*.

Table 3 shows that $\overset{\infty}{\gamma}_1$ for CCl_4 varies only slightly with temperature; hence no reliable figures for $\Delta_e\overset{\infty}{H}_1$ could be obtained. However, the temperature variations of $\overset{\infty}{\gamma}_1$ do show that the mixing process is accompanied by evolution of heat, i.e. $\Delta_e\overset{\infty}{H}_1$ is negative.

Tables 5 and *6* give the partial molar excess entropies of CCl_4 and ethanol at various temperatures, together with their component parts. The geometrical part is the largest for both substances; it is counteracted by a relatively small thermal expansion effect. For ethanol the last term of eqn (19) makes a positive contribution which is twice as great as that from the cubical expansion term, making the partial molar entropy, as a whole, positive.

Table 5. The partial molar excess functions of carbon tetrachloride in DNP

Temp. $T°K$	$RT \ln \overset{\infty}{\gamma_1}$ cal mol.$^{-1}$	aT	bT	$T(\Delta_e \overset{\infty}{S})_{\Delta w}{}^0$ cal mol.$^{-1}$	$(\gamma_1)_{\Delta w \quad 0}$	$\left[\left(\frac{v_2{}^0}{v_1{}^0}\right)^{\frac{1}{3}} - \left(\frac{v_1{}^0}{v_2{}^0}\right)^{\frac{1}{3}}\right] \Big/ \frac{\Delta w}{kT}$
293·20	−340	−420	66	354	0·486	6
298·18	−331	−426	69	357	0·487	5
303·18	−334	−432	71	361	0·488	5
308·17	−337	−438	73	365	0·489	5
313·16	−347	−444	75	369	0·490	5
318·15	−339	−449	78	371	0·491	4

$$a = R\left[\ln \frac{V_1{}^\circ}{V_2{}^\circ} + \left(1 - \frac{V_1{}^\circ}{V_2{}^\circ}\right)\right], \quad b = RT(\alpha_1 - \alpha_2)\left(1 - \frac{V_1{}^\circ}{V_2{}^\circ}\right)$$

$$\alpha_1 = 12{\cdot}2 \times 10^{-4} \text{ deg.}^{-1} \quad \alpha_2 = 7{\cdot}2 \times 10^{-4} \text{ deg.}^{-1}$$

Table 6. The partial molar excess functions of ethanol in DNP

Temp. $T°K$	$RT \ln \overset{\infty}{\gamma_1}$ cal mol.$^{-1}$	aT	bT	cT	$T(\Delta_e \overset{\infty}{S_1})$ cal mol.$^{-1}$	$\left[\left(\frac{v_2{}^0}{v_1{}^0}\right)^{\frac{1}{3}} - \left(\frac{v_1{}^0}{v_2{}^0}\right)^{\frac{1}{3}}\right] \Big/ \frac{\Delta w}{kT}$
293·19	650	−661	53	−95	703	0·39
298·17	638	−670	55	−98	712	0·39
303·21	623	−680	57	−104	729	0·40
308·18	611	−692	59	−108	741	0·41
313·16	581	−702	61	−128	769	0·42
318·16	590	−712	62	−112	762	0·42

$$\Delta_e \overset{\infty}{H}_1 = 1352 \text{ cal mol.}^{-1}; \quad a = R\left[\ln \frac{V_1{}^\circ}{V_2{}^\circ} + \left(1 - \frac{V_1{}^\circ}{V_2{}^\circ}\right)\right]$$

$$b = RT(\alpha_1 - \alpha_2)\left(1 - \frac{V_1{}^\circ}{V_2{}^\circ}\right), \quad c = \sqrt{\frac{V_1{}^\circ}{V_2{}^\circ}}\left[\tfrac{1}{2}(\alpha_1 - \alpha_2)\Delta w + \frac{\mathrm{d}}{\mathrm{d}T}(\Delta w)\right]$$

$$\alpha_1 = 10{\cdot}8 \times 10^{-4} \text{ deg.}^{-1} \quad \alpha_2 = 7{\cdot}2 \times 10^{-4} \text{ deg.}^{-1}$$

(b) *Physical interpretation of excess functions*

On statistical mechanical grounds, the excess entropy of mixing may originate from:

(i) difference in molecular volumes of the components of the solution
(ii) relative orientational distribution of molecules, and
(iii) relative spatial distribution of molecules.

The contribution to excess entropy due to (iii) is usually small. On the other hand, the excess heat of mixing is strongly dependent on (iii), to a lesser extent on (ii), and receives no contribution whatsoever from (i).

The physical interpretation of (i) is the simplest of all. The packing of particles of different sizes is less uniform or more disorderly, i.e. it gives rise to a larger number of distinguishable configurational arrangements with molecules of unequal size than with molecules of equal size. Thus, it should always give a positive entropy of mixing.

The negative contribution to $\Delta_e\bar{S}_1^{\infty}$ due to the difference in the thermal expansion of CCl_4 and DNP or ethanol and DNP, indicates a tendency toward compensation of volume differences, nullifying the disorder resulting from the mixed population of big and small molecules.

The positive contribution to the partial molar entropy of ethanol from the energetic effect shows that, during the mixing process, the solution becomes less ordered. The high degree of order which existed in the pure state of ethanol is at least partially destroyed. The ethanol molecules have a greater randomness and 'wander about' more freely in DNP than in their own atmosphere.

The large positive heat of mixing at infinite dilution (or a large value of $\Delta_e\bar{H}_1^{\infty}$) suggests the breakage of hydrogen bonds during the mixing process. This is followed by a loss of orientational order, making the energetic part of excess entropy positive.

The small amount of heat evolved when CCl_4 is mixed with DNP indicates weak interactions (absent in pure CCl_4), which come into play when the easily polarizable molecule of CCl_4 is surrounded by moderately polar molecules of DNP.

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LIST OF SYMBOLS

B second virial coefficient
$\mathscr{F}$ total Helmholtz free energy
F molar Helmholtz free energy
$\mathscr{G}$ total Gibbs free energy
G molar Gibbs free energy
$\mathscr{H}$ total enthalpy
H molar enthalpy
M molecular weight
N number of molecules
$\mathscr{P}$ total pressure
Q configurational partition function or configurational integral
R gas constant
$\mathscr{S}$ total entropy
S molar entropy
T temperature in degrees Kelvin
U configurational potential energy of all the molecules

$\mathscr{V}$ total volume
V molar volume
V_o gas flow rate at the column outlet
V_g specific retention volume
V_g^t retention volume per gramme of the stationary phase at the column temperature and average column pressure
g molecular Gibbs free energy
h Planck's constant
k Boltzmann's constant
l column length
m mass of a molecule
p pressure
r radius of the capillary
s molecular entropy
t temperature in degrees Celsius
u linear flow rate
v molecular volume
w average molecular potential energy, related to the total potential energy of the whole assembly when all the molecules are on their sites
Δw interchange energy
α coefficient of cubical expansion
γ activity coefficient
η viscosity of the carrier gas
ϕ product of $\left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}}$ and the partition function for all internal degrees of freedom
$(\mathrm{d}\tau)^N$ product of the N elements of volume containing the centres of all the N molecules in the assembly
Γ Raoult law deviation factor
Δ change in a thermodynamic function

Subscripts

1,2 solute and solvent, respectively
e excess ($\Delta_e G$ and $\Delta_e S$ referring to excess free energy and excess entropy)
i, o column inlet and outlet, respectively
j any individual component

Superscripts

M mixing of components
$^\circ$ pure component
* averaged value
$^-$ partial ($\Delta_e \bar{S}_1 \ldots$, etc.), refers to partial molar excess functions of component 1
∞ infinite dilution

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DISCUSSION

Author's Additional Comments

Since this paper was written Smith has published a letter in *Nature*[20], claiming that the use of methane for the determination of the free gas volume of a column is unreliable.

The validity of this method was checked in the course of the work described here. This was done by comparing the free gas volume of the column determined with methane with that determined by weighing the column empty and then full of water.

It was found that at both the lowest and the highest temperatures used in our experiments (20 and 56°C), the methane value of the free gas volume was 2 per cent higher than that obtained by the water method. Since the difference was the same at both temperatures it may be due to the small dead volumes in the detector, sample introduction system and connecting pipes, which were not completely accounted for in the latter method.

We would agree with Smith that the methane method is open to suspicion as a generally applicable technique. It is apparent, however, that in our case, where the retention volumes being measured were large compared to the free gas volume, a small error in the latter will have a negligible effect on the accuracy of retention data obtained in this way.

We have found four systems for which the heat of mixing is either very small or zero—two from our own work and two from the paper of Freeguard and Stock (page 102) on static systems. *Table 7* shows the experimental values of $\overset{\infty}{\gamma}_1$, and the values calculated from the equation

$$\ln \overset{\infty}{\gamma}_1 = \ln \frac{V_1^0}{V_2^0} + \left(1 - \frac{V_1^0}{V_2^0}\right)$$

under the assumption that the last term of eqn. 17 is equal to zero.

With the exception of the last system, i.e. the CCl_4/squalane system, there is a reasonably good correlation between the experimental and the calculated values.

Table 7. Comparison between experimental and calculated values of activity coefficients

System	$\overset{\infty}{\gamma}_1$ exp.	$(\overset{p}{\gamma}_1)_{w=0}$ calc.
CCl_4/DNP at 40°C	0·57*	0·49
Benzene/DNP at 50°C	0·51*	0·46
CH_2Cl_2/DNP at 30°C	0·38†	0·35
CCl_4/Squalane at 40°C	0·54†	0·42

* Experimental values from our work.
† Experimental values of Freeguard and Stock.

J. F. Smith (*prepared contribution*): The excellent agreement between the results on packed and capillary columns is testimony to the experimental skill in obtaining these results. There are, however, one or two points of technique which require comment, and the elimination of which would render even more remote the possibility that such good agreement is fortuitous.

In the first place the authors clean the capillaries with petroleum ether. In our experience many metal capillaries as received from the manufacturers are frequently coated internally (presumably with the lubricant used for drawing). This material is not soluble in petroleum ether and is incompletely soluble even in hot chloroform. The significant absence of this material can be easily checked by the absence of a retentive and resolving effect of the capillary before it is coated with stationary phase. Unfortunately on removing this layer we have found that metal capillaries produce severe tailing of polar solutes; this may explain why the authors did not observe tailing with ethanol.

In order to determine the amount of stationary phase in the column the authors extract the column with petroleum ether until no further material is removed. A residual monolayer of stationary phase could be tenaciously retained, however. A check that the column neither retained nor resolved appropriate solutes after removal of the stationary phase would confirm or eliminate this complication.

In the paper methane has been used as a 'dead volume marker'. It would be interesting to know whether the value for the dead volume obtained in this way coincides with the value required to 'linearize the log plot' for the n-paraffins; since in our experience the latter gives a more accurate value for the dead volume than the use of methane, which can have a small but significant retention volume, even at 50°C.

Finally, before the Symposium I made the comment that the close agreement of specific retention volumes determined with capillary and packed columns would indicate that there is very little interfacial adsorption; because I thought at that time that the surface area–volume ratios in packed and capillary columns would be

greatly different. However, during the last few days we have been looking with optical and electron microscopes at the distribution of stationary phase on packed materials; our preliminary calculations indicate that in rough terms a 2 per cent stationary phase level on a packed column has an identical surface area–volume ratio as a 0·1-μ thick film on a 0·010-in. capillary, and similarly for 20 per cent and a 1-μ thick film.

E. R. Adlard: In reply to Dr Smith's question about the close agreement between results from packed and capillary columns, and his conclusion that gas–liquid and liquid–solid interfacial adsorptions can make no contribution I should agree with his statement, but modify it as follows: in the systems benzene/DNP and CCl_4/DNP it appears that gas–liquid and liquid–solid adsorptions make no contribution to the retention volume. As Dr Khan pointed out yesterday (page 17), any given system may or may not have interfacial resistance; the systems for which Mr Winters reported interfacial adsorption (page 54) involve highly polar stationary liquids.

In the case of the benzene/DNP and CCl_4/DNP systems, which are not very polar, adsorption effects appear to be negligibly small.

I think the question regarding the use of methane for the determination of the dead volume of the column is adequately covered in the 'authors' additional comments', but I should agree with Dr Smith that in general the methane method is suspect; and each case must be considered on its merits.

Concerning the point, whether the stationary liquid was completely removed by petroleum ether: we did in fact check this by washing the column with diethyl ether, but no more stationary liquid was removed by this treatment. I suspect, however, that this point is not very important, since I imagine that if a monolayer of stationary liquid were left behind it would have a negligibly small weight.

Finally, in answer to Dr Smith's first point: we did indeed get tailing with ethanol, but this was not serious; the retention time did not alter with quite large variations in sample size, in marked contrast with the behaviour of ethanol on packed columns, where retention times were completely unrepeatable.

A. V. Kiselev: I should like to ask Mr Adlard what is the precision and reproducibility of his ΔH value on page 95.

M. A. Khan: The accuracy with which one can determine the heat of mixing depends on the variation of the activity coefficient with temperature. We believe our values are correct to within ± 5 per cent.

A. Goldup: I should like to mention in support of Mr Adlard that, when I was doing my work on the measurement of retention volumes on capillary columns for the Edinburgh meeting[21], I measured very carefully the precision with which a given amount of stationary phase could be put on to, and taken off, a column. For all these measurements I used a micro-balance. I much prefer this technique to the method which Mr Adlard used. The amount of stationary phase put on to a column would be of the order of 5–10 mg, and this one could measure with 0·1 per cent accuracy on a more or less standard micro-balance.

E. R. Adlard: I agree that Dr Goldup's suggestion is a reasonable one, but in our case the column used was heavier than the maximum load of the micro-balance available. We were therefore forced to adopt the technique described of washing the stationary liquid out of the column.

M. B. Evans: I should like to ask whether Mr Adlard has considered the possibility of using an infra-red spectroscopic determination of DNP at the strong carbonyl absorption band at 1,720 cm^{-1}. If the column were washed out with a known volume of solvent, this would not have to be removed for the measurement.

E. R. Adlard: As Dr Martin pointed out in his opening lecture (page xxvii), weighing is one of the most accurate measurements which one can make; and I think it

unlikely that a better simple method could be devised for the determination of the amount of stationary liquid in the column.

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7

SOME STATIC MEASUREMENTS ON GAS–LIQUID CHROMATOGRAPHIC SYSTEMS INVOLVING DINONYL PHTHALATE AND SQUALANE

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Gas–liquid chromatography is a rapid and convenient method for the determination of activity coefficients at infinite dilution (γ^∞) of vapours in non-volatile liquids. Owing to the many experimental variables involved, however, great care must be taken when such measurements are made. Values of γ^∞ from independent methods are scarce and difficult to obtain, although there is an obvious need for them for comparative purposes. Partition isotherms of CCl_4, $CHCl_3$ and CH_2Cl_2 in dinonyl phthalate and squalane have therefore been determined at different temperatures under static conditions, by means of a McBain-type balance. From the data obtained the values of γ^∞ have been obtained by extrapolation, and excess heats and entropies of mixing have been evaluated by a graphical method from the temperature dependence of γ^∞. A technique is suggested by means of which values of γ^∞ can be rapidly estimated with reasonable accuracy by GLC; it involves the use of standard solutes with known activity coefficients.

The shapes of the partition isotherms suggest that 'fronting' (diffuse front, sharp tail) of chromatographic peaks is an inherent tendency in GLC. Tailing, when it occurs, cannot be due to non-ideal solution behaviour except when the most pronounced negative deviations from Raoult's law are observed.

Sorption isotherms for cyclohexane in various mixtures of dinonyl phthalate and squalane have also been measured; these prove to correspond almost exactly to those which would be predicted on the assumption that each component of the mixture behaves independently of the other.

ACTIVITY coefficients (γ) are useful parameters in the study of mixtures because they afford a measure of the interactions between the different molecular species, and since in GLC separations are due to differences in the solubility of the vapours of the various substances in the stationary liquid, at extreme dilution, it is to be expected that the specific retention volume (V_g) is related to the activity coefficient at infinite dilution (γ^∞). The relationship derived by Khan[1] is:

$$V_g = \frac{273R}{M_L p^0 \gamma_p{}^\infty} \tag{1}$$

where M_L = molecular weight of the involatile liquid (stationary phase)
p^0 = equilibrium vapour pressure of the pure absorbate at the temperature of the column

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γ^{∞} = activity coefficient at infinite dilution (which is a measure of the combined imperfections of the absorbate in vapour and liquid phase)*

Conversely it is also possible to estimate γ^{∞} from retention data, and this has been done by a number of workers[2–5,8,9]. This 'dynamic' method for determination of γ^{∞} is both rapid and convenient, but a large number of experimental variables is involved, such as flow rate and nature of the carrier gas, sample size, sample injection method, column length and so on, which can all be eliminated in a static method. It was with the intention of (a) comparing the GLC values of γ^{∞} with those obtained by a static technique, (b) investigating the nature of the partition isotherm, and (c) observing the effect of mixtures of stationary phases on the absorption of vapours that we carried out the following experiments. Some similar measurements have been made by Everett and co-workers[3,4].

The static method adopted was found to possess the following advantages for measurements involving gas–liquid systems:

(a) measurements could be carried out under equilibrium conditions, and the reversibility of the absorption process established;
(b) the effect of the solid support on the absorption of vapour by the involatile liquid could be ascertained;
(c) the partition isotherm could be constructed for a wide range of concentrations, so that the variation of γ with concentration could be studied;
(d) measurements could be made in the absence of a carrier gas.

Some disadvantages were:

(a) only small samples of support plus involatile liquid could be used; it is possible to use the pure liquid alone but equilibrium times are greatly increased (see below);
(b) uptake of vapour at very low pressures was difficult to measure; hence an extrapolation method was necessary for the evaluation of γ^{∞};
(c) the experiments were time-consuming.

Dinonyl phthalate and squalane were chosen as the stationary phases for two reasons: firstly, they are standard chromatographic materials and are widely used; secondly, preliminary experiments showed the uptake of vapour by these liquids was such that reasonably accurate measurements could be made. Carbon tetrachloride, chloroform and dichloromethane were chosen as absorbates because of their physical properties, such as fairly high molecular weight and convenient vapour pressures. Different combinations of the involatile and volatile liquids just mentioned represent examples of the following systems;

polar vapour/polar liquid, polar vapour/non-polar liquid
non-polar vapour/polar liquid, non-polar vapour/non-polar liquid

In addition to measurements made with the chlorinated hydrocarbons the

*(In the discussion, Dr Stock has indicated that the statement in brackets should be deleted—*Ed.*)

absorption of cyclohexane at 30° by mixtures of dinonyl phthalate and squalane was measured for the following systems:

15 per cent dinonyl phthalate/ 5 per cent squalane/80 per cent Celite
10 per cent dinonyl phthalate/10 per cent squalane/80 per cent Celite
5 per cent dinonyl phthalate/15 per cent squalane/80 per cent Celite

These experiments were suggested by the fact that a number of workers have used mixed stationary phases in GLC.

Experimental

The apparatus used for the static measurements was a McBain-type balance: a small glass bucket containing the sample was suspended from a fused silica spring. The spring itself was suspended in a water-jacketed column to maintain it at constant temperature. Careful calibration showed that the extension of the spring was a linear function of the increase in weight of the sample. This system was similar to that described by Ashworth and Everett[3], but with the following important differences: first, two springs were used in the same apparatus (in separate jackets), so that partition isotherms of a given compound could be measured in two different stationary phases at the same time; second, very sensitive springs were used (extension approximately 100 cm g $^{-1}$); third, a simple optical device was used to form a magnified image of the extension of the springs for very small amounts of absorbed vapour.

The procedure adopted to measure an isotherm was as follows: the absorbent was degassed to a pressure of about 10^{-5} mm of mercury, and the glass limb surrounding it immersed in a constant-temperature bath. Small charges of vapour were then admitted to the system through a greaseless tap. The extension of the spring and the pressure of vapour were measured by means of a katharometer.

For the most part, measurements were made with the involatile liquids coated on Celite. It was convenient to do this because it was established that isotherms obtained for the pure liquid alone were identical with those obtained when it was coated on Celite, and sorption equilibria were obtained much more slowly with the pure liquid, particularly at the higher relative pressures of vapour. The effect of Celite on the isotherms was found to be negligible, but this was not true of crushed Firebrick used as a support. Adsorption effects were particularly noticeable when small amounts of liquid were used (5 per cent or less by weight)—in fact at low relative pressures the uptake by the Firebrick alone was greater than that by the coated solid.

Sorption experiments were carried out at a number of temperatures within the range 0–50°.

Results

Values of γ were calculated by substitution of the experimental values of pressure (p) of the absorbate and the mole fraction (x) taken up by the involatile liquid, in the equation:

$$\log \gamma = \log \frac{p}{xp^0} - \frac{B(p^0 - p)}{2{\cdot}303RT} \qquad (2)$$

where p^0 is the equilibrium vapour pressure of the pure absorbate at temperature T, and B is the second virial coefficient of the vapour at the same temperature. Values of B were calculated for carbon tetrachloride, chloroform and cyclohexane by means of the Berthelot equation[6]:

$$B = \frac{9}{128} \cdot \frac{RT_c}{P_c}\left(1 - \frac{6T_c^2}{T^2}\right) \tag{3}$$

where T_c and P_c are the critical temperature and pressure respectively. Values of B for dichloromethane were calculated from[7]:

$$\ln(-B) = 9{\cdot}160 - 8{\cdot}28 \times 10^{-3}T \tag{4}$$

Values of $\log \gamma^\infty$ at the various temperatures were obtained by extrapolation to $x=0$ of a plot of $\log \gamma$ versus mole fraction x.

Table 1. Values of the excess heats and entropies of mixing

System	$\Delta H^{e\infty}$ cal	$\Delta S^{e\infty}$ e.u.
CCl_4/SQ	0	+1·20
$CHCl_3$/SQ	+540	+2·62
CH_2Cl_2/SQ	+1,150	+3·64
CCl_4/DNP	0	+1·04
$CHCl_3$/DNP	−1,020	−0·56
CH_2Cl_2/DNP	0	+1·93

SQ = Squalane DNP = dinonyl phthalate

Table 1 gives the values of the excess heat of mixing ($\Delta H^{e\infty}$) and excess entropy of mixing ($\Delta S^{e\infty}$), estimated from the temperature variation of γ. For this purpose the equation:

$$\log \gamma^\infty = \frac{\Delta H^{e\infty}}{2{\cdot}303RT} - \frac{\Delta S^{e\infty}}{2{\cdot}303R} \tag{5}$$

can be used; in a plot of $\log \gamma^\infty$ against $1/T$ the slope is $\Delta H^{e\infty}/R$ and the intercept $\Delta S^{e\infty}/R$.

The results of the determination of γ^∞ are summarized in *Tables 2* and *3*,

Table 2. Activity coefficients at infinite dilution (γ^∞) in squalane

Absorbate		0°C	20°	30°	40°	45°	50°
CH_2Cl_2	$\log \gamma^\infty$	0·122	0·064	0·032	0·022	0·002	$\bar{1}$·980
	γ^∞	1·324	1·159	1·076	1·052	1·005	0·955
$CHCl_3$	$\log \gamma^\infty$	$\bar{1}$·860	$\bar{1}$·830	$\bar{1}$·815	$\bar{1}$·806		
	γ^∞	0·724	0·676	0·653	0·640		
CCl_4	$\log \gamma^\infty$			$\bar{1}$·742	$\bar{1}$·735		
	γ^∞			0·552	0·543		

Table 3. Activity coefficients at infinite dilution (γ^{∞}) in dinonyl phthalate

Absorbate		0°C	20°	30°	40°
CH_2Cl_2	$\log \gamma^{\infty}$	$\bar{1}$·579	$\bar{1}$·579	$\bar{1}$·579	$\bar{1}$·580
	γ^{∞}	0·379	0·379 (0·44)	0·379	0·380 (0·43)
$CHCl_3$	$\log \gamma^{\infty}$	$\bar{1}$·320	$\bar{1}$·370	$\bar{1}$·400	$\bar{1}$·425
	γ^{∞}	0·209	0·234	0·251	0·266 (0·33)
CCl_4	$\log \gamma^{\infty}$	$\bar{1}$·774		$\bar{1}$·778	$\bar{1}$·774
	γ^{∞}	0·594		0·600	0·594 (0·71)

Figures in parentheses are values obtained by Hardy[5] at approximately the same temperature.

together with some of the values obtained by Hardy[5] at temperatures very close to those used in the present work. *Figure 1* shows the isotherms of some of the systems listed in *Tables 2* and *3*, and *Figures 2* and *3* show the corresponding Raoult law plots.

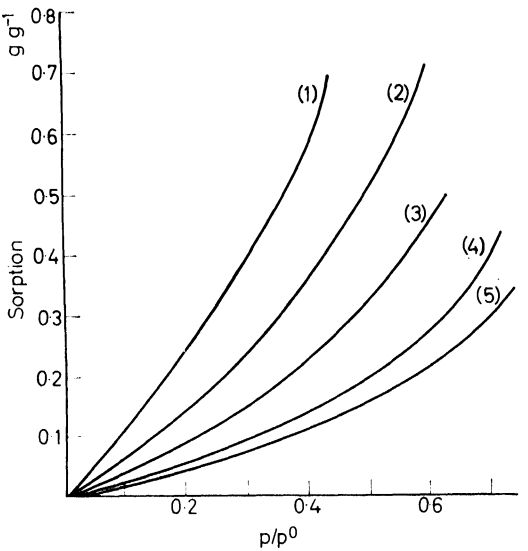


Figure 1. Absorption isotherms at 30°C. (1) Chloroform in dinonyl phthalate; (2) carbon tetrachloride in dinonyl phthalate; (3) cyclohexane in squalane; (4) cyclohexane in dinonyl phthalate; (5) dichloromethane in squalane.

At the time of writing the only values of γ^{∞} for chlorinated hydrocarbons, obtained by GLC, are those measured by Hardy[5]; and since the static values and the GLC values show quite a large discrepancy it is difficult to assess the

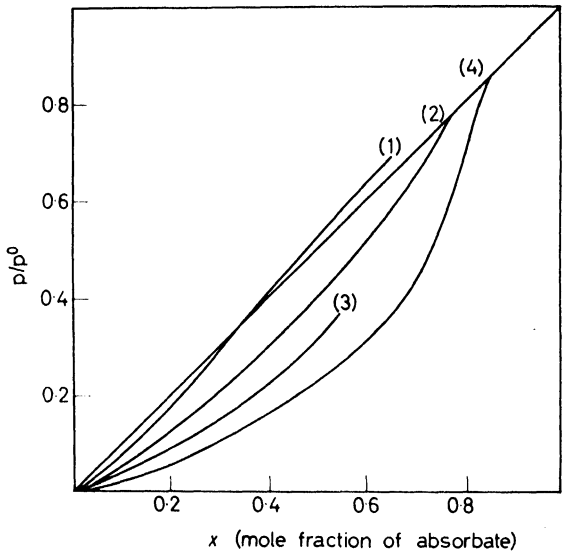


Figure 2. Deviations from Raoult's law at 30°C. (1) Cyclohexane; (2) carbon tetrachloride; (3) dichloromethane; (4) chloroform (all in dinonyl phthalate)

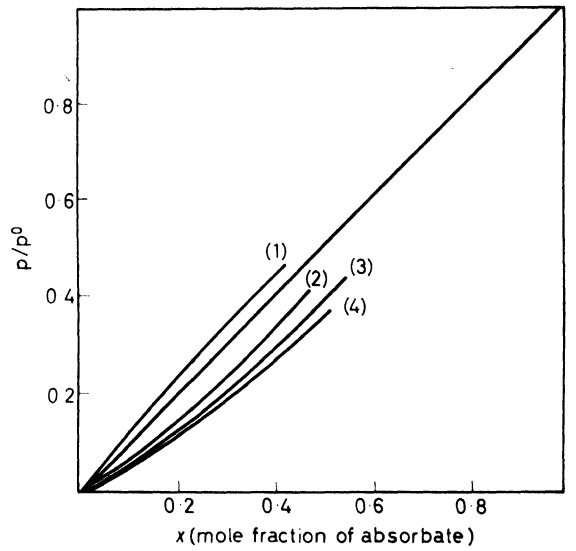


Figure 3. Deviations from Raoult's law at 30°C. (1) Dichloromethane; (2) chloroform; (3) carbon tetrachloride; (4) cyclohexane (all in squalane)

accuracy of either series of results. It seemed reasonable to us, however, to assume that the data obtained by static measurements correspond more nearly to the actual values in the present instance, because values of γ^{∞} for cyclohexane in dinonyl phthalate and squalane, obtained by us, agree well

with those predicted by Ashworth and Everett[3] (static technique), and others obtained by GLC[4,8,9]; and we believe our values in *Table 3* to be of comparable accuracy. A more detailed comparison of Hardy's results with our own nevertheless shows that relative values of γ^{∞} agree quite well, and this suggests a simple method to obtain reasonably accurate values of γ^{∞}. Provided that an accurate value of γ^{∞} is available for a standard absorbate from either 'static' measurements or a careful GLC measurement, other values can be estimated from relative retention volumes. If s designates the standard and x the unknown, it follows directly from eqn (1) that

$$\gamma_x^{\infty} = \gamma_s^{\infty} \frac{p_s^0 V_{gs}}{p_x^0 V_{gx}} = \gamma_s^{\infty} \frac{p_s^0}{p_x^0} T_r \qquad (6)$$

where T_r is the ratio of the retention times.

In this expression the contribution of a second term, which is a function of the second virial coefficient, is neglected; hence values of γ^{∞} obtained in this way will be the same as those defined in eqn (1).

The actual values of γ^{∞} obtained for the series of chlorinated hydrocarbons investigated are much as would be expected in view of the chemical nature of the absorbents, but a detailed discussion is outside the scope of this paper and will appear elsewhere.

Partition isotherms

It is noteworthy that all partition isotherms sketched in *Figure 1* have the same general shape: they curve in a direction convex to the pressure axis, in spite of the fact that some show negative deviations from Raoult's law; one shows a positive deviation and one both a positive and a negative deviation. A simple calculation shows that a system obeying Raoult's law will also give an isotherm of the same shape as those in *Figure 1*. De Vault[10] has shown theoretically that, in so far as the isotherm shape determines the chromatographic behaviour, isotherms like those depicted in *Figure 1* will tend to produce 'fronting', i.e. elution peaks with diffuse fronts and sharp tails. A gas–solid system showing this behaviour was described by Gregg and Stock[11]. It would seem that tailing can only result from negative deviations from Raoult's law if the corresponding partition isotherm is concave to the pressure axis. Calculation shows that very pronounced deviations are necessary to produce such isotherms; these are likely to be encountered only very rarely in GLC. Tailing probably results from adsorption on the solid support or at the gas–liquid interface, or possibly from non-ideal behaviour exhibited by the vapour/carrier gas system.

Mixed stationary phases

The experiments with various mixtures of dinonyl phthalate and squalane as the absorbent and cyclohexane as the absorbate showed that there must be very little interaction between the two involatile liquids, since the isotherms obtained were almost exactly those predicted on the assumption that each component of the mixture behaved independently of the other. There would appear to be no advantage (other than that of convenience) in the use of these

particular mixed phases rather than two separate columns, each containing one component of the mixture. On the other hand the results suggest that tailing in GLC, due to adsorption on the solid support when a non-polar stationary phase is used, might be reduced by addition of a small proportion of a polar involatile liquid during coating of the support. The desirable properties of the non-polar liquid should be little changed by this treatment.

Some measurements made on a thermobalance showed little increase in the volatility of the mixtures relative to that of the pure liquids.

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DISCUSSION

M. A. Khan: I am very pleased to read this Paper. The more I read it the more fascinating I have found it.

Looking at *Table 1* on page 105, where you find a loss in entropy and where there is evolution of heat with the chloroform/dinonyl phthalate system, we can form a physical picture. I think there is an indication of hydrogen bonding between the molecules of the dinonyl phthalate and the chloroform. This results in restricted orientation of the molecules, with concomitant loss in entropy. This is further confirmed by the evolution of heat where the heat of mixing is negative.

Another thing which I found interesting was the dichloromethane/dinonyl phthalate system, for which the heat of mixing is zero. In other words, the non-ideality is due to the difference in volume, even though the components concerned are polar. It might be interpreted that the over-all field around the dinonyl phthalate molecule has more or less the same symmetry as the molecule of dichloromethane. The interaction energy may thus be taken as the arithmetic mean, i.e. $\epsilon_{12} = \frac{1}{2}(\epsilon_{11} + \epsilon_{22})$.

There is a very interesting effect regarding the temperature. For the dichloromethane/squalane system, the activity coefficient is greater than unity. As the temperature increases, the activity coefficient decreases; the system tends towards ideality. On the other hand, for the chloroform/squalane system we see that as the temperature increases the activity coefficient decreases, the system becoming

more and more non-ideal. These are rather interesting systems. I think further studies are necessary to clarify the physical picture.

R. Stock: I am happy to agree with Dr Khan's comments.

A. V. Kiselev: The most interesting point for me in the beautiful paper by Dr Stock is the evaluation of the activity coefficient at high concentration. In this connection, I should like to ask Dr Stock whether the Berthelot equation has a molecular statistical explanation or not.

R. Stock: I regret that I am unable to answer Professor Kiselev's question, since we have not considered our results in these terms.

F. Sjenitzer: The activity coefficient is a measure of the 'imperfection' of the absorbate in the liquid phase only, and not in the vapour phase as stated in line 2 on page 103.

R. Stock: We agree and should like lines 1–3 on that page to read: 'γ^{∞} = activity coefficient at infinite dilution'.

8

A NEW TYPE OF POLAR STATIONARY PHASE WITH ADJUSTABLE SELECTIVITY COEFFICIENT

H. ROTZSCHE
Institut für Silikon- und Fluorkarbonchemie Radebeul-Dresden, D.D.R.
(Presented by W. Trieselt)

A new class of silicone oils is described, to which polar characteristics are imparted by cyanoalkyl groups. Contrary to most other polar stationary phases, these compounds can to some extent also be used at temperatures above 150°C. Even at 250°C they show excellent selectivity for the separation of aromatic from aliphatic hydrocarbons with comparable boiling points. It is shown that the selectivity and polarity of the oils can be adjusted to any value within certain limits by control of the number of cyanoalkyl groups introduced during preparation of the compound. The basic structure of the liquid phase remains the same, so that retention volumes for different oils can be easily assessed. With two, three or four such standard liquids many separation problems can be solved, including those involving multicomponent mixtures, for which up to now the most favourable stationary phase had to be selected by means of a lengthy series of experiments. Lastly the oils can also be used at normal temperatures; thus they are effective over a wide range of temperature and may be used in programmed temperature work.

COMPOUNDS belonging to a homologous series can generally be separated without difficulty by gas chromatography. The vapour pressure ratio p_1^0/p_2^0 for adjacent members of the series is sufficiently different from unity, so that their corrected retention volumes V'_{R_1} and V'_{R_2}, as given by the fundamental relation[1]

$$\log \frac{V'_{R_2}}{V'_{R_1}} = \log \frac{p_1^0}{p_2^0} + \log \frac{\gamma_{13}^0}{\gamma_{23}^0}$$

are sufficiently wide apart even when the activity coefficients in the liquid phase are equal, as may be the case for adjacent homologues. Substances with equal or nearly equal boiling points (which must therefore belong to different homologous series) must be treated differently. Here the term $\log p_1^0/p_2^0$ has only minor importance. If the vapour pressures of the two components are equal at the operating temperature, the term drops out completely. Therefore the ratio of the activity coefficients γ_{13}^0 and γ_{23}^0, describing the interactions with the stationary phase, 3, is decisive. Bayer[2] introduced the selectivity coefficient σ as a measure of the separation efficiency of a stationary phase for substances belonging to different homologous series:

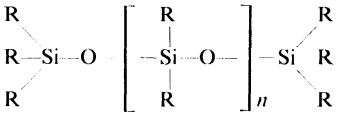
$$\sigma = \frac{V'_{R_1}}{V'_{R_2}} = \frac{V_{g1}}{V_{g2}} \quad \text{(b.p. 1 = b.p. 2)}$$

V_g is the specific retention volume, b.p. is the boiling point.

The parameter can be calculated from the retention volumes of two substances with equal boiling points, or from the boiling point *v.* log V'_R diagrams of two homologous series. A selectivity coefficient much larger or much smaller than unity represents a highly selective stationary phase, which will effectively separate substances with equal boiling points, resp. members of different homologous series, from one another. Selectivity coefficients of different liquid phases have already been calculated for the separation of hydrocarbons[2,3], oxygen-[2] and fluorine-containing[4] compounds. The $\beta\beta'$-oxydipropionitrile used by Eggertsen and Groenings[5] has an excellent selectivity which is most likely due to the presence of the ether oxygen and nitrile groups and the attendant polarizability and high dipole moment. This liquid interacts strongly with substances having large dipole moments or large polarizability. Unfortunately the high vapour pressure precludes its use above 70°C. Other polar compounds, such as diglycerol, polyesters, polyethylene glycol, tricresyl phosphate, etc., have lower selectivity coefficients.

We have therefore searched for a stationary phase with good selectivity which can also be used at higher temperatures.

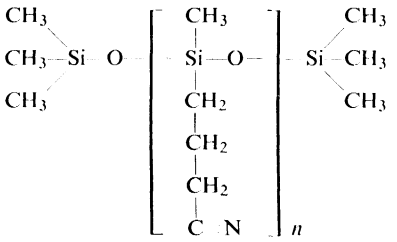
Silicone oils have been widely used in gas chromatography because they allow operation at temperatures up to 150–200°C. This applies to oils with the general structure



(1)

where R may stand for an alkyl or an aryl group. Aryl substituents impart a better thermal stability. Methyl and phenyl groups are the most widely used substituents. The oils possess low selectivity, however, and may be compared to the silicone greases, which also consist only of silicone oils to which various fillers have been added.

We have tried to prepare an oil with the structure



(2)

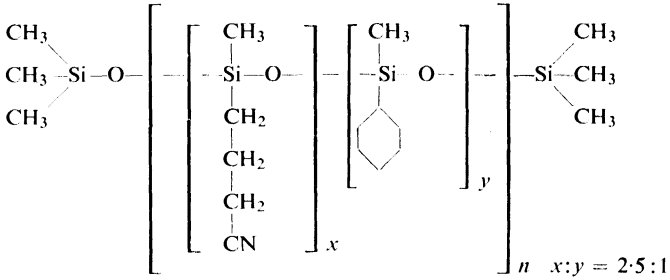
by introducing polar groups into the silicone molecule. Such a molecule would have a higher dipole moment which would give rise to better selectivity. The compound in question is a viscous liquid which is thermally stable up to 150°C and, when suitably prepared, at even higher temperatures. *Table 1* shows that the oil (2) retains polar compounds more strongly than the other liquids included in the table.

Dichloromethane has a greater retention time on (2) than carbon tetrachloride, although the latter has a 35°C higher boiling point and is eluted after dichloromethane from all other stationary phases. The relative retentions on

Table 1. Relative retentions of some halogenated hydrocarbons ($CCl_4 = 1{\cdot}00$)

Compound	B.p. °C	μ D	*Column*				
			Paraffin[6]	*Silicone fluid* MS710[6]	DNP[6]	TCP[6]	*Silicone oil* (2)
			77°C	77°C	77°C	77°C	77°C
$CH_3CHClCH_3$	36·5	2·1	0·19	0·22	0·28	0·21	0·46
CH_3CH_2Br	38·4	2·00	0·20	0·31	0·33	0·34	0·74
CH_2Cl_2	41·6	1·57	0·23	0·41	0·50	0·61	1·08
$CHCl_3$	61·2	1·10	0·58	0·84	1·19	1·41	2·06
CCl_4	76·7	0	1·00	1·00	1·00	1·00	1·00
$CHCl{=}CCl_2$	87·2	0·94	1·42	1·48	1·89	1·90	2·20

paraffin, silicone fluid MS 710[a], dinonyl phthalate (DNP) and tricresyl phosphate (TCP) have been calculated from the corrected retention volumes given by Harrison[6]. The μ values given are the dipole moments in Debye units. The polarity of the oil (2) can be decreased by introduction of methylphenylsiloxane groups:



(3)

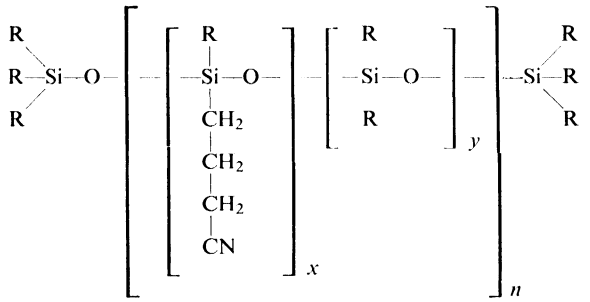
The oils (2) and (3) were aged at 200, resp. 250°C and tested for selectivity. Results are given in *Table 2.*

Table 2. Relative retentions on two polar silicone oils (naphthalene = 1·00)

Compound	B.p. °C	μ D	*Column*	
			Silicone oil (2)	*Silicone oil* (3)
			200°C	250°C
Propionic acid	140·7	1·69	—	0·29
Dibutyl ether	140·9	—	—	0·08
Nitrobenzene	210·9	3·95	1·25	1·10
Naphthalene	218·0	0	1·00	1·00
Benzyl cyanide	233	3·5	2·25	1·37
Biphenyl	254·9	0	1·67	1·58
p-Bromo-nitrobenzene	255	2·65	6·37	2·48
Hexadecane	287	0	0·29	0·63

At 200°C the strongly polar oil (2) retains naphthalene more than three times as long as n-hexadecane, although the latter has a 69°C higher boiling point. The liquid (3), which has a slightly lower selectivity, still gives a higher retention for naphthalene than for the hexadecane. Thus we can control the characteristics of partitioning liquids and obtain excellent selectivity at elevated temperatures, e.g. for the separation of aliphatic from aromatic hydrocarbons.

The shift in selectivity caused by the insertion of relatively unpolar siloxane groups (*Table 2*) encouraged us to investigate further modifications in order to obtain a wider range of stationary phases with different selectivities. Accordingly silicone oils with the general formula (A) were prepared:



(A)

The following oils were studied:

Silicone oil (4)	$x : y = 3 : 1$	R = CH_3—
Silicone oil (5)	$x : y = 1 : 1$	R = CH_3—
Silicone oil (6)	$x = 0$	R = CH_3— or C_6H_5—
Silicone oil (7)	$x = 0$	R = CH_3—

Oil (7) corresponds to type (1) with R = CH_3. This compound and another oil, (6), of type (1), in which part of the R groups are phenyl groups, are the silicone oils generally used in gas chromatography. Owing to the absence of polar groups these liquids are selective for only a few classes of compounds. Oil (3) also belongs to type (A), with $x:y = 2{\cdot}5:1$ and R representing methyl as well as phenyl groups.

Table 3 lists all oils introduced thus far, in order of increasing polarity. The notation refers to formula (A).

Table 3

Silicone oil (7)	$x = 0$	R = CH_3—
Silicone oil (6)	$x = 0$	R = CH_3— resp. C_6H_5—
Silicone oil (5)	$x : y = 1 : 1$	R = CH_3—
Silicone oil (3)	$x : y = 2{\cdot}5 : 1$	R = CH_3— resp. C_6H_5—
Silicone oil (4)	$x : y = 3 : 1$	R = CH_3—
Silicone oil (2)	$y = 0$	R = CH_3—

Columns of 1·5 m length were prepared with these oils, coated on to Sterchamol from ether or acetone solution. Corrected retention volumes were

determined for a large number of hydrocarbons and oxygen-containing compounds belonging to various homologous series, and from these data the selectivity coefficients were obtained by graphical means, as described by Bayer[2]. Operating temperature was 100°C, carrier gas flow was 50 ml hydrogen per minute.

Table 4 lists the values obtained, together with Bayer's[7] estimates for silicone oil DC703[b], polyethylene glycol 2000 (PG2), tricresyl phosphate (TCP) and Dow-polyglycol 166–450 (PCG)[c].

Table 4. Selectivity coefficients at 100°C

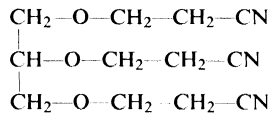
Separation	*Stationary phase*										
	(7)	(6)	(5)	(3)	(4)	(2)	DC703	TCP	PG2	PCG	ODP*
Alkylbenzenes/ n-paraffins	1·2	1·7	3·0	3·7	4·1	6·1	1·8	3·4	2·2	4·8	16·1
Alkylbenzenes/ cyclohexanes	1·1	1·5	1·9	1·9	2·4	3·0	1·4	2·4	1·5	3·0	9·2
Alkylbenzenes/ cyclo-olefins	—	—	—	1·6	2·0	2·2	1·2	1·7	1·3	2·0	4·2
Ketones/prim. alcohols	2·1	2·6	1·5	1·5	1·3	1·3	2·4	1·3	1·0	1·5	1·2
Prim. alcohols/ ethers	0·4	0·4	1·5	1·4	1·7	2·1	0·4	—	1·4	1·9	6·0
Ketones/ethers	0·8	1·0	2·2	2·1	2·3	2·8	1·0	—	1·3	3·1	8·0
Alkylformates/ ethers	0·9	1·3	1·8	1·8	1·8	2·1	1·0	—	1·2	2·5	5·5
Max. column temperature (°C)	150	200	150	250	170	200	180	150	220	—	—

* Data presented by W. Trieselt at the Symposium.

It can be clearly seen how the selectivity coefficient is affected by the introduction of polar groups into the silicone molecule. While for example with increasing polarity of the oil the selectivity increases for the separation of alkylbenzenes from n-paraffins or primary alcohols from ethers it decreases for the separation of ketones from primary alcohols. In many cases it is important to select the proper selectivity. When a mixture of three components, *a*, *b*, and *c*, of which *a* and *b* have the same boiling point, is analysed with a non-polar partitioning liquid, *a* and *b* will be eluted together. On a highly polar column, however, simultaneous elution of, for example, *b* and *c* might occur. Therefore it is important that liquids with medium selectivity be available, particularly for the analysis of complex mixtures, where the overlap described can occur. James and Martin[8,9], Raupp[10], Keulemans[11] and Tenney[12] have drawn attention to the selectivity, which depends on the polarity of the partitioning liquid. Not only in analytical work, but also in preparative-scale separations, it is especially important to

use phases with a high degree of selectivity, so that good separations can be obtained even with overloaded columns. The fact that the selectivity may be controlled is an advantage in this case as well, particularly for 3- and multicomponent mixtures. Although a number of stationary phases with various selectivities are already available, they differ so much in their chemical structure that retention volumes cannot be predicted. With the silicone oils, however, the selectivity is determined solely by the number of cyano groups in the molecule, while the basic structure (A) remains unaltered, so that an estimate can be made of the change in retention volume with change to the liquid with the next higher polarity.

Until now the choice of the best stationary phase for a particular separation problem could only be made after a lengthy series of tests. A great number of liquid phases is available and the choice is not always easy. This raises the question whether the majority of the widely-occurring separation problems could be solved by means of a few standard liquids. The new silicone oils appear to be suitable for this task because they can be prepared with the same basic structure but with different degrees of selectivity. In addition the compound



which may be even more polar than (2), could possibly be used. This compound was described by Anderson[13] and by Bayer[14]; it is produced in the reaction between glycerol and acrylonitrile and seems to be stable at temperatures up to 180°C.

As expected, the viscosity of the new silicone oils is greater at lower temperatures, but at 20°C it is still so low that the oils may be used for the separation of a number of gases at this temperature. Owing to the large temperature interval, from 20°C to 150 resp. 250°C, in which they may be used, the oils are suitable as stationary phases in programmed temperature gas chromatography.

The author thanks the Director of the Institute, Prof. Dr Richard Müller, for permission to publish this paper and E. M. Lorenz and H. Hahnewald for their experimental work and Dr R. Köhne for the preparation of the oils.

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[a] Midland Silicones, Ltd.
[b] Dow Dorning Corp.
[c] Dow Chemical Corp.

DISCUSSION

M. B. Evans (*prepared contribution*): Though not recommended for use as stationary phases, certain of the nitrile silicones described in Dr Rotzsche's paper have recently been made commercially available by the General Electric Company of the U.S.A.

Since the preparation of copolymers of well-defined structure is very difficult I should like to ask Dr Rotzsche on what evidence he suggests that his nitrile silicones are molecules of the form A (page 114) rather than a mixture of types 1, 2 (page 112) and A. Also, what chemical and/or physical methods have been used to characterize these materials?

Recently there have been numerous publications describing new polar stationary phases, but these contained no details of GLC or chemical evaluation. We at N.R.P.R.A. feel that before a substance can be recommended as a stationary phase the following should be thoroughly investigated:

(*1*) The constancy of retention data with column usage over the range of temperatures proposed for its use.

(*2*) The constancy of retention data for materials obtained from different commercial sources or by different methods of synthesis.

(*3*) The influence of molecular weight range and effect of end groups on retention.

(*4*) The effect of moisture on retention times, particularly with strongly hydrophilic substances and when detectors insensitive to water are used.

We are at the present time concluding an investigation of the polyethylene glycols, which we hope will serve as a general procedure for the GLC evaluation of polar stationary phases; details of this work will be published shortly.

Factors (*2*) and (*3*) should not be observed with pure compounds, provided adequate criteria of purity are available. Elemental analysis can be particularly deceptive in this respect, a case in point being the cyano-ethylated glycerol mentioned on page 116. Whereas we found that elemental analyses were correct with respect to C, H and N for the products of three independent preparations and one commercial product, the infra-red spectra revealed approximately one $-OH$ group per mole in each case. The fact that C, H and N values were correct is presumably due to the presence of polyacrylonitrile. I should certainly like to know about the purities of the compounds prepared by Dr Anderson and Dr Bayer which are referred to in the paper.

W. Trieselt: I am very sorry that I cannot give you any detailed answer, but I will read you a general reply from Dr Bayer.

Obviously the use of only well characterized, uniform materials as partitioning phase is desirable, as suggested by Mr Evans. This is a fundamental question, which applies not only to the silicone oils of Dr Rotzsche, but to all liquid phases which may be used at temperatures above 180°C.

All high-temperature phases (polyglycols, silicones, diol-dicarboxylic acid esters, asphalt extracts and polyphenyl tars) are polymers, the uniformity of which is strongly dependent on the conditions of preparation. This imposes a limit on the reproducibility we may expect for retention data on these phases. The preparation of uniform high molecular weight materials of this type would certainly be very desirable. However, this would require a large amount of work which would deserve to be published, like the work on polyglycols Mr Evans has told us we may look forward to.

Regarding the purity of cyano-ethyl ethers, we may note that complete cyano-ethylation is only possible for mono-alcohols and diols. Ethylene glycol di(propionitrile) ether, which we recommend for use instead of glycerol cyano-ethyl ether, can be distilled, and analysis as well as spectroscopic data indicate that the material may be obtained in 100 per cent purity. It can be used up to 150°C for analytical purposes. As may be seen from the table, the selectivity is comparable to that of oxydipropionitrile.

Selectivity coefficients for various separations on $\beta\beta'$-di-(propionitrile) ether (ODP) and ethylene glycol di-(β-cyano-ethyl) ether (CDP)

Separation	*Stationary phase*	
	ODP	CDP
Cyclohexanes/n-paraffins	2·1	2·2
Alkylbenzenes/cyclohexanes	9·2	9·0
Alkylbenzenes/n-paraffins	16·1	15·8
prim. Alcohols/sec. alcohols	1·4	1·4
prim. Alcohols/tert. alcohols	1·5	1·5
sec. Alcohols/tert. alcohols	1·2	1·2
Cyclic ketones/methyl ketones	—	1·7
Methyl ketones/ethers	8·0	7·8
prim. Alcohols/ethers	6·0	6·0
Fatty acid ethyl esters/acetic acid esters	—	1·1

Figure 1 shows that we can also adjust the selectivity by changing the number of CH_2 groups between the ether oxygen and the nitrile group. The materials to which this figure refers are uniform compounds, as will be discussed in a paper we hope to publish in the near future.

Cyano-ethylation of higher alcohols, such as glycerol, sorbitol, penta-erythritol, results in products which cannot be purified by crystallization or distillation; these materials therefore still contain alcohols which are only partially cyano-ethylated. A product free of acrylonitrile can be obtained by precipitation, however, and analysis and infra-red spectra both indicate more than 90 per cent cyano-ethylation. Selectivity and temperature limit were comparable to ethylene di(propionitrile) ether.

Lastly, an example may be given of how much the selectivity may vary with the purity of the partitioning phase. The cresols cannot be separated on commercial tricresyl phosphate. Whereas with pure p-tricresyl phosphate, 2,000 plates are sufficient for the separation of o-, m- and p-cresol, these compounds cannot be separated on o-tricresyl phosphate, and much higher plate numbers are required with m-tricresyl phosphate. Here we find interesting problems concerning structure and selectivity, the importance of which extends beyond gas chromatography to such fields as the stereo-specificity of catalysts and enzymes.

M. B. Evans: Whereas one would expect the base-catalysed addition of acrylonitrile to ethylene glycol to lead to the fully cyano-ethylated compound, the weaker

acidity of the secondary hydroxyl group of glycerol and steric effects would preclude the formation of the compound shown on page 116. However, if the primary hydroxyl groups are chemically protected, strongly basic conditions can be used to add the acrylonitrile on to the secondary hydroxyl group. Subsequent removal of the protecting groups and further base-catalysed addition should lead to the fully cyano-ethylated compound. I think we ought to have a get-together some time and discuss these points.

H. J. Coleman: With reference to the opening paragraph on page 111 of this paper, I should like to present some data on some compounds which do not form a true homologous series, although they are of the same type. You will note the change in polarity and its effect on the retention times (*Figure 2*). With silicone oil DC-550

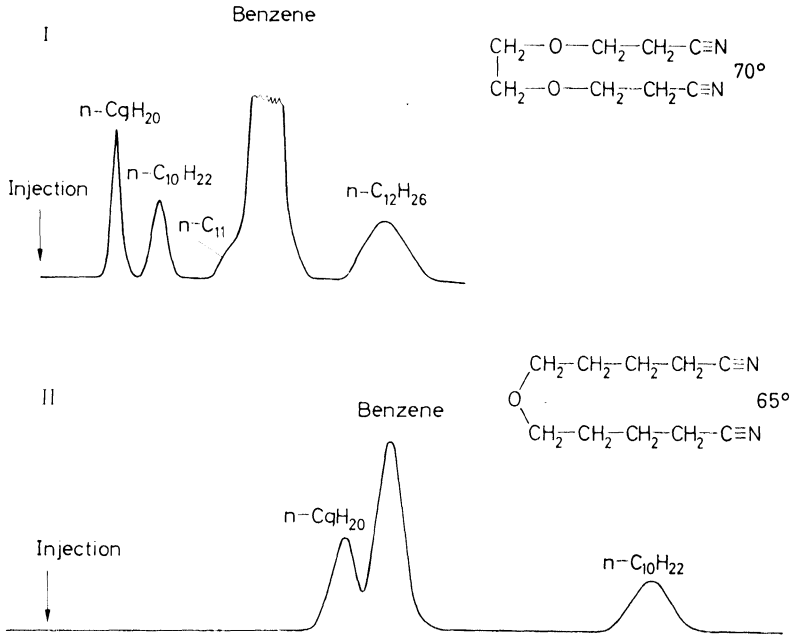


Figure 1. Chromatograms of some hydrocarbons on two partitioning phases with different numbers of CH_2 groups between the ether oxygen and the nitrile group

(Dow Corning) we get a straight relationship of increasing retention time with increasing molecular weight. With the Reoplex 400 we were quite surprised to get a decrease in retention time with increasing molecular weight. I put this forward as a matter of interest. It is not entirely due to polarity, but to the type of polarity; because we also ran this same series on sucrose acetate isobutyrate and got a line which runs parallel to the curve for the silicone DC-550.

J. F. Smith: Several years ago, Professor Gee and his co-workers at NRPRA showed that solute solubility in a mixture of miscible polar and non-polar solvents is not a linear interpolation between the solubility in the pure solvents. In fact, maxima are observed when the cohesive energy densities of solvent and solute are the same. To achieve linear interpolation of retention data one should choose immiscible pairs of solvents (e.g. squalane/PEG 400), as was found by Cheshire and myself some years ago at the Beecham Laboratories.

W. Trieselt: We also believe that linear relationships cannot be obtained when the column is coated with mixtures of different polar materials.

A. V. Kiselev: I found this paper by Dr Rotzsche most interesting, because here is an approach to a rational limitation of the number of liquid immobile phases. It is important from my point of view that the polar functional groups in these large polymer molecules are not located close to each other, but at large distances. This makes the surface of the liquid film more homogeneous and selective for adsorption of components of different natures. I think there is only one step between this paper and our attempt to graft a polymer film on to the surface of a wide-pore support by chemical reaction. If we could prepare a material with the combined properties of these selectively interacting polymers and the high thermal and chemical stability of a layer grafted on to a large-pore solid surface, we could perhaps join the successes of gas–liquid and gas–solid chromatography. If we can graft such

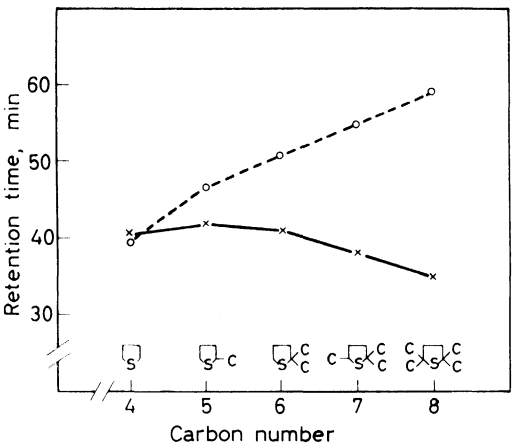


*Figure 2.** Retention times for a series of compounds with varying type of polarity
○ Stationary phase silicone oil DC-550 (Dow Corning)
× Stationary phase Reoplex 400

polymer films on to the surface of solid supports by chemical bonds, the functional groups would be arranged with a wide spacing. This is important if we want to obtain isotherms with a linear initial region, for adsorption as well as for absorption. If we try and graft polymer films with different functional groups on to a solid support by chemical reaction, we shall be able to prepare selective adsorbents with a high thermal and chemical stability, which we can use at high temperatures.

J. C. Winters: Is there any direct relationship between the polarity of the silicones and their thermal stability?

W. Trieselt: I have not received any further details about these compounds. Dr Rotzsche sent me a somewhat more detailed manuscript, but it contained no data on the properties or preparation of these compounds.

G. A. P. Tuey: First of all, I should like to express my agreement with what Mr Evans has said about the need to evaluate polar stationary phases very critically. We have made and tested some 100 compounds, none of which has in fact proved to have sufficiently high thermal stability, even though sometimes the extrapolated boiling points were high enough. The most selective of these compounds were

* Figure reconstructed from a photograph of projected slide, courtesy S. J. Hawkes.—Ed.

always those containing nitrile groups and were, in fact, derivatives of acrylonitrile; we found that these compounds were uniformly unstable, pyrolysing to regenerate acrylonitrile. I suggest the observations of Mr Evans on his glycerol condensation product were the results of decomposition during attempted distillation or purification at the end.

I notice that Dr Rotzsche's compounds contain the CN group attached by a 3-carbon chain. This seems to me very interesting, and I wonder whether Dr Rotzsche chose the cyano-propyl group because it has a higher thermal stability than the cyano-ethyl group.

W. Trieselt: Apparently the stability of the cyano-silicones of Dr Rotzsche doesn't extend above 150°C either, and that we can also reach with our ethylene glycol cyano-ethyl ether. The question is whether we can find materials at all which contain cyano groups and which have a higher thermal stability.

H. Boer: Page 113 states 'up to 250°C'!

W. Trieselt: Elsewhere in the manuscript it is stated that they can only be used up to 150°C.

W. Heinemann: The principle of combining two chemical functions in one substance has been seen in the case of β-indolyl acetonitrile. This substance combines the properties of condensed rings, which give good separations of, e.g., the xylene isomers, with the function of the nitrile groups, which give these compounds a high selectivity towards aromatics. The vapour pressure of this compound is 10^{-4} mm Hg at 120°C, but above this temperature it possibly degrades, so it cannot be used as a stationary phase for gas chromatographic purposes.

J. Janak: We have prepared and tested the condensation product of pentaerythritol with acrylonitrile by the method described by R. Komers[15]. This stationary phase is thermally stable at 220°C for at least two weeks, and it doesn't interfere with the operation of ionization detectors. The selectivity according to Bayer's criterion is higher than 10 for alkyl benzenes/paraffins.

W. Trieselt: The same compound has also been investigated by Dr Wahl; this will be published in the near future. Indeed, the thermal stability seems to be somewhat better, and the volatility is also very small. However, when the liquid is heated as such, there is some discoloration in the long run. From what I know from the work of Dr Wahl, this compound won't be so stable after all, for long periods of time.

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SECTION II

APPARATUS AND TECHNIQUE

Chairmen:

D. H. DESTY

W. W. BRANDT

PANEL DISCUSSION

QUANTITATIVE ASPECTS OF GAS CHROMATOGRAPHY

Chairman: G. W. A. RIJNDERS

9

RATIONAL INTEGRATION PROCEDURES IN GAS CHROMATOGRAPHY INVOLVING NOVEL COMBINATIONS OF INSTRUMENTS

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QUANTITATIVE evaluation of chromatograms (recorder strips) is still the most unattractive step in gas chromatographic analysis, since the use of conventional differential detectors necessitates integration. It has been theoretically proved and established in practice that integration is basically more accurate than any other method of evaluation (e.g. via peak height or by triangulation)[1]. Up till now, two fundamentally differing roads have been followed:

1. The elution diagram is recorded on a strip chart by a potentiometric recorder. The diagrams are subsequently evaluated at a time independent of the time of recording. (Integration by means of the polar planimeter; if desired, with the aid of suitable auxiliary devices and approximation procedures[1,2,3,4].) This technique is still used with relatively sluggish separation processes. An asset of the method, which should not be underestimated, is that the evaluator keeps in close contact with the analytical problem and frequently is able to introduce essential corrections (for drift, superposition of elution zones, components not belonging to the system). Even with unsatisfactory separations, or elutions, acceptable results can thus still be obtained.
2. Alternatively, an integrating device is coupled to the recorder. Operating while the elution of the components is in progress, this device yields the integrated value of the chromatograms.

   For this application numerous types of instruments have been developed, partly commercially, partly by individual users. The principles of operation have been discussed in detail elsewhere and will be only briefly outlined below:

   (a) mechanical integration with a ball and disc integrator[7,a];
   (b) electromagnetic integration with an integrating motor, or rather with an integrating motor coupled to a servo-amplifier; see, e.g., refs [5,6,b-d];
   (c) electronic integration by means of an analogue operational amplifier[7,e-h];
   (d) electronic integration by means of an analogue-to-digital converter and counter; with such instruments integration can be effected by various principles and with differing degrees of accuracy (see also refs [8-10,i,j]).

Most of the above instruments normally are connected to the transmitting

slidewire of the compensating recorder, since the detector output is generally insufficient to operate an integrating unit directly. Consequently, the accuracy can at best be equal to that of the recorder, i.e. not better than 0·1–0·2 per cent of full scale deflection. The inherent inertia of the recorder limits the rate of response (for very fast processes this limit is unacceptable) and hence also the reading accuracy. Signals exceeding the recorder range cannot be integrated without recourse to additional accessories.

Furthermore, the integration can be executed only once: during elution. Obviously the recorder can be replaced by suitable amplifiers. However, the accuracy of a good integrating system can only be fully utilized if a precision amplifier is used; this entails a considerable increase in cost. We have attempted to avoid the difficulties mentioned by using a set of instruments satisfying the practical requirements as nearly as possible, particularly with respect to adaptability and economy[11].

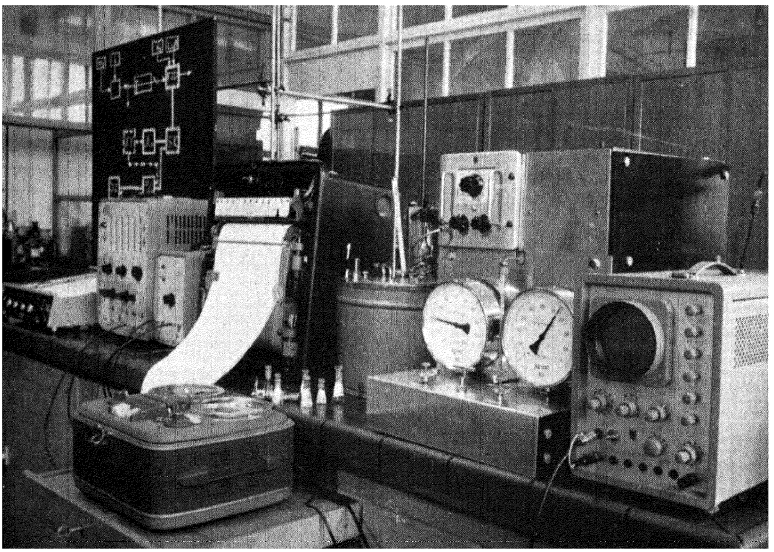


Figure 1. Building blocks. From right to left: oscilloscope (not required for routine operation); gas chromatograph with gas flow control, gas purifier, and vibrating reed amplifier (upper left), thermostat with column and flame ionization detector; recorder; analogue-digital converter; counter; X-Y recorder; tape recorder (in front)

Principle of the system (Figure 1)

1. An analogue-digital converter is coupled to the detector (katharometer or amplifier of the flame ionization detector)[k]. The device operates on the principle of an analogue operational amplifier with integrating capacitor. Charging of this capacitor is compensated by accurately defined rectangular pulses of opposed polarity; the pulses are supplied by an oscillator which is actuated by the output voltage of the operational amplifier via a trigger stage. Since only a very small part of the charging curve is utilized,

the linearity is excellent. The manufacturer supplies the following data for pulse frequency $F = F_{max} (= 10{\cdot}000/\text{sec})$:

Table 1.

Input for $F = F_{max}$ (V)	*Input resistance* (kΩ)	*Drift per day*	*Deviation at 10% mains fluctuation* ($\times F_{max}/100$)	*Linearity, maximum deviation*
1	1000	0·03	0·02	0·002
0·1	100	0·08	0·05	0·01
0·01	10	0·52	0·35	0·05

The values compiled in columns 3 and 4 of *Table 1* can be slightly improved. From column 5 it can be seen that the linearity is excellent.

2. The pulses supplied by the converter (at a separate output) are summated by an electronic counter[1].

A brief discussion of the errors observed in the arrangement described under 1 and 2 presents the following picture.

The error consists of the parts:

1. a fixed contribution, including systematic errors of converter and counter;
2. a variable contribution, depending on deflection and time (see also *Table 1*).

The fixed contribution comprises:

1.1. the systematic error of pulse counters, ± 1 pulse;
1.2. an error inherent in the operation of the analogue-digital converter, which manifests itself when the input voltage to the converter changes in polarity. The error amounts to − 10 pulses.

Error 1.2 can be completely suppressed by application of a small positive bias, which causes the converter to give approx. 1 pulse in every 5–10 seconds.

The variable contribution is composed of:

2.1. instability at constant mains voltage + temperature: ± 0·03 per cent of maximum count rate per day,
2.2. influence of ± 10 per cent mains voltage fluctuations: ± 0·02 per cent,
2.3. converter linearity: ± 0·002 per cent,
2.4. temperature coefficient (between 20 and 40°C): ± 0·01 per cent of maximum count rate, per °C.

These values refer to maximum pulse frequency of the converter in the 1 V range. Under normal working conditions (calibration: once daily; drift; mains voltage fluctuations: 10 per cent; temperature fluctuation: ± 5°C; nonlinearity) one may expect that the total value of error 2 will be ± 0·06 per cent of the maximum count rate.

As observed earlier, the error contributions 2.1, 2.2 and 2.4 can be reduced in a simple way.

3. Via a code adapter a printer and/or other read-out device may be connected to the counter. Addition of a storage stage eliminates the inactive time of the counter during the printing cycle.

4. A commercial tape recorder forms a very effective complement to 1 and 2. The tape serves as storage for impulses supplied by the analogue-digital converter and permits counting to be done later and as often as may be desired.

5. A curve follower[m] makes possible the evaluation of normal strip chart records by fully automatic planimetry. The instrument operates in conjunction with the analogue-digital converter and the counter, so that the latter may, in principle, serve three different purposes:

(a) direct evaluation of chromatograms during elution;
(b) evaluation of tape-recorded chromatograms at a later moment, especially of chromatograms with closely-spaced peaks;
(c) in conjunction with the curve follower, for evaluation of chromatograms recorded on strip charts, corresponding to the technique used until now.

Additional remarks

The use of building blocks permits adaptation to the various problems that may arise, particularly to evaluation of fast processes (high-speed chromatography). The combination analogue-digital converter + counter yields very exact area integrals, since the response time is negligible. Owing to the high pulse frequency the range is a factor of 10 larger than that of a conventional recorder. In pursuing further automation of the integration step one might equip the system with an electronic minimum detector which determines the beginning and end of a peak and effects printing-out of the corresponding integral value. It is not easy, however, to develop a system which operates equally well with fast and slow elutions, even when errors resulting from insufficient resolution (small superimposed peaks, etc.) are disregarded. It would be more advisable to combine the analogue-digital converter with the tape recorder, since magnetically recorded chromatograms will then be obtained. The only difference with regard to chromatograms written on recorder strips would be that the peaks are magnetically stored in the form of a pulse frequency starting at zero and increasing up to the peak maximum (listening to such chromatograms is quite impressive). The tape or tapes from several recorders can be evaluated later. The cost of this arrangement is low since only an analogue-digital converter and a tape recorder are needed for each chromatograph, with evaluation of the tapes by means of one centrally located electronic counter. Furthermore, to permit determination of the retention time, time marks might be recorded on the second track of the tape. The latter step, however, has not yet been realized experimentally. In the practical realization of this technique provision will be made for a device permitting high-speed evaluation of recorder tapes; this device is still in the development stage. It is possible, of course, to run a recorder of a most simple design as indicator in conjunction with each of the above arrangements, for the sake of convenience.

As stated, it will not be possible in the near future to replace the conventional strip chart records by tape records in all cases. For a long time to come we shall probably not be concerned exclusively with ideal chromatograms accessible to automatic integration. In principle, the device outlined under 5 permits chromatograms with drift and/or partially resolved peaks to be automatically evaluated in the same way as has so far been done manually with the aid of the polar planimeter. It is therefore possible to draw in certain corrections before evaluation of the chromatograms, and to make allowance for them during evaluation. The elution curve is scanned with the head of the optical curve follower and the output signal is fed to the counter via the analogue-digital converter. In this case no closed curves are measured, as with the polar planimeter, but integration yields the value $\int f(x)\mathrm{d}x$. A second pass along a drawn-in zero line or peak flank can also yield the area under the peak as the difference between two areas. Although the price of a curve follower is relatively high, the method appears rational, because the evaluation proceeds extremely rapidly and a curve follower can replace at least ten planimeters. The optical curve follower is not commercially available as yet. Working with the combination outlined above, we tested a model placed at our disposal by the firm of Hewlett-Packard; this device was equipped with a magnetic head. The reproducibility of the integral values for peaks of normal size was excellent. The standard deviation in the most unfavourable case amounted to 0·2 per cent of the final value. It was quite immaterial whether the scanning rate was 5·5 cm/sec or 0·5 cm/sec. The scanning speed of the optical curve follower of the same firm, on the other hand, is at most 1 cm/sec, owing to the larger head mass, but the gain in time and improvement in accuracy are still considerable.

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[c] Instron integrator; Instron Engineering Corp., Canton, Mass, U.S.A.
[d] Servo-Riter integrating recorder; Texas Instruments, Inc., Houston, Texas, U.S.A.
[e] Pye integrating amplifier, type 12360; W. G. Pye & Co., Ltd, Granta Works, Cambridge, Great Britain

[f] Polygrator; Beckman Instruments, GmbH., München, DBR
[g] Integrators, types IB 6 BN 800 and NIF BN 810; Alb. Knott, München, DBR
[h] Integraton; Dr. Virus KG, Bonn, DBR
[i] Integrator; Siemens & Halske, A. G., Wernerwerk für Messtechnik, Karlsruhe, DBR
[j] Digital integrator-recorder-controller; Infotronics Corp., Houston, Texas, U.S.A.
[k] Analogue-digital converter, Dymec, type DY2210; Hewlett-Packard Co., Frankfurt/Main, DBR
[l] Electronic counter, type 522B, Hewlett-Packard Co.*
[m] Autograf 2D; F. L. Moseley Co., Pasadena, Calif., U.S.A., with optical curve following head, type F2; Hewlett-Packard Co.

DISCUSSION

Authors' Additional Comments

Since the manuscript was submitted, the measurement of retention times (see page 128) has been elaborated in detail. A second track of the magnetic tape is used for that purpose. On this track a 100 c/sec signal from the mains is recorded. It starts at the same time as the chromatogram.

For evaluation, the pulses of the time track are fed into a reversing counter, whose direction of counting is coupled with that of the tape recorder. The pulses can be played back in two directions. The final direction of counting is preserved until the tape comes to rest. The tape can be played back at normal speed (19 cm/sec) as well as at high speed, up to 50 times of the normal one, without any impairment in counting. At high play-back speed only the time counter is active. The counting of peak pulses is not advisable, mainly because of the upper frequency limit of the tape recorder used.

The purposes of the evaluating system are:

(a) to sum up and print out the retention times from track No. 2 at the peak maxima;
(b) to sum up and print out at the end of the peaks the pulses which represent the area integrals.

This is achieved as follows:

Evaluation of a tape starts with both counters and the logic system (see over) switched to a starting position. An operator then plays back the tape (at high speed) until he hears the typical sound of a rising peak. Then he rewinds the tape as far as necessary and switches over to normal speed. All following steps are done automatically. If a certain value of pulse frequency (1–10 p/sec), determined by the setting of a limit detector, is exceeded, the gate of the area counter is opened and a detector of maximum/minimum is unlocked. This detector may be set for detection of maxima or minima; it compares pulse counts of successive 0·1 second intervals. As soon as the count decreases by more than a given amount (adjustable between 1 and 10 pulses) from one counting period to the next, a maximum is indicated. Minima are similarly detected. Such a digital system is preferable to a circuit operating on an analogous basis, because it has a relatively short time constant and because it operates in an exactly defined manner. As soon as the detector of maximum has responded, the time counter is stopped and the value is scanned and printed (time for these steps: 0·7 sec). One second later, the gate of the time counter is reopened and at the same time 100 pulses are fed into the counter

* Although the precision timing signal incorporated in this counter is not essential for the work described here, it can be used to advantage for adjustment and periodic inspection, to which end the counter is used, in combination with the analogue-digital converter, as an accurate digital voltmeter.

to compensate for the pulses lost during the printing cycle. Meanwhile pulse counting of area is going on unimpaired until the limit detector or the detector of minimum gives a signal. The tape is then stopped, and the peak area is printed out. The tape then begins to move again, and the detector of maximum/minimum is reset to detection of maxima.

The whole process is repeated until the end of the chromatogram. When the peaks are very far apart, high speed can be used alternatively to shorten evaluation time.

The detector of max/min, the limit detector (both digital) and other signal-handling elements not described here in detail form the so-called logic system, which controls the interaction between the tape recorder, the 2 counters, and the printer.

With this arrangement chromatograms can be evaluated automatically, if zero drift is negligible and if the peaks are sufficiently resolved.

We use an adding machine with electrical input (Addo X-41 E; Addo-Data Vertriebs-G.m.b.H, Frankfurt/Main, DBR) as the printer. This makes it possible to type in additional information by means of the keys. If necessary, one can sum up the peak areas.

The complete equipment is relatively inexpensive because of the use of commercially available digital building blocks (Akkord-Radio G.m.b.H, Herxheim bei Landau/Pfalz, DBR), which allow the construction of special systems. Tape Recorder (Type Telefunken M 24; AEG, Büro Frankfurt/Main, DBR), VFC[k] and printer may also be easily obtained.

Prices:	VFC	*ca.*	DM 3,600	
	Tape recorder	,,	,, 800	recording system
			DM 4,400	
	Tape recorder	*ca.*	DM 2,000	
	Printer	,,	,, 2,200	evaluating system
	Building blocks	,,	,, 6,000	
			DM 10,200	

W. Heinemann (*prepared contribution*): A semi-automatic gas chromatographic integrator and digitizer has been constructed and successfully used for about one year by Esso Research Laboratories, U.S.A. Its advantages are as follows:

(a) Performance is independent of the precision of the recorder used.
(b) Dynamic range is very wide.
(c) Base line drift is automatically corrected.
(d) Minimum manpower cost is involved, as one operator can handle a number of chromatographs.

The lay-out of this apparatus is shown by *Figures 2–4*. The procedure runs as follows:

The signal from the chromatograph is converted to a pulse frequency by a Dymac electronic converter. The pulses are then recorded on one channel of a 2-channel tape recorder. A sixty-cycle signal from the power line is recorded on the other channel.

A central high-speed read console plays back the tapes of various chromatographs at 2–10 times the recording speed. The pulses from channel one are reconverted to the original signal with high precision and linearity up to 15,000 c/sec.

The regenerated signal is adjusted for base line drift by a helipot and servo system. Then the corrected signal

(a) is recorded by a normal laboratory recorder;
(b) is differentiated, the differential being used to provide control signals at the start, top, and end of each peak;
(c) drives a (second) voltage-to-frequency converter.

When the start of a peak is sensed by (b), zero adjustment is stopped and the output of (c) is switched to a counter. The end of the peak causes the accumulated

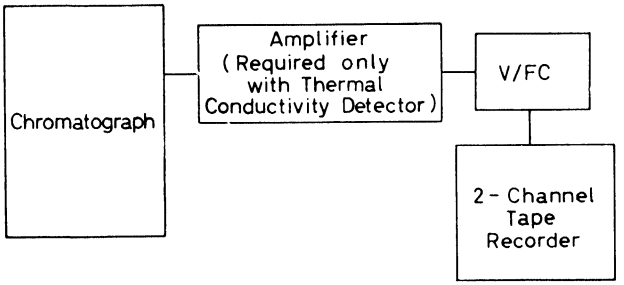


Figure 2. Chromatape system, block diagram of recording equipment

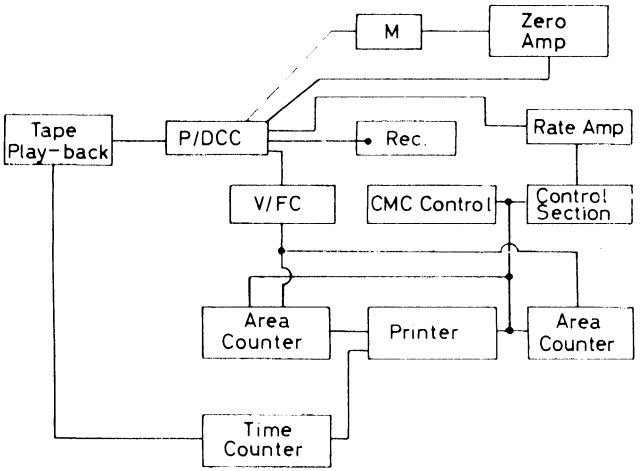


Figure 3. Chromatape system, block diagram of play-back console

count to be printed out, the counter to be reset, and the zero adjustment to be switched on again. A second counter is provided to count a second peak if this follows within the 0·25 seconds required for printing and resetting the first counter.

The sixty-cycle signal from channel 2 is fed to a time counter, which is started automatically by the sample injection. Print-out takes place (in hundredths of a minute) when the top of a peak is sensed by (b). Chromatographic data thus obtained are punched on cards and fed to a computer.

Satisfactory performance was obtained with both capillary and conventional columns. Linearity of the system should be within 0·2 per cent, estimated from the performance of the components used.

To test the apparatus, square wave peaks were recorded and integrated. The standard deviation was found to be considerably under 0·1 per cent for each peak. Similar results were obtained with simulated gas chromatographic peaks.

A time loss is encountered owing to combination of the time constants in the peak sensor, switching delays, and integrator. With regular gas chromatographic peaks, this loss was estimated to be less than 0·5 sec. The useful dynamic range is 5,000/1 to 10,000/1. Apparatus costs are as follows: $8,000 for read console; $1,200 for each recording device. From these costs it is seen that the application of tape recorders for intermediate storage of information considerably reduces cost, if more than one gas chromatograph is employed.

Furthermore, tape recorders can make possible the determination of olefins or other hydrocarbons extracted in a short scrubber column, by the following method: At first, a normal run is recorded on one track of a magnetic tape. Then a second

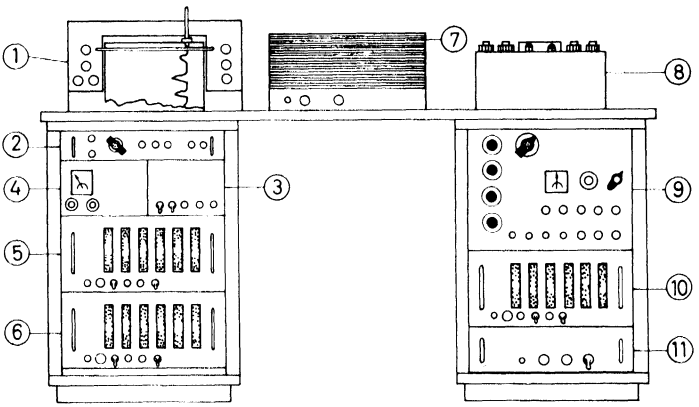


Figure 4. Chromatape system, front view of play-back console

1. Analogue recorder
2. Voltage-to-frequency converter
3. Power panel
4. Pulse frequency-to-voltage converter
5. Area counter
6. Time counter
7. Printer
8. Tape read-out
9. Control panel
10. Area counter
11. CMC control panel

run is recorded on the second track, with a scrubber column connected in series to the chromatographic column. Finally, both tracks are played back simultaneously, the signals being adjusted and superimposed so that only the extracted components show up.

I. Halasz: In the following, we intend to report on quantitative analyses requiring a few seconds only and carried out with packed capillary columns in combination with sufficiently fast automatic digital integrators.

A description of packed capillary columns has recently been published[12] and the present discussion will be restricted to the essential facts.

A packed capillary column is made by drawing a glass tube loosely filled with a solid on the capillary machine described by Desty. *Figure 5* shows a longitudinal cross section of a capillary with an inner diameter of 0·3 mm. The solid in this case was aluminium oxide having a grain size of 0·10–0·15 mm. Regardless of the irregularity of the loose packing, this column has a performance of 1,000–3,000 plates/m, corresponding to that of a well-packed classical column of 4 mm i.d. filled with the same solid. Gas permeability of the packed capillaries is about

Table 2. Analyses of Hydrocarbon Blend by means of Capillary Chromatograph and Flame Detector (Detector output fed to V/F Converter-tape, and Automatic Read-out)

Component	*Weight per cent*									*Average*	*Std. Dev.*
	1	2	3	4	5	6	7	8	9		
n-C_5	5·00	4·91	4·97	4·54	4·73	4·56	4·62	4·77	4·70	4·76	0·17
2,2-DMB	10·59	10·36	10·18	9·94	9·99	9·78	9·81	9·67	9·55	9·98	0·38
CyC_5	3·55	3·54	3·70	3·71	3·81	3·77	3·84	4·04	3·93	3·77	0·17
2,3-DMB	9·34	9·12	8·89	9·09	8·92	8·97	8·90	8·87	8·86	9·00	0·16
2-MP	18·46	18·10	17·88	18·53	18·22	18·33	18·32	18·10	17·98	18·21	0·22
3-MP	10·81	11·01	10·77	10·70	10·73	10·71	10·57	10·77	10·65	10·75	0·12
n-C_6	20·15	20·00	20·01	20·60	20·61	20·69	20·54	19·35	20·67	20·29	0·30
MCP	10·67	11·41	11·03	11·34	11·66	11·45	11·56	12·13	11·73	11·44	0·41
CyC_6	11·43	11·55	12·57	11·55	11·33	11·69	11·84	12·30	11·93	11·80	0·32

Table 3. Repetitive Read-outs of Tape Record of Analysis 6 in *Table 2*

Compo-nent	*Weight per cent*										*Average*	*Std. Dev.*
	1	2	3	4	5	6	7	8	9	10		
n-C_5	4·59	4·56	4·58	4·51	4·59	4·51	4·54	4·53	4·60	4·55	4·56	0·04
2,2-DMB	9·73	9·75	9·74	9·78	9·74	9·80	9·84	9·82	9·78	9·86	9·78	0·05
CyC_5	3·77	3·77	3·77	3·76	3·78	3·76	3·77	3·77	3·78	3·78	3·77	0·01
2,3-DMB	8·98	9·02	9·00	9·35	8·97	9·38	9·06	9·07	8·97	8·96	9·08	0·16
2-MP	18·35	18·35	18·36	18·27	18·35	18·24	18·29	18·27	18·25	18·28	18·30	0·05
3-MP	10·70	10·68	10·68	10·67	10·69	10·70	10·71	10·70	10·67	10·71	10·69	0·02
n-C_6	20·70	20·72	20·74	20·62	20·75	20·59	20·69	20·72	20·79	20·72	20·70	0·06
MCP	11·50	11·48	11·46	11·42	11·46	11·40	11·45	11·45	11·47	11·45	11·45	0·03
CyC_6	11·68	11·67	11·67	11·62	11·67	11·62	11·65	11·67	11·69	11·69	11·66	0·02

five to seven times that of classical columns; the average linear flow rate at a pressure drop of 2 atm is as low as 10 cm/sec, whereas in a capillary column of the same length (2 m) it was 80 cm/sec.

The packed capillary columns, therefore, have the following advantages:

(*1*) Lower pressure drop than packed classical columns, when they are used under comparable conditions. This means that either rather long capillary columns can be chosen for difficult separations, or that quick separations can be carried out with a high linear flow rate without the need for special high-pressure equipment.

(*2*) Capillary columns can be directly connected to a FID, so that dead space is eliminated.

A flame ionization detector is the favoured instrument for the evaluation of such quantitative analyses, because its reading is linear over several orders of magnitude, and because the peak areas of the chromatogram are a direct measure of the size of the sample injected, without being affected by minor variations in the flow rate of the carrier gas.

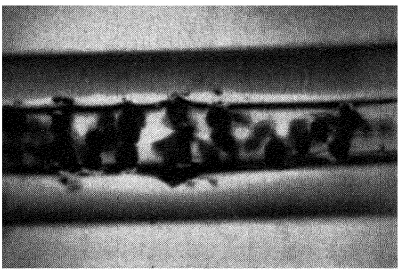


Figure 5. Microscopic view of a longitudinal cross-section of a packed capillary column. Inside diameter of the capillary, 0·3 mm. Packing material, Al_2O_3, grain size, 0·1–0·15 mm

Integration was carried out with a voltage-frequency converter connected to an electronic counting device. The converter gives an output of 100 kc/volt input signal. The peak area counts are automatically printed at the end of each peak. As the mechanical printing is the slowest process of the system, taking $\frac{1}{3}$ of a second, we have installed several counters, to ensure that closely spaced peaks can be counted while the printing of the integral of the first peak is still in progress. An electronic sensing element is installed to switch on the appropriate counter at the beginning of a peak as soon as a predetermined threshold value is reached (100–1,000 c/sec), to switch off the counter at the end of the peak and to start the printing cycle. The instrument is designed to allow for intervals of less than 0·1 seconds between peaks. Preliminary results obtained with this apparatus are given in *Figure 6* and *Table 4*.

Figure 6 shows a chromatogram of methane, ethylene, propane, propylene, and isobutane, which was obtained in less than 35 seconds. *Table 4* contains the results of 30 subsequent quantitative analyses. Sample injection was done with a gas syringe. The figures shown are the measured values in units of area per cent × 100 and the deviation from the average (Δ). The last column contains the index values for the isobutane peaks. As may be seen from this column, reproducibility of the sample injection was ± 2·5 per cent. In the runs represented by the last nine lines, amplifier sensitivity was reduced by a factor of three and sample size was approximately tripled. The last row of the table shows the average and the reproducibility expressed in percentages (± 0·3–2 rel. per cent).

Design of the system is but a preliminary one. It may be expected that the reproducibility can be increased by at least a factor two.

The apparatus and column were constructed by Mr W. Schneider and Mr E. Heine, the integration system by Mr W. R. Marx.

H. Boer: Apparently computers nowadays can be instructed to solve almost any problem, including the integration of chromatograms with base line drift and incompletely resolved peaks. It seems to me that it is much more economical to

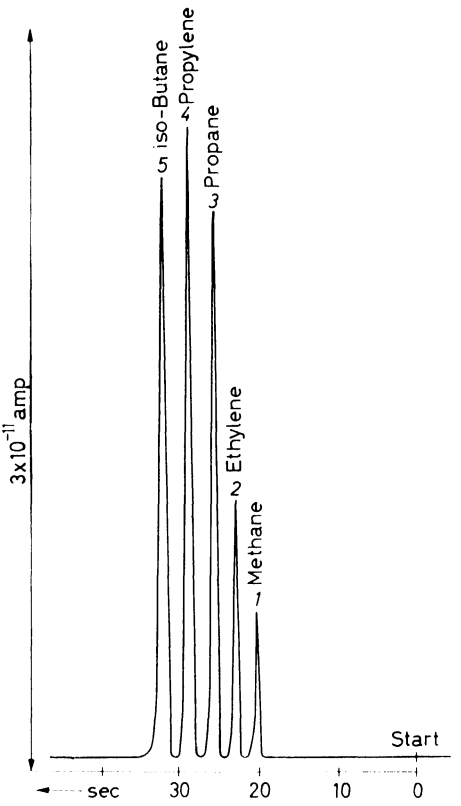


Figure 6. Quantitative separation of (*1*) methane, (*2*) ethylene, (*3*) propane, (*4*) propylene, (*5*) isobutane. Column length, 2 m; inside diameter 0·25 mm. Packing material Al_2O_3 (particle size 0·1–0·15 mm). Temperature 150°C. Carrier gas N_2 (moistened over $Na_2SO_4.10H_2O$). Inlet pressure 5·2 atm. Flow rate 1·2 ml/min (NTP). Sample size $\sim 5{\cdot}10^{-8}$g. Flame ionization detector with electrometer amplifier and 2 mV potentiometric recorder (full scale deflection 0·3 sec)

improve on the chromatograph proper to obtain maximum stability and separation than to use an expensive computer.

My second point is, that after integration, a lot of work still remains to be done; namely multiplication of the individual peak areas by specific calibration factors, and normalization to 100 per cent. Apparently this type of apparatus solves only part of the problem.

W. Heinemann: The most important thing is that this apparatus has been developed for routine analysis, and it has to be used with existing equipment. This is already there; it cannot be changed a lot.

Secondly, the apparatus is used with programmed temperature gas chromatographs, and there base line drift cannot be avoided entirely. In addition, the automatic correcting device for the base line drift is not very expensive. It is not an important part of the cost of the apparatus.

Table 4. Repeated rapid analyses evaluated with an automatic digital integrator. Measured values and errors (Δ) are given in units of area per cent × 100

Full scale deflection of amplifier [amp]	*Methane*	(±Δ)	*Ethylene*	(±Δ)	*Propane*	(±Δ)	*Propylene*	(±Δ)	*iso-Butane*	(±Δ)	*Index of the isobutane peak*
$1 \cdot 10^{-11}$	550	+8	1,078	+26	2,349	−7	2,847	−22	3,173	−17	44·475
,,	548	+6	1,074	+22	2,349	−7	2,849	−20	3,177	−13	44·393
,,	558	+16	1,092	+40	2,345	−11	2,838	−31	3,158	−32	45·124
,,	542	0	1,066	+14	2,349	−7	2,857	−12	3,182	−8	44·147
,,	523	−19	1,028	−24	2,358	+2	2,883	+14	3,206	+16	42·054
,,	536	−6	1,045	−7	2,352	−4	2,873	+4	3,190	0	42·750
,,	536	−6	1,045	−7	2,354	−2	2,874	+5	3,189	−1	42·750
,,	527	−15	1,027	−25	2,356	0	2,888	+19	3,200	+10	41·259
,,	520	−22	1,014	−38	2,357	+1	2,898	+29	3,207	+17	40·603
,,	534	−8	1,043	−9	2,354	−2	2,874	+5	3,192	+2	42·249
,,	527	−15	1,032	−20	2,353	−3	2,884	+15	3,200	+10	41·543
,,	533	−9	1,043	−9	2,355	−1	2,874	+5	3,191	+1	42·477
,,	539	−3	1,054	+2	2,436	+80	2,993	+24	3,216	+26	40·778
,,	528	−14	1,034	−18	2,355	−1	2,882	+13	3,198	+9	41·880
,,	541	−1	1,055	+3	2,350	−6	2,864	−5	3,186	+4	43·026
,,	544	+2	1,057	+5	2,347	−9	2,862	−7	3,187	−3	43·118
,,	542	0	1,055	+3	2,347	−9	2,866	−3	3,186	−4	42·888
,,	520	−22	1,021	−31	2,358	+2	2,894	+25	3,203	+13	41·195
,,	516	−26	1,013	−39	2,357	+1	2,897	+28	3,213	+23	40·783
,,	528	−14	1,031	−21	2,354	−2	2,884	+15	3,199	+9	41·856
,,	531	−11	1,038	−14	2,354	−2	2,874	+5	3,197	+7	42·397
,,	515	−27	1,005	−47	2,429	+73	2,871	+2	3,177	−13	115·203
,,	560	+18	1,078	+26	2,352	−4	2,849	−20	3,159	−31	113·299
$3 \cdot 10^{-11}$	544	+2	1,059	+7	2,352	−4	2,856	−13	3,185	−5	112·246
,,	547	+5	1,062	+10	2,349	−7	2,854	−15	3,183	−7	112·396
,,	556	+14	1,081	+29	2,351	−5	2,841	−28	3,167	−23	115·016
,,	555	+13	1,079	+27	2,348	−8	2,839	−30	3,174	−16	115·480
,,	562	+20	1,086	+34	2,344	−12	2,837	−32	3,169	−21	114·492
,,	559	+17	1,081	+29	2,347	−9	2,839	−30	3,170	−30	114·829
,,	562	+20	1,088	+36	2,343	−13	2,835	−34	3,169	−21	117·046
Average	542	±2 rel.-%	1,052	±2 rel.-%	2,356	±0·3 rel.-%	2,869	±0·6 rel.-%	3,190	±0·4 rel.-%	

Regarding the second question: this is an apparatus for routine operation, and calibration factors will be the same in most analyses; making these corrections isn't as complicated as it looks at first sight. In a research laboratory, of course, this apparatus would not be of any use; you would not install it there.

I. Halasz: I should like to answer the first question by Dr Boer: over a period of a few hours the noise and drift of the flame ionization detector amount to about 10^{-13} amp, whereas the ion current amounts to 10^{-10}–10^{-8} amp. For that reason

we didn't have to put much effort into the stabilization of the base line for the fast quantitative analyses I have reported here.

On Dr Boer's remark I should like to say the following: if only hydrocarbons are analysed, the operating conditions of the detector can be chosen so that the response factor is independent of the sample—within an error of 1–2 per cent. The flow velocity of the hydrogen burner gas is very important in this respect; we hope to publish this in more detail in the near future. If we can do without calibration factors, we are no longer faced with any substantial computing work.

REFERENCE

[12] HALASZ, I. and HEINE, E. *Nature* 1962 **194** 971

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A NOMOGRAPHIC APPROACH TO SOME PROBLEMS IN LINEARLY PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

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A rigorous nomographic approach to certain problems in programmed temperature gas chromatography has been developed, and its validity is demonstrated experimentally. The usefulness of the method greatly depends upon the degree to which a linear rate of change may be impressed on to the column temperature. Small deviations from the linear time–temperature profile may be corrected for, if these corrections are made, agreement between actual and calculated retention times and retention temperatures is excellent.

STANDARD GAS chromatographic instruments for use with the column held at isothermal conditions are operated with constant inlet and outlet pressures of the carrier gas. Mass flow and average velocity are then also constant; the theory for operation under these conditions is well established.

Not long ago it was found that some advantages can be realized if the temperature of the entire column is raised during analysis, in order to accelerate the elution of higher-boiling components. A number of authors have dealt with various theoretical aspects of this new technique and with the problems of interpretation and prediction of retention data[1–11].

At constant inlet and outlet pressures the mass flow rate of the carrier gas changes with column temperature. As thermal conductivity detectors normally used with commercial programmed temperature equipment are affected by changes in flow, the mass flow rate is kept constant by control of the inlet pressure. The result is that both average gas velocity and pressure drop along the column change with temperature. Since both parameters are complex functions of column temperature, the calculation of peak positions involves relatively complex mathematics. Alternatively inlet and outlet pressures may be kept constant. The pressure profile along the column is then independent of temperature, provided the column is uniformly heated, and only the average velocity is a function of temperature. This simplifies the mathematical treatment considerably. From a theoretical standpoint, operation at constant pressure drop is therefore more useful. However, since carrier gas flow is not constant under these conditions, detectors which are affected by flow rate are less suitable.

In this paper a theoretical treatment is given for a system operated at constant inlet and outlet pressures, as well as a nomographic solution for three crucial problems in programmed temperature gas chromatography. The validity of the theory is demonstrated by means of data obtained with a gas chromatograph designed to fulfil certain special criteria significant in programmed temperature gas chromatography.

Theory

It is assumed that pressures at column inlet and outlet are kept constant during a run, and that temperature affects all gas passages in the column in a similar manner. The pressure gradient at any point along the column is then also constant during a run. Furthermore the treatment is restricted to linearly programmed temperature gas chromatography, i.e. to operation with constant rate of change of temperature.

The following problems will be discussed:

(1) Given the capacity ratio $k(T)$ for any one substance, determine the elution time t_s of this substance when the column temperature at time $t \geqslant t_h$ is given by

$$T = T_0 + r_T(t - t_h) \tag{1}$$

where T_0 designates the reference temperature. The column temperature eventually levels off at an upper temperature, T_1.

(2) Given a desired elution time t_s for a substance for which $k(T)$ is known, as well as an upper temperature T_1, determine the rate of temperature rise r_T required after any given starting time t_h.

(3) Given $\theta = E/R$, where R is the molar gas constant and E is the molar change in free energy for the solution of a substance into the fixed phase, and given also elution times t_a and t_s of a non-retarded component and of the retarded substance, respectively, for given values of r_T and T_1, determine $k_0 = k(T_0)$. (The solution of this problem should lead to a standard procedure for the comparison of retention times at one reference temperature.)

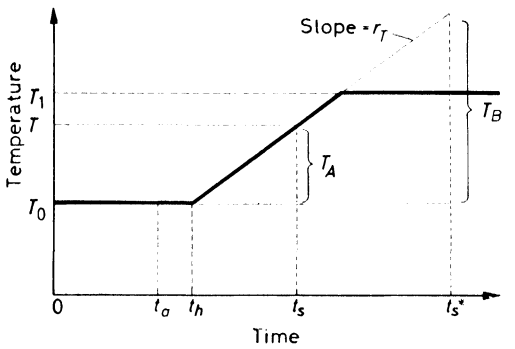


Figure 1. Diagram showing correlation of symbols used in the text, for a typical temperature programme. The solid line represents the normal temperature programme

If the pressure gradient at a distance x from the inlet of a column of length L remains constant with time, we can write for the velocity $v_c(x, T)$ of the carrier gas at any point and any time:

$$v_c(x, T) = v_c(x) f(T) \tag{2}$$

where $v_c(x)$ is the carrier gas velocity at point x and at the reference temperature T_0, and where $f(T)$ represents a function of temperature. Since the

variation of the gas passages with temperature is negligible for both packed and tubular columns, $f(T)$ is essentially proportional to the inverse of the function describing the change of carrier gas viscosity with temperature.

The velocity v_s of a retarded component is given by the expression:

$$v_s(x, T) = \frac{v_c(x, T)}{1+k(T)} = \frac{v_c(x)f(T)}{1+k(T)} \tag{3}$$

The elution time t_a of a non-retarded component at temperature T_0 ($t_a < t_h$) is given by:

$$t_a = \int_0^l \frac{\mathrm{d}x}{v_c(x)} \tag{4}$$

Recalling that a component eluted at time t_s travels a distance $\mathrm{d}x$ in a time $\mathrm{d}t = \mathrm{d}x/v_s(x, T)$, and substituting eqn (3) for the velocity $v_s(x, T)$, we can rewrite eqn (4):

$$t_a = \int_0^{t_s} \frac{f(T)\,\mathrm{d}t}{1+k(T)} \tag{5}$$

or

$$t_a = \int_0^{t_h} + \int_{t_h}^{t_s} = \frac{t_h}{1+k_0} + \int_{t_h}^{t_s} \frac{f(T)\,\mathrm{d}t}{1+k(T)} \tag{6}$$

Multiplication of both sides with $(1+k_0)$ leads to:

$$t_s^* - t_h = (1+k_0) \int_{t_h}^{t_s} \frac{f(T)\,\mathrm{d}t}{1+k(T)} \tag{7}$$

where $t_s^* = t_a(1+k_0)$ is defined as the reference elution time. The 'virtual temperature rise', T_A, which is always positive, will be defined by:

$$T_A = r_T(t - t_h) \quad \text{for} \quad t > t_h \tag{8}$$

and we shall have:

$$T = T_0 + T_A \quad \text{when} \quad T_0 + T_A < T_1 \tag{8a}$$

$$T = T_1 \quad \text{when} \quad T_0 + T_A \geqslant T_1 \tag{8b}$$

Both sides of eqn (7) may be multiplied by r_T, and $\mathrm{d}T_A$ may be substituted for $r_T\mathrm{d}t$. A 'parametric temperature', T_B, will now be defined:

$$T_B = r_T(t_s^* - t_h) = (1+k_0) \int_0^{T_A} \frac{f(T)\,\mathrm{d}T_A}{1+k(T)} \tag{9}$$

Determination of $f(T)$ and $k(T)$

The empirical expression

$$\frac{\eta_T}{\eta_0} = \left(\frac{T}{T_0}\right)^{0.7} \tag{10}$$

has been verified experimentally for the viscosity of helium in the temperature range between 323 and 473°K [12]; accordingly we may write:

$$f(T) = \left(\frac{T_0}{T}\right)^{0.7} \tag{11}$$

Over the temperature range of interest the relation between k and T can be written:

$$k(T) = k_0 \exp\left(\frac{\theta}{T} - \frac{\theta}{T_0}\right) \tag{12}$$

Substitution of the expressions for $f(T)$ and $k(T)$ in eqn (9) gives:

$$T_B = (1+k_0)\int_0^{T_A}\left(\frac{T_0}{T}\right)^{0.7}\frac{dT_A}{1+k_0\exp\left(\frac{\theta}{T}-\frac{\theta}{T_0}\right)} \tag{13}$$

In *Figure 2*, values of T_B, obtained by numerical integration*, are plotted as functions of T_A for one value of θ and three values of k_0. The value of θ is given by the slope of a plot of ln k versus $1/T$, as shown in *Figure 3* for n-hexane, n-heptane, n-octane, n-nonane and n-decane at 323, 373 and 423°K.

By means of the T_B versus T_A curves, the three problems stated earlier can be solved as follows:

(1) Given k_0, θ, t_h, t_s* and r_T, determine t_s:

Solution:

The parametric temperature T_B is defined by eqn (9):

$$T_B = r_T(t_s^* - t_h)$$

The intersection of a horizontal line at height T_B with the curve for the proper k_0 on the appropriate θ chart gives the temperature rise T_A, from which t_s is calculated by means of the relation

$$t_s = t_h + \frac{T_A}{r_T} \tag{14}$$

(2) Given k_0, θ, t_h, t_s*, and a desired elution time t_s, determine r_T:

Solution:

A line through the origin, inclined at an angle arc $tg(t_s^* - t_h)/(t_s - t_h)$ intersects the curve for the proper value of k_0 at a point (T_A, T_B), from which

$$r_T = \frac{T_A}{t_s - t_h} \quad \text{or} \quad r_T = \frac{T_B}{t_s^* - t_h}$$

The value of the integral may be computed for $\theta < T_A < (T_1 - T_0)$ as the sum of a series:

$$T_B = (1+k_0)\sum_{i=1}^{T_1-T_0}\left(\frac{T_0}{T_0+i}\right)^{0.7}\frac{1}{1+k_0\exp\left(\frac{\theta}{T_0+i}-\frac{\theta}{T_0}\right)}$$

Calculations were made at 1°C increments with a desk-sized digital computer, Royal McBee type LGP 30, utilizing ACT III simplified algebraic language. For $T_A > (T_1 - T_0)$, the T_B versus T_A curves are extended as straight lines.

(3) Given θ, t_a, t_h, t_s and r_T, determine k_0:

Solution:

The expression

$$T_B = r_T(t_s^* - t_h) = r_T\{t_a(1+k_0) - t_h\}$$

can be written:

$$k_0 = \frac{T_B + r_T t_h - r_T t_a}{r_T t_a} \tag{15}$$

A transparent chart is now prepared with lines going through its origin, and slanting to the left at various angles, arc $tg\ k_0$ with the horizontal. If this chart is placed on the T_A, T_B chart for the appropriate value of θ with its origin at the point (T'_A, T'_B) defined by $T'_A = r_T(t_s + t_a - t_h)$ and $T'_B = -r_T(t_h - t_a)$, then on the vertical line corresponding to $T_A = r_T(t_s - t_h)$ there will be a point P for which the k_0 value interpolated from the T_A, T_B chart is equal to the k_0 value interpolated from the transparent chart. This point represents the correct value of T_B, for which eqns (9) and (15) are both satisfied, and gives the correct value of k_0.

A number of charts, for different values of θ, will be required for the solution of these three problems by interpolation for the correct value of k_0.

Experimental

Apparatus

For the experimental verification of the theory a gas chromatograph was used which had been designed to fulfil the following requirements[a]:

(a) operation at constant and at linearly rising temperature, as illustrated in *Figure 1*;
(b) constant pressure differential across the column;
(c) uniform column temperature;
(d) minimum difference between actual and desired temperature at any time.

A flame ionization detector was used, which is insensitive to changes in carrier gas flow. At constant inlet pressure, temperature programming did not produce appreciable base line drift. The design considerations and performance of the instrument have been reported elsewhere[13]; nevertheless, requirement (d) merits a brief discussion here. When a column is mounted in an air bath, the temperature may vary along the length of the column, and often lags appreciably behind the oven temperature during programming[7]. In our instrument columns are wound into a flat spiral and mounted between two circular aluminium discs, each $\frac{1}{32}$ in. (0·8 mm) thick and with a diameter of $8\frac{1}{4}$ in. (21 cm). This assembly is pressed evenly on to a heater cast into an aluminium disc of similar size and 0·2 in. (5 mm) thick, in order to ensure good thermal contact. The entire unit is surrounded by insulating bricks. With an initial temperature of 50°C, measured lag at 200°C was only 2·2°C at a heating rate of 18·75°/min, and 6·7°C at a heating rate of 50°C/min.

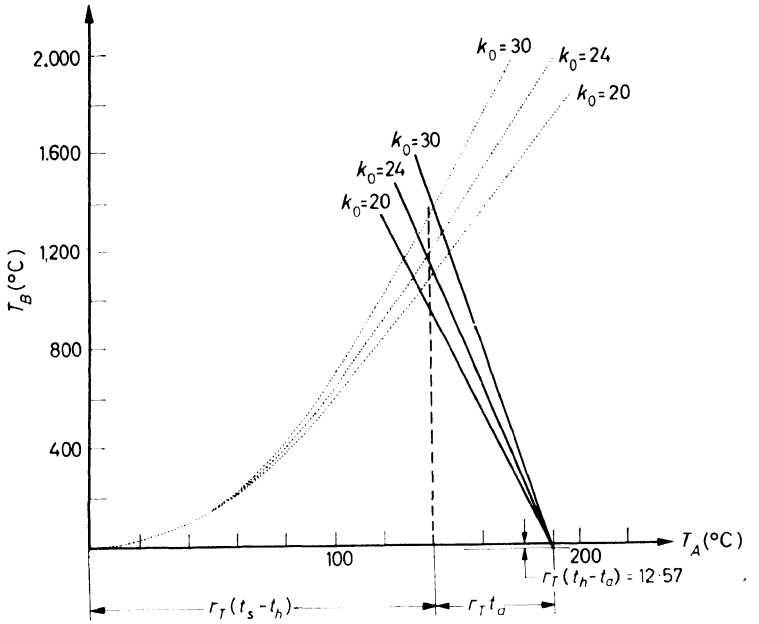


Figure 2. Computer-drawn curves for three values of k_0, in a T_A, T_B diagram, as seen with transparent chart correctly superimposed. Sample: n-decane; $\Theta = 5282$

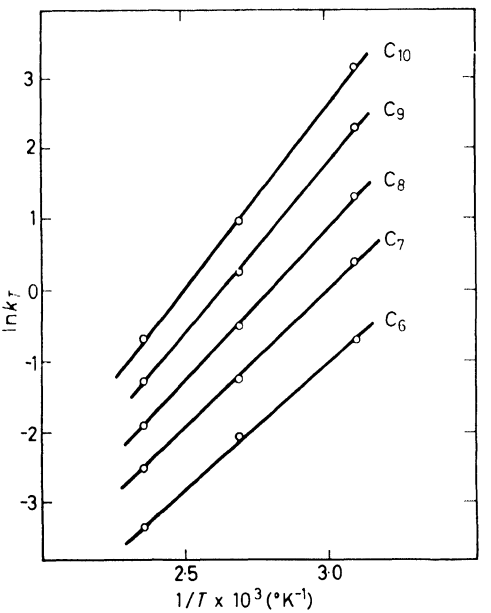


Figure 3. Plots of ln k_T versus reciprocal absolute temperature, $1/T$, for normal paraffins from C_6 to C_{10}. Column: 90 m stainless steel tube, 0·25 mm i.d., coated with Apiezon L. Carrier gas: helium. Inlet pressure: 40 psig (2·7 atm). Outlet pressure: atmospheric

It will be shown later that calculations can be made to an accuracy of about 8 per cent when this lag is neglected. Improvement is possible if actual column temperatures, measured with separate iron-constantan thermocouples in direct contact with the column, are used in the calculations.

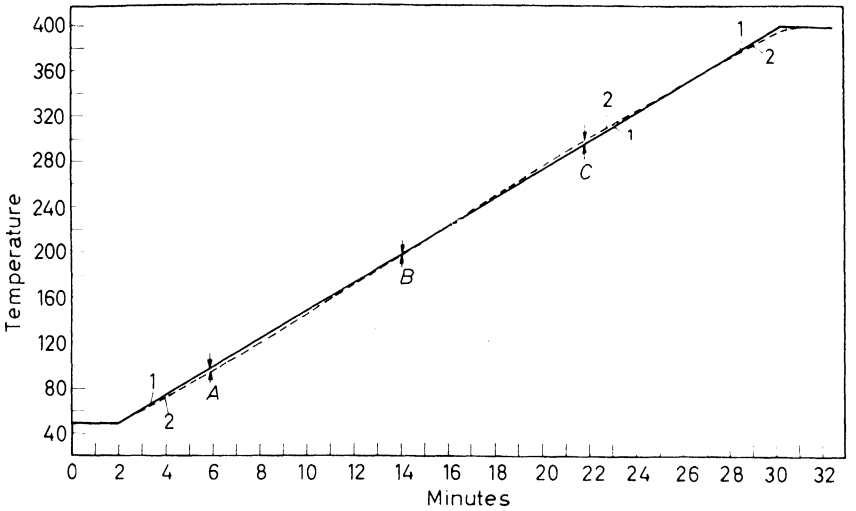


Figure 4. Comparison of nominal and actual column temperatures for a nominal heating rate of 12·5°C/min. Curve 1: nominal temperature; Curve 2: actual column temperature. Deviations are as follows: 100°C, 3·6°C; 200°C, 0°C; 300°C, 1·3°C

Figure 4 shows curves of nominal and actual column temperatures for the programme setting used in the experimental work (nominal heating rate 12·5°C/min between 50 and 400°C). The data of these curves were used in the calculations.

Experimental data

Values of T_B for individual components were calculated by eqn (9) from data obtained at 50°C; values of T_A were obtained from programmed temperature runs by means of eqn (8). The T_A values thus obtained were compared with those derived from the actual chromatogram (*Figure 5*) by reference to the nominal temperature programme. It was found that the observed values exceeded the calculated values by as much as 8 per cent. Although this might be tolerable in practice, it was decided that the discrepancies were too large to permit verification of the nomographic procedure. Since programmed temperature gas chromatography derives its usefulness from the strong temperature dependence of the partition ratio, it is obvious that precise knowledge of the temperature–time profile is required for any system for prediction of retention times. As shown in *Figure 4*, actual column temperatures differ slightly from those corresponding to the nominal programme. Nominal values of t_R and r_T were therefore corrected for each peak to represent the best straight-line approximation to the heating curve over the

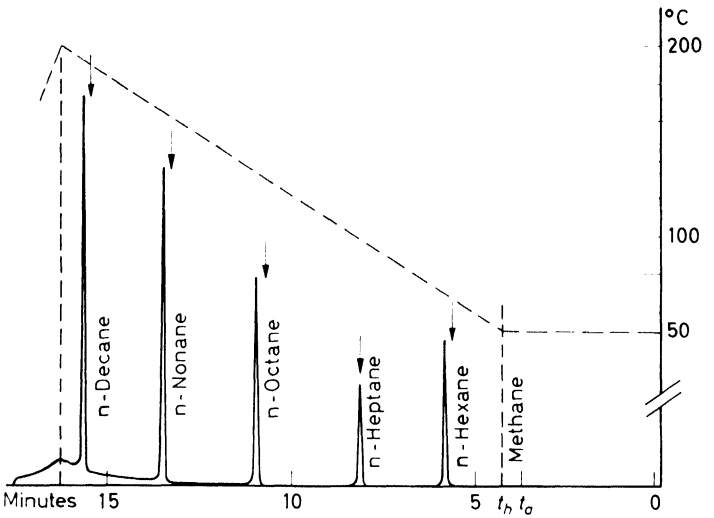


Figure 5. Programmed temperature chromatogram of normal paraffins from C-6 to C-10. Nominal heating rate: 12·5°C/min. Column, carrier gas, inlet and outlet pressures the same as for *Figure 3.* Solid curve: detector signal; dotted lines: nominal temperature programme. Arrows indicate the calculated elution times

Table 1. Linear approximations to the effective heating programme

Time from nominal start of heating programme, min	*Effective heating rate*, °C/min	*Delay between nominal and effective start, as extrapolated from linear approximation*, min
1·5	11·5	0·20
4·0	12·0	0·26
7·0	12·7	0·35
9·0	12·9	0·50
12·0	12·9	0·50

Table 2. Comparison of calculated k_0 values with values observed at the reference temperature. Extrapolated t_h values and observed heating rates were used in the calculation

Component	t_s*	T_B	T_A				t_s			k_0		
			calc.	*obs.*	*dev.*		*calc.*	*obs.*	*dev.*	*calc.*	*obs.**	*dev.*
	min	°C	°C	°C	°C	%	min	min	%			%
n-Hexane	5·68	14	13	15	+2	14	5·62	5·79	3	0·55	0·49	12
n-Heptane	9·44	59	43	43	—	—	8·13	8·11	0·25	1·5	1·5	—
n-Octane	17·57	164	77	80	+3	3·8	10·72	10·91	1·8	4	3·6	11
n-Nonane	40·72	464	110	112	+2	1·8	13·29	13·47	1·3	10	9·7	3
n-Decane	95·25	1,167	138	140	+2	1·4	15·49	15·65	1·0	24	24	2

* Isothermal operation at 50°C

part corresponding to the time each component remained in the column. Values of these corrections are given in *Table 1*. When the corrected values are used for the calculation of T_A and t_s by means of eqn (10), the agreement between calculated and observed value is excellent, as shown in *Table 2* and by the arrows in *Figure 5*, and the results confirm the validity of the solution proposed for problems 1 and 2. As a test for the validity of the solution for problem 3, values of k_0 were obtained from the programmed temperature run by means of the nomographic procedure, as illustrated in *Figure 2*. Corrected values of r_T and t_h were used in this calculation. The data are summarized in *Table 2*; it is clear that knowledge of accurate values of r_T and t_h is even more important here than for the calculation of t_s.

Discussion

Even the small deviations from a linear temperature programme illustrated in *Figure 4* can introduce definite errors, although approximate calculations may be made without further correction. If actual time–temperature data are used, values for T_A and t_s can be predicted with a high degree of accuracy. It may be expected that the method will prove to be even more successful for strongly retained substances, as, with the longer heating time, small departures from the desired temperature programme may tend to cancel out.

Packed columns, with their inherently greater thermal mass and temperature gradients, appear to demand more elaborate instrumentation for effective utilization of the procedure, although the large k values obtainable may partly offset the disadvantage of these effects, particularly if moderate heating rates are employed.

We anticipate that further studies will accentuate the practical significance of the nomographic approach described above.

The authors wish gratefully to acknowledge the assistance of W. Averill and H. Gill in the experimental work and the help and advice of A. Savitzky and R. Bernard in the computer calculation and in the interpretation of the computer data.

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DISCUSSION

Authors' Additional Comments

At a given reference temperature the resolution of a gas-chromatographic column may be defined as[14]:

$$R = \frac{t - t_a}{\delta t} = \frac{k_0 t_a}{\delta t} \tag{16}$$

in which δt designates the band width at midheight of a retarded component.

As defined above, the resolution is a function of the elution time and therefore varies from component to component. The essential virtue of this definition is that the relative separation, S, of two neighbouring components with reference temperature elution times t and $t+\Delta t$, and capacity ratios k_0 and $k_0+\Delta k_0$ may be expressed as:

$$S = \frac{\Delta t}{\delta t} = R \frac{\Delta t}{t - t_a} = R \frac{\Delta k_0}{k_0} \tag{17}$$

in which $\Delta k_0/k_0$ depends essentially upon the intrinsic characteristic properties of the two neighbouring components and of the fixed phase of the chromatographic column, but does not depend upon the design parameters of any particular column.

Since at the reference temperature we have:

$$t_a = \frac{\Delta t}{\Delta k_0} \tag{18}$$

the resolution can be written:

$$R = k_0 \frac{\Delta t}{\Delta k_0} \frac{1}{\delta t} \tag{19}$$

This last expression, in which Δt designates the differential elution time during a temperature-programmed run, will be taken as the definition of the resolution in temperature-programmed chromatography. We shall still have for the relative separation:

$$S = \frac{\Delta t}{\delta t} = R \frac{\Delta k_0}{k_0} \tag{20}$$

but eqn. 18 is no longer valid.

The task of evaluating R for any given temperature programme can be subdivided into the two sub-tasks of evaluating $\Delta t/\Delta k_0$ and δt.

The evaluation of $\Delta t/\Delta k_0$ can be made as follows by means of the nomogram illustrated in *Figure 2*, in which it must be imagined that curves have been drawn for, e.g. every integral value of k_0: starting at the distance $r_T(t_h - t_a)$ below the T_A axis, and at every $k_0 r_T t_a$ point so obtained, a horizontal line is drawn to intersect the corresponding k_0 curve (this has to be done only for the points above the T_A axis, as below it eqn. 18 is valid and this construction would be trivial). Vertical lines are then drawn through these points of intersection on the k_0 curves; the successive intervals thus marked off on the T_A axis, divided by r_T, then give the corresponding values of Δt for unit increments of k_0.

The value of δt is calculated from the specific second moment of mass[15], w, at the column exit, to which δt is related by:

$$\delta t^2 = 5{\cdot}54 \frac{w}{p_0^2 v_s^2(l,T)} = 5{\cdot}54 \frac{w[1+k(T_e)]^2}{p_0^2 v_c^2(l) f^2(T_e)} \tag{21}$$

where T_e designates the elution temperature.

The product $p(x)v_c(x)$ is constant throughout the column, and is equal to:

$$p(x)v_c(x) = \frac{p_1^2 - p_0^2}{2r} \tag{22}$$

where r designates the pneumatic resistance of the column.

We also have:

$$p^2(x) = p_0^2 + (p_1^2 - p_0^2)\left(1 - \frac{x}{l}\right) \tag{23}$$

where l designates the length of the column. Eqns 22 and 23 may be utilized to evaluate t_a in eqn. 4:

$$p(x)v_c(x) = \frac{2}{3} \frac{p_1^3 - p_0^3}{p_1^2 - p_0^2} \frac{l}{t_a} \tag{24}$$

Hence, δt^2 can now be written:

$$\delta t^2/w = 5{\cdot}54 \frac{9}{4} \frac{(p_1^2 - p_0^2)^2}{(p_1^3 - p_0^3)^2} \frac{t_a^2}{l^2} \frac{[1+k(T_e)]^2}{f^2(T_e)} \tag{25}$$

The specific second moment of mass w must be utillzed, rather than the second moment u, in order to allow for the effect of decompression, which is caused by the component moving from regions of high pressure to regions of low pressure; for w remains invariant for any change of pressure, but u does not.

The rigorous evaluation of w would be somewhat complex; but a general method is sketched below, which will lead to a workable expression for w, when two simplifying assumptions are made.

Any incremental value of w is given by:

$$\mathrm{d}w = p^2 h \, \mathrm{d}x = p^2 h v_s(x,T) \, \mathrm{d}t \tag{26}$$

where p and h designate respectively the pressure and the HETP at the point where a given component is moving with the velocity $v_s(x,T)$.

The first simplifying assumption will be that the presence of an oil diffusion term in h can be ignored, so that h may be considered to be only a function of k and of the ratio, $D/v_c(x)$, of the diffusivity of the given component over the velocity of the carrier gas. Since both k and $D/v_c(x)$ are functions of the temperature, and since the ratio D/v_c is constant throughout the column for any one temperature, h can be written:

$$h = h(p_1, p_0, T) = h(T) \tag{27}$$

The effect of p_1 and p_0 is felt through their influence on the carrier gas velocity, which is also affected by the temperature, T. Since p_1 and p_0 are maintained constant throughout a run, h will be written simply as a function of the temperature, $h(T)$.

We now utilize eqns 24 and 27 to rewrite $\mathrm{d}w$:

$$\mathrm{d}w = p^2(x)h(T)v_c(x) \frac{f(T)}{1+k(T)} \mathrm{d}t = \frac{2}{3} \frac{p_1^3 - p_0^3}{p_1^2 - p_0^2} \frac{l}{t_a} \frac{p(x)h(T)f(T)}{1+k(T)} \mathrm{d}t \tag{28}$$

The exact role of $p(x)$ in the integration of eqn. 22 would be difficult to evaluate, since it would imply following the travel of the component throughout the column during a temperature-programmed run. This will be avoided by means of the second assumption, namely that the average effective value of $p(x)$ will be the same during a temperature-programmed run as at the reference temperature. The average effective value of $p(x)$ at the reference temperature can be calculated from the expression:

$$\overline{p(x)} = \frac{\int p(x) \frac{dx}{v_c(x)}}{\int \frac{dx}{v_c(x)}} = \frac{\int p^2(x)\, dx}{\int p(x)\, dx} \tag{29}$$

in which the second equality is a direct result of eqns 22 or 24. The evaluation of $\overline{p(x)}$ can then proceed, and utilizing eqn. 23 we obtain:

$$\overline{p(x)} = \frac{3}{4} \frac{p_1^4 - p_0^4}{p_1^3 - p_0^3} \tag{30}$$

Since $p(x)$ may now be taken out of the integral required for the evaluation of w, we derive from eqn. 28:

$$w = \frac{2}{3} \frac{p_1^3 - p_0^3}{p_1^2 - p_0^2} \frac{l}{t_a} \frac{3}{4} \frac{p_1^4 - p_0^4}{p_1^3 - p_0^3} \int \frac{h(T) f(T)}{1 + k(T)}\, dt \tag{31}$$

Substitution of this expression for w in eqn. 25 gives:

$$\delta t^2 = 5{\cdot}54 \frac{9}{8} \frac{(p_1^2 - p_0^2)(p_1^4 - p_0^4)}{(p_1^3 - p_0^3)^2} \frac{t_a}{l} \frac{[1 + k(T_e)]^2}{f^2(T_e)} \int_0^t \frac{h(T) f(T)}{1 + k(T)}\, dt \tag{32}$$

Since the value of the term in p_1 and p_0 lies between 8/9 and 1 for all values of p_1 from near p_0 to very large, eqn. 32 may be simplified to:

$$\delta t^2 = 6 \frac{t_a}{l} \frac{[1 + k(T_e)]^2}{f^2(T_e)} \int_0^t \frac{h(T) f(T)}{1 + k(T)}\, dt \tag{33}$$

with an error in δt of less than $\frac{1}{2}$ per cent when p_1 is between $1{\cdot}9p_0$ and $2{\cdot}4p_0$.

When the parametric temperature is utilized instead of real time, as was done for the evaluation of T_B, we obtain for δt:

$$\delta t^2 = 6 \frac{t_a}{l} \frac{[1 + k(T_e)]^2}{f^2(T_e)} \left[\frac{h(T_0) t_h}{1 + k_0} + \frac{1}{r_T} \int_0^{T_A} \frac{h(T) f(T)}{1 + k(T)}\, dT_A \right] \tag{34}$$

The application of this formula for the evaluation of δt will require an experimental determination of $h(T)$ at several fixed temperatures.

F. Sjenitzer (*prepared contribution*): I have the following question with regard to *Table 2* on page 146. There are three columns of deviation given in this table in percentages of the quantities T_A, t_s, and k_o. The relative deviations between calculated and observed temperatures, T_A, have to my mind very little meaning, since these percentages depend on the zero points used. I think it is more interesting to note the simple absolute differences, which appear to be approximately constant for the five paraffins studied. These I find to be 2, 0, 3, 2, and 2°C.

(As requested by the authors, a column indicating deviations of T_A in °C has been inserted in *Table 2—Ed.*)

J. C. Sternberg: Does the method presented require separate numerical calculation for each value of k_0, each value of θ and each value of T_0? If so, wouldn't it be better to define a more general parameter T/θ, so that the difficult numerical portion of the computation would have to be carried out for only one set of values

of k_0 and for required values of T_0? This would eliminate the need for separate calculations for each value of k. Such a procedure has been utilized by Dr A. S. Said[16]; in a private communication Dr Said has indicated the applicability of this method here, and even the possibility of eliminating the need for separate computations for different values of T_0.

M. J. E. Golay: It is correct that the virtual temperature rise could be replaced by the parameter $x = T/\theta$; but, since $f(T)$, which represents the variation of viscosity with temperature, would have to be replaced by $f(\theta x)$, the presence of θ in the argument would require a double multiplicity of tables, as in the original treatment. In addition, the terminal temperature T_1 would have to be replaced also by θx_1; for the same terminal temperature various values of x_1 would have to be selected, corresponding to several values of θ; this would cause a further complication.

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11

SUBAMBIENT PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

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A programmed temperature gas chromatograph has been built. The equipment is cooled with liquid carbon dioxide and may be used from −75 to +400°C. Rapid cooling of the column is possible with the carbon dioxide cooling system.

The subambient temperature range is very useful in programmed temperature gas chromatography. Samples containing gases and having a wide boiling range can be analysed easily. Use of fixed starting conditions near and below ambient temperature allows reproducible retention times to be obtained.

Initial freezing of the sample is advantageous, since peak widths for homologous series are constant and peak heights can be used directly for quantitative measurements. At low temperature materials may also be effectively concentrated in the first section of the gas chromatographic column. After concentration, the components can be eluted at an appropriate setting of the temperature programmer.

Liquid phases are evaluated for application at low temperatures.

Methods of applying corrections for pressure drop in programmed temperature work are evaluated and a new method is presented. It is shown that retention temperature may be correlated better with boiling point than with carbon number over a wide temperature range. Methods for the calculation of retention temperatures from isothermal data are described and applied to homologous series of normal paraffins, aromatics and primary alcohols.

Description of the instrument

The instrument utilizes liquid carbon dioxide for cooling. The cooling apparatus is illustrated in *Figure 1*. The on-off temperature controller is a Resistrotrol Model 1215*. A synchronous motor is used to change the temperature setting linearly. A No. 1146C temperature probe[a] is used in conjunction with the Resistotrol. This probe is reported to be usable in the range −75°C to 480°C. It has been operated very successfully in the range −75°C to 300°C. The column oven can be used from −75°C to 400°C. The detector ovens operate from ambient temperature to 400°C.

Cooling

Use of liquid carbon dioxide to cool the column oven provides a large saving in time. Without carbon dioxide cooling, about 1 hour was required to cool from 240 to 40°C. With cooling, this could be done in 10 minutes. Cooling to 0°C takes less than 13 minutes. In addition, the cooling process is automatic. The operator need only set the temperature controller for the

desired minimum temperature. After cooling, the unit will maintain the temperature at this level.

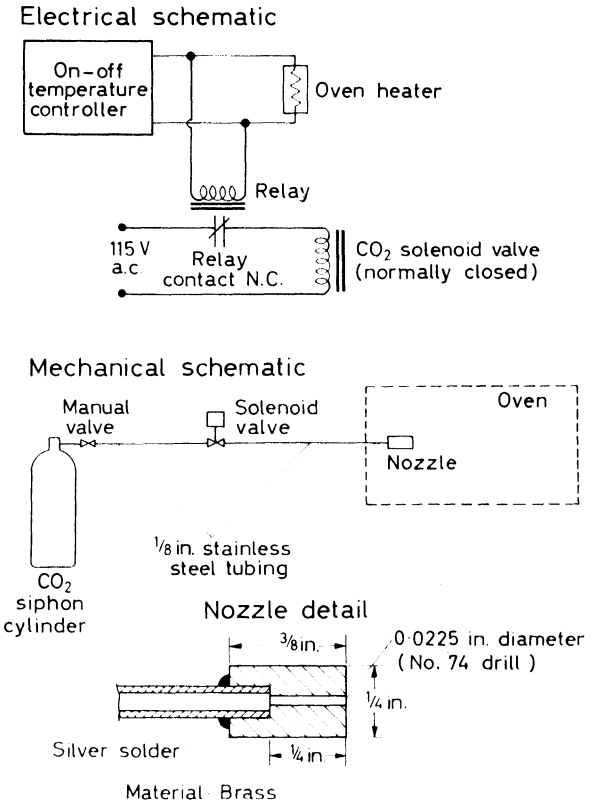


Figure 1. Carbon dioxide cooling apparatus

Liquid phases

Subambient programmed temperature gas chromatography requires columns which can be operated at both low and high temperatures. *Table 1* shows results of a survey of liquid phases. The silicone polymers appear to be very

Table 1. Practical temperature limits for liquid phases in gas chromatography

Liquid phase	*Temperature range* °C
Polypropylene Glycol 150[d]	−20 to 80
Polyethylene Glycol 200[d]	No separation at −20
Silicone oil 550[c]	−20 to 270
Silicone gum rubber SE 30[b]	Above 0
SF 96 (50)[b]	−60 to 270
Fluorosilicone oil QF-1-0065[c]	−20 to 220
Nitrile silicone fluid XF-1112[b]	−40 to 200

suitable for this application. Silicone oil, SF 96 (50)[b], is particularly outstanding. No loss of resolution was observed at −60°C, and the oil can be heated to 270°C without base line drift. With dual columns the upper limit may be extended to 300°C.

Most polar materials have high melting points. However, the recent appearance of polar silicone fluids offers hope of finding polar liquid phases with a wide temperature range. Data for nitrile silicone fluid, XF-1112[b], and fluorosilicone oil, QF-Z-0065[c], are included in *Table 1*.

Analytical applications

The instrument has been used for the separation of volatile hydrocarbons. With a 50 ft (15·5 m) by $\frac{1}{4}$ in. (4·3 mm ID) column containing 28·6 per cent silicone fluid SF 96 (50)[b] on silicone-treated Chromosorb W (60–80 mesh), all the C_1–C_4 olefins and paraffins can be separated with the exception of 1-butene and isobutene. The initial temperature is −20°C; after elution of ethane the temperature is raised at 4·0°C per minute. The separations between air and methane and between ethane and ethene are excellent. Under isothermal conditions, these pairs are difficult to separate because of the relatively high temperature required for the C_4 components.

Wide-boiling mixtures, C_1–C_{16}, have also been separated with our technique. Even in such mixtures, methane and air can be separated, as well as ethene and ethane, propene and propane, and the C_4 olefins and paraffins, with the exception of 1-butene and isobutene. A high-pressure sampling syringe was used for injection of such samples.

Wide temperature range studies

Theory

Programmed temperature gas chromatography can be described by:

$$\int_{T_o}^{T_R} \frac{F}{r} \frac{1}{(V_R^o)_T} \, dT = 1 \tag{1}$$

where T_o and T_R are the injection temperature and the retention temperature, respectively; r is the linear heating rate in degrees per minute; $(V_R^o)_T$ is the corrected retention volume measured from the injection; and F is the flow rate. $(V_R^o)_T$ and F are measured at a standard temperature (25°C) in this study, rather than at the column temperature as recommended[1]. They must be corrected for the pressure gradient. Neglecting velocity gradients along the column and assuming r/F to be temperature-independent, we may write eqn (1):

$$\int_{T_o}^{T_R} \frac{1}{(V_R^o)_T} \, dT = \frac{r}{F} \tag{2}$$

These appear to be minor approximations[2,3,5]. Since the temperature dependence of $(V_R^o)_T$ cannot be represented by easily integrated equations, a graphical integration method was developed by Habgood and Harris[2].

If the gas holdup volume is neglected, the temperature dependence of the retention volume can be expressed as:

$$\log (V_N)_T = \frac{A}{T} + \log B \tag{3}$$

where $(V_N)_T$ is the net corrected retention volume, measured from the air peak. Substitution of $(V_N)_T$ for $(V_R^0)_T$ and combination of eqns (2) and (3) gives:

$$\int_{T_A}^{T_R} \exp(-A/T)\, dT = \frac{Br}{F} \tag{4}$$

where T_A is the temperature at which the air peak emerges. Giddings[3] and Rowan[5] developed analytical methods for the calculation of retention temperatures based on eqn (3).

Experimental

The subambient programmed temperature gas chromatograph described above was used for all measurements. It has an inlet pressure gauge to measure column inlet pressure and a constant differential flow regulator to ensure constant flow rate with changing temperature. A high resistance thermal conductivity detector with tungsten filaments was used; the instrument volume was 5 c.c.

A 10 ft. (3·10 m) by $\frac{1}{4}$ in. (4·3 mm ID) copper column packed with 28·6 per cent SF 96 (50)[b], silicone fluid, on hexamethyldisilizane-treated Chromosorb W (60–80 U.S. standard mesh) was used for all measurements. The interstitial volume was 45 c.c. Helium was used as the carrier gas.

Retention temperatures were measured with a thermocouple placed at the end of the column, isolated from the walls and surrounded by packing.

Pressure corrections

If isothermal retention volumes corrected for pressure gradient are used in a calculation of retention temperatures, the flow rate must also be corrected for pressure. This correction is difficult to apply since the factor changes with temperature, owing to changes in viscosity of the gas. On the other hand, uncorrected flow rates may be used in the calculation of retention temperatures if uncorrected isothermal data are likewise used. The results of avoiding pressure corrections by this method are shown in the *A* rows of *Table 2*. This table contains data for C_2–C_{14} normal paraffins. In general, good agreement was obtained with the empirical retention temperature over a wide temperature range. The disadvantage of this method is that the isothermal data at differing flow rates cannot be correlated by eqn (3). Separate plots of $\log (V_N)_T$ versus reciprocal of the absolute temperature must be prepared for each flow rate. The values of *A* and *B* used in the analytical method also depend on flow rate; they were obtained from these plots. Plots of the logarithm of the uncorrected isothermal retention volume versus reciprocal of the absolute temperature deviate more from linearity over a wide temperature range than plots of corrected retention volume. Linear relationships were obtained in the temperature ranges of interest: higher

Table 2. Retention temperatures, corrected for pressure drop by various methods

Row *A* Uncorrected isothermal data
Row *B* Average pressure
Row *C* Rough retention temperature; uncorrected flow rate
Row *D* Corrected for pressure drop at rough retention temperature

Run	*Method*	*Row*	*Retention temperature*, °C							*Heating rate*, °C/minute	*Flow rate*, ml/minute	*Temperature rise to air peak*, °C
			C_2	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}			
1	Experimental		−44	26	87	140	181	219	248	4·00	50	5
	Graphical	*A*	−54	34	90	133	177	213	240			
	Graphical	*B*	−49	32	95	138	173	210	236			
	Graphical	*C*	−59	18	75	122	161	193	224			
	Graphical	*D*	−54	29	95	139	176	215	242			
	Analytical	*A*	−53	28	89	139	178	212	249			
	Analytical	*B*	−42	31	90	137	176	209	237			
	Analytical	*C*	−48	18	81	122	161	193	218			
	Analytical	*D*	−45	28	89	138	179	213	241			
2	Experimental		−28	55	116	168	213			8·43	50	9
	Graphical	*A*	−33	58	119	165	209					
	Graphical	*B*	−25	59	122	168	205					
	Graphical	*C*	−41	41	107	147	183					
	Graphical	*D*	−32	56	123	169	211					
	Analytical	*A*	−38	50	115	167	205					
	Analytical	*B*	−28	56	115	163	204					
	Analytical	*C*	−37	39	98	145	186					
	Analytical	*D*	−32	51	115	165	208					

temperatures for the higher members; lower temperatures for the lower members. The technique presented no difficulty and is satisfactory if all the data are obtained at a single flow rate.

The alternative method of calculating retention temperatures involves the use of pressure-corrected isothermal data and application of a correction for pressure gradient to the flow rate:

$$j = \frac{3}{2}\left\{\frac{(p_i/p_o)^2-1}{(p_i/p_o)^3-1}\right\} \tag{5}$$

where p_i and p_o are the column inlet and outlet pressures, respectively. At moderate heating rates the increase in flow rate due to expansion of the carrier gas can be neglected, and at constant mass flow the pressure increases linearly with column temperature.

Rowan[5] has suggested that the pressure gradient correction factor could be made for the average temperature. However, this requires *a priori* knowledge of the retention temperature. Row *B* of *Table 2* contains data for which the correction was made at the mean column temperature during a run. This does not require *a priori* knowledge of the retention temperature. Fair agreement is obtained, but this method results in over-correction for compounds with low retention temperature and undercorrection for those with high retention temperatures.

An alternative method is offered here which is based on preliminary calculation of a rough retention temperature from pressure-corrected isothermal data but with uncorrected flow rate. The final retention temperature is then calculated by applying the pressure gradient correction at this rough temperature. The rough retention temperatures are shown in the *C* rows of *Table 2* and the final retention temperatures in the *D* rows. Good agreement with the experimental data is observed over a wide temperature range. The data calculated by the analytical method show a negative bias. This may be due to the neglect of the gas holdup volume. No correction for this has been made.

Correlation of parameters

Correlations of retention temperatures and retention times with carbon number have been reported[3,4]. Measurements over a wide temperature range indicate that retention temperature shows a better correlation with boiling point. This is illustrated in *Figure 2* for C_1–C_{16} normal paraffins. The initial temperature has no effect in the linear range. Similar relationships were obtained for alcohols and aromatics. With plots, such as given in *Figure 2*, retention temperatures of other homologues can be obtained without measurements, once two points are established. This is valuable for qualitative identification. However, the curves in *Figure 2* only hold for a specified heating rate and flow rate.

More general methods of correlating isothermal data for the prediction of retention temperatures are available. The familiar logarithmic correlation of isothermal retention volumes with carbon number can be used to produce data for subsequent calculations of retention temperature for homologous series. However, when the parameters needed for calculations of retention temperature are correlated, only the terminal calculations need be performed.

The graphical method utilizes curves of the integral in eqn (2) versus retention temperature. These exponential curves have the same shape for many compounds but are displaced along the temperature axis. They can, however, be reduced to a single curve by means of the concept of reduced temperature. Such a reduced temperature plot is shown in *Figure 3*. The reduced retention temperature is defined as:

Reduced Retention Temperature = Retention Temperature
− Reduced Temperature Factor

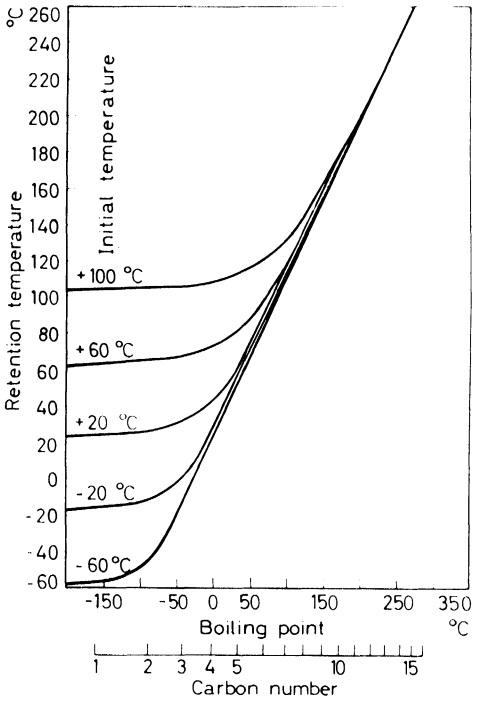


Figure 2. Retention temperature *v.* boiling point for normal paraffins

The reduced temperature factors were obtained from the retention temperature at $r/F = 0{\cdot}2$ by reference to normal octane:

Reduced Temperature Factor = 155°C − (Retention
Temperature of Component at $r/F = 0{\cdot}2$)

Figure 3 shows that correlation is good for normal paraffins, alcohols, and aromatics over a wide temperature range.

The reduced temperature factors correlate very well with boiling point, as is shown in *Figure 4*. By means of the relationship illustrated in *Figure 4*, the retention times for members of homologous series may be predicted at any flow rate and heating rate from isothermal data on two homologues, at two temperatures.

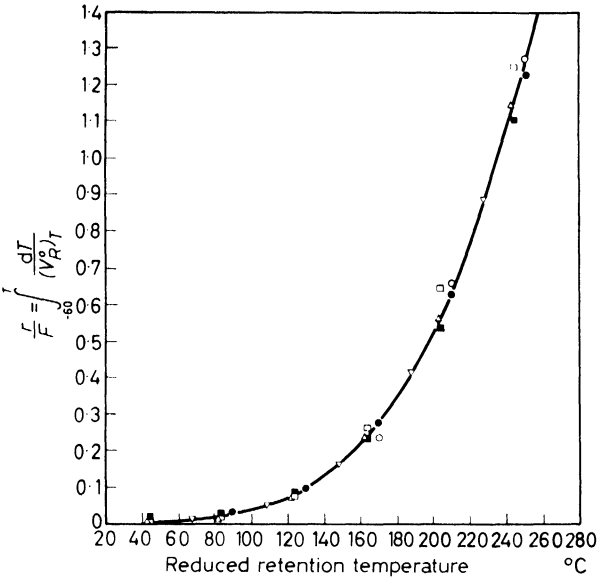


Figure 3. r/F *v.* reduced retention temperature. (○—Ethane; □—n-Hexane; ■—n-Decane; △—n-Tetradecane; ●—Toluene; ▽—n-Hexanol)

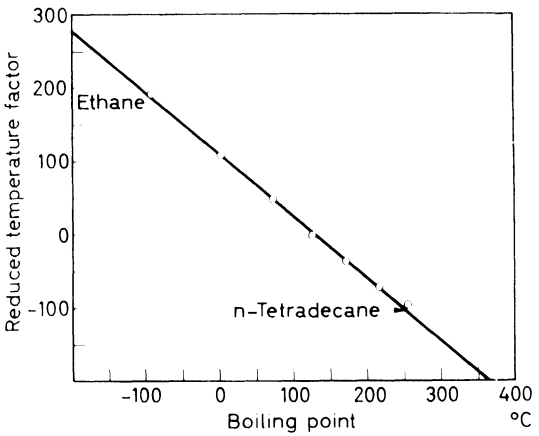


Figure 4. Reduced temperature factor, correlation with boiling point

The analytical method of calculating retention temperatures utilizes the constants A and B defined in eqn (3). A and log B give an almost linear correlation with carbon number over a large temperature range (*Figure 5*). Log B tends to fall off at high carbon numbers for the normal paraffins, but can be considered linear over a moderate range of carbon numbers. The correlation with boiling point is worse.

Retention temperatures for homologous series of normal alcohols and aromatics were calculated by means of the relationships described above. The calculated retention temperatures are shown in *Table 3*. The pressure

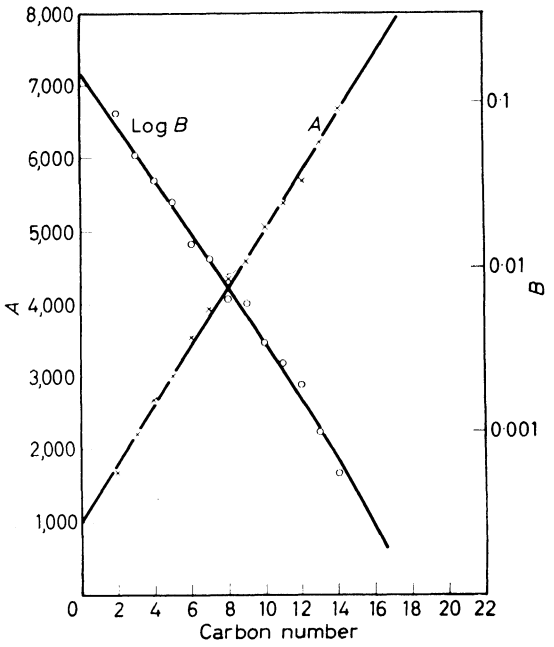


Figure 5. A and log B *v.* carbon number for n-paraffins

Table 3. Retention temperatures for normal alcohols and aromatics

Compound	*Method*		
	Analytical (°C)	*Graphical* (°C)	*Experimental* (°C)
Alcohols			
Methanol	20	49	40
Ethanol	47	66	58
1-Propanol	83	88	89
1-Butanol	109	116	117
1-Pentanol	137	142	142
1-Hexanol	164	167	165
1-Heptanol	188	190	185
1-Octanol	212	215	207
1-Nonanol	232	241	232
1-Decanol	253	266	255
Aromatics			
Benzene	116	116	116
Toluene	144	144	143
Ethylbenzene	165	164	165
o-Xylene	171	171	172
n-Propylbenzene	184	185	186
n-Butylbenzene	203	206	206
n-Pentylbenzene	218	225	224

gradient correction was applied at the rough retention temperature, as discussed above. Excellent agreement between calculated and experimental values was obtained for the aromatics by both methods. No gas holdup correction was applied to the analytical result.

Some discrepancies are observed with the alcohols. The graphical results for the higher alcohols are high. This might be accounted for by an error in the extrapolation of the plot of reduced temperature factor *v.* boiling point (similar to the curve for normal paraffins, *Figure 4*). The results for methanol and ethanol show rather large discrepancies by both methods of computation. These compounds exhibit anomalies which are characteristic of terminal members of homologous series; hence, care should be exercised where terminal members are concerned.

The aid of Mr G. L. Duffel, who performed the experiments and calculations, is gratefully acknowledged.

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[a] Hallikainen Instruments, Berkeley, Calif., U.S.A.
[b] General Electric Co., Willoughby, Ohio, U.S.A.
[c] Dow Corning Corp., Midland, Mich., U.S.A.
[d] Union Carbide Chemicals Company, Division of Union Carbide Corp., New York, N.Y., U.S.A.

DISCUSSION

H. Schulz: We have just heard two papers on programmed temperature work, and calculations were given for retention times and retention temperatures. I should be very interested to hear about any experience on the quantitative evaluation of the chromatograms obtained with this technique. Could one of the gentlemen perhaps give some information about this?

F. Baumann: I can speak from my experience on this. We have looked at mercaptans and sulphides, both isothermally and by the temperature-programmed method, using the apparatus described here today. We evaluated weight correction factors, numbers with which one multiplies the areas in order to get the weight percentages. We measured these factors at 50°, using the isothermal method, and at 150°C, using the temperature-programmed method. Essentially identical factors were obtained in both cases; they were within 2 per cent.

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THE DESIGN OF HIGH EFFICIENCY PACKED COLUMNS FOR USE WITH KATHAROMETER DETECTORS

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The performance of small diameter packed columns operated at high pressures and used in conjunction with katharometer detectors has been examined. Practical details of column construction are given and a new sample introduction system for operation at high pressure is described. For the analysis of C_3–C_5 hydrocarbon mixtures improved resolution and reduced analysis times were obtained by the choice of optimum values for column diameter, support size, percentage liquid phase and operating temperature. Use of improved column conditions resulted in a higher analytical precision. The column performance was ultimately limited by the sensitivity of the katharometer detector.

OWING to the rugged characteristics and relative simplicity of the katharometer detecting system, gas chromatographic equipment utilizing this detector is particularly suited to plant monitoring and routine analysis. However, with $\frac{1}{4}$ in. o.d. (5 mm i.d.) columns the resolving power is often inadequate and analysis times tend to be long. It has been shown that choice of column diameter[1], support grade[2,3,4,5], percentage liquid phase on support[1,2,6] and operating temperature[7,8,9] can affect resolving power and analysis time. Optimum values of parameters, producing the required separation of a C_3–C_5 hydrocarbon blend in the shortest possible time, were determined for columns of $\frac{1}{8}$ in. o.d. (1·5 mm i.d.).

Apparatus and materials used

A Perkin-Elmer 154B Fractometer was modified so that the column could be immersed in an ice–water mixture or a solid CO_2–IPA mixture contained in a Dewar flask external to the Fractometer. With the Dewar flask sealed by a cork, it was found that the temperature remained constant during a 30 minute run without further addition of CO_2. The fractometer oven was maintained at 60°C by means of the Perkin-Elmer temperature controller. The carrier gas flow issuing from a 200 p.s.i. pressure controller was split at the inlet. One part flowed through the column and through the sensing side of the detector, the other part flowed through a diaphragm valve and through the reference side of the detector. Fine control of the reference flow was obtained by means of a capillary tube connected to the reference side of the detector block. Control of column exit pressures was achieved by means of a length of packed column equal to 10 per cent of the length of the partition column, attached down-stream from the detector.

A simple but effective sample introduction device was developed (*Figure 1a*) which allowed injection of liquid samples directly on to the head of the column with a Hamilton microsyringe. The silicone rubber septum was held in position by a retaining nut in which was drilled a hole just large enough to admit the syringe needle. Such a system withstood repeated injections at high pressures (e.g. 200 p.s.i.) owing to the self-sealing property of the rubber septum. The sample chamber was designed to have minimum dead volume to minimize diffusion of the sample 'plug', and was efficiently flushed to avoid peak tailing.

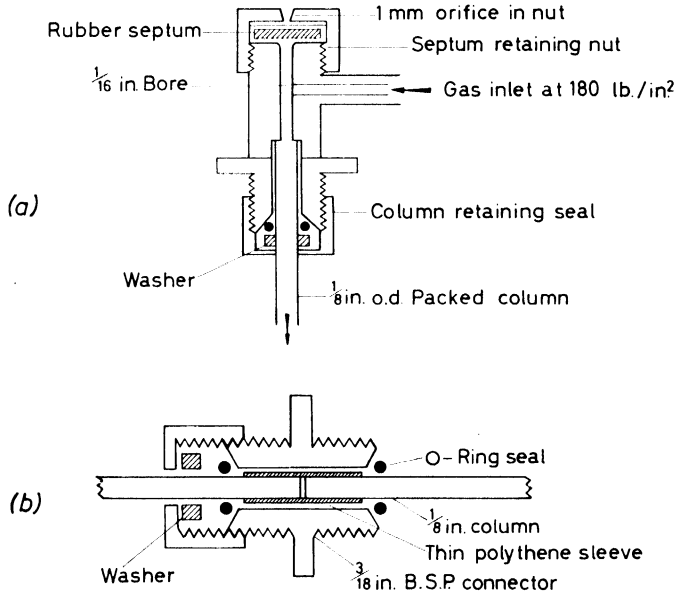


Figure 1. Column construction. (*a*) sample introduction system, (*b*) column connector

Gas samples were introduced from a 0·1 ml sample loop attached to a six-way gas valve which in turn was connected to the column by a narrow bore connecting tube. PTFE tubing, 0·1 in. o.d. by 0·03 in. i.d., was found to be suitable for this purpose.

The columns used in this work were prepared from copper tubing having an internal diameter of 1·5 mm. They were packed with 2:5-hexanedione on Firebrick. For the preparation of long, small-diameter columns of high efficiency, removal of degradable particles and fines from the column packing to minimize flow resistance was essential. To this end the coated support was fluidized with dry nitrogen for about an hour. A glass absorption drying tower was one-third filled with the coated support. A wad of cotton wool was placed at the head of the tower. Dry nitrogen was passed up through the support, so that the latter was fluidized to occupy approximately two-thirds of the vessel. Most of the fines were entrained and trapped in the cotton wool at the top. The coated support was then resieved before the

column was packed. It was found that 15 per cent by weight of the original material was degraded by this attrition procedure.

Short columns may be rapidly filled with the packing; excessive vibration or tapping should be avoided since this only results in particle degradation and increases resistance to gas flow. We preferred to prepare long columns by packing a series of short columns, e.g. 4·5 m lengths, and joining them together with the connector illustrated in *Figure 1b*.

Results

Columns prepared in this manner were found to have efficiencies of the order of 1,500 plates per metre when measured for cyclopentadiene in the usual way[10]. The data in *Table 1* confirm previous work[1], indicating that at high exit pressures column efficiencies are linearly dependent on column length. However, this was not true for unrestricted columns longer than 7 m.

Table 1. Effect of column length on efficiency for cyclopentadiene, for columns with and without restriction

Column length (m)	*Without restriction*			*With restriction*		
	Inlet pressure (atm)	*Outlet pressure* (atm)	*Efficiency (plates)*	*Inlet pressure* (atm)	*Outlet pressure* (atm)	*Efficiency (plates)*
4·5	4	1	4,500	4	1	4,500
9·0	9	1	8,100	9	2·3	8,700
13·5	13	1	10,300	13	3	13,200

Effect of sample size

With gas velocities above the optimum gas velocity, OGV[6], measurements on a C_3–C_5 hydrocarbon blend showed that sample charges of 0·3 μl were required to give good signal-to-noise ratio (i.e. 10:1 or greater) for components present at concentrations in the range 0·1–5 per cent. These relatively large sample charges imposed limitations on column design. For example, an 0·5 μl sample of the same blend was found to be the maximum charge a column packed with 3 per cent hexanedione on 85–100 mesh Firebrick could take without overloading.

Effect of stationary phase concentration

The efficiencies of various columns carrying different percentages of hexanedione were determined for 0·3 μl samples of the same blend of C_3–C_5 hydrocarbons. The results (*Figure 2*) show that efficiencies increase sharply when the stationary phase concentration is reduced below 6 per cent. No measurements were made at hexanedione concentrations below 3 per cent since below this level the maximum acceptable sample charge was inadequate for determination of minor components.

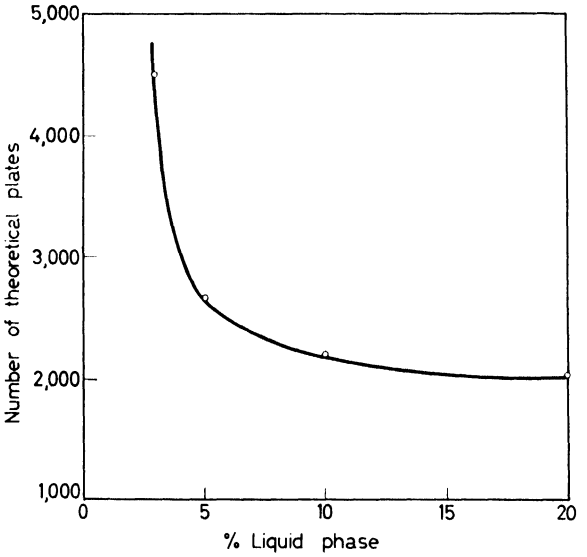


Figure 2. Effect of concentration of liquid phase on column efficiency for a 1/8 in. o.d. column of hexanedione on 85–100 mesh Firebrick

Effect of column exit pressure

Higher column exit pressures resulted in remarkable improvement in resolution, especially at high gas velocities, owing to the lower inlet to outlet pressure ratio. This effect is demonstrated in *Figure 3* which is part of a chromatogram showing the improvement in resolution of the C_5 olefins obtained with a 6 per cent hexanedione column.

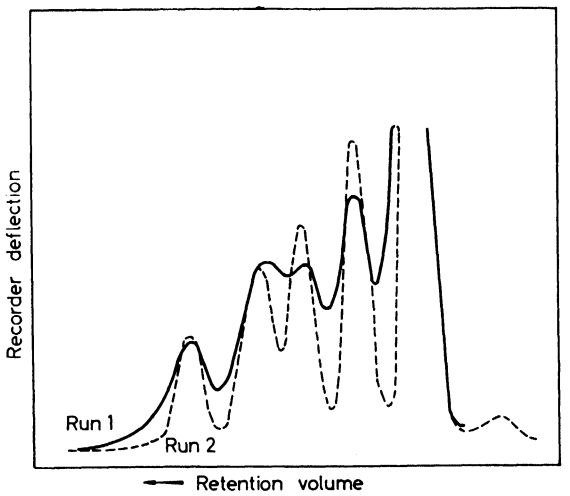


Figure 3. Improvement in resolution obtained by constriction of the column exit. Run 1: exit not constricted. Run 2: exit constricted

Effect of gas velocity

Figure 4 illustrates that the HETP of a column with a restricted exit showed only a gradual increase for gas velocities between 5 and 10 cm/sec.

Effect of temperature

The work described so far was carried out at a column temperature of 0°C. Hexanedione is relatively volatile and columns supporting 3 per cent of this substance were found to have a limited life, especially above 0°C. In fact, it was impractical to study the effect of temperature on resolution at temperatures above 0°C, but below this temperature resolution improved to give a

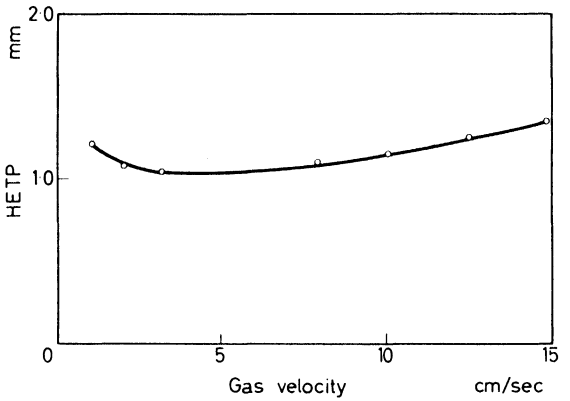


Figure 4. Variation of HETP with gas velocity for a 9 m hexanedione column

maximum at −7°C. Even at this temperature, however, loss of stationary phase occurred, as indicated by loss in resolution of the butene-1/isobutene doublet; the most poorly resolved pair present in the blend under study. However, a 6 per cent hexanedione column on 72–85 mesh Firebrick was found to be much more stable. The resolution of the butene-1/isobutene doublet was found to increase below +10°C to a maximum at −7°C as can be seen from *Figure 5*. Below this temperature, resolution collapses quite dramatically. The effect of temperature on analysis time, with the gas velocity at each temperature adjusted to give the same resolution, is shown in *Figure 6*. A temperature of −8·5°C gave the minimum analysis time for the butene-1/isobutene doublet. However, at this temperature the retention time of the last component (cyclopentadiene) was rather long.

Selection of best operating conditions

At the optimum temperature of −8·5°C for the best analysis of isobutene and butene-1, the total time for analysis of the complete sample was still rather long. Therefore, the temperature was raised to 0°C to shorten the total analysis time, while the resolution of butene-1/isobutene was maintained by an increase in the length of the column. The net result of this was a reduction of the analysis time from 40 to 26 minutes. The comparison between the optimum conditions for the separation of butene-1 and isobutene and the

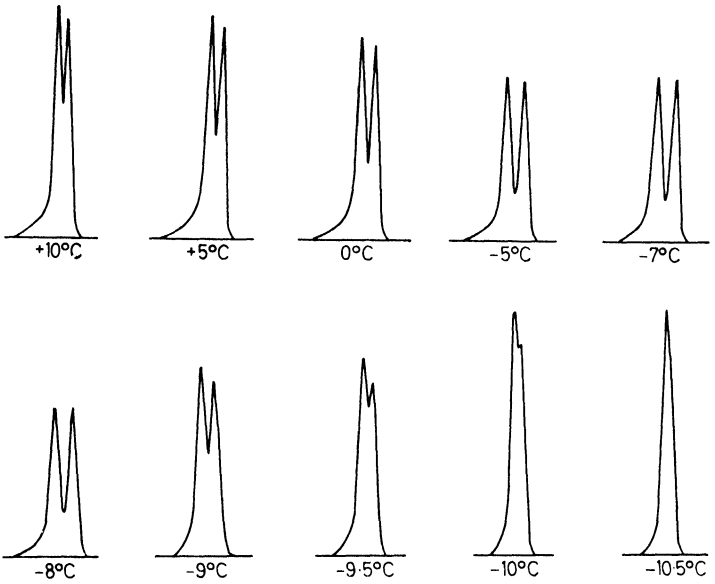


Figure 5. Effect of temperature on column resolution

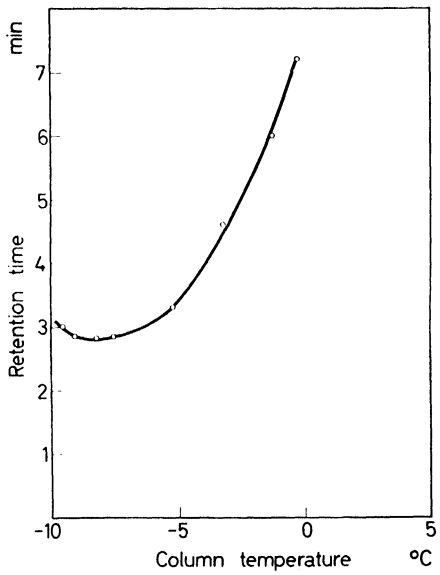


Figure 6. Effect of temperature on retention time of butene-1 at constant resolution for a 9 m column with 6 per cent hexanedione on 72–85 mesh Firebrick

best practical operating conditions for the analysis of the C_3–C_5 hydrocarbon blend is given in *Table 2.*

Table 2. Comparison of optimum conditions and best operating conditions for a C_3–C_5 hydrocarbon analysis

	Optimum conditions for butene-1/isobutene separation	*Best operating conditions for complete analysis*
Support size (acid washed Firebrick)	72–85 mesh	72–85 mesh
Stationary phase/100 g support	6 g	6 g
Sample size	0·5 μl	0·5 μl
Column length	9 m	13·5 m
Column internal diameter	1·5 mm	1·5 mm
Inlet pressure	120 lb./in.^{2}	180 lb./in.^{2}
Outlet pressure	20 lb./in.^{2}	30 lb./in.^{2}
Gas velocity	7 cm/sec	5 cm/sec
Column temperature	−8·5°C	0°C
Efficiency (butene-1)	10,400 theoretical plates	17,900 theoretical plates
Retention time for butene-1	5 min	8 min
Total analysis time	40 min	26 min

The performance of a column operated under these conditions was compared with data from the best of our 5 mm hexanedione columns. The best practical operating conditions were obtained with a 7 m column containing 20 per cent stationary phase at 0°C. Standard deviations listed in *Table 3* indicate the superiority of the small bore high pressure columns. It will be noted that the time for a complete analysis was reduced as well by a factor of three.

Table 3. Comparative precision with small bore and conventional columns
Results are means of 10 runs in each case

*Type of column component**	7 m *of* 20% *hexanedione in a* 5 mm *i.d. column*		13·5 m *of* 6% *hexanedione in a* 1·5 mm *i.d. column*	
	wt %	2 σ	wt %	2 σ
Butane	0·10	0·03	0·08	0·040
Butene-1	2·17	0·952	1·99	0·176
Isobutene	1·06	0·276	0·88	0·098
cis-Butene-2	0·96	0·108	0·81	0·092
trans-Butene-2	0·85	0·124	0·77	0·108
Pentane	0·36	0·133	0·43	0·070
Pentene-1	20·33	2·040	21·02	1·006
Cyclopentene	4·23	1·05	4·30	0·120
trans-Pentene-2	6·05	0·776	6·26	0·316
2-Methylbutene-1	7·92	1·140	8·55	0·126
3-Methylbutene-1	1·87	0·124	1·93	0·162
2-Methylbutene-2	3·67	0·402	3·84	0·126
cis-Piperylene	6·10	0·794	5·95	0·600
trans-Piperylene	10·72	0·398	10·33	0·414
Isoprene	16·16	1·116	16·38	0·392
Cyclopentadiene	3·99	0·758	3·42	0·478
Total analysis time	90 minutes		26 minutes	

* Only components completely separated on both columns have been included, in order to simplify a comparison of component levels.

Several other 1·5 mm i.d. columns with different stationary phases (e.g. Apiezon L, squalane, hexamethylphosphoramide) have since been prepared and used as replacements for 5 mm i.d. columns on routine applications. In all instances, greater precision has been achieved and analysis times have been reduced by at least a factor of two.

Discussion

High column inlet pressures, up to 200 p.s.i., are usually required to obtain the optimum gas velocity through a long, small-bore column. The great improvement in column efficiency achieved at elevated column exit pressures was similar to that previously reported by R. P. W. Scott. A length of packed column equal to 10 per cent of the analytical column, attached downstream from the sensing side of the detector, was found to be a better control than a needle valve.

The introduction of samples into such a high pressure system presented a problem. Convenient, reproducible and representative sample introduction methods are essential for all gas chromatographic procedures. It is difficult to introduce liquid charges of less than 0·5 μl by direct methods, particularly where column inlet pressures are much greater than atmospheric. Sample splitting devices often fail to deliver representative samples to the column.

Although direct injection procedures have been employed with charges even smaller than 0·3 μl, most simple methods do not produce a sample 'plug' as sharply defined as the column performance warrants. However, our experience with a direct injection system designed specifically for the introduction of small samples indicates that the problems associated with direct injection at high pressures may perhaps have been somewhat magnified. For example, although charges of 0·3 μl were used for all the measurements described earlier, work with smaller charges indicated that the system described would probably be satisfactory for charges as small as 0·05 μl.

The maximum detector sensitivity available sets a limit to the minimum charge that can be used. The smaller the diameter of the column, however, the smaller the charge must be to prevent overloading. These two effects act in opposition and thus the detector sensitivity also sets a limit on the minimum column diameter that can be employed. However, the charge size that can be permitted without overloading is also dependent on the quantity of liquid phase present on the support, so the minimum column diameter is determined by both the quantity of liquid phase on the support and the maximum detector sensitivity.

The resolving power of a column and the time required for analysis of a given mixture is dependent on the percentage liquid phase on the support, the support size and the operating temperature. In fact, column diameter, support size and the percentage liquid phase on support, operating temperature, detector sensitivity, resolving power and analysis time are all interdependent variables. Thus, in practice, the choice of optimum values is possible only after experimental examination of the effect of these variables for the particular sample to be analysed.

The results obtained indicate that for optimum results with the katharometer as a detector the column diameter should be fixed at 1·5 mm i.d.

and a narrow range of support particle size between 70–100 B.S. mesh should be used. The optimum quantity of liquid phase can be assessed by determination of the resolving power of the column at a constant gas velocity above the OGV[6] for various ratios of liquid phase to support. In a similar manner, the optimum operating temperature can be determined by examination of the analysis time for a given resolution over a range of operating temperatures.

Conclusions

The direct introduction of liquid samples into high pressure small-bore columns may be easily accomplished with a system such as the one described.

With all high pressure small-bore columns, conditions can be determined to give optimum resolution with minimum analysis time and these will be a great improvement over those obtainable with larger bore columns containing high concentrations of liquid phase.

Attention must be paid to choice of stationary phase in order to ensure that changes in column characteristics due to loss of stationary phase are negligible.

The use of an insensitive detector such as a katharometer will set the lower limit on the amount of liquid phase that may be employed, although this may not interfere with the choice of optimum operating conditions.

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DISCUSSION

Author's Additional Comments

We have examined the performance of small-diameter packed columns operated at high pressures and used with katharometer detectors, and our paper describes the

modification of a Perkin-Elmer 154B Fractometer which has been used for the analysis of C_3–C_5 hydrocarbon mixtures.

We have also used high-pressure small-bore columns with an F. & M. Model 500 Gas Chromatograph. This was a convenient apparatus to use when it was desirable to run such columns at temperatures above ambient, and gave us the additional facility of temperature programming. The only modification necessary was to build a completely new sample introduction system, since it soon became apparent that the internal volume of the F. & M. injection port was too great.

The modification (*Figure 7*) consists essentially of a rectangular brass block, through which a hole is drilled just large enough to accommodate the inlet of the

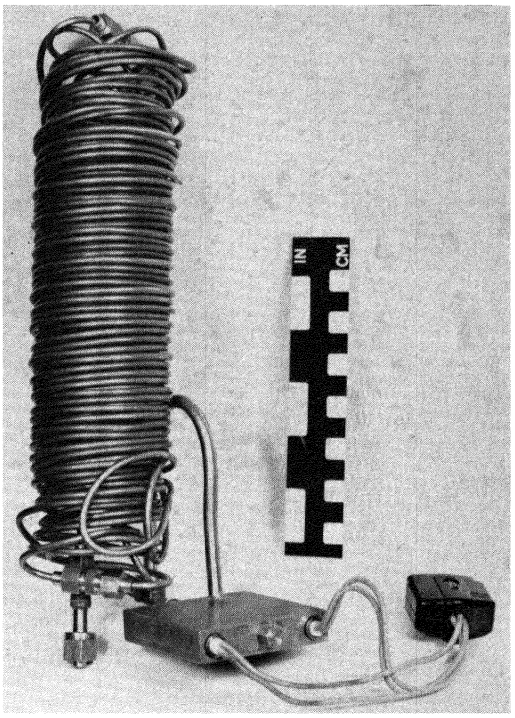


Figure 7. Photograph of assembled column and detector block

column. The latter, which enters at the back of the block, is pushed right up adjacent to the carrier gas inlet, about 5 mm behind the face of the silicone rubber septum, which in turn is covered by the retaining nut seen at the front of the block. The F. & M. injection port is blanked off, and the carrier gas enters the modified assembly via the pipe seen on the right. The block is heated by two 75 W tubular heaters located as shown in the figure, and its temperature may be measured with the thermocouple of the F. & M. injection port. Hence, the essential features of this injection point are identical with those of the system used with the Perkin-Elmer Fractometer (*Figure 1a*).

The column–injection point assembly is now interchangeable with a normal conventional column, and is attached to the detector oven by Swagelok fittings.

The column shown in *Figure 7* consists of four 4·5-m lengths of 1·5 mm i.d. copper tubing filled with 85–100 mesh Firebrick coated with 2 per cent Apiezon L.

For each column section a 15-ft. length of $\frac{1}{8}$ in. o.d. copper tubing is folded in the form of a U. This shape is then suspended vertically and clamped top and bottom to a framework of laboratory tubing. A hand vibrator is attached to a laboratory clamp and mounted equidistant from the vertical parts of the U form. The vibrator hammer does not strike the column or assembly. The movement of the vibrator body transmits enough vibration to ensure a regular flow of packing down the column without degrading the support.

The column is packed at both ends simultaneously through glass funnels. Care is taken to ensure that the 'head' of support in each funnel does not exceed $\frac{1}{2}$ in.

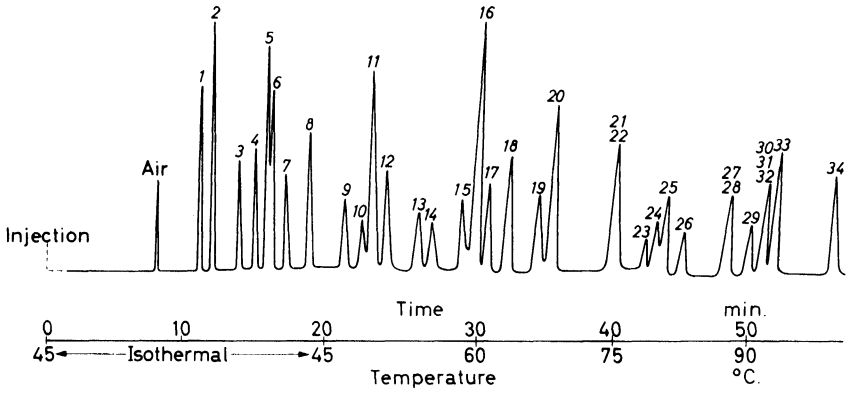


Figure 8. Chromatogram of C_5–C_8 saturates

Column dimensions	20 m long, 1·5 mm i.d.
Column packing	2 per cent Apiezon L on 85–100 mesh Firebrick
Packing density	5·5–5·7 g. packing/5 m length
Carrier gas	helium
Inlet pressure	170 p.s.i.g.
Outlet pressure	atmospheric
Flow rate (measured at exit)	30 ml/min
Heating programme	20 min at 45°C, followed by a heating rate of 1·5°C/min
Detector	4-filament hot-wire katharometer
Sample size	1 µl
Column efficiency	Approx. 21,000 theoretical plates for n-hexane

1 iso-pentane
2 n-pentane
3 cyclopentane
4 2,2-dimethyl butane
5 2,3-dimethyl butane
6 iso-hexane
7 3-methyl pentane
8 n-hexane
9 methyl cyclopentane
10 2,2-dimethyl pentane
11 2,4-dimethyl pentane
12 2,2,3-trimethyl butane
13 cyclohexane
14 3,3-dimethyl pentane
15 iso-heptane
16 2,3-dimethyl pentane
17 3-methyl hexane
18 3-ethyl pentane
19 2,2,4-trimethyl pentane
20 n-heptane
21 methyl cyclohexane
22 2,2-dimethyl hexane
23 2,5-dimethyl hexane
24 2,4-dimethyl hexane
25 2,2,3-trimethyl pentane
26 3,3-dimethyl hexane
27 2,3,3-trimethyl pentane
28 2,3-dimethyl hexane
29 4-methyl heptane
30 3-methyl heptane
31 3-ethyl hexane
32 3,4-dimethyl hexane
33 3-methyl 3-ethyl pentane
34 n-octane

during the operation in order to reduce differences in packing density. The time taken to pack a 15 ft. length of column by this method is usually between four to six minutes and is constant for any one system to within ± 15 sec.

The efficiency of each column length is then measured before the column is coiled and put into service.

The assembled column (4 sections) easily fits inside the circulating air oven. With silicone rubber 'O' rings and PTFE sleeves in the column connectors this column has been operated up to 200°C at an inlet pressure of 180 p.s.i.g. A $\frac{1}{2}$-in. thick asbestos block placed around the inlet system and resting on the detector oven provides a smooth support for the column oven.

Figure 8 shows a chromatogram obtained on the saturated fraction of a simulated gasoline. This compares favourably with the similar but isothermal chromatogram shown by R. P. W. Scott at a previous Symposium. The chromatogram was produced by charging 1 μl. of sample on to the column, which was maintained at 45°C until after n-hexane had been eluted.

The column was then heated at a rate of 1·5 °C/min. It was found necessary to hold the column temperature initially at 45°C in order to get maximum separation of the pair of C_6 paraffins most difficult to resolve; i.e. 2,3-dimethylbutane and isohexane (*Figure 8*, peaks *5* and *6*). The optimum temperature for this separation is undoubtedly below 45°C, but this is the minimum practical operating temperature for the F. & M. Model 500 Gas Chromatograph. The efficiency of this column, measured for n-hexane under isothermal conditions, was 21,000 theoretical

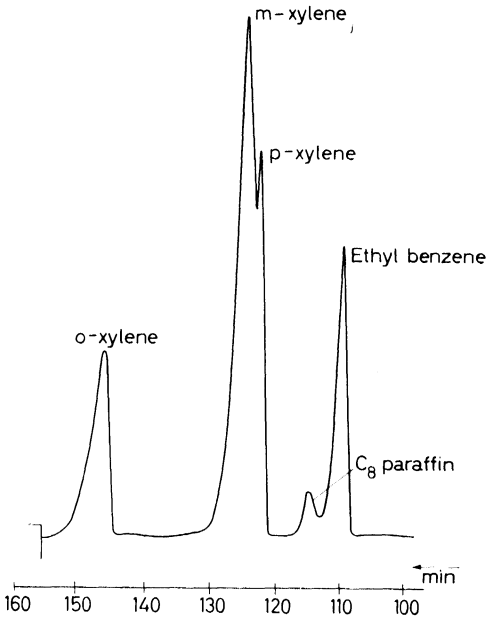


Figure 9. Chromatogram of C_8 aromatics on the Apiezon L column described, operated at 55°C

plates. The effect of combining a short isothermal run with a temperature-programmed run is to resolve completely all C_6 and C_7 saturates, with the exception of methyl cyclohexane, which is not separated from 2,2-dimethylhexane (peaks *21* and *22*). The elution time for n-heptane was 34 min, and n-octane was eluted after 56 min.

It is of interest to note that the four-filament tungsten hot wire detector has adequate sensitivity to give a reasonable recorder deflection throughout this multicomponent chromatogram, even though the sample charge was only one μl. This sample size could be readily accepted by this column without overloading. Since the peak width barely increases throughout the chromatogram, lower limit for quantitative estimation for any component is about 0·2 per cent.

Mixtures containing aromatic hydrocarbons have also been separated on this column, and *Figure 9* indicates the resolution obtainable for the xylenes with the

same Apiezon L column at a constant temperature of 55 °C. It will be noted, however, that considerable tailing of aromatics occurs—a fact that has facilitated identification of components in, e.g., gasoline samples. This phenomenon does not assist in quantitative estimation, however, but efforts to improve peak shape have only met with partial success. Pre-treatment of the support with Siliclad* (a water-soluble silicone compound) or coating with silver[11] only slightly improved peak shapes. Raising the temperature only produced a further deterioration. Further work is at present in progress, involving Theed and polyethylene glycol as stationary phase.

J. F. Smith: I wonder if I might make one or two comments which are relevant to both this paper and some of the papers on adsorption presented earlier (pages 18 and 36). A question arises about the distribution of stationary phase on supports. This is of considerable importance, in so far as it does decide the optimum level of stationary phase, which will result in the highest efficiency. When we look at *Figure 2* on page 165, we find, broadly speaking, an inverse square log curve coming down to a constant plate height. Giddings has suggested on theoretical grounds that, when Celite or Firebrick is coated, an initial monolayer is formed; the rest of the stationary phase then goes into the micro pores of the Celite structure. This was what we also anticipated; and we have recently done some electron microscopy and optical microscopy on Celite and Firebrick. The supports were coated with squalane; this was then cross-linked with osmium tetroxide, which acts both as an electron stain and as an optical stain. Much to our surprise, we found that the stationary phase, instead of being concentrated in the pores at 20% loading, was in fact very uniformly distributed over the surface. I offer no explanation for this, but this is the experimental result; and it certainly ties in with *Figure 2* of this paper.

R. A. Hurrell: I should like to make the observation here, that in the determination of the optimum amount of stationary phase to use, the actual working life of the column is usually a more important criterion than the desirable amount of stationary phase which one would like to use. For this reason we nearly always use concentrations of stationary phase rather above the optimum, and choose a slightly longer column.

B. T. Whitham: In *Figure 5* (page 167) the authors show the separation of butene-1 and isobutene. I note that at −9 °C the separation suddenly decreases; and at −10·5 °C there is no separation at all. I believe that the melting point of the 2,5-hexanedione used as stationary phase is, in fact, −9 °C, although I stand to be corrected on this point. The effect we see then is due to the change from gas–liquid to gas–solid chromatography. A similar change in separation was shown in the paper by Scott (page 40) for benzophenone as the stationary phase. I should like to ask Dr Hurrell whether he can make any comment on this point.

R. A. Hurrell: I must accept that point. I had some information that the melting point was about half a degree lower than that; but it is certainly of that order, and I believe that this is the explanation for the change in resolution.

A. Goldup: Referring back to *Figure 2* (page 165), I wonder if you could tell me what the k' factor might be for the columns with a low percentage of stationary phase, say 5 per cent—in other words, when you measure the efficiency for a certain peak, how much time is there between the elution of this peak and the air peak?

R. A. Hurrell: It was about 2½ times the retention distance of the air peak.

A. Goldup: About a year ago Desty and I presented a paper discussing this number n, the number of theoretical plates[12]. It is rather a misleading concept, I always feel, in that it only indicates the extent to which a band broadens as it passes through a column. You find that, if you only have a very small amount of stationary phase on a column, the band moves through quite quickly; and you

* Clay-Adams Inc., New York 10, N.Y., U.S.A.

always get high efficiency: the less stationary phase you put on, the higher the efficiency. This accounts for the shape of the curve in *Figure 2*. If you express column performance in terms of what we call the effective number of theoretical plates—and this is the column efficiency measured from the air peak—you will find that the curve does not take this shape, but is more or less linear with the amount of stationary phase.

I should like to make another point about *Table 1* (page 164). You examine three columns of increasing lengths—4·5–13·5 m—with and without restriction; and you come to the conclusion that if you have a restriction on the column, then the efficiency of the column increases roughly with column length. The point which occurs to me on looking at the table is that if you change from the 4·5 m column to the 13·5 m column, you change the inlet-outlet pressure differential from 3 to 12 atm; so you increase the pressure differential by a factor of 4. You have increased the column length by a factor of 3, so that on the longer column you have a higher linear gas velocity. I should like to put this point to you, that generally the optimum linear gas velocity goes down with increasing column length. In fact, U is approximately proportional to D_g, and D_g is inversely proportional to the mean absolute column pressure. Did you determine the figures in *Table 1* by doing HETP-u curves and picking out the efficiency at the optimum linear gas velocity, or are they just values obtained at a constant gas velocity?

R. A. Hurrell: These are somewhere near the optimum practical gas velocity, which is much higher than the optimum gas velocity. I don't know the gas velocities offhand, but I think the optimum gas velocity is about 5 cm/sec for a 1-unit column, i.e. 4½ m in length; and we used gas velocities of some 6–10 cm/sec.

A. Goldup: I just wanted to make the point that, if you are going to compare two columns, it is important to compare efficiencies under comparable conditions; to measure both efficiencies at the optimum linear gas velocity.

R. A. Hurrell: The curve is very flat, and I think it is unlikely that it would change very much. If you look at the HETP curve in *Figure 4* (page 166), you will see that you can't be very far off.

A. Goldup: Could I make a general comment about columns operated at elevated outlet pressures. As a general principle, I don't feel that one would gain very much by putting the column outlet above atmospheric pressure. If you increase the mean absolute column pressure, this has the effect of shifting the minimum of the H–u curve to the left and downward. The result is that generally you increase the column efficiency slightly, but you pay very dearly for this in terms of time. I should recommend that, if you want to have a few more plates, much the better way of doing it is to stick a little more on to the end of the column; instead of pushing the column outlet above atmospheric pressure. By this method you don't have to pay quite so dearly for your few extra plates in terms of time.

S. J. Hawkes: I am intrigued by *Figure 2* (page 165), which has given rise to comments by other people about the increase in efficiency with decreasing amount of stationary phase. This was also mentioned at the Amsterdam Symposium; and after that I did a fair amount of work to try and demonstrate it in practice, but failed completely. I was using a Pye Argon Chromatograph and found that as the amount of stationary phase was reduced, so the number of theoretical plates was also reduced; not linearly, but nevertheless quite seriously. This was independent of the amount of sample I used, and it did not vary when I changed from the normal Pye method of injecting a sample—stopping the gas flow and taking the top off the column—to the pressure injection system, which involves injection of the sample while the gas is flowing. After some time I gave it up as a bad job and decided that, in fact, efficiency goes down and not up with the amount of stationary

phase. For a long time I had used 5 per cent of stationary phase on my columns; and some time ago I saw some curves produced by Dr Holness on the samples I had also done, and found he was getting better resolution using a 10 per cent column than I was getting with a 5 per cent column. I then made my 10 per cent columns and repeated his results almost peak for peak.

C. G. Scott: Mention has been made of the effect of column temperatures above and below the melting point of the liquid phase. *Figure 5* of my own paper (page 40) shows the effect with an aromatic liquid phase, benzophenone, where there is

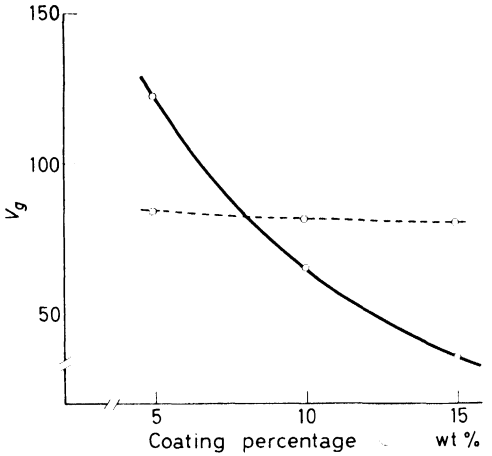


Figure 10. Retention of n-heptane per gramme of benzophenone deposited on Celite —— −5°C (solid benzophenone); ---- +60°C (liquid benzophenone)

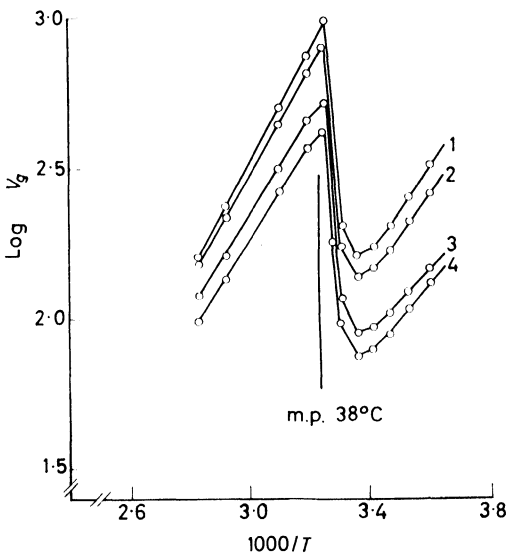


Figure 11. Retention of some hydrocarbons on eicosane (10 wt% on Celite) as a function of the reciprocal absolute temperature

1: n-heptane; 2: iso-octane; 3: cyclohexane; 4: benzene

a sharp drop in retention and a change-over from partition to adsorption when the column temperature is taken below the melting point of the liquid phase. In *Figure 10* the retention of n-heptane per gramme of benzophenone is plotted for two temperatures as a function of the coating percentage on Celite. At 60°C, when the benzophenone is in the liquid state, retentions are almost proportional to the amount of liquid phase. At −5°C the benzophenone is in the solid state, and the retentions show no such relation; there is, however, a good correlation with the measured surface areas of the packings. This sharp drop in retention and change-over to adsorption only take place when benzophenone is deposited on a reasonably active support, such as Celite. If benzophenone is deposited on a glass capillary column this effect does not occur: we get supercooling, which results in retentions continuing to increase as the temperature is taken below the melting point.

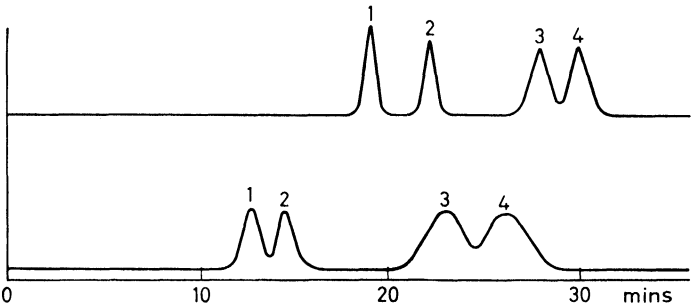


Figure 12. Separation of some hydrocarbons on eicosane (10 wt% on Celite) at 80°C (top) and at 15°C (bottom)

1: benzene; 2: cyclohexane; 3: iso-octane; 4: n-heptane

Figure 11 shows plots of log V_g vs reciprocal absolute temperature for some hydrocarbons on an aliphatic liquid phase, eicosane, on Celite. There is no indication of supercooling. Retentions do not drop as sharply at the melting point as with benzophenone, however; and there is no reversion of elution order. Further, even when the column temperature is some 20, 30 or 40°C below the melting point, retentions are found to be almost proportional to the amount of liquid phase on the column. Retention is due essentially to a solution effect, even though there are indications of a phase change. This change is accompanied by a loss of column performance, as shown by the chromatograms at 15 and 80°C reproduced in *Figure 12*.

As a start to investigating these differences we looked at the behaviour of the even-numbered fatty acids from C_{10} to C_{18} deposited on Celite. With stearic acid the behaviour is similar to that obtained with eicosane. As the length of the paraffin chain is reduced there is a gradual trend towards the type of behaviour shown by benzophenone, but down to C_{10} there is no definite change-over to adsorption at temperatures below the melting point.

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[12] DESTY, D. H., GOLDUP, A. and SWANTON, W. T. ISA Symposium on Gas Chromatography, Lansing, Mich., U.S.A.

13

EXPERIENCES IN CONNECTION WITH THE DETECTION OF SUBSTANCES PRESENT IN MINIMAL AMOUNTS BY MEANS OF A CATALYTIC COMBUSTION CELL

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IT IS obvious that the sensitivity of a normal katharometer cell may be increased by several orders of magnitude if the rise in temperature of the wire is effected by the heat of combustion of the respective organic substance, instead of the change in heat conductivity of the gas mixture. For example, with 10^{-4} parts by volume of benzene vapour in H_2, a rough estimate (temperature drop to the walls 100°C, gas flow rate 30 ml/min) predicts a temperature rise of about 10^{-3} degrees only in a frontal analysis, whereas the same amount of benzene burned in a stream of air results in a rise of about 10 degrees, i.e. an increase in sensitivity of about four orders of magnitude. The frontal experiment can be carried out under steady conditions, but if the latter are not fulfilled (e.g. in the case of an elution peak), then the heat capacity of the combustion cell may also become relevant. In this case it is favourable to use a measuring wire as thin as possible.

In practice, combustion cells have hitherto been used only to a limited extent, the main causes for this being: (1) the unusually high temperature of the wire (500–900°C), requiring a substantial amount of stabilized power; (2) the short life, i.e. the great variability with time, likewise caused by the high temperature; and (3) the small variation of the relative resistance, due to the same cause. Thicker wires are commonly used in order to increase their lifetime, but this is accompanied by a reduction of the absolute value of the resistance, so that the sensitivity of the usual devices is less than that of a normal katharometer.

All these drawbacks may be avoided if the temperature of the burning process can be reduced to a reasonable level. To this end, we prepared a catalytic coating of sufficient activity and stability on thin platinum wire, so that reaction with the oxygen or air used as carrier gas sets in with the speed needed for gas chromatographic purposes at about 200°C for the slowest-burning chlorinated hydrocarbons and methane, and at about 150°C for alcohols and aromatic compounds. The operating parameters of the cell and some results characteristic of its performance are described below.

The cell is a glass capillary, 10 cm long, of 0·18 ml volume. The diameter of the axially mounted Pt-wire in its untreated state was 50 μ, the cold resistance (with coating) 7·2 ohm. The measuring cell constitutes one arm of a Thomson bridge, the other arm being a control cell of almost identical geometrical dimensions and of about the same resistance. Normally, the

burned-out gas mixture is led through the latter cell. The bridge works with a supply voltage of 13 V, and a current of 0·45 amp. The read-out device is a null-balance recording millivoltmeter with 50 mV span (or, if no recording is needed, a simple millivoltmeter having the same sensitivity), connected directly to the bridge terminals.

The frontal experiments described below were made with oxygen as carrier gas, loaded in a spiral saturator with the vapour of the liquid in question. The saturator temperature was carefully controlled in order to maintain the required vapour pressure. The mixture was led through a short column, about 5 cm long and 0·5 cm wide, packed with Firebrick (0·1 mm diameter, wetted with about 5 per cent polyglycol). Since, in this experiment, we did not intend to carry out separations, the only role of the column was to provide a

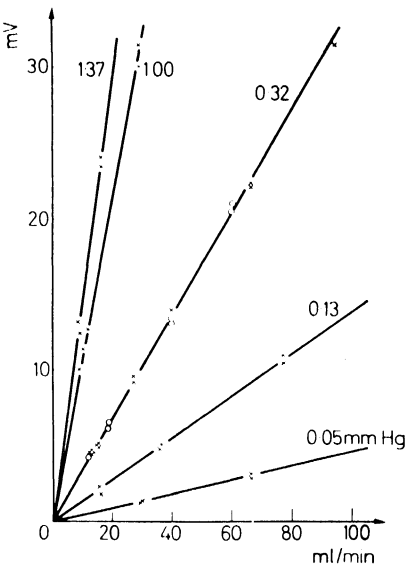


Figure 1. Detector output *v.* flow rate of carrier gas containing amyl alcohol at different partial pressures
Wire temperature: 200°C (×) or 240°C (o)

convenient throttle to stabilize the gas stream. The flow rate of the carrier gas was varied between 5 and 90 ml/min. Above a certain flow rate, the combustion is incomplete in the measuring cell and some of the substance burns in the control cell, resulting in a decrease in signal. In such cases the control cell was by-passed, which action restored the signal to its original level. The performance of the measuring cell could then be investigated at higher flow rates as well.

Figure 1 shows the results of frontal experiments carried out with amyl alcohol, the pressure of which was varied between 0·049 and 1·37 mm (saturation pressure at −20 to 18°C). The temperature of the wire was 200°C (240°C for the points marked with a circle). It may be seen that under the given conditions the signal varies strictly proportionally with the flow

rate of the carrier gas, the slope of the straight lines depending on the concentration of the burning substance. At lower wire temperatures the linear relationship fails and the curve shows a tendency to flatten out at the higher velocities. Surprisingly, the linear relationship continues to hold even with incomplete combustion in the measuring cell at high sample concentrations. (As described above, the control cell was by-passed in this case.) Incomplete combustion sets in at flow rates of 35–40 ml/min; nevertheless the linear region extends to about 90 ml/min, as can be seen from the graphs. The sensitivity of detection amounts to 12·5 mV μg^{-1} sec^{-1} or 1·39 V cal^{-1} sec^{-1} for amyl alcohol. In *Figure 2* the same data are represented as functions of the concentration, for different flow rates. The linearity of the graphs is a proof

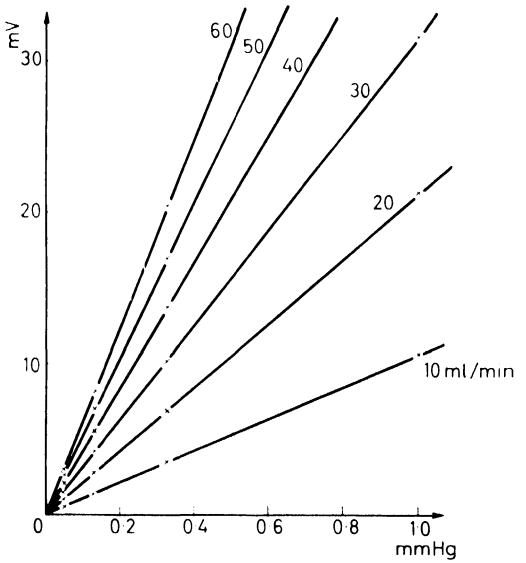


Figure 2. Detector output *v.* partial pressure of amyl alcohol in carrier gas, at different flow rates

that the slopes of the straight lines in *Figure 1* are determined by the concentration of the combustible substance.

Figure 3 shows the dependence of the detector signal on the temperature of the wire. The initial rise may be explained by the increase in the rate of combustion, the flat region determines the operating range of the cell. A further increase in temperature results in a smaller signal, owing partly to the increase of the absolute resistance of the wire, and partly to the increase of the heat losses.

Experiments with xylene gave similar results and, in addition, confirmed our expectation that the magnitude of the signal is proportional to the heat of combustion.

The 50 mV maximum deflection of the instrument used imposed a limit of 1·5 mm Hg for the partial pressure of the sample component, except for very low flow rates. Under such conditions, however, the measurements

were markedly affected if the gas line contained rubber or polyethylene connections. The appearance or disappearance (after a switch to pure carrier gas) of the front of the burning substance was then accompanied by a protracted creep (of several minutes) of the pointer. This shows that the

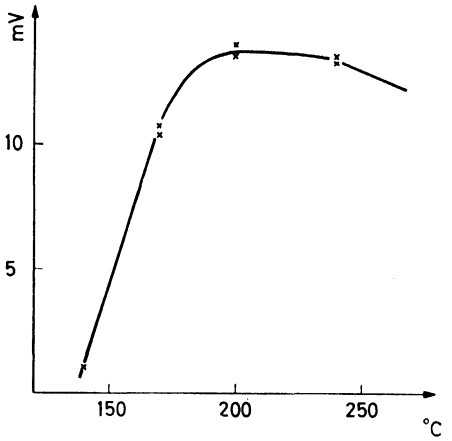


Figure 3. Detector output *v.* wire temperature
Sample: amyl alcohol, partial pressure 0·32 mm Hg

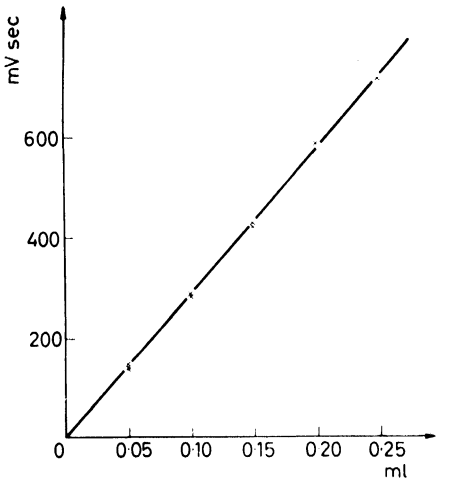


Figure 4. Peak area *v.* sample size
Sample: oxygen containing benzene at a partial pressure of 70 mm Hg
Eluting gas flow 8·5 ml/min

sensitivity of detection is great enough to reflect the sorption and desorption processes occurring on even very small rubber or polyethylene surfaces.

Higher pressures could be applied in elution experiments. *Figure 4* shows the area of elution peaks of benzene, in mV sec. The volumes indicated on the abscissa represent plugs of oxygen saturated at room temperature with

benzene vapour (tension about 70 mm Hg). It can be seen that the magnitude of the signal varies linearly with the amount introduced.

Figure 5 shows the results of the elution of plugs of 0·05 ml air containing about 10 per cent by volume benzene, at different flow rates. The appearance of unburned material in the control cell occurs at flows of 42 ml/min or greater. As can be seen from the figure, detector response up to this point is quite linear: curve *a*, showing peak areas, is horizontal (the scattering of the points indicated on the diagram is the result of inaccurate introduction in the earlier experiments), while the peak height, shown in curve *b*, increases linearly with the flow rate.

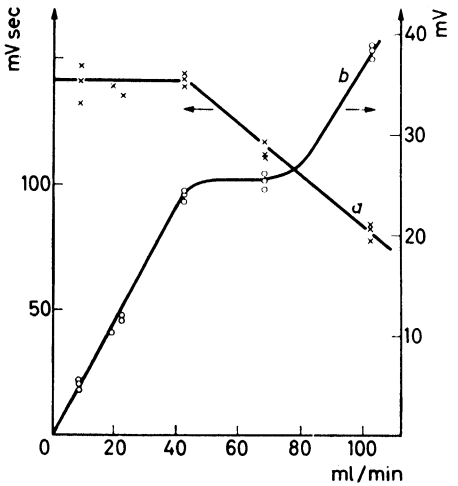


Figure 5. Detector response *v.* eluting gas flow
Sample: 0·05 ml air containing 10 per cent v/v benzene
Curve *a*: peak area
Curve *b*: peak height

Similar experiments, by both the frontal and the elution method, were carried out with a variety of different substances, including light hydrocarbons and chlorinated compounds. Even CH_4 and CCl_4 are oxidized smoothly and quantitatively at 200°C, at the flow rates indicated above. The flow rate at which combustion in the cell begins to become incomplete depends on the geometry and on the concentration of the burning substance in the frontal experiment, or on its absolute amount in the case of elution. The geometry is a decisive factor: in a cell of larger diameter radial diffusion is the main rate-determining process; the critical flow rate becomes independent of the amount of burning substance and decreases with increasing diameter. Even with small diameters radial diffusion is by no means negligible, as is proved by the observation that the critical flow rate decreases together with the concentration of the combustible substance. The critical flow rate depends also on the temperature of the wire: it increases with increasing temperature. Obviously, the performance of the cell depends also on

the temperature of the capillary wall. In the experiments described here, this temperature was maintained at about 120°C by asbestos packing.

In view of its satisfactory sensitivity and because it needs no extra amplification, the catalytic cell may be used advantageously as a detector in almost the same range as the now widespread ionization detectors.

Author's Additional Comments

After the printed text was submitted to the editor we proceeded to use the described cell for real analytical purposes. We found that at higher column temperatures (e.g. 70°C), impurities were released from the rubber tubing connecting the cell to the column. In order to eliminate this difficulty we constructed the all-metal cell

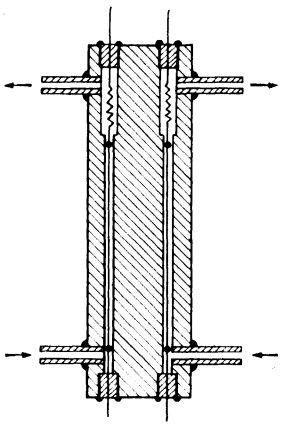


Figure 6. All-metal catalytic combustion cell

shown in *Figure 6*. Because of the somewhat less favourable geometry of this cell (length of Pt wire 6 cm, bore diameter 3 mm), its sensitivity was about one-half that of the glass cell.

Figure 7 shows a chromatogram of 0·6 ml oxygen saturated with technical xylene vapour at room temperature, corresponding to 24 μg of the main component. The peak area of the main component amounts to 123 mVsec, independent of flow rate between 10–30 ml/min; this corresponds to 5,130 mVsec/mg. A katharometer cell of similar construction, but with tungsten wires, gave a signal of only 30 mVsec/mg at the same flow rate.

Quantitative evaluation of the chromatogram gives the following data for the composition of the vapour:

	Per cent
Xylene isomers (together)	97·07
Toluene	1·30
Benzene	1·63

A normal chromatographic analysis of the liquid gave 99·5 per cent xylenes, 0·38 per cent toluene and 0·12 per cent benzene. If the mixture is assumed to

behave ideally the composition of the vapour may be calculated: xylenes 97·02 per cent; toluene 1·32 per cent and benzene 1·66 per cent. The excellent agreement between the two sets of data may certainly be somewhat fortuitous, but proves beyond doubt the reliability of the combustion cell.

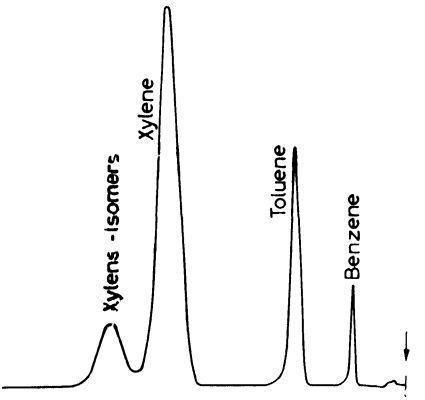


Figure 7. Chromatogram of technical xylene, injected as saturated vapour in oxygen. Column: 1 m long, 3 mm ID. Stationary phase: 5 per cent w/w silicone oil on 0·1–0·2 mm Firebrick. Operating temperature: 70°C. Carrier gas: 18 ml/min O_2. Cell heating current: 0·45 amp. Recorder: 2 mV. Sample: 0·6 ml O_2, saturated with sample vapour at room temperature, corresponding to 24 μg of the main component

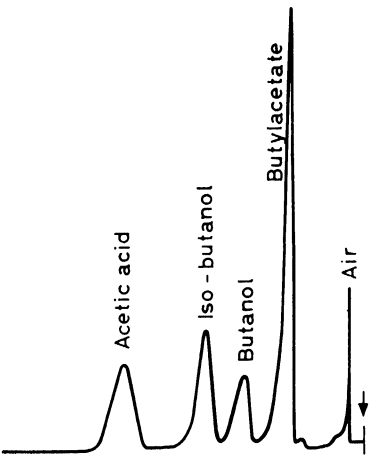


Figure 8. Chromatogram of industrial butyl acetate, injected as saturated vapour in air. Conditions as for *Figure 7*

Figure 8 shows a chromatogram of industrial butyl acetate. The sample consisted of air saturated with vapour, and a normal heat conductivity peak for nitrogen may be observed.

Discussion

G. A. P. Tuey: I should like to ask Professor Schay what material he uses for the connection to his filament, and whether it is a fairly thin wire. If so, one would expect from the geometry of the cell that one would get a thermocouple effect, and that the detector in fact would be acting as a combined katharometer plus a Scott flame detector. Does this effect contribute to the sensitivity of the detector?

G. Schay: It is not very probable, because the effective temperature rise is not so great. I cannot say exactly how much, perhaps 1 or 2°C. I do not think there would be any thermocouple effect. Perhaps in principle there would be, but effectively I do not think so.

E. R. Adlard: I think Professor Schay has answered my question in his presentation, but perhaps he could repeat in English, what is the catalytic coating and how is this applied to the platinum wire?

G. Schay: It is platinum and palladium black together. Exactly how it is done I cannot tell you. It is my staff who have done this and they have not given me the exact details. They have merely told me that one must take care of current density and temperature and composition of the base, so that the coating is sufficiently active and does not peel off. If somebody intends to try such a cell, I must warn him that it cannot be overloaded, for then the platinum black loses its activity. It works only with very small amounts.

L. Rohrschneider: If the detector is de-activated even by the plasticizer of the rubber tubing, then one might expect the stripping of stationary phase to have the same adverse effect. I should like to ask how long such detectors can be operated.

G. Schay: I don't have any definite data on that aspect. The whole problem didn't arise from gas chromatography, but originated with the Mining Research Institute.

For their purposes the various mine gas indicators weren't adequate, and we were approached to look into this problem. This gave us the idea to decrease the size of the thick wires used there and to reduce the temperature a bit. This works well in the laboratory, but the cell has not yet been used in actual service. We have run a cell practically continuously for some seven or eight months with gasoline vapour and have not observed any changes yet.

Of course, with compounds of high molecular weight something may happen when the cell is connected to a chromatograph.

PANEL DISCUSSION

QUANTITATIVE ASPECTS OF GAS CHROMATOGRAPHY

Chairman: G. W. A. RIJNDERS
Panel: G. R. PRIMAVESI and H. KELKER
Report by: D. AMBROSE

In a characteristically forthright and humorous manner Mr G. R. Primavesi introduced the subject of detectors and their failings, comparing the elegant and satisfying qualitative aspect of gas chromatography with its dismal record as a quantitative technique. The main faults can be attributed to detectors. We hardly ever measure a property which is stoichiometric or calculable; it is as if we did acid-base titrations without a knowledge of the equivalents of the acids we were titrating. Dr Martin started with a detector which did measure a stoichiometric property—an acid titrator; his next detector measured a readily calculable property —density. Only one other detector reaches the standard of these—the Janak method—but this unfortunately is restricted to gases. Scott's flame/thermocouple detector bravely attempts to measure a calculable property—the heat of combustion —but does not quite succeed. The argon and flame-ionization detectors are invaluable because of their great sensitivity, but it is not clear what they measure— apart from a current—and their response to a given substance cannot be calculated.

The commonest detector is based on thermal conductivity, because it is the simplest and easiest to maintain; but the price is heavy in other respects. Either we must calibrate for every substance (especially if nitrogen or argon is the carrier gas) or, probably more commonly, we are consciously or unconsciously inaccurate because we do not calibrate when we should. It is easy enough to find data on the thermal conductivities (if that is what we measure) of pure gases and vapours, but it is another matter when we come to what is needed—data on mixtures.

Mr Primavesi concluded with some suggestions for the improvement of quantitative gas chromatography:

(*1*) The development and use of detectors based on a calculable property, such as density; but with sensitivities one or two orders of magnitude greater than those available at present.

(*2*) The collection and critical appraisal of responses of other detectors to as many different substances as possible with different carrier gases.

(*3*) The development of a simple system of calibration for all substances at all levels.

Dr H. Luy was prepared to take up Mr Primavesi's challenge with regard to the thermal conductivity of mixtures (when one of the components is helium) and presented an equation based on that of Mason and Saxena[1]. The molar response A of a substance k in the carrier gas is given by

$$[A_k]_{\text{mol}} = \text{Constant}\left[B_{ik} - \frac{\lambda_k}{\lambda_i}\cdot\frac{1}{B_{ki}}\right] \tag{1}$$

$$B_{ik} = \frac{\sigma_{ik}^2}{\sigma_{ii}^2}\left[\frac{2}{1+\frac{m_i}{m_k}}\right]^{1/2} 1{\cdot}065 \tag{2}$$

$$\sigma_{ik}^2 = (r_i + r_k)^2 \tag{3}$$

where λ = thermal conductivity, m = mass of molecules, σ = collision diameter and r = collision radius.

When values obtained from eqn. 1 are compared with experimental results[2] on relative responses good linear correlation is obtained, although substances with polyatomic molecules fall on a line other than that theoretically predicted. The deviations can be explained because the collision diameters used have been obtained from results of experiments on collisions between like particles. In fact the interaction forces between the molecules and those of the carrier gas are appreciably smaller than those between like molecules, and eqn. 2 must therefore be modified by the inclusion of a correction factor in the numerator on the right hand side. These correction factors have been empirically determined as:

Type of molecule	*Correction factor*
Monatomic	1·00
Diatomic	0·98
Polyatomic	0·75

When these factors are applied, excellent agreement is obtained and all points fall approximately on a single line.

Mr S. Thorburn was able to provide one suggestion in answer to Mr Primavesi's first request—for a genuinely quantitative detector—when he reported on work by himself and Dr S. C. Bevan in developing a detector based on mass which is now in use in courses on gas chromatography given at Brunel College, London.

In a typical procedure a modified recording thermobalance is used, but the initial success was achieved with an analytical balance. The effluent gas from the column is fed by means of a capillary into an adsorption vessel of suitable geometry which contains an appropriate reagent (concentrated sulphuric acid has been found suitable for the quantitative absorption of most organic compounds). The solute is transferred from the mobile phase by gaseous diffusion. The detection system is characterized by its mass response (so that no correction factors are required); it gives integral detection (so that no expensive integrator is required); it gives a stable base line and there is quantitative recovery of the sample.

Dr H. Kelker introduced the second subject under discussion, that of data handling. Although there are occasional exceptions, as when chromatograms are evaluated from peak heights, an integration process is normally necessary in quantitative work. For this integration one of two courses may be followed:

(a) the use of a so-called integral detector—which may be considered a form of preparative system—with which micro-analytical methods may be used;
(b) the application of a time-summation, in which the determination of concentration is employed as a basis for integration.

Method (a) has the outstanding advantage that the determination may be carried out independently of the separation, and there is a relatively free choice in the use of the most sensitive or most accurate method of determination. It is essential, of course, that there should be quantitative recovery of the sample; if this is achieved we may be sure that the classical methods of micro-analysis will give results of good accuracy.

Method (b), the differential detector, gives as its final product a picture of the separation process, and the auxiliary equipment limits the accuracy possible: the integration is applied not merely to the substance but to the instrumental values, and this is a basic disadvantage. Integration is nearly always synchronous with the separation (with the exception of the evaluation of recorded chromatograms) and

it is questionable whether this is necessary or desirable. In general, we think not. It may be desirable for industrial control processes; in the laboratory it is superfluous and sometimes irrational, because the information content of a chromatogram usually occupies only a small proportion of its running time. This is true even for very rapid separations, and what is needed is temporal independence of the separation and integration, so that the latter can be done under optimum conditions. The maximum rationalization of procedure therefore requires good data storage, for which the following considerations are relevant:

(a) Availability of the data: the primary data should preferably be reproducible before the integration.
(b) The maximum amount of information should be stored with the greatest possible accuracy. (The system must in practice have higher accuracy than the detection itself.)
(c) The values should be readable.
(d) Correction by an observer may be desirable.
(e) Correction factors may have to be included in the stored signal.

It should be noted that most automatic integrators are unable to store the original measured values; they merely store the integrated data provided at the time of elution. The variety of procedures in use shows that the ideal solution still eludes us despite intensive search.

In the development of integration procedures the following suggestions appear widely acceptable:

(a) The use of an analogue-digital converter directly at the source of measurements.
(b) Storage on magnetic tape instead of paper strip charts.
(c) The ability to assign timing marks, so that the peaks can be related to retention times.
(d) The retention of strip chart chromatograms, with improved planimetry. Here the curve follower is a possibility. The method is adaptable for the analyst who has to deal with a wide variety of problems.
(e) The use of impulses provided by an electronic counter.

In amplification of Dr Kelker's remarks, Dr H. Boer gave the following table of the types of integrator currently available:

1	Planimeter, triangulation, cutting out and weighing, etc.	Very simple; time consuming; inaccurate; corrections can be applied
2	Motor and counter, operated from retransmitting slide wire	Simple; fairly accurate; coupled to recorder
3	Motor + counter + printer	Rather expensive; accurate only with good separations because of printing time
4	Ball- and disc-mechanisms with pipping pen or integral presentation	Moderately expensive; rather poor presentation; coupled to recorder
5	RC-integration and integral presentation	Moderately expensive; accurate. In the case of ionization detectors: simple and inexpensive. No range switching ('folded integral'). Unlimited dynamic range
6	Voltage-to-frequency conversion and pulse counting + printing	Accurate; rather expensive. In the case of very rapid or incomplete separations the additional printing-out memory makes it more involved and expensive
7	Curve follower + *6*	Very expensive; coupled to recorder; corrections can be applied

8	Computing integrator*	Expensive; accurate; wide dynamic range; applies calibration factors and normalizes to any desired percentage. Adaptable to differential as well as to integral detectors; especially suited for routine analyses
9	Integration by a coupled digital computer	Presents the ultimate in GC-data processing. Is considered to be uneconomical

* Design of Koninklijke/Shell Laboratory, Amsterdam. Patent applied for.

Dr E. Palm made some suggestions for improvements in the presentation of chromatograms. As is well known, peaks with long retention times give a small signal because they are more diffuse than those eluted earlier; the total amount of information is the same, however, because the signal lasts for a longer time. By increasing the amplification in proportion to the time elapsed we can make the peak heights for a given amount of each component approximately the same (if we assume equal response), and analyses based on peak heights can be made directly. Measurement of peak areas is, however, preferable, but the later peaks have now become unduly large. This difficulty may be overcome by changing the time-scale, viz. adjusting the chart speed so that it is inversely proportional to the time elapsed. The scale thus becomes a logarithmic one, the peaks are restored to their correct areas, and the relative retention of two substances is given by the differences between their retention distances and not, as normally, their ratio. During the chromatogram the signal/noise ratio can be adjusted and kept substantially constant by adjustment of the time constant of the system.

Dr P. A. T. Swoboda described a simple method for the calibration of sensitive detectors[3]. The absolute calibration of very sensitive detectors requires the preparation of accurately measured samples of masses less than 1 μg. In the method described, which has been developed by Dr M. G. Burnett, the diluent gas is saturated with the vapour of a very dilute solution. Sub-microgram samples of the solute are thus obtained in a convenient volume of gas. At the very low concentrations involved, Henry's law applies and vapour–liquid equilibrium data from the literature can be used to calculate the size of sample required for calibration of the detector. For example, a 0·1 per cent solution of ethanol in water at 25°C gives a saturated vapour containing 0·2 μg of ethanol per ml. Experimentally, the procedure is very simple and it avoids the errors due to adsorption by the surface of the containing vessel which arise when dilutions are carried out in the vapour phase. The use of a short pre-column of diglycerol allows the water vapour in the sample to be back-flushed if its presence is liable to interfere with the response. This procedure for the absolute calibration for one component can be combined with the determination of relative responses for mixtures with other compounds, and the sensitivity of the detector for them thereby obtained. Since the Henry's law coefficient for dilute solutions can be determined from retention volume measurements, we have here the possibility that the results obtained for the qualitative analysis of a mixture may be used for the calibration of the quantitative response of the detector for its components.

The last speaker, Professor E. Cremer, described the halogen detector in use at Innsbruck and illustrated its use with several slides. This detector works on the so-called Langway-Kingston effect and is very suitable for the detection of halogens, halogenated hydrocarbons and any other compounds containing halogens. Linearity is very good and for halogens the detector is much more sensitive than the katharometer (as was illustrated by comparative chromatograms from the two detectors). Other compounds which appear in the katharometer trace are virtually missing from the halogen-detector trace. It is highly selective. An example of its

use was shown in the determination of the surface area of glass by means of chlorine.

In his concluding remarks the Chairman said:

'When you consider the rapid development of gas chromatographic methods you cannot escape from the impression that the study of quantitative aspects lags somewhat behind.

'When we restrict ourselves to detectors—and we have heard today of some new ones—the katharometer gives the best precision. Good katharometers can be constructed and are commercially available; and if they are carefully applied their linear dynamic range does not differ very much. Generally the calibration constants are also very nearly the same, at least for carrier gases with high thermal conductivities such as hydrogen and helium, and are not very sensitive to changes in temperature or flow. Some investigators have tried to deduce these constants from the kinetic theory of gases.

'We have far less knowledge of the newer ionization detectors, the flame ionization and argon β-ray detectors. With flame ionization one of the main points is that the cause of ionization is still unknown. Thus the construction and the use of the detector up to now have had no theoretical background and it is generally a case of trial and error. There is one general rule (which is valid also for the Argon β-ray detector): for a sensitive detector all the ions must be collected at the electrode; in other words, the measurement must be carried out at some point on the saturation curve. However, there is a difference in sensitivity when oxygen is used and when air is used; also, the way in which the air is introduced, and whether hydrogen or hydrogen and nitrogen is used, influences the result. Although flame ionization detectors are widely used, it is rare that two chromatographers use the same apparatus, the same design; this diversity is reflected in the quantitative data available now. There is no unanimity as to the linear dynamic range. There is only unanimity as to the frank statement that it is large. The same is the case for the relative response for different compounds which Mr Primavesi discussed. The rapid development of GLC and its wide application as an analytical tool have reached the point at which the rapid conversion of the chromatogram into quantitative figures becomes too time-consuming, hence there is a tendency to carry out the required measurements and calculations automatically. In general, the data required for calibration consist of peak areas, although there is some doubt whether this is the only method. At present, different methods are being used for the integration of the curve to produce peak areas and the conversion of peak areas into analytical results; matters which have been discussed by Dr Kelker and Dr Boer.

'To keep this summary short, I will not go into details and I will finish by expressing the hope that this discussion will have contributed to a more rapid development in this underdeveloped side of GLC, the quantitative aspect.'

The meeting concluded at the end of its scheduled hour. Several interesting contributions had been presented, but it is to be regretted that there had not been a little more spontaneity in replies to the opening speakers.

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14

MASS SPECTROMETRIC IDENTIFICATION IN CAPILLARY GAS CHROMATOGRAPHY

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The application of a gas chromatograph in conjunction with a mass spectrometer is discussed. Possibilities and advantages of a combination based on the method of fixed masses are explained with the aid of two examples; the first concerns the analysis of aromatics in a gasoline cut, the second the identification of 37 components constituting 97–98 per cent of a gasoline cut containing more than 70 components.

Preliminary remarks about application of a gas chromatograph (GC) in combination with a mass spectrometer (MS)

Since multicomponent mixtures can be separated by modern gas chromatographic equipment, there is need for a structure-sensitive detector. Retention times alone do not suffice for identification of complicated mixtures because of overlap of peaks and lack of calibration substances.

The mass spectrometer is such a structure-sensitive detector. It is sufficiently sensitive and may be used for almost any category of substances. Technically the combination of GC and MS does not present unresolvable problems. Prerequisite for successful identification, however, is the availability of calibration spectra, or knowledge of general relations between structure and mass spectra. The API catalogue already contains a considerable number of calibration spectra. Numerous, mostly recent, investigations in the field of mass spectrometry are aimed at elucidation of the relation between structure and mass spectrum. Application of the combination GC–MS both requires this type of work and stimulates it by making accessible the mass spectra of substances that cannot otherwise be obtained in a pure state.

In the continuous procedure part of the GC eluate is continuously fed into the MS ion source. Two methods can be discerned:

(a) Fast scan method: the complete mass spectrum is scanned so quickly that the change of the partial pressure of a component during the scan is negligible compared with the partial pressure. A multiplier collector and photographic registration of the spectrum displayed on an oscilloscope screen are required[1].

(b) Fixed mass method: during a complete chromatogram the MS is focused on one characteristic mass, and this is repeated for other masses[2,3]. Sufficient information is obtained for identification. A good electrometer amplifier is adequate.

Another method not yet applied might be based on the use of a Mattauch-type MS, which simultaneously registers all masses on a photographic plate, thereby eliminating the change of concentration with time.

The method of Lindemann and Annis[4] is intermediate between the methods (a) and (b). These authors scan the spectrum in 30 seconds and repeat this

continuously. Identification is achieved by consideration of peak heights in subsequent spectra, i.e. as in the fixed mass method. Ebert jr.[5] uses a time-of-flight MS without applying its high scan speed. Difficulties in the evaluation of the photographs of the oscilloscope forced him to use a discontinuous technique. Packed columns have been used in both cases. A detailed comparison of procedures, with reference to their application to various examples, will be published[6].

Procedure of the combination GC–MS at fixed mass; discussion of examples

A complete elucidation of molecular structure never demands a complete mass spectrum. The relative intensities of 5–12 selected masses suffice, if the category of the substance is known. If it is not, the mass spectrum of the unseparated sample will give clear indication of the peaks required. Determination of the class of substance or of the carbon number is already possible after measurement at 1–3 masses.

In order to illustrate the capabilities of the combination GC–MS, two mixtures, prepared from distillation fractions of a catalytic reformer product, were analysed; mixture 1 having an upper boiling limit of 135°C (*Figure 1*), mixture 2 of 130°C (*Figure 2*).

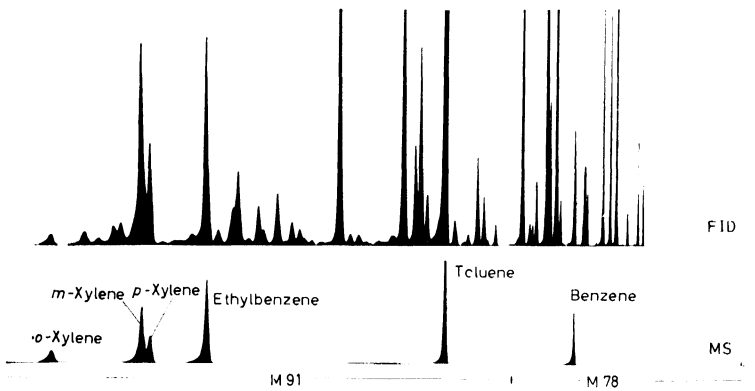


Figure 1. Analysis of a gasoline cut with upper boiling limit of 135°C (mixture 1). Upper curve: flame ionization detector. Lower curve: mass spectrometer, initially focused on mass 78 for benzene, subsequently on mass 91 for alkylbenzenes

Behind the capillary column a MS (structure-sensitive) and a flame ionization detector (FID, non-specific) are connected in parallel. The operation is similar to that described elsewhere for analogous equipment[3].

Determination of substance class by one 'characteristic mass'

A mass is characteristic when it occurs in the spectra of members of one class of compounds only. When focused on this mass the MS will register a peak only when the eluate contains a compound belonging to this class. An excellent example is mass 91, characteristic of all alkylbenzenes. *Figure 1* demonstrates how in a single measurement all aromatics in a mixture can be

recognized. Because of the low carbon number the retention times will then suffice to identify them. Similarly lead alkyls could be recognized in gasolines by mass 208 (Pb-isotope).

Identification

For identification of a substance knowledge of the relative ion intensities of a few selected masses is required; i.e. a characteristic extract of the dissociation pattern. These relative intensities are obtained as follows: The MS peak height is proportional to the concentration of the compound in the carrier gas and to the response S_M of the compound for the mass selected. Likewise the FID peak height is proportional to the same concentration and to the response S_{FID} in the FID. On division of the former peak height by the latter the concentration factor cancels out. In the quotient S_M/S_{FID} the denominator S_{FID} remains constant for the measurements of the same FID peak at different masses. For a series of selected characteristic masses the quotients are normalized to a value of 100 for the largest. In this way the required relative intensities are obtained; they can be compared with literature data.

The elimination of the concentration factor from the MS signal does not necessarily require an independent detector. An internal standard can be measured at one mass value all the time; or known sample quantities may be introduced.

Analysis of mixture 2

The important results are contained in *Tables 1* and *2* and in *Figure 2*. The discussion is restricted to features illustrating interesting aspects of the method, and to classification, where this is not immediately clear from *Table 1*. The following abbreviations are used:

M 83	= mass 83
P 12	= GC peak No. 12
M 83 chromatogram	= chromatogram during which the MS is focused on mass 83

Selection of the masses for analysis is performed after consideration of the mass spectrum of the whole mixture. It clearly contains mainly paraffins, along with benzene, toluene and small amounts of C_nH_{2n} compounds (olefins or cycloparaffins). For P36 and P37 *Table 1* shows a special choice of fixed mass, M83 and M100 respectively. The masses 43, 57, 71, 85 and 99 are especially important for the paraffins. The other masses complete the paraffin spectra but serve as a check for C_nH_{2n} compounds as well, in particular M69 and, in *Figure 2*, M83.

Discussion of results

(1) *Aromatics*

P23 and P52 do not show up in the MS to an extent corresponding to a relative intensity larger than 1 per cent. This indicates benzene and toluene in this mixture.

Table 1. Results of analysis of mixture 2 (*Figure 2*). Relative intensities at selected masses, and identification by comparison with calibration spectra. (See also *Table 2*)

Peak No.	*Mass number*											*Reference spectrum*	*Identified as:*	*Concentration (%)*
	41	42	43	55	56	57	69	70	71	85	99			
1	23·4	46·9	100·0									API i-C_4	i-C_4	0·01
	38·4	32·3	100·0											
2	23·2	11·1	100·0	0·5	0·5	2·0						E* n-C_4	n-C_4	0·08
	29·3	12·1	100·0	0·9	0·7	2·3								
3	55·2	83·9	100·0	3·6	13·0	45·4			1·3			E* i-C_5	i-C_5	2·15
	61·6	79·3	100·0	3·7	12·6	45·3			1·3					
5	35·0	55·0	100·0	2·3	1·7	11·3			0·3			E* n-C_5	n-C_5	1·91
	39·9	50·2	100·0	2·3	1·7	10·3			0·3					
7	44·7	3·9	100·0	9·0	24·0	90·7		2·3	56·7			E* 2,2-DMC_4	2,2-DMC_4	0·46
	49·9	4·0	100·0	10·7	24·0	86·5	0·5	2·2	54·6					
10	25·6	59·9	100·0	4·4	3·0	7·4	0·4	4·6	21·0	0·5		E* 2-MC_5	2-MC_5	3·89
	28·4	52·2	100·0	4·2	4·0	9·8	0·4	4·7	21·3	0·5				
12	52·4	4·3	28·3	6·5	70·0	100·0	0·4	1·1	5·0	0·4		E* 3-MC_5	3-MC_5	2·65
	63·5	5·4	31·1	6·8	70·4	100·0	0·4	1·2	7·4	0·5				
15	62·9	41·7	84·8	6·5	43·7	100·0	1·0	0·6	4·4	0·3		E* n-C_6	n-C_6	3·24
	79·0	42·6	88·8	6·8	40·6	100·0	0·5	0·6	4·2	0·3				
18	37·5	3·4	78·4	3·8	35·1	100·0	1·7		0·6	27·4		API 2,2-DMC_5	2,2-DMC_5	0·89
	42·0	2·5	71·4	4·8	40·7	100·0	1·5	0·2	0·6	33·0				
19	36·5	25·1	100·0		33·3	65·1			0·7	12·0		API 2,4-DMC_5	2,4-DMC_5	1·33
	40·0	25·0	100·0	3·6	36·0	67·0	2·04	0·3	0·9	16·6				
20	73·0	42·0		25·0	100·0		28·8	2·0				E* MCC_5	MCC_5	0·92
	61·0	31·0	13·7	24·0	100·0	5·7	29·5	2·1						

22	41·0 53·0	4·0 3·7	83·0 71·0	5·0 5·3	63·0 62·0	100·0 100·0	2·0 2·5			29·0 29·5		API 2,2,3-TMC_4	2,2,3-TMC_4	0·10
23	Small peaks corresponding to relative intensity smaller than 1% or no signal at all.												Benzene	2·27
27	12·4 19·8	2·6 3·2	100·0 100·0	8·7 11·6	1·7 1·3	4·3 5·1	0·7 1·0	14·3 18·6	50·6 62·0	11·9 16·0		API 3,3-DMC_5	3,3-DMC_5	0·91
28	32·6 34·0	37·1 37·7	100·0 100·0	3·8 4·8	16·6 19·7	23·3 25·6	0·5 0·7	1·1 1·3	1·8 1·7	23·7 31·5	0·1 0·01	API 2-MC_6	2-MC_6	8·08
30	50·2 65·0	24·8 25·0	100·0 100·0	8·7 11·0	85·9 100·0	64·6 72·0	0·9 1·7	6·4 9·8	28·8 34·8	3·3 5·6		API 2,3-DMC_5	2,3-DMC_5	3·03
31+32	34·3 44·7	10·3 10·7	100·0 100·0	10·9 13·0	27·7 32·0	41·1 47·0	1·0 1·0	28·2 37·5	38·8 46·7	2·9 4·2	0·05 0·07	API 3-MC_6	3-MC_6+1,1-$DMCC_5$*	9·60 +0·30
33+34	28·1 22·4	11·5 8·0	100·0 100·0	20·3 16·0	18·4 3·2	4·0 3·9	4·6 0·8	49·4 45·0	37·3 45·0	0·3		API 3-EC_5	3-EC_5+*cis*-1,3-$DMCC_5$*	0·90 +0·40
35	100·0 78·0	27·3 28·0	62·0 12·0	62·0 71·0	78·5 100·0	41·3 13·0	41·3 33·0	64·5 83·0	18·0 4·0	18·0 26·0		API $DMCC_5$	*trans*-1,3-$DMCC_5$*	0·49
36	99·1 77·0	35·2 33·0	12·0	69·6 76·0	100·0 100·0	23·1 13·0	41·7 31·0	60·9 91·0	5·0	(M 83: 16·0) (M 83: 14·0)		API $DMCC_5$	*trans*-1,2-$DMCC_5$*	0·48
37	38·7 41·8 48·5	21·1 21·3 23·0	100·0 100·0 100·0	8·4 7·6 11·0	22·4 21·0 25·7	42·2 40·0 47·0	1·1 0·6 0·9	13·8 11·4 17·0	36·6 31·7 43·0	1·5 1·0 1·7	(M 100: 4·7) (M 100: 4·0) (M 100: 12·1)	E n-C_7 API n-C_7	n-C_7	7·20
38	See text												*cis*-1,2-$DMCC_5$	0·15
39	21·3 26·0 28·0	1·1 1·8 1·5	16·4 15·9 17·7	2·4 4·5 4·3	27·1 32·0 27·0	100·0 100·0 100·0	0·38 0·7 1·3	0·18 0·3 0·1	0·45 0·7 0·3		3·5 5·5 6·2	API 2,2-DMC_6 API 2,2,3,3-TMC_4	2,2-DMC_6	0·50
42+43	32·5 38·0	34·1 34·0	100·0 100·0	13·9 10·9	13·2 7·5	80·4 80·3	4·2 1·3	9·8 9·7	15·2 18·8	0·3 0·6	10·5 17·2	API 2,5-DMC_6	2,5-DMC_6+C_nH_{2n}	1·09
44+45	39·0 43·0	14·8 11·0	100·0 100·0	17·6 10·0	28·6 29·0	67·6 73·0	5·5 4·2	9·9 9·8	12·1 14·8	32·4 46·0	1·0 1·0	API 2,4-DMC_6	2,4-DMC_6+C_nH_{2n}	2·00

Table 1. (Continued)

Peak No.	Mass number											Reference spectrum	Identified as:	Concentration (%)
	41	42	43	55	56	57	69	70	71	85	99			
47+48	34·8	26·1	39·1	43·5	82·6	100·0	21·7	30·4					2,2,3-TMC_5 + C_nH_{2n}	0·10
	32·6	2·3	22·8	5·5	56·6	100·0	1·1	0·5		3·0	3·0	API 2,2,3-TMC_5		
49+50	24·4	5·6	100·0	17·8	5·7	34·7	3·7	27·6	41·8	24·9	3·1		3,3-DMC_6 + C_nH_{2n}	0·73
	29·2	3·7	100·0	11·5	5·0	41·0	3·5	17·0	47·0	36·0	5·0	API 3,3-DMC_6		
	28·5	5·4	100·0	15·5	1·5	35·0	3·5	35·0	45·0	25·0	3·5	API 2,3,3-TMC_5		
52	Small peaks corresponding to relative intensity smaller than 1% or no signal at all.												Toluene	28·20
53	28·0	5·5	100·0	8·3	2·8	11·0	2·8	22·0	33·0				2,3,4-TMC_5	0·08
	24·0	7·0	100·0	16·0	2·0	16·0	1·0	40·0	62·0	0·2		API 2,3,4-TMC_5		
54+55	21·3	16·5	100·0	13·2	1·4	14·5	0·9	43·6	37·6	0·9			2,3-DMC_6 + C_nH_{2n}	1·00
	28·4	18·8	100·0	19·4	1·6	16·8	1·57	57·0	46·0	1·5		API 2,3-DMC_6		
56	27·9	38·1	100·0	8·9	7·3	65·7	1·0	15·5	12·6	1·8	7·0		2-MC_7	3·74
	38·0	42·0	100·0	11·0	8·0	73·0	1·28	17·0	17·8	1·8	12·5	API 2,MC_7		
57+58	19·6	17·0	100·0	11·3	3·0	21·6	1·2	30·2	39·2	2·9			4-MC_7 + C_nH_{2n}	1·80
	26·0	13·0	100·0	15·0	2·3	14·0	1·3	46·0	52·0	4·45		API 4-MC_7		
60	30·0	6·8	100·0	8·0	31·0	53·0	2·1	3·2	4·4	30·0	0·4		3-MC_7	6·03
	46·0	8·0	100·0	11·0	38·0	67·0	2·7	2·5	3·1	49·0	0·8	API 3-MC_7		
62+63	29·0		100·0	14·0		40·0	8·0	20·0	20·0	33·0			3-EC_7 + C_nH_{2n}	0·10
	23·0	7·0	100·0	11·0	6·0	12·0	2·5	13·0	13·5	28·0		API 3-EC_7		
71+72	28·0	13·3	100·0	8·0	14·5	30·4	1·2	9·0	18·5	20·0			n-C_8 + C_nH_{2n}	2·62
	30·0	13·0	100·0	7·9	15·1	30·1	1·3	8·7	17·7	19·2		E n-C_8		
	38·1	15·6	100·0	10·1	18·8	34·2	1·3	12·3	23·3	29·5		API n-C_8		

(2) *Accuracy of the spectra*

The accuracy of our measurements must be known for a classification to be justified. In *Table 1* the relative intensities, measured by GC–MS for each peak, are given in the top row as percentage of the base peak. The following calibration spectra have been used:

calibration spectra on our apparatus for n-C_7 and n-C_8 (referred to by E); calibration spectra obtained elsewhere on the same type of apparatus (CEC[a] 21–620) (referred to by E*);

API[b] spectra, largely obtained on instruments of a different type (CEC[a] 21–103) (referred to by API).

The agreement between data obtained by the GC–MS combination and those from spectra measured directly on our instrument is good, as may be judged from the first and the second row for P37 (n-C_7) and for P71+72 (n-C_8+trace of C_nH_{2n}). Comparison of the second with the third row for these peaks shows the degree of agreement between E- and API-values to be expected. Our M41 and M71 appear somewhat small compared with the API data; M85 and M99 amount to about two thirds; M100 to about half the API value.

These deviations depend upon the properties of individual ion sources and may be expected to pertain to other compounds as well.

The agreement between E- and E*-values from P1 to P15 and for P20 is likewise good. Larger deviations between calibration spectra may be attributed to coincidence of GC peaks.

(3) *Complete or partial coincidence of peaks*

The increase of the values for masses 41, 42, 55, 56, 69 and 70 of the peaks P33+34, P42+43 to P49+50 and of P62+63 points to overlap of the paraffin peaks by C_nH_{2n} peaks.

A small peak may be completely masked by an adjacent large peak, but will become visible when measured at a mass at which the minor component has a high response and the high-concentration component a low response. This can be seen for P22, P31+32, P38 and P54+55. *Figure 3* illustrates this demasking for peak 38 at M83.

Figure 2 demonstrates the degree of coincidence. The peaks in the M85-chromatogram arise from paraffins; the paraffins P33, P39 and P53 are not visible owing to their low intensity at mass 85. The contribution to mass 83 of identified components can be calculated from the M85 chromatogram on the basis of their mass spectra.

This contribution has been left white in the M83 chromatogram (*Figure 2*) run at higher sensitivity. The remainder of the peaks represents C_nH_{2n} compounds hitherto indistinguishable. For the C_6 range the corresponding procedure has to be performed for M69. Whereas the FID chromatogram shows 40–45 peaks, the M69 and M83 chromatograms show positive evidence for at least 72. This figure must be seen as a minimum, since coincidence of C_nH_{2n} peaks has not been recognized in this investigation. All peaks C_nH_{2n} above P37 appearing in the M83 chromatogram are estimated to amount to 2–3 per cent only of the mixture.

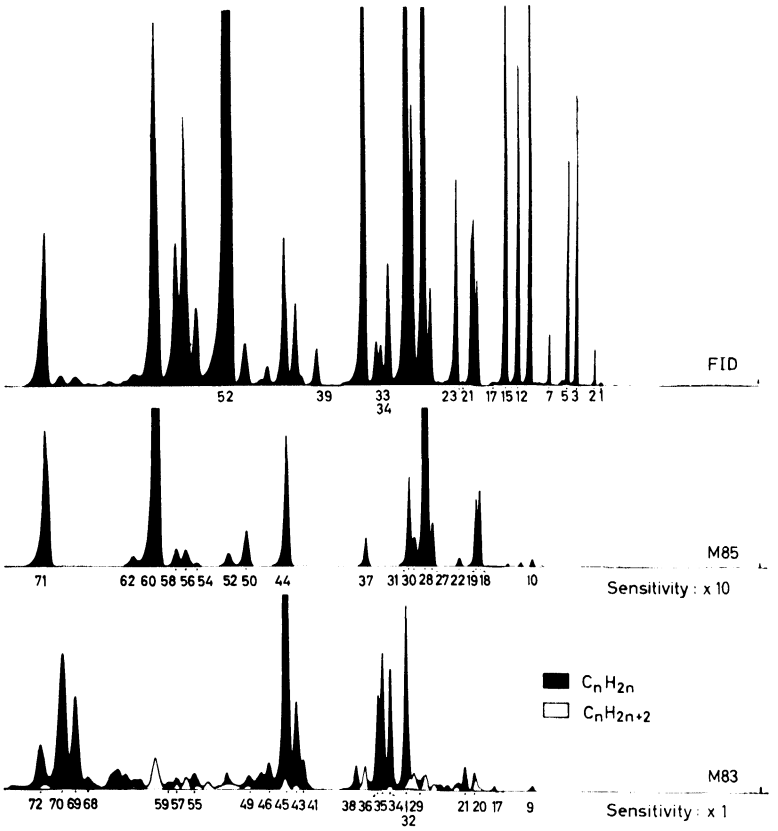


Figure 2. Analysis of a gasoline cut with upper boiling limit of 130°C (mixture 2), recorded by flame ionization detector and mass spectrometer at masses 85 and 83

Thus the possibility of measuring chromatograms at characteristic masses leads to a kind of trace analysis which can hardly be realized with a normal chromatograph because of overlap of peaks. The fast scan method does not offer any advantage in this respect, since it provides mixed spectra only. In the fixed mass method the constant background of the MS does not introduce any complications.

(4) *Dimethylcyclopentanes*

For the identification of P35 and P36 we referred to 29 spectra of C_7 olefins and 8 spectra of C_7 cycloparaffins. The peaks proved to be dimethylcyclopentanes, but the data of *Table 1* do not allow identification, owing to insufficient accuracy. An auxiliary mixture of 4 out of the 5 isomeric dimethylcyclopentanes provided the necessary additional data via the retention times. These four peaks had to be identified in a separate analysis along the same lines (*Table 2*). The *cis*-1,2-dimethylcyclopentane (P38) was identified from its MS peak 83 and from its retention time, which was estimated from the

Table 2. Identification of 4 isomeric dimethylcyclopentanes. Upper row: measured relative intensities. Lower row: relative intensities of API spectrum

Peak No.	*Mass number*							*Identified as:*
	41	55	56	69	70	83	98	
31	52 69	63 77	100 100	60 70	24 28	40 55	4 8	1,1-dimethylcyclopentane
34	60 80	63 73	100 100	29 29	86 96	22 25	7 15	*cis*-1,3-dimethylcyclopentane
35	62 78	60 71	100 100	30 33	77 84	21 26	8 15	*trans*-1,3-dimethylcylcopentane
36	59 68	59 66	100 100	25 30	53 58	11 13	13 27	*trans*-1,2-dimethylcyclopentane

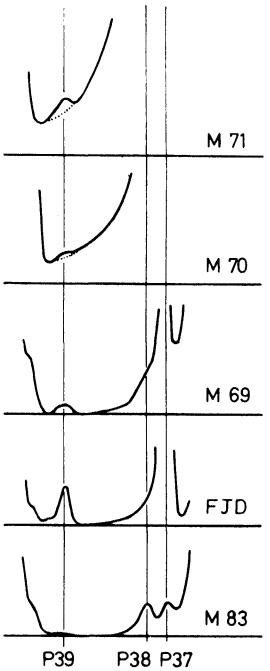


Figure 3. Measured curves of FID and MS for the section between P36 and P40 of mixture 2 illustrate advantages of the fixed mass method.

FID, M83: Trace analysis on a specific mass with high response for P38 and low response for P37

FID, M69–71: The tail of P37 does not interfere with peak height measurement at P39

boiling point. Part of the higher C_nH_{2n} compounds could have been determined in the same way.

(5) *Peak No. 39*

Two API spectra show similarity: 2,2-dimethylhexane and 2,2,3,3-tetramethylbutane. They can only be distinguished via the relation between masses 69, 70 and 71. P37 is several 100 times stronger on masses M70 and M71, so that P39 appears as a slight elevation on the tail of P37 (*Figure 3*, FID and M69–71); the fixed-mass method allows reliable measurement, however. The ratio of the three masses led us to the conclusion that the compound was 2,2-dimethylhexane.

(6) *Peak No. 47+48*

A comparison of the measured data with those from the API spectrum does not make our identification look plausible. The values for M43 and M57 point to a paraffin, which is characterized by a lack of response at M71, M85 and M99. Apart from 2,2-dimethylhexane three octanes only show this behaviour: 2,2,3- and 2,2,4-trimethylpentane and 2,2,3,3-tetramethylbutane. The second one can be rejected since it would appear before P39, according to its boiling point. The boiling point of the third compound is not very favourable either, and it should have a relative intensity of 6 per cent at M99. This leaves 2,2,3-trimethylpentane.

(7) *Peak No. 50*

Because of the ratio between M70, M71 and M85 the two spectra listed in *Table 1* need only be considered. The intensities of M85 and M99 should, according to (2), amount to about two-thirds of the API values. For this reason, and in view of the inconsistency between its boiling point and the observed retention time, 2,3,3-trimethylpentane is rejected. The high values at M55 and M70 seem to favour 2,3,3-trimethylpentane, but these arise from overlap with a C_nH_{2n} compound.

(8) *Sensitivity of this arrangement*

The concentration of P8 is 50 p.p.m.; it was measured at M69 with a signal-to-noise ratio of 15. Compounds may be detected in concentrations of 5–10 p.p.m. at a mass at which the compound in question gives a high response. Obviously the sensitivity will be lower for peaks with long retention time and large half-width.

Independent checking measures on this identification method have been effected:

(a) correlation between logarithm of retention time and boiling point;
(b) correlation between logarithm of retention time and carbon number for C_6, C_7 and C_8 homologues of the same branching type;
(c) comparison with a chromatogram of the heptanes by Desty, Goldup and Whyman[8];
(d) comparison with a chromatogram of the octanes by Simmons, Richardson and Dvoretzky[9], containing most of the octanes identified by us.

No contradictions were found.

Technical part

The gas chromatographic separation

A squalane column, 90 m long and 0·25 mm i.d., was used. Temperature 85°C, carrier gas helium. Carrier gas velocity 4·8 cm^3 min^{-1} at inlet pressure of 2·7 atg. With a split ratio of 1:400 10 mm^3 were injected. With n-octane 70,000 plates were obtained, no increase being observed for smaller sample size.

The mass spectrometer

An instrument of the type CEC 21-620 was used with the following modifications: ionization current was increased to 50 μA, the leak R_2 (*Figure 3*), was enlarged, and the amplifier was replaced by a Cary model 31[c], with a critically damped input circuit. A 40-turn potentiometer was installed to permit accurate mass focusing.

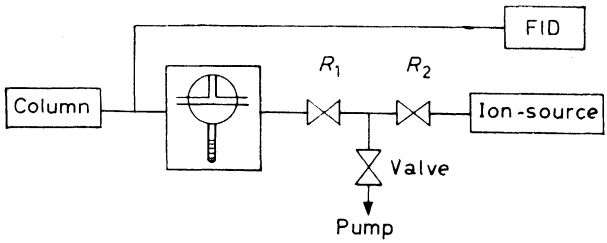


Figure 4. Spectrometer inlet system of the combination gas chromatograph–mass spectrometer

The inlet system

Figure 4 shows a block diagram of the arrangement between the exit of the capillary column and the ion source. Part of the effluent flows through the FID, the remainder to the MS after passing a gadget administering to the carrier gas a very small constant flow of a suitable liquid[10]. This provides a constant background to the MS, allowing focusing of the masses required.

Subsequently the gas flows through the first throttle R_1, originally a narrow capillary about 1 m long. A pump is connected between R_1 and the second throttle R_2 (a gold leak) leading into the ion source. The valve V limits the pumping speed and thereby regulates the pressure in the ion source, permitting an increase in sensitivity. The upper limit of the pressure in the ion source is set by the capacity of the ion source pump and by space charge effects. Helium was used as the carrier gas because of its low ionization efficiency and because it is rapidly pumped off.

The capillary R_1 is particularly inappropriate for high-boiling and polar substances, since it causes delay of peaks and tailing, as evidenced by comparison of MS and FID peaks. Coating of the capillary with the stationary phase brings about some improvement, but all troubles are disposed of when the capillary is replaced by a gold leak. Work on this problem is being done.

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[b] American Petroleum Institute, Pittsburgh, Pa., U.S.A.
[c] Applied Physics Corp., Monrovia, Calif., U.S.A.

Discussion

H. Boer: I think Dr Henneberg is to be congratulated on his nice piece of work which he has just presented. I have not tried to discover any shortcomings in his method, but I have a general remark on the method as such.

Table 1 on page 195 shows that for a mixture boiling up to 130 °C one needs at least eleven successive injections and scans on a mass spectrometer. I assume that subsequently a lot of calculation has to be made. I wonder how this would work out for a hydrocarbon fraction boiling above 130 °C. It seems to me that a more promising approach would be to evaluate the chromatogram on two different stationary phases with, e.g. the retention index of Kovats, and then to trap out any double peaks or unidentifiable peaks and analyse them by a mass spectrometer; or maybe in addition use the method of methylene insertion described by Dvoretzky and co-workers[11]. I think that for the higher-boiling fractions this is an approach which would bring us much closer to finding out what really is present. I wonder if you have any comments on that.

D. Henneberg: Much of what you have said is right, but I should like to say something else first. One shouldn't expect a mass spectrometer to do what the chromatograph, which precedes it, cannot do. If you cannot separate a mixture and cannot get an excellent chromatogram, you should not expect that the mass spectrometer is a detector which can tell you all you want to know.

Another thing is that if you have a mixture with more than, say, 30 peaks and you want to work with two columns, with a polar and a non-polar phase, you cannot say which peak is which in the two chromatograms.

H. Boer: I do not quite agree. Although there is something in this, it is not easy to identify every peak. We currently are working on oil fractions with an even higher boiling range, about 200 °C. There, of course, you have more or less to limit yourself to type separation and type analysis. It is impossible to identify every component, but up to at least 180 or 190 °C one should be able to work out such a scheme, doing most of the work by gas–liquid chromatography, trapping out fractions which can be analysed further and identifying even the components as such. I think that is definitely possible, and it has been proved by different people. The mass spectrometer is a wonderful tool and we cannot do without it, but on the application for which you have been using it here—although I really

admire the work you have been doing—I think it would be much better to use it in the other way.

G. Dijkstra: I should like to add a few arguments. A mass spectrometer is a very expensive instrument, and in a set-up like this we waste valuable instrument time. The instrument is, in fact, 'twiddling its thumbs' between peaks; and in addition, because of the dilution by the carrier gas and the consequent pumping away of your sample, a lot of sensitivity is lost. That means that you only work with very strong peaks. Therefore, you waste time and you waste a lot of information. You can improve this by condensing and subsequently taking a full mass spectrum. In that case, you do not waste any time and you have the full information.

The situation might be changed radically if there were a simple, inexpensive mass spectrometer, manually operated, manually set to certain masses, and of sufficient resolution.

D. Henneberg: In this case, may I ask you a question. Can you trap a trace peak emerging from a capillary column?

G. Dijkstra: I am not quite sure. We have come down to catching a few micrograms; and we have traps which can be connected at one end to the column—packed columns so far—and at the other end to the mass spectrometer, so there are no losses in transfer. This system could be applied to a mass spectrometer with a direct inlet, which would improve sensitivity. I suppose there would be no problem in condensing from a capillary column, if there were no problem in condensing from a packed column. I know there is a problem: it is difficult to catch a representative sample, to catch the famous 85 per cent which all people seem to get, and exactly 85 per cent of all peaks! However, you can have your normal detection system for quantitative work—we know the difficulties there—and just use condensation for the identification of unknown peaks.

H. Zech: I have a technical question. We have found that often strong adsorption occurs between the column and the ion source, particularly with compounds such as carboxylic acids. Have you also had similar experiences in your work, and if you have, how have you eliminated this difficulty?

D. Henneberg: We have seen such things, but they can be avoided if you have a minimum area at high pressure between the end of the column and the inlet of the mass spectrometer. That is the way to overcome this difficulty.

May I give a short answer to Dr Dijkstra. I must confess that we also try to work with systems which work discontinuously behind capillary columns, and we agree that even in such difficult cases a mass spectrometer is a useful aid. For instance, before you trap the peak you may as well check and see whether it is one peak, or two or three peaks. In this case a mass spectrometer is very helpful.

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15

A CRITICAL STUDY ON GOLAY COLUMNS

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GOLAY columns, i.e. tubes of a relatively small inner diameter with the inside wall coated with a film of stationary phase, have been known since 1957[1]. In comparison with the packed columns exclusively used until then, one of the advantages of the Golay columns is the fact that a high number of theoretical plates can far more easily be obtained. The first gas chromatographic applications therefore essentially involved the separation of multi-component hydrocarbon mixtures[2]. Subsequent studies[3] dealt with the possibility of carrying out rapid analyses by means of appropriate selection of the column parameters and of the operating conditions. Until recently the selected column radii and the small sample quantities permitted the use of these columns only in connection with high sensitivity ionization detectors.

Theory and application

As problems concerning reproducible manufacture and operating characteristics of the Golay columns in qualitative and quantitative analysis[4,5] have been solved for practical purposes, the way is free for their general application also in those fields which so far were specifically reserved for the packed columns.

The following new applications are of particular interest:

1. Separation of mixtures consisting of components other than hydrocarbons.
2. Analysis of high-boiling mixtures by the use of temperature-resistant stationary phases.
3. Analysis of mixtures with great differences in component concentrations (trace analysis).
4. Separation of larger sample quantities, to permit condensation at the column exit and subsequent qualitative analysis.

The design of columns for these four applications must, among other features, be based on a careful consideration of the theoretical relations existing between the HETP and other parameters, such as the column radius r, the film thickness d_F, and the carrier gas flow u. According to van Deemter[6] and Golay[7] the following equation applies:

$$\text{HETP} = \frac{2D_G}{u} + \frac{r^2}{D_G}\left(\frac{1+6k+11k^2}{24(1+k)^2}\right)u + \frac{d_F{}^2}{D_L}\left(\frac{2k}{3(1+k^2)}\right)u \qquad (1)$$

or in a simplified formula:

$$\text{HETP} = \frac{B}{u} + (C_G + C_L)u \qquad (2)$$

Accordingly the column radius r considerably influences the HETP, without any limitation being imposed on the magnitude of the column radius. Columns with a relatively large radius, e.g. $r = 0{\cdot}5$ mm, can therefore successfully be used, if a sufficiently large number of theoretical plates is obtained by an appropriate choice of the column length (100 m). For the separation of mixtures of compounds present in comparable concentrations, the admissible sample size of these columns permits the use of thermal conductivity detectors, provided their linearity range and time constant are adequate. When used with a flame ionization detector, such columns make possible the trace analysis of larger sample quantities (in comparison with columns of smaller radius) with higher resolution than can be obtained with packed columns. A high admissible sample size of the column and the use of thermal conductivity detectors are essential prerequisites for the condensation of components separated in Golay columns. In practical operation the duration of an analysis is an important factor. According to eqn (3) the retention time t_r' of a component is:

$$t_r' = K \cdot \frac{2d_F}{r} \cdot t_M \tag{3}$$

Accordingly d_F should be as small as possible. For columns with a larger admissible sample size, the ratio d_F/r must be greater. However, as—through the intermediary of C_L in eqn (2)—the magnitude of the film thickness also influences the HETP, the general applicability of the column will rapidly meet its limits.

It is recalled that eqn (1) only applies to the linear range of the partition isotherm. In trace analyses or for the separation of larger quantities, e.g. for the purpose of subsequent qualitative analysis, this range must often be exceeded. The dependence of the peak shapes—recorded under these circumstances—on the operating conditions, such as temperature and pressure, required detailed investigations. In addition, the behaviour of low concentration components in the presence of very high concentrations had to be studied.

A number of important aspects which have a decisive influence on, e.g., the separations of non-hydrocarbons are not covered by the theory. An example is the so-called 'tailing' effect (asymmetry between the peak tail and the peak front), which affects the resolution. Therefore two different ways to reduce such effects were studied.

When the gas chromatographic problems are studied with simultaneous consideration of the individual parameters which influence the column performance, it will be recognized that one single Golay column cannot satisfy all requirements. However, the advantage of the Golay columns lies in the fact that both the column parameters (radius, length, film thickness) and the operating conditions (flow, pressure) can easily be adapted to the analytical problem.

The results obtained with different columns are as follows.

Instrumentation

The measurements were made with the Model F6 Fractometer of Bodenseewerk Perkin-Elmer & Co. GmbH, Überlingen. This fractometer can be

fitted optionally with a thermistor, a hot wire, or a flame ionization detector. The injection block temperature is adjustable up to 450°C, independent of the oven temperature. A thermostat (integral controller) guarantees a high temperature stability in the column oven.

Results

(a) Golay columns, between 50 and 100 m length, internal radius 0·125 to 0·25 mm.

Golay columns of these dimensions with their high number of theoretical plates are known to be suitable for the separation of multi-component mixtures. The undesirable 'tailing' effect can be reduced by two methods which simultaneously result in a better stability of the film.

Coating of the tube with an inert, temperature-stable 'intermediate phase' before application of the stationary phase results in a strong, perhaps even complete, reduction of the effects impairing the separation. It moreover results in surfaces that can be more uniformly coated with a film. With regard to its melting point the 'intermediate phase' should be selected so that it has practically no share in the partition process. For example, copper capillaries lined with silicone rubber SE52[a] as 'intermediate phase' and subsequently coated with 7,8-benzoquinoline, had a longer lifetime. The isomeric xylenes gave completely separated symmetrical peaks.

Another method—the elimination of 'active centres' of the metal surface with certain corrosion inhibitors—also results in symmetrical peaks for polar substances, according to Averill[8]. Our own detailed investigations revealed that the influence of the wall on the shape of the peak makes itself felt already for aromatic hydrocarbons (benzene, toluene, xylenes) in copper capillaries. By addition of 'alkaterge T' the shape of the peak can be improved in these cases as well and thus the separating power can be increased.

(b) Golay columns with a length between 12·5 and 25 m with an internal radius of 0·125 to 0·25 mm.

The plate number of these relatively short columns is smaller than that of 50 or 100 m columns; it is sufficient, however, for the separation of samples with large partition coefficients, according to Purnell[9]. With temperature stable stationary phases (e.g. Apiezon grease L or M or silicone rubber SE 52) high-boiling mixtures from tar chemistry can be separated within a few minutes at low temperatures (compared with the boiling temperatures) which do not stress the thermal stability of the column. *Table 1* shows the evaluation of corresponding chromatograms.

The use of these columns for the separation of isomers (borneol/isoborneol; menthyl-methyl-ether/isomenthyl-methyl-ether; axial-/equatorial-t-butyl-methyl-cyclohexanol; α-fenchol/α-isofenchol) allows kinetic investigations by virtue of the short time of analysis and the good resolution.

(c) Golay columns with a length of 100 m and an internal radius of 0·5 mm.

Columns of this dimension are characterized by a bigger plate volume, which allows the introduction of larger sample quantities. Thereby the limits of detection of thermal conductivity detectors are exceeded, so that application of these detectors is readily possible[12]. A stream splitter before the column is no longer necessary.

Table 1. Quantitative separation of high-boiling samples by means of Golay columns (25 m and 50 m steel columns, 0·125 mm inner radius), coated with Apiezon L grease. Operating temperature 170°C. (Retention time t_r, half band width $b_{1/2}$, number of theoretical plates n, $k = t_r'/t_M$, carrier gas (helium) flow u.)

Sample	*Boiling point* °C	25 m					50 m				
		t_r min	$b_{1/2}$ min	n	k	u ml/min	t_r min	$b_{1/2}$ min	n	k	u ml/min
Benzene	80	1·60	0·025	23,000	0·68	1·6	4·50			1·40	1·3
Ethyl benzene	136	2·30	0·030	32,000	1·42	1·6	5·00			1·66	1·3
trans-Decalin	185	3·25	0·036	46,000	2·42	1·6	7·05	0·06	77,000	2·75	1·3
cis-Decalin	193	3·55	0·046	33,000	2·74	1·6	7·80	0·06	94,000	3·20	1·3
Naphthalene	218	4·35	0·056	34,000	3·58	1·6	9·60	0·08	80,000	4·10	1·3
β-Methyl naphthalene	241–2	6·10	0·207	48,000	5·41	1·6	13·60	0·11	85,000	6·20	1·3
α-Methyl naphthalene	240–3	6·55	0·223	48,000	5·90	1·6	14·55	0·12	82,000	6·80	1·3
Fluorene*	293	14·0	0·178	34,200	25*	2·3					
Dibenzothiophene	334	30·2	0·360	38,700	55	2·3					
Phenanthrene	340	34·8	0·485	28,800	62	2·3					
Anthracene	351	36·5	0·400	46,000	66·5	2·3					

* In this run the isotherms were selected so that quantitative separation of the following compounds was possible: benzene, indene, naphthalene, α-/β-methylnaphthalene, fluorene, dibenzothiophene, phenanthrene, anthracene.

If the ratio of film thickness d_F to column radius r becomes sufficiently small and is selected in the same order of magnitude as for the columns mentioned under (a) and (b), the maximum number of theoretical plates of a column with $r = 0{\cdot}5$ mm is about one fourth of the number obtainable with a column with $r = 0{\cdot}125$ mm.

Since columns with a d_F/r ratio of 1/1200 to 1/1700 have a relatively large gas volume V_g besides the volume of the liquid phase V_L, the influence of C_g (see eqn (2)) on the term $(C_g + C_L)$ predominates, according to Scott[10]. It is then recommended that a carrier gas of lower density—e.g. helium—be

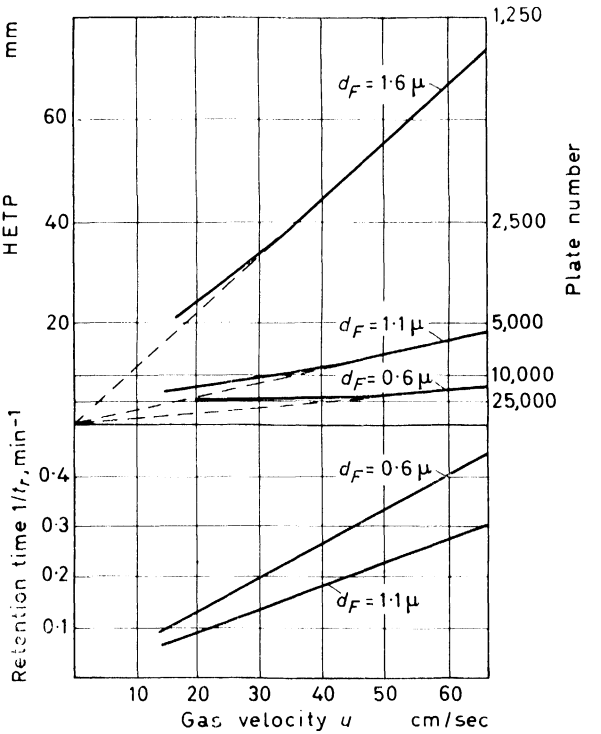


Figure 1. HETP and $1/t_r$ for n-pentane, as a function of linear gas velocity. Operating temperature 40°C; copper tube, length 100 m, inside radius 0·5 mm, coated with squalane

used, which allows faster diffusion of the sample in the gas phase. This is immaterial for ionization detectors; it is an advantage when thermal conductivity detectors are used with columns with a radius $r = 0{\cdot}5$ mm.

Figure 1 shows the HETP as a function of the flow u for three different coatings that would correspond to the film thicknesses of 0·6, 1·1 and 1·6 μ, when the coating is assumed to be uniform. The smallest film thickness results in the smallest slope, as expected, so that this coating would be most favourable for analytical problems. However, in view of the admissible sample size (see below), preference was given to the medium coating. Thus a plate number of 20,000 to 25,000 can be achieved for n-pentane under the

given operating conditions. In accordance with theory this is approximately one quarter of the plate number which can be obtained with a Golay column of a diameter of 0·25 mm.

Whereas the purpose of previous studies[11] on different component concentrations primarily was a determination of the linear range of the partition isotherm, this region was deliberately exceeded here, so that the peak form at higher concentrations could be investigated.

The results on the admissible sample size are given for the column with the computed film thickness of $d_F = 1{\cdot}1\ \mu$. *Figure 2* shows how the peak shape

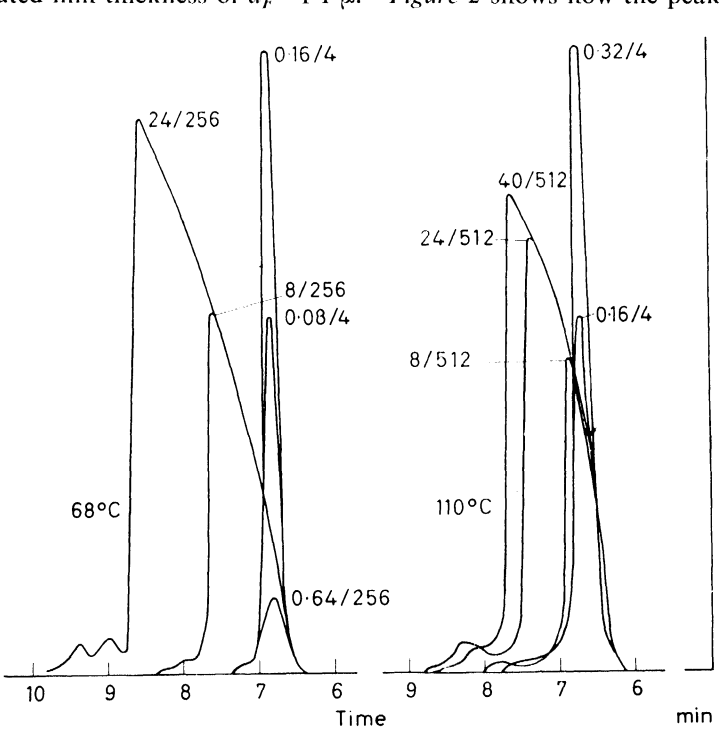


Figure 2. Peak shape for different quantities of 2,4-dimethyl pentane, at 68 and 110°C. Copper tube, 100 m length, inside radius 0·5 mm, coated with squalane, computed film thickness $d_F = 1{\cdot}1\ \mu$. The numbers represent substance quantity in microlitres resp. attenuation factor of the detector signal

changes with increasing quantity from the symmetrical to a triangular form for 2,4-dimethyl pentane. The operating temperature of 68°C is below the boiling point of the sample (80·5°C). An increase in operating temperature to 110°C results in a Gaussian peak again; at this temperature an even larger sample is needed to produce an asymmetric peak.

Owing to the relatively small pressure drop, which occurs with Golay columns with a radius of 0·5 mm over a length of 100 m, the flow along the column length is more uniform than with other column types. A more detailed study of the behaviour at higher pressures in the column, obtained by incorporation of a flow restriction at the column end, therefore seemed to be useful.

The values compiled in *Table 2* show that the operating pressure in the column appreciably affects the plate number n only if the boiling temperature of the component in question is lower than the column temperature. When

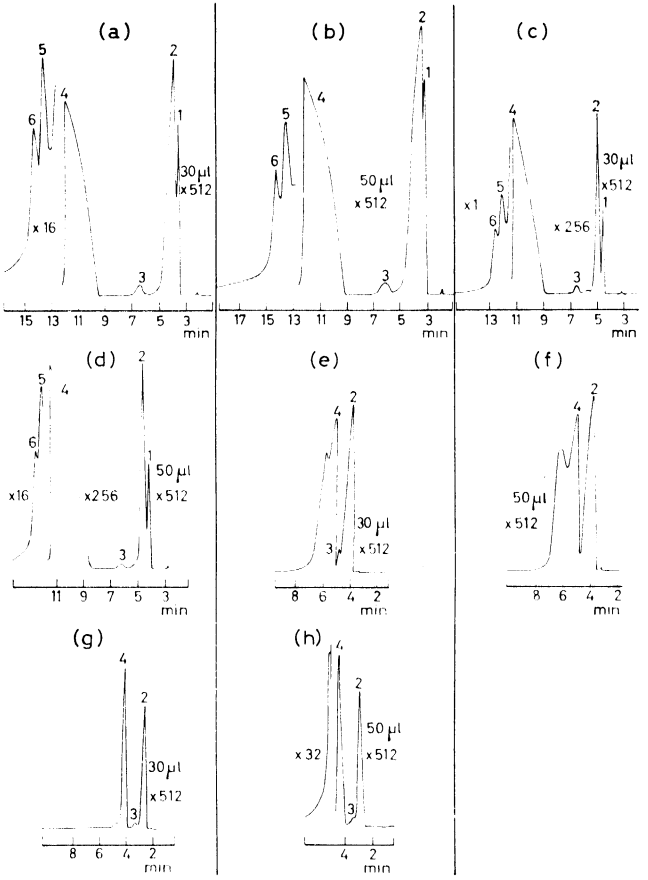


Figure 3. Influence of operating temperature and pressure on peak shape. Sample mixture 40 per cent v/v pentane, 60 per cent v/v dimethylpentane. Copper tube, length 100 m, inside radius 0·5 mm, coated with squalane, computed film thickness $d_F = 1{\cdot}1\ \mu$

Curve	Temp. °C	Pressure atm	Gas flow ml He/min.	Sample size µl
a	70	0·4	20·3	30
b	70	0·4	20·3	50
c	70	2·0	24·5	30
d	70	2·0	24·5	50
e	110	0·4	24·2	30
f	110	0·4	24·2	50
g	110	2·0	23·4	30
h	110	2·0	23.4	50

the operating temperature is raised above the boiling temperature of the 2,4-dimethylpentane, the influence of the pressure on the plate number is the same for this component. This effect could also be observed with numerous other substances (benzene, toluene, xylenes).

If a high admissible sample size is to be achieved with a constant ratio of the film thickness to the column radius, one should proceed as follows:

(a) At operating temperatures above the boiling point of a component a Gaussian shape of the corresponding peak can again be obtained (*Figure 2* and peak 4 in *Figure 3*).
(b) This increase in temperature reduces the separation power (peak 3 in *Figure 3*).
(c) A simultaneous increase of pressure in the column acts to further improve the symmetry of the peak, thus increasing the separation power again. This can clearly be seen for peaks 1 and 2 in *Figure 3a* and *3c*, and *3b* and *3d*, as well as for peaks 2 and 4 in *Figure 3e* and *3f*, and *3g* and *3h*.

Table 2. Influence of the pressure in the column on the theoretical plate number n for n-pentane (14 per cent by volume) and 2,4-dimethylpentane (81 per cent by volume) at 68°C. (The carrier gas flow was adjusted so that i- and n-pentane could be separated quantitatively.) Copper column, 100 m length, inside radius 0·5 mm, coated with squalane, computed film thickness 1·1 μ

Sample size	*n-Pentane*			*2,4-Dimethylpentane*			*Pressure* atm	*Flow* ml/min
μl	t_r min	$b_{1/2}$ min	n	t_r min	$b_{1/2}$ min	n		
0·4	6·02	0·09	22,300	8·02	0·15	17,000	0·45	19·4
4·0	5·90	0·15	8,590	8·37	0·43	2,110	0·45	19·4
10·0	5·82	0·20	4,470	8·72	0·77	704	0·45	19·4
0·4	6·10	0·10	20,680	8·07	0·16	14,130	2·02	21·2
4·0	6·08	0·13	13,100	8·60	0·47	1,810	2·02	21·2
10·0	6·08	0·16	8,000	9·10	0·82	673	2·02	21·2

The results show that the selection of the operating conditions is of great importance for the admissible sample size. A general interpretation of the results seems to be possible only after further systematic studies.

Summary

A critical consideration of the indicated results shows that the principle of gas chromatographic separating columns described by Golay is neither confined to certain geometric parameters nor to certain groups of samples in its application. A prerequisite for the work with Golay columns is the proper adaptation of the column dimensions and of the treatment of the column wall to the analytical problem.

The use of 'intermediate phase' for coating or the addition of corrosion inhibitors reduces the tailing effect with polar substances.

Columns of limited length (12·5–25 m) are especially suitable for the separation of substances with great partition coefficients. This allows the application of Golay columns to the field of high-boiling samples, permitting their analysis under non-stressing conditions.

Golay columns of a larger radius with appropriate length also have high plate numbers and high resolution. They can above all be charged with

greater sample quantities. This allows the use of thermal conductivity detectors. In conjunction with an ionization detector there are new possibilities for trace analysis.

The low pressure drop along the column length allows the setting of new operating conditions with regard to the pressure in the column. Since the admissible sample size grows with increasing pressure in the column, it is possible for the first time to work on a preparative scale with Golay columns.

The studies made until now have shown that these Golay columns have the largest operating range that has been known until now for *one* column type: with optimum carrier gas flow one obtains high plate numbers and high resolution; with higher gas velocities separations are effected in the same time as with packed columns, but with higher resolution.

Under special operating conditions one can make use of a high admissible sample size that combines good resolution with the possibility of sample collection at the column end.

Symbols

$b_{1/2}$	Band width at mid-height
d_F	Film thickness of the stationary phase in Golay columns
HETP	Height equivalent to a theoretical plate
K	Partition coefficient
$k = t_r'/t_M$	
n	Theoretical plate number, computed according to $n = 5{\cdot}54\,(t_r/b_{1/2})^2$
r	Inside radius of the Golay columns
t_M	Uncorrected retention time of a non-absorbed sample
t_r	Uncorrected retention time
$t_r' = t_r - t_M$	Corrected retention time

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Discussion

Authors' Additional Comments

In addition to the material presented in the Preprints, *Figure 4* shows a chromatogram of trace impurities in n-hexane.

The effect of the high load capacity of a macro Golay column and its importance in trace analysis are clearly demonstrated in this figure.

J. F. Smith (*prepared contribution*): In the design of Golay columns to accommodate large samples there is inevitably a serious increase in HETP and analysis time,

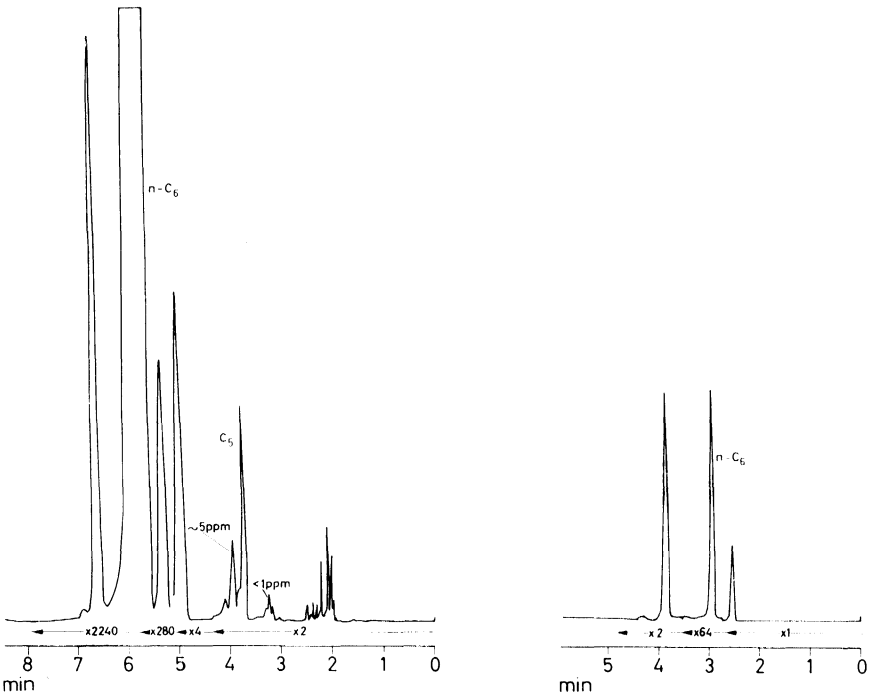


Figure 4. Analysis of trace impurities in n-hexane with macro Golay columns. Detection by flame ionization detector

Right: Column diameter, 0·5 mm; temperature, 60°C; sample size, 0·015 μl; injected via 1:500 stream splitter

Left: Column diameter, 1·0 mm; temperature, 60°C; sample size, 5 μl

compared with conventional Golay columns. In so far as the choice between Golay and packed column must be made early in any particular application, it is important to define the sphere of application of each type of column.

It would seem that, unless high efficiencies are required (> 10,000 plates), samples of about 1 μl can be analysed more rapidly on packed columns. Thus a 5 per cent squalane (on 60–72 mesh Celite) column, 6 m × 4 mm, has an efficiency of 10,000 plates for n-pentane with an analysis time of about 5 minutes at 40°C. A Golay column with $d_F = 1{\cdot}1$ μ (*Figure 1*, page 208) operating at this efficiency would have an analysis time of about 6 minutes. At higher efficiencies the packed column becomes troublesome, owing to the high inlet pressures required, and this would seem the region where the type of Golay column described in this paper is supreme.

A more serious limitation of Golay columns in our (and many others') experience is the tailing with highly polar or polarizable solutes. Metal capillaries as received from the manufacturers are frequently coated internally with material which has a retentive effect and sometimes reduces tailing. Cleaning the capillary (e.g. with hot chloroform) eliminates this retention, but results in serious tailing of polar solutes.

The use of an 'intermediate layer' to reduce tailing is therefore no surprise, but further evidence regarding the absence of retentive effect of this layer is clearly desirable; particularly with silicone rubber SE52, which has no melting point in the normal sense. Since, moreover, a polar stationary phase might be expected to eventually displace a non-polar layer from the metal surface, information on the life of these 'double coated' columns would be interesting.

The overloading effects of *Figure 2* (page 209) are attributed to non-linearity of the isotherm; it is important to note that a system which is ideal in respect of Raoult's law can deviate from a linear isotherm at a lower concentration than one which deviates from Raoult's law strongly in such a way as to be convex towards the mole fraction axis. The condition for a linear isotherm, which means deviation from Raoult's law, is that

$$\frac{d\gamma}{df} = \frac{1}{1-f}$$

where

$$\gamma = \frac{d\left(\frac{P}{P_0}\right)}{df}$$

f = mole fraction of solute.

Thus chloroform on dinonyl phthalate, as shown by Freeguard and Stock (*Figure 2*, page 107), should give an approximately linear isotherm up to much higher concentrations than cyclohexane in the same system, in spite of the fact that the cyclohexane approximately obeys Raoult's law. Chloroform strongly deviates from that law, but in the right way to give an approximately linear isotherm. This type of deviation from Raoult's law is usually found with selective stationary phases.

The non-linearity of an isotherm can produce overloading; in the case cited (2:4 dimethylpentane on squalane) this is probably the cause, in so far as this system obeys Raoult's law too well! In fact a rough calculation shows that the curve for the 24 μl sample has a concentration in the liquid phase at peak maximum of 44 g/g of stationary phase at the elution end of the column! In the circumstances overloading is not surprising, but the fact that the stationary phase is not washed out of the column is!

Column overloading can arise from causes other than non-linearity of the isotherm. In particular non-isothermal conditions in the column and extended injection volumes both produce loss of efficiency and peak distortion. Consequently it is important to establish the role of the injection system in column overloading.

At N.R.P.R.A. we have been studying both practical and theoretical aspects of column overloading, and we hope to publish the results shortly.

D. Jentzsch: I think it would be a good idea in this discussion, if we could find a few minutes to do so, to compare the different columns. I would say the real advantage of the Golay columns is that you have three possibilities for using this type of column. You can use it with flows lower than 5 ml/min, which gives you an excellent plate number and excellent resolving power. Then you have a range between 10 and 25 ml/min, that is, a range a little above the optimum, where the

efficiency is much better than for the packed column. Above that range, that is with flows of more than 25 ml/min, you have the possibility of running the column as a high-speed column. For all these applications the advantage of a small pressure drop is retained. You will probably remember the column described by Dr Halasz yesterday (page 133), which is a similar packed column which also has a small pressure drop.

Regarding the question raised by Dr Smith regarding the lifetime of the double-coated columns: this depends on the problem for which you use these columns. I should say that normally we have a lifetime of 1,000 working hours for the Golay column; sometimes much more; and of about 500 hours for the double-coated column. This reduction in lifetime is not due to washing-out of the stationary phase, but to diffusion of the partitioning fluid into the underlying film.

The cause of the overloading is not, I am absolutely certain, a non-isothermal condition for the column. We use an excellent instrument for these measurements, and the volume of the injection system is only such as is necessary to vaporize liquids.

G. Dijkstra: I wish to make a remark on the idiom. I don't think that we should unnecessarily increase the jargon of gas chromatography by calling these things Golay columns instead of capillary columns. If we had started doing this in gas chromatography, in the same publication we might have had James columns, and efficiencies of columns expressed in Martins or 'Martinis' instead of theoretical plates!

D. H. Desty: I am a little puzzled by these enormous sample sizes. We did some work some years ago, if I remember rightly, on the effect of sample size with conventional capillary columns of about $\frac{1}{4}$ mm in diameter. I forget the figures, but if I remember rightly, critical sample size must have been of the order of 1γ. With solutes which have a reasonably high partition coefficient the plate capacity is directly related to the diameter, and it would seem on this basis that a 1-mm column has a critical sample size of less than 10γ, whereas here Dr Jentzsch is talking in terms of fractional milligrams at least. I find this very surprising. I wonder if he could comment about the situation when the k' factor is, say, 10+. Perhaps there is some indication that this is so from the data in *Table 2*. There seems to be a rather more dramatic fall in the efficiency with increasing sample size in the case of heptane than in the case of pentane.

D. Jentzsch: I should say that the first time we tried to work with these sample sizes we were also very much surprised at what we could do with these columns. I should like to refer to the pure peak shapes given on page 209, for column outlet at atmospheric pressure. It can be seen that the peak shape becomes unsymmetrical at sample sizes of about 1 µl. This would appear to be a reasonable order of magnitude; the fact that we also get symmetrical peaks with much larger samples is due to the application of pressure, which results in completely different conditions in the column and apparently changes the relative concentration in the gas phase.

I don't think there is time for a detailed discussion at this moment, and I should prefer to further discuss the matter privately with Mr Desty.

16

ADSORPTION CHROMATOGRAPHY OF HYDROGEN ISOTOPES WITH CAPILLARY COLUMNS

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(Presented by G. Schay)

IT IS well known that enrichment of hydrogen isotopes and their nuclear spin isomers can be achieved by selective adsorption at low temperatures[1,2,3]. In 1958 Moore and Ward[4] successfully used columns packed with aluminium oxide for the gas chromatographic separation of *ortho*- and *para*-hydrogen. Since that time the gas-chromatographic procedures for the analysis of hydrogen isotopes have been improved, especially by the use of column packings consisting of an adsorbent which contains a catalyst for *ortho–para* conversion. Separation of *ortho*-protium and protium deuteride, together with the separation of the nuclear spin isomers of deuterium, has not yet been possible because difficulties of a practical nature set a limit to the separating power of packed columns. We have therefore attempted to use capillary columns for this purpose, because much higher separating power may be expected when capillary columns are used.

Although the technique of gas–liquid chromatography (GLC) has been used with packed, as well as capillary columns, gas–solid chromatography (GSC) has so far been restricted to packed columns only.

In principle it should be possible to achieve the desired separations with an appropriate liquid stationary phase. Since, however, the differences in the energies of rotation of the hydrogen isotopes and their nuclear spin isomers make gas chromatographic separation possible at temperatures below 100°K only, and since suitable liquids for use at these low temperatures are not known, a solid stationary phase had to be used for our purpose. These considerations have led to the opening of a new field of gas chromatography; that of adsorption chromatography with capillary columns.

After several unsuccessful attempts to coat the inner wall of a capillary with an adsorptive layer, we discovered that such a layer may be prepared by corrosion of the inner wall of a glass capillary. The procedure is very simple indeed.

A glass[a] capillary is filled with a 17 per cent aqueous ammonia solution and sealed at both ends. It is then heated to 170°C for 70 hours. After this treatment the capillary is opened and the ammonia solution is removed by means of compressed air. Then the temperature is raised very carefully, the air stream being continued, until the capillary is dry and annealed. The temperature may be raised to 190°C.

By this treatment a layer of 20 μ thickness is formed at the inner wall of the capillary. *Figure 1* shows a cross-section of a capillary treated in this manner: the SiO_2 layer can clearly be seen. (The unsharpness arises from unevenness of the cut.)

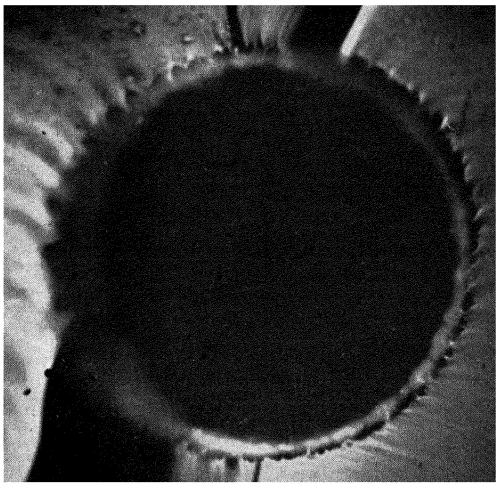


Figure 1. Cross-section of an adsorption capillary. ID of capillary = 0·27 mm

A capillary obtained in this manner was used in a gas chromatograph which is schematically depicted in *Figure 2*. Neon was used as carrier gas; it was purified in a special pre-column, *C*.

Precision needle valves *D* and *E* allow accurate control of carrier gas flow. A special valve *F* served as sample injector; the sample size could be varied between 0·7 and 3·2 μl. The sample gas is contained in a small vessel *G*, the 80 m column *H* is connected to the sample injector. A microkatharometer *K* of our own design was used as detector; the detector outlet could be connected to a soap film flow meter *L*.

At an operating temperature of 77·6°K complete separation of the stable hydrogen isotopes and their nuclear spin isomers was obtained. The chromatogram (*Figure 3*) shows the separation of a mixture of the isotopes. The mixture also contained some helium, which is inert towards the adsorbents at 77·6°K, so that the break-through time of He represents the 'dead time'

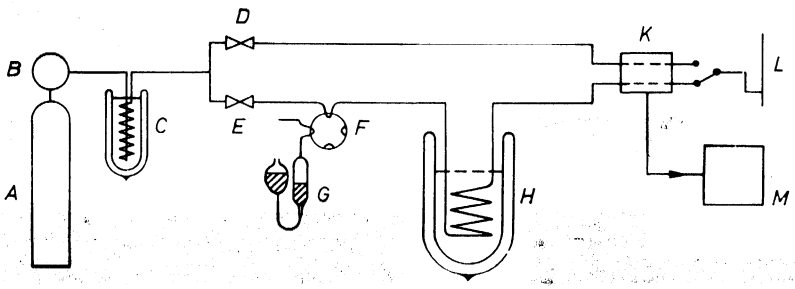


Figure 2. Flow sheet of GC apparatus: *A*=neon flask, *B*=reducing valve, *C*=purification column, *D*,*E*=precision needle valves, *F*=sample injector, *G*=sample container, *H*=capillary column, *K*=katharometer, *L*=soap film flow meter, *M*=recording potentiometer

(t_d) of the capillary, and the differences in break-through time between He and the other components represent the corrected retention times ($t_{R'}$) of these components.

In order to obtain data about the energies of adsorption, we also carried out separations at other temperatures. Temperatures below 77·6°K can easily be obtained with liquid nitrogen at reduced pressure. The temperatures were measured with a nitrogen vapour pressure thermometer.

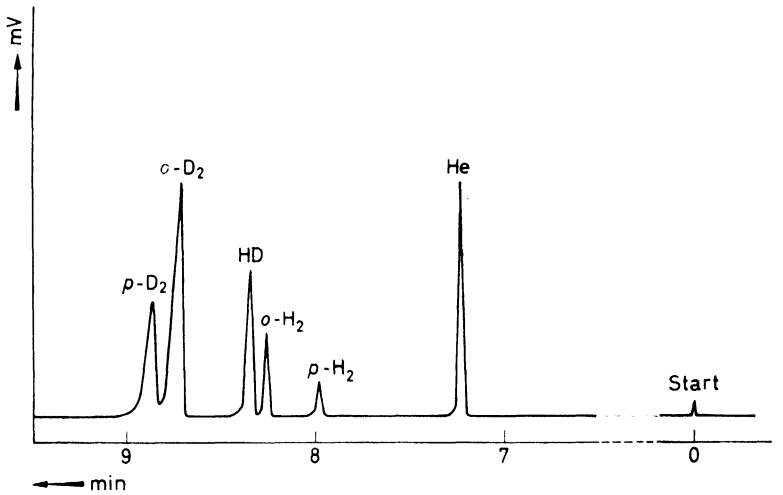


Figure 3. Separation of hydrogen isotopes and their nuclear spin isomers. Column length 80 m; temperature = 77·6°K; carrier gas flow 2 ml Ne/min.; sample size 1·5 µl

Table 1 is a compilation of the data obtained. The enthalpies of adsorption for the respective components can be determined from the slope of the plots of $\ln (V_{R'}/V_d)$ versus $1/T$ (*Figure 4*) if the relation

$$\ln \frac{V_{R'}}{V_d} = \frac{\Delta H}{RT} + C$$

is assumed to be valid. ($V_{R'}$ is the corrected retention volume, V_d is the dead volume of the column.) The linearity of the curve indicates that ΔH is constant over the temperature range studied.

The integration constant C is a measure of the adsorption entropy, which can be determined from the ordinate intercept ($1/T = 0$). The following energies of adsorption were obtained:

	$p-H_2$	$o-H_2$	HD	$o-D_2$	$p-D_2$
ΔH kcal/mole	0·77	0·93	0·92	1·00	1·09

HD is eluted after o-H_2; nevertheless its enthalpy of adsorption is smaller.

Table 1. Net retention times and separation factors for hydrogen isotopes and their nuclear spin isomers

	$T = 77{\cdot}6°K$ $1/T = 0{\cdot}01289°K^{-1}$ $t_d = 6{\cdot}28$ min $V = 2{\cdot}16$ ml/min			$T = 70{\cdot}2°K$ $1/T = 0{\cdot}01426°K^{-1}$ $t_d = 6{\cdot}50$ min $V = 2{\cdot}14$ ml/min			$T = 67{\cdot}8°K$ $1/T = 0{\cdot}01473°K^{-1}$ $t_d = 6{\cdot}97$ min $V = 2{\cdot}18$ ml/min		
	$t_{R'}$ min	α	$\frac{V_{R'}}{V_d}$	$t_{R'}$ min	α	$\frac{V_{R'}}{V_d}$	$t_{R'}$ min	α	$\frac{V_{R'}}{V_d}$
p-H_2	0·644		0·1024	1·125		0·174	2·94		0·211
		1·391			1·513			1·653	
o-H_2	0·895		0·1427	1·705		0·262	4·12		0·324
		1·085			1·085			1·080	
HD	0·973		0·1418	1·845		0·284	4·45		0·349
		1·350			1·419			1·557	
o-D_2	1·312		0·2090	2·620		0·403	6·93		0·511
		1·095			1·151			1·221	
p-D_2	1·438		0·2290	3·02		0·464	8·47		0·602

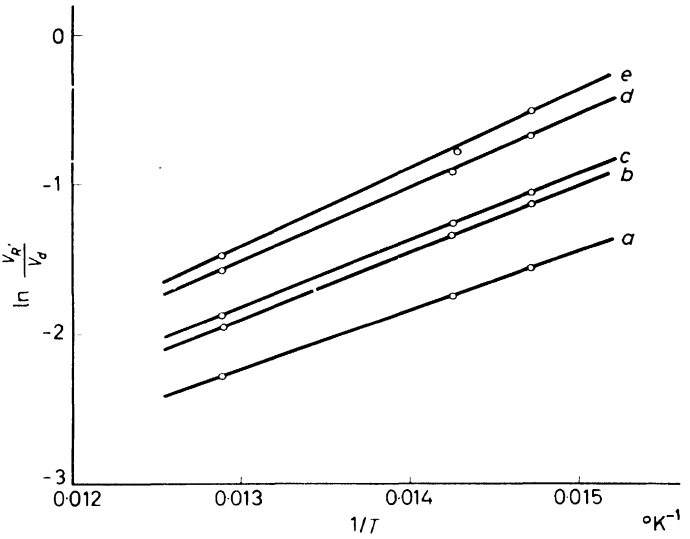


Figure 4. Plot of ln (V_R'/V_d) versus $1/T$
$a = p\text{-}H_2$, $b = o\text{-}H_2$, $c = HD$, $d = o\text{-}D_2$, $e = p\text{-}D_2$

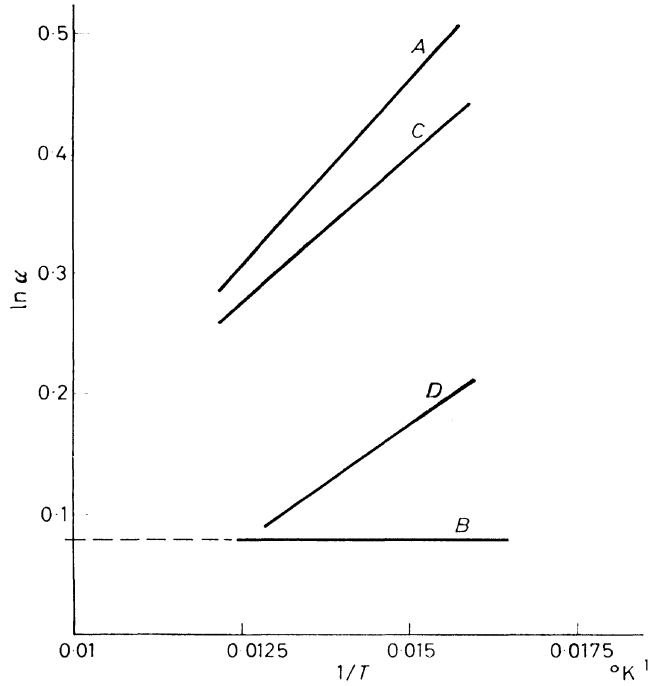


Figure 5. Plot of ln α versus $1/T$

Curve	
A	$o\text{-}H_2/p\text{-}H_2$
B	$HD/o\text{-}H_2$
C	$o\text{-}D_2/HD$
D	$p\text{-}D_2/o\text{-}D_2$

The observed separation between these components must therefore be ascribed to the difference in adsorption entropy, which is larger for HD than for o-H_2. In agreement with this fact the separation factor between HD and o-H_2 decreases with decreasing temperature as shown in *Figure 5*. The difference in adsorption entropy between HD and o-H_2 in our case amounts to 2·6 cal mole^{-1} deg^{-1}.

It should be noted that the enthalpy and entropy values obtained depend upon the activity of the adsorption layer in the capillary. This was also shown by Moore and Ward[6]. The chromatograms obtained with the procedure described can be quantitatively evaluated with the aid of an integrator when detectors of sufficient sensitivity are used.

The results, obtained with capillary gas–solid chromatography, justify the hope that other difficult separation problems may be solved with this technique.

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[a] Jenaer Gerateglas 16 III, SiO_2: 67·5%, Al_2O_3: 2·5%, B_2O_3: 2·0%, CaO: 7·0%, Na_2O: 14·0%, ZnO: 7·0%.

DISCUSSION

G. P. Cartoni (*prepared contribution*): In connection with the application of gas chromatography for the separation of isotopes I wish to present some preliminary results obtained in the separation of hydrogen and deuterium compounds. Benzene and hexa-deuterobenzene can be separated by means of a partition glass capillary column, as shown in *Figure 6*.

The nature of the liquid phase is of the greatest importance when chromatographic resolution is to be achieved for this type of isotopic material. Three liquid phases have been tried: silicone oil (702), squalane, and dinonyl phthalate, on glass capillary columns of about 50 m length. The columns had a comparable efficiency in terms of theoretical plates. A complete separation has been obtained only with the first two liquids at temperatures between 0 and 50 °C.

In *Table 2* are reported the ratio of the corrected retention volumes for C_6D_6 and C_6H_6, together with the ratio of the vapour pressures, which were taken from Bailey and Topley[10]. In the squalane column this ratio is higher than the vapour pressure ratio; the converse is observed on the silicone oil. The activity coefficients (γ) of the two compounds consequently are not equal and have different values in different liquid phases.

From the plot of the logarithm of the ratio of retention volumes versus reciprocal absolute temperature (*Figure 7*), the difference between the ΔH values related to the chromatographic process may be calculated for these compounds. By comparing this value with the difference between the heats of vaporization we may

Table 2. Ratio of corrected retention volumes and ratio of activity coefficients for hexadeuterobenzene/benzene (dBz/Bz) on silicone oil (702) and squalane

		Silicone oil 702		*Squalane*	
T	$\frac{P_{dBz}}{P_{Bz}}$	$\frac{V_{R,Bz}}{V_{R,dBz}}$	$\frac{\gamma_{Bz}}{\gamma_{dBz}}$	$\frac{V_{R,Bz}}{V_{R,dBz}}$	$\frac{\gamma_{Bz}}{\gamma_{dBz}}$
273·2	1·0370			1·0421	0·9951
283·2	1·0332	1·0205	1·0124	1·0395	0·9939
293·2	1·0315	1·0198	1·0112	1·0357	0·9939
303·2	1·0304	1·0191	1·0111	1·0336	0·9969
313·2	1·0295	1·0186	1·0112		
323·2	1·0286	1·01787	1·0102		

evaluate the difference between the heats of solution of the two compounds. Thus for solution in squalane we find $45{\cdot}5 - 20{\cdot}96 = 24{\cdot}54$ cal, and for silicone oil (702): $11{\cdot}4 - 20{\cdot}96 = -9{\cdot}56$ cal.

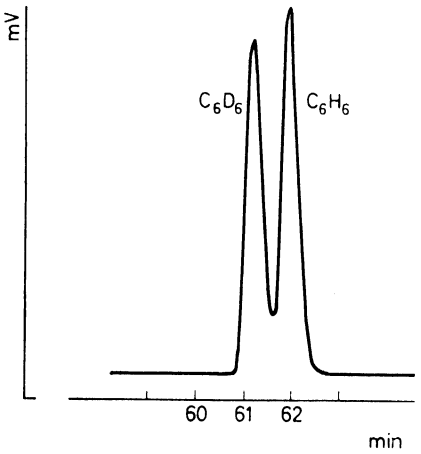


Figure 6. Separation of benzene and hexa-deuterobenzene. Column: 85 m glass capillary, coated with silicone oil (702); temperature 35°C; inlet pressure 160 mm Hg; flow rate 0·5 ml/min; 160,000 theoretical plates

These values should be regarded as a relative measure of the interaction of the solutes with the two liquid phases. Thus the squalane column is much more effective for the desired separation, because the difference between the heats of solution operates in the same direction as the difference between the vapour pressures.

G. Schay: I have only one remark to make on the contribution by Dr Cartoni. From an analytical standpoint it is a different problem to separate the deuterated compounds, rather than to separate the gases themselves into the different rotational isomers; and this is the achievement of Dr Mohnke.

E. Cremer: For one who has worked for many years on ortho- and para-hydrogen it is a pleasure to see such a beautiful separation of all the isomers of the hydrogen–deuterium mixture. At the time we had concluded from kinetic measurements that ortho- and para-hydrogen show different adsorption behaviour, because conversion of para-hydrogen was inhibited, but conversion of the ortho isomer was not. After adsorption on SiO_2 and subsequent pumping we could indeed

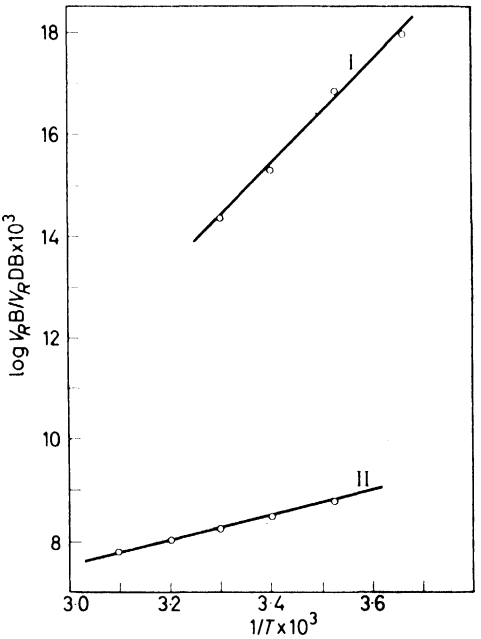


Figure 7. Separation of benzene and hexa-deuterobenzene. Log relative retention as a function of reciprocal absolute temperature
I: squalane column; II: silicone oil (702) column

observe an enrichment of ortho-hydrogen. We have now also done experiments on the separation of ortho- and para-hydrogen on molecular sieves.

I have admired the fact that the peaks here show so little tailing; the surfaces obtained with these glass capillaries must be very homogeneous. With the molecular sieves one gets pronounced tailing; this has the advantage that one can determine the adsorption isotherms from these tails, as we have done.

I might add that the adsorbent should be very pure. One is always faced with the problem of paramagnetic conversion. When the molecular sieve is not very pure, it contains iron, and this causes paramagnetic conversion. Again, this is an advantage in certain respects. To some extent one can actually test the catalytic activity of the molecular sieves, by noting whether the peaks are completely resolved or not.

G. Schay: I believe that the absence of tailing is due to the thinness of the adsorbing film, which has a thickness of about 50 μ, according to the authors. I

have no authority to discuss this, because it is not my work. However, very recently I have heard that work is being done on very thin adsorbing films, and that other persons also have found that tailing is more or less eliminated with these very thin films. Probably the tailing is related not only to the shape of the adsorption isotherm, but to other factors as well; because at very low concentrations the isotherm can be regarded as linear in practically all cases. I have never really believed that tailing has anything to do with the shape of the isotherm at the low concentrations—perhaps 0·1 per cent or less—which occur in capillary columns.

Probably the effect is related to the retarding effect of the long desorption path on the diffusion; this may cause tailing. Apparently this retarding effect becomes insignificant when the adsorbing film is very thin, say a few microns. I don't know whether this is the correct explanation, but this would be my way of looking at it.

M. M. Wirth: Could you perhaps say whether the surface area/m of these capillaries has been determined, and whether hydrocarbons can be separated with such columns?

G. Schay: Unfortunately I cannot answer that question. I have not talked to Dr Mohnke; the only information I have, in addition to what you can read in the Preprints, is the composition of the glass.

A. V. Kiselev: Dr Mohnke's method of the geometrical modification of the walls of the capillary column is very similar to our own. The only difference is that he produces a porous film by hydrochloric acid treatment of sodium borosilicate glass. I have mentioned this possibility and showed a few examples in my lecture (page xlvii). In this connection, I should be very grateful to Professor Golay, Professor Schay and Dr Jentzsch if they could let me have their opinion about the use of capillary columns with porous walls in gas–solid or gas–liquid gas chromatography; not packed capillary columns, but capillary columns with porous walls. This would be interesting to me.

G. Schay: My opinion is—as the present example shows, and as I have heard elsewhere, as well as from Professor Kiselev's own contribution—that capillary columns with porous walls may be used to advantage as adsorption columns. The question on the wetting liquid: certainly in my opinion it can be used also with a wetting liquid; only one has to be careful and investigate every individual case, because on such a thin film you cannot put much stationary liquid, and it has to be spread out also in a very thin film. I believe that, as a consequence of the cohesive forces and the modified surface tension of the thin film on the porous support, the retaining properties of the liquid may be more or less—I believe rather more than less—modified. This should certainly be investigated. We have already got some experience ourselves along these lines.

A. V. Kiselev: The adsorption version on porous walls would be useful, perhaps?

G. Schay: Certainly, I am convinced of it.

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CONTINUOUS COUNTER-CURRENT SEPARATION UNDER CONDITIONS OF ELUTION GAS CHROMATOGRAPHY

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THE QUANTITATIVE comparison, described in this paper, of the effect on separation efficiency of the counter-current between gas phase and sorption material under chromatographic conditions with that of the counter-current between vapour phase and liquid in rectification is the continuation of a previous publication by Pichler and Schulz[1] on continuous separation under the conditions of elution gas chromatography.

The well-known efficiency of elution gas chromatography, together with the special selectivities reported for particular column materials, has stimulated many research workers to try separations of larger amounts of mixtures by this method. Separations with columns of large diameter were investigated: e.g. Bayer[2] found a relatively low HETP of 0·31 cm, using a column of 10·1 cm diameter. Techniques for automatic sampling and fraction collecting were also developed.

For continuous separation a second velocity component must be superimposed on the migration velocities of the components to be separated, either in opposite or in transverse direction. This is achieved by a corresponding movement of the sorption material.

Utilizing counter-current adsorption on active charcoal, Berg[3] developed the 'hypersorption' process, which was later elaborated as 'continuous gas chromatography' by Freund and co-workers[4]. At the Symposium on Vapour Phase Chromatography, held in London in 1956, it was recommended that the term chromatography be used only for those methods where the sorption-material is not moved[5]. If the process of Berg and Freund is to be named in terms of chromatography it might then be called 'continuous gas displacement chromatography'. Being a displacement method the process is limited to the use of adsorption materials. In contrast to the method already mentioned, 'continuous separation under conditions of elution gas chromatography' is a technique which may utilize the large number of special substances available as sorption material, and which is as widely applicable as elution gas chromatography for separation of mixtures that may be vaporized without undergoing decomposition.

From analytical discontinuous elution gas chromatography the following conditions can be deduced for the continuous method. If components A and B move with velocities u_{AS} and u_{BS}, relative to the sorption material, then this must be moved with a velocity u_{SC}, relative to the column, so that

$$|u_{AS}| > |u_{SC}| > |u_{BS}| \qquad (1)$$

Then the less sorbed component A will move upward with velocity $u_{AC} = u_{AS} - u_{SC} > 0$, relative to the column, and component B will move downward with velocity $u_{BC} = u_{BS} - u_{SC} < 0$. These velocities are schematically indicated in *Figure 1*. Ideally the various linear velocities are constant; it remains to be proved that they may be assumed to be constant in practice.

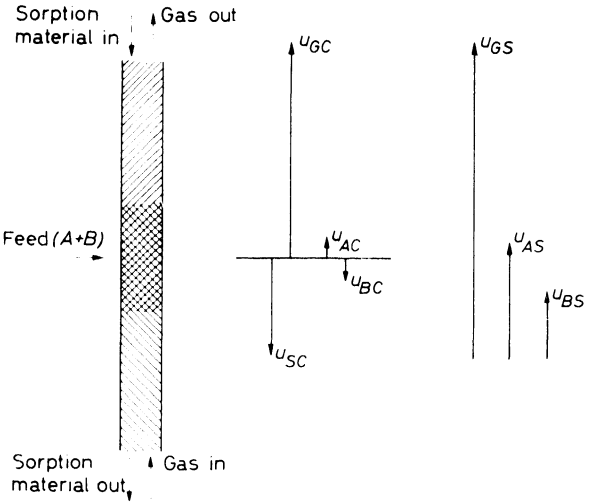


Figure 1. Continuous separation of a two-component mixture.

Component	*Linear velocities*	
	Relative to column	*Relative to sorption material*
Sorption material	$-u_{SC}$	0
Gas phase	u_{GC}	u_{GS}
Component A	u_{AC}	u_{AS}
Component B	$-u_{BC}$	u_{BS}

$$u_{SC} = -\tfrac{1}{2}(u_{AS} + u_{BS})$$

An apparatus used for continuous separation under conditions of elution gas chromatography is shown schematically in *Figure 2*.

The sorption material is moved downwards in the column with a definite velocity and conveyed continuously to the top (1) by means of a gas lift (2). The velocity of the sorption material is regulated by means of orifice (3). The sorption material moves downwards as a fixed bed and the particles of the sorption material do not displace each other. Uniform packing and transport of the sorption material is favoured by vibration (4) of the column in the vertical direction.

A counter-current of carrier gas is introduced at the bottom of the column (5) and flows upwards. The two-component mixture is fed into the middle of the separation zone (6). Gas and packing flows have to be adjusted to

fulfil the condition of eqn. (1). At the top and bottom of the separation zone (7;8) components *A* and *B*, along with the carrier gas, can be removed from the column. The linear gas velocity is greater between the point of introduction of the carrier gas and the point of removal of component *B* than in the separation zone, resulting in upward movement of *B* and allowing its removal from the column. Samples of the gas phase can be taken at different points along the column and analysed by gas chromatography for control purposes.

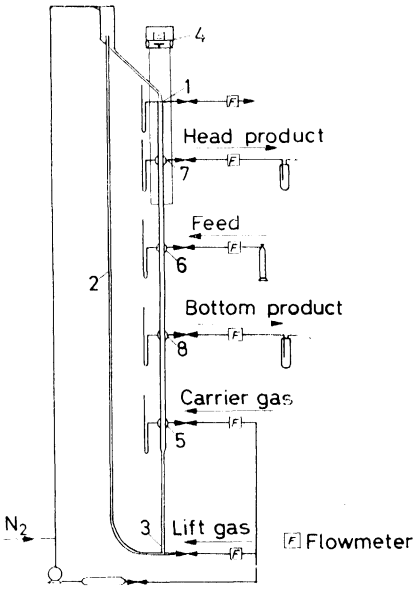


Figure 2. Schematic diagram of equipment for continuous counter-current elution

By this method, separations which cannot normally be realized by means of rectification can be achieved; e.g. with a column with a separating zone of 1 m length, a feed mixture of isobutene (b.p. −6·9°C) and n-butene-1 (b.p. −6·26°C), could be separated into a top product of more than 99 per cent pure isobutene and a bottom product of more than 99 per cent pure n-butene-1 (calculated on carrier gas free basis)[10]. However, it must be mentioned that in this case a highly selective sorption material, silver nitrate in benzyl cyanide on Sterchamol, was used ($R_A/R_B = 1{\cdot}27$).

In order to allow an estimation of the possibilities of the new continuous separation method, a quantitative comparison with the rectification method will be established. The separability of an ideal two-component mixture can be represented by the relative volatility, i.e. the ratio of the vapour pressures of the pure components at the distillation temperature. According to Fenske[6], the number of theoretical plates required to yield a product of concentration x_E at total reflux is given by

$$n+1 = \frac{1}{\log \psi} \log \frac{x_E(100-x_B)}{x_B(100-x_E)} \qquad (2)$$

where n = number of theoretical plates,
$\psi = P_A/P_B$ = relative volatility,
x_B = concentration in mole % in reboiler.

Conversely, the number of theoretical plates of a rectification column may be calculated from the results of a particular separation.

The separability of two components by means of gas chromatography can be similarly represented by the ratio of the retention values (R_A/R_B). For a comparison of the effectiveness of counter-current in continuous separation under conditions of elution gas chromatography with that of rectification, the number of theoretical plates required for rectification of a mixture with the same separation factor (relative volatility numerically equal to relative retention) has been calculated for the results obtained by the method described here.

Experimental data for the continuous separation under conditions of elution gas chromatography of a mixture of *trans*-butene-2 and *cis*-butene-2 are given in *Table 1*. According to eqn (2), 81 theoretical plates are required to separate a mixture having an equal separation factor into products of the same purity at total reflux.

Table 1. Continuous separation of *cis*- and *trans*-butene-2

Column	Effective length 100 cm cross-section 1·0 cm²
Feed	*trans*-butene-2 37·6 vol.% *cis*-butene-2 62·4 vol.% total 78 ml/hour
Sorption material	Dibutyl phthalate on Sterchamol 30 ; 100 particle size: 0·3–0·4 mm material flow: 540 g/hour 15·8 cm/min
Carrier gas	5·1 l. nitrogen per hour
Relative retention	R_A/R_B = 1·14
Pressure drop over separation zone	26·6 mm Hg
Pressure at top of column	Atmospheric
Temperature	22°C
Analyses of gas phase*	
32 cm above feed point	*trans*-Butene-2 99·73 vol.% *cis*-Butene-2 0·27 vol.%
32 cm below feed point	*trans*-Butene-2 0·76 vol.% *cis*-Butene-2 99·24 vol.%

* After removal of carrier gas

A rectification column with the same efficiency must have an HETP of only 0·80 cm. This may be compared with optimum HETP values of 2 cm for spinning band- and 5 cm for Vigreux and Jantzen columns, cited in the literature[7].

The high counter-current efficiency under chromatographic conditions, as in the process described here, results from the peculiar flow pattern, called percolation, in which the gas–liquid interface has a large area, the film thickness of the liquid phase is small, and diffusion in the interstitial gas volume is fast, so that equilibrium is rapidly attained.

It should be noted that reported values of the number of theoretical plates

needed for comparable separations by gas chromatography and by rectification differ considerably, and calculations according to chromatographic theory lead to a number of plates approximately ten times as large[8]. However, the special advantage of the continuous separation under conditions of elution gas chromatography lies in the fact that a stable phase with special selectivity for a particular separation may be used, which results in a substantially higher separation factor for the desired separation than would be possible on the basis of relative volatility of the mixture.

As an illustration, relative volatilities of some two-component mixtures are compared with the corresponding relative retention volumes in *Table 2*.

Table 2. Relative volatility and ratio of the retention volumes of some two-component mixtures

Mixture	B.p. °C	B.p. °C	ΔB.p. °C	$\varphi = \frac{P_A}{P_B}$	$\frac{R_A}{R_B}$	*Stat. phase*	*Temp.* °C
Propene/ propane	−47·1	−42·1	5·0	1·25	2·14	Silica gel	25
Isobutene/ n-butene-1	−6·9	−6·26	0·64	1·03	1·27	Silver nitrate in benzyl cyanide	25
n-Butane/ *trans*-Butene-2	−0·5	+0·88	1·38	1·05	2·32	Silica gel	25
trans-Butene-2/ *cis*-Butene-2	+0·9	+3·7	2·8	1·14	1·65	Silver nitrate in benzyl cyanide	25

Thus the relative volatility φ of a mixture of n-butene-1/isobutene is 1·03, and relative retention R_A/R_B of these two components on silver nitrate in benzyl cyanide is 1·27; and the relative volatility of a n-butane/*trans*-butene-2 mixture is 1·05 whereas the relative retention on silica gel is 2·32.

In addition to the continuous separation of two-component mixtures referred to above, group separations of, e.g., olefins and paraffins from narrow boiling-point cuts may be effected with column materials having appropriate selectivity.

Theoretical considerations

Figure 3 serves to correlate the different experimental quantities of the continuous separation under conditions of elution gas chromatography.

Under steady-state conditions the flow of carrier gas through a cross-section of the column may be represented by v ml/min, with s representing the flow of sorption material in g/min. Above the feed point a_G ml/min of component A will flow upwards with the gas phase and a_S ml/min is transported downwards with the sorption material.

Under conditions producing quantitative separation A will not be transported downward and B will not be transported upward, so that

$$a_G - a_S = a \tag{2a}$$

Similarly, in the column section below the feed point

$$b_S - b_G = b \tag{2b}$$

The feed of components A and B in ml/min is represented by a, resp. b. The gas stream g above the feed point contains carrier gas and component A:

$$g = v + a_G \tag{3}$$

As the separation is assumed to be quantitative, we may further write

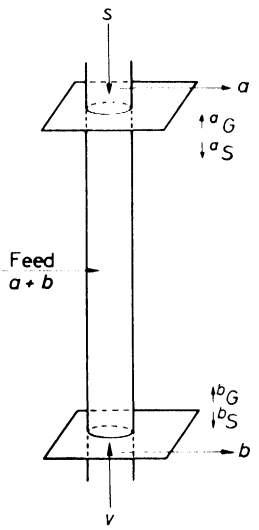
$$\frac{a_G}{g} = \frac{p_A}{P} \tag{4}$$

where p_A is the partial pressure of A, and P is the total pressure. Substitution of eqn (3) into eqn (4) leads to:

$$\frac{a_G}{a_G + v} = \frac{p_A}{P} \tag{5a}$$

or

$$a_G = \frac{p_A}{P - p_A} v \tag{5b}$$



s = sorption material
v = carrier gas
a_G and b_G = mass transport of gaseous A and B
a_S and b_S = mass transport of sorbed A and B

Figure 3. Mass flows of various components in the column.

The downward transport velocity a_S of sorbed A in the upper segment of the column is given by

$$a_S = s p_A \sigma_A \tag{6}$$

where σ_A is the sorption coefficient of A.

Similar expressions can be derived for b_G and b_S:

$$b_G = \frac{p_B}{P - p_B} v \tag{7}$$

$$b_S = s p_B \sigma_B \tag{8}$$

From the known quantities v; s; P; σ_A; and a, the values of a_G; a_S; and g may now be calculated with the aid of eqns (2), (5) and (6).

Eqns (2), (5) and (6) may further be combined to give an expression for p_A:

$$p_A = -\frac{a+v-sP\sigma_A}{2s\sigma_A} \pm \left\{\left(\frac{a+v-sP\sigma_A}{2s\sigma_A}\right)^2 + \frac{aP}{s\sigma_A}\right\}^{\frac{1}{2}} \quad (9)$$

The sorption coefficient σ_A for component A at the operating temperature is determined separately, e.g. from the retention volume measured with an analytical column packed with the same sorption material.

Experimental values of p_A, obtained from analysis of the gas phase under conditions of quantitative separation, were in good agreement with values calculated from eqn 9.

Owing to space limitations a discussion on such aspects as the relationship between loading capacity and counter-current velocity, the influence of pressure drop in the separation zone, the recovery of the product in the highest possible concentration in the carrier gas, separation in columns of larger diameter, and a further theoretical treatment of the continuous separation under conditions of elution gas chromatography could not be presented. The continuous separation of mixtures at higher temperatures is under investigation.

Lastly, it must be noted that the definition of chromatography as a method involving stationary (i.e. non-moving) sorption material presents a terminological difficulty. In accordance with this definition, the term chromatography may justly be used for a continuous method in which sorption material is placed in a special tube, so that gas inlet and outlet may be moved as demanded by the conditions of the separation. Such a method is, however, equivalent to the technique described here.

For further information on the process described in this paper, the theses of the author and of Dr B. Firnhaber can be referred to [9, 10].

The author wishes to thank Professor Dr H. Pichler for his continued encouragement and valuable advice during this investigation.

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Discussion

F. Sjenitzer (*prepared contribution*): I should like to make the point that I am rather surprised that in the whole of the paper no mention was made of extractive distillation. Actually, on the third line of page 229 I find the statement, 'However, the special advantage of the continuous separation under conditions of elution gas chromatography lies in the fact that a stable phase with special selectivity for a particular separation may be used. . . .' I should like to remind the author that exactly the same advantages are obtained with extractive distillation executed in an ordinary distillation column. Here the same increased selectivity between components is obtained when a liquid phase is used, the selective properties of which have been modified in a suitable way. In fact, it is well known that the separation between the saturated and unsaturated C_3 and C_4 components which are enumerated in *Table 2* is quite feasible when a suitable selective solvent, such as e.g. acetonitrile, is used. This gives relative volatilities of the component pairs to be separated in the range of 1·4–1·6, so that sharp separation by extractive distillation is quite easy.

I am glad to announce that later on in the discussion my colleague from the Amsterdam Shell Laboratory, Dr Rijnders, will mention a laboratory method where extractive distillation with a stripping gas has been used.

G. W. A. Rijnders: I will try and reach a compromise between the feelings of those who are defenders of gas chromatography and feel deeply against extractive distillation, and those who believe in distillation. In our laboratory we have already used for some time a method first developed by Mr Huppes, which resembles the one described here. Mr Huppes started with the same idea of moving the stationary support, but the disadvantage of this system was the pulverization of the supporting material which occurred. The conclusion which could be drawn was to omit the supporting material, and the result was an ordinary Oldershaw distillation column with a certain number of plates. The solvent was introduced at the top of the column, and inert gas at the bottom. The feed was introduced in the middle. By a proper choice of column temperature and gas velocity the mixture could easily be separated into two fractions; the top and the bottom fraction. If the process is repeated on one of these fractions in a second column, a given component can be obtained in pure form.

H. Schulz: I have prepared an answer to the first remark, which I will read for the sake of simplicity and accuracy.

No doubt there is an analogy between the process described here and extractive distillation, with respect to the increase in selectivity for the separation of two-component mixtures. For this reason the selectivity of the column material was eliminated in the Paper and the separation process was compared with rectification for the same separation factor. In a comparison with extractive distillation it should be noted that for the process described here the introduction of a third selective component does not result in a decrease of the separating efficiency of the counter current. I would guess that in extractive distillation the number of plates per column length would be smaller than the number attainable in normal distillation.

Furthermore practically all liquids and adsorbents used in elution gas chromatography are suitable for the process described here, whereas in extractive distillation only a few of these might be successfully employed; thus the advantage of using selective sorption materials can be utilized particularly in the continuous separation under conditions of elution chromatography.

Regarding the remark by Dr Rijnders: it was said there that the support was omitted and that a normal rectification with a third selective component was again reverted to.

If one wanted to compare these processes, this would only make sense if one had definite data, with percentages for mixture and products. For example, the remark that a certain number of plates was attained there is of little use for a comparison of the two processes.

G. W. A. Rijnders: Did you have any trouble with the pulverization of your support material?

H. Schulz: Undoubtedly it is somewhat difficult to find suitable supports. We have occasionally used Sterchamol coated with dinonyl phthalate and other liquids, and with the prototype equipment we could use this material for at least two or three weeks. However, materials such as, e.g., silica gel coated with 3 per cent dimethylsulpholane proved to be much better. With that support we have had no trouble from pulverization over operating periods of two weeks—I don't think we have made longer single runs than that.

F. Sjenitzer: In reply to Dr Schulz's remark I should like to say that if one has relative volatilities of the order of 1·5 there simply is no difficulty at all in the separation by distillation. Further, if one wants to have a distillation column with a high number of theoretical plates, it is always possible to use empty cylinders (Kuhn columns); and then one will have an enormous number of theoretical plates, at a low capacity, of course; but I understand that low capacity is a general feature of all chromatography.

H. Schulz: In my presentation I have also mentioned the high plate numbers of empty tubes and concentric tube columns, although this was not in the Preprints. Most of the work on these columns was done by Kuhn. I have tried to find definite experimental results, and from a curve by Kuhn I could derive comparable data for this process. I found that the capacity for equal efficiency of the counter current—referred to equal cross section, length, etc.—is about equal; I even think it is a bit higher here. This may be due to the fact that in the concentric tube columns and also in the empty tubes the liquid must flow downward as a film. Then the diffusion in the liquid is less favourable than it should be in our case, where the fixed liquid phase moves uniformly downward, so that the mass transfer is as favourable as it is in gas chromatography. For good mass transport to the liquid phase the thickness of the film should be as uniform as possible.

G. A. P. Tuey: I should like to make the comment which I felt impelled to make earlier in the Symposium in connection with the talk by Dr R. P. W. Scott on continuous gas chromatography (p. 63). This seems once again to be a very inefficient use of the column capacity. A column of 1 cm diameter in 1 hour is putting out, according to the arithmetic I have just done, only 0·2 g of separated material. We can do better than that by batch-wise operation. This only reinforces my suspicion that continuous gas chromatography—if it *is* gas chromatography—is something of a snare and a delusion. Is it not a very elaborate way of attacking a problem which can be solved by orthodox methods—extractive distillation if one wants to work on a very large scale, or batch-wise operation of chromatographic columns?

18

PROCESS CONTROL WITH AUTOMATIC PROCESS GAS CHROMATOGRAPHY

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Process control with automatic gas chromatography

ATTENTION was first drawn some three years ago to the economies which can be achieved through the use of process control by means of gas chromatography in the chemical industry. Thus Fraade[1] reported on the use of a gas chromatograph to control the vaporization process in a depropanizer column. The apparatus had been in use for 1½ years at Phillips Petroleum Company and it was found that the equipment paid for itself every two weeks as a result of increased production, every 6 weeks through improvements in the quality of the products and every 3 months through economies in power. This means that the gas chromatograph pays for itself within a period of 10 days.

Similar results have been obtained elsewhere in the petroleum industry, although the results were not always so satisfactory. In other branches of industrial chemistry we may take as an average that the gas chromatograph used for process control pays for itself within 1 month, when employed at the right place and under the right conditions.

In spite of the great advantages offered by the gas chromatograph, there is considerable reluctance to employ it on any large scale. The object of this communication is to remove these doubts and at the same time to explain what is meant by the 'right place' and the 'right conditions' for the use of the gas chromatograph in process control.

The gas chromatograph provides a large volume of information and is specific. Process control in the chemical industry largely depends on methods which indicate and record mono-dimensional physical conditions such as pressure, temperature, pH, density and viscosity. In only a few cases such values are specific for the material in question, and only when very simple mixtures are involved. Thus, the normal methods of process control only give values which are the sum of the values for the constituents. In practically all cases these values have to be recorded continuously or intermittently with a sampling period of less than 100 seconds.

Process control by gas chromatography differs fundamentally from the methods hitherto employed in two respects. Thus, a positive characteristic of the method is that it shows simultaneous and multiple specificity in the majority of cases. The negative characteristic is represented by the greater sampling period as compared with the other methods. The ability to supply

multiple and absolutely specific values opens the way for completely new possibilities in process control.

An example of a distillation process will be discussed later in which data for several components of a mixture can be simultaneously obtained if the distillation plant is controlled by means of gas chromatography. The relatively large time interval, i.e. the sampling period, between the individual measurements presents certain difficulties and is a disadvantage of the gas chromatograph. The question will be discussed as to how far this property influences the control of processes which are in themselves difficult to control.

Desty [2] has employed specially designed capillary columns and has achieved a speed of analysis which is much greater than that obtained with the usual methods. He was thus able to separate and measure quantitatively 5 components in 1 second. The time interval between the measurements can thus be reduced to seconds in gas chromatography. A more or less continuous supply of data can be obtained by storage of analytical values and by the use of electronic or pneumatic regulation, as in the Taylor system. Although in certain cases the gas chromatograph yields only intermittent data, it should be remembered that the total information supplied is much greater than can be dealt with by a controller or computer.

The majority of manufacturers of process control equipment still design this equipment to provide for a dense sequence of data. The time interval from measurement to measurement, i.e. the sampling period, is only given by the difference of the pure retention times of the fastest and slowest components in the mixture if the continuous carrier gas stream through the column is not interrupted for injection of the sample. The time required for the injection of a sample is mostly much less than the retention time difference and can therefore be neglected.

The difference in the retention times can be kept as small as possible by various methods, cf. Jentzsch and Rödel [3]. Columns giving rapid separation should be employed, and the use of back-flush columns which operate without interruption of the continuous carrier gas stream may be necessary if the gas mixture contains slow components which are of no significance from the point of view of process control. The column should be as short as is compatible with optimum resolving power, this being achieved by selection of the most suitable stationary phase and temperature of separation. The sampling device, detector and recorder should be adapted for use with the column employed.

Programmed temperature gas chromatography should be used in preference to the isothermal method if the time necessary to cool the column is considerably shorter than the time required for the normal isothermal method. In certain countries, programmed temperature gas chromatography is used almost exclusively. Point recorders should be employed with gas chromatographs in order to conform with the usual methods of data recording.

Line recorders are usually unsuitable for recording values of more than two parameters from a gas chromatograph. Instruments for analysis of more than one stream should be provided with colour point recording. Line recorders are practically useless in the plant.

The application of gas chromatography to distillation problems

Distillation problems are still largely investigated by means of simple Engler distillation, analogous to the simplest A.S.T.M. analytical distillation method, and the theoretical Engler distillation method is only seldom employed on account of the time involved in this method.

Kögler[4] has compared results obtained by the Engler distillation method and by means of gas chromatography. These results show that gas chromatography is a particularly useful tool in the control of distillation operations. It is only possible to deal in general terms with the application of gas chromatography in process control of technical distillation processes. Numerous and outstanding examples could be cited for the application in synthetic processes, in purification and other processes.

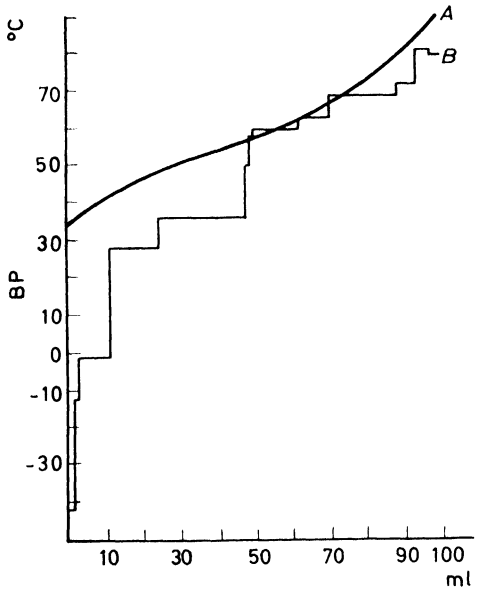


Figure 1. *A*, Engler distillation curve for a hydrocarbon fraction. *B*, theoretical distillation curve (from GC data) corresponding to Engler curve *A*

Figure 1 shows a distillation curve obtained by the Engler method; *Figure 2* shows the actual composition of the individual Engler fractions. It is well known that reliable information concerning the distillation behaviour of a mixture can only be obtained with the aid of the theoretical Engler distillation method, which involves the use of an efficient fractionating column. A comparison of *Figures 1* and *2* leads, however, to the conclusion that the thousands of Engler distillations which are carried out daily are in reality useless. This has been amply demonstrated by Kögler and other workers. It is true, of course, that the Engler distillation method is not employed directly for process control in distillation and rectification on the industrial scale.

A comparison of *Figure 1* with *Figure 2* provides a convincing demonstration of the value of the gas chromatograph in the field of distillation. In addition, the technique offers new potentialities for process control.

The gas chromatograph is particularly useful in cases where the mixtures to be separated are complicated or show non-ideal behaviour and the simple measurement or pressure and temperature is not sufficient. Distillation columns are normally fitted with additional plates which compensate for the effect of the various factors which can influence the composition of the distillate. Thus the heat input, the feed, the composition of the feed and the temperature of the feed may all vary.

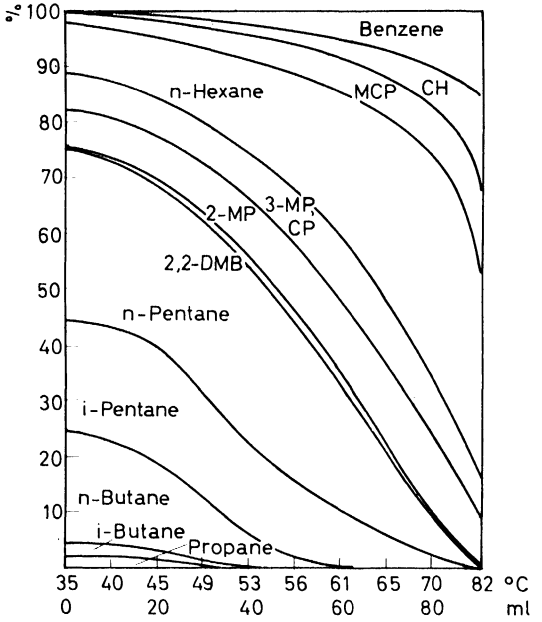


Figure 2. Composition of the individual drops from the Engler distillation of a hydrocarbon fraction, cf. *Figure 1*

In the case of binary mixtures, the relation between the distillation temperature and the composition of the mixture is normally quite simple. In the case of multi-component mixtures, however, this relation is often very complicated, as shown in *Table 1*. In the case of distillation, therefore, process control by means of gas chromatography has two important characteristics. It provides specific data which are largely independent of the degree of complexity of the mixture and can be used to control the heat input and the reflux ratio. Further, it is often possible to employ shorter distillation columns, i.e. columns containing a smaller number of plates. This, in turn, yields a considerable improvement in the space, time and energy yield.

The control of distillation columns is a difficult matter and it is therefore interesting to determine whether gas chromatography, in spite of its fairly

Table 1. Composition of the liquid phase in equilibrium with the vapour phase at constant temperature and pressure

$T = 110{\cdot}5°C$; $p = 760$ mm

3-component system: 3,3,5-trimethylpentane/toluene/phenol

	3,3,5-TMP	*Toluene*	*Phenol*	
a (liquid)	7·1	82·6	10·4	mol. %
b	27·5	8·9	63·6	
c	29·4	41·4	29·1	
d	30·4	14·8	54·8	
e	39·2	18·9	41·9	

Composition of the vapour phase in equilibrium with the liquid phase *a* and *d*:

a (vapour)	14·6	83·2	2·2	
d	79·4	15·9	4·7	

Kogan, W. B., W. M. Fridemann, ed. E. Krell, *Handbuch der Dampf-Flüssigkeits-Gleichgewichte*, p. 441, Deutscher Verlag der Wissenschaften, Berlin, 1961 (Translated from the Russian)

large sampling period, does not render the control so difficult that no practical advantages are achieved.

The dynamic behaviour of distillation columns has been investigated recently by Rijnsdorp and Maareveld[5], who used an analogue computer. They investigated a binary mixture at constant pressure, neglecting the pressure drop over the plates, and obtained useful information where the column shows linear behaviour. Their results showed very good agreement with the results obtained by us, which are given below.

For multi-component mixtures with non-ideal properties it has been shown that calculation of the dynamic behaviour is much too complicated. The behaviour of the column over all the plates can be determined accurately as a function of the various conditions by means of gas chromatography. A single sampling point on any plate provides good information concerning the dynamic behaviour of the column if the analytical values for the composition are recorded rapidly.

The results given below were obtained during an investigation of the dynamic behaviour of a small distillation column. The column had the following dimensions:

Volume of the column	20,300 l.
Number of plates	60 bubble cap plates
Feed input at the 35th plate	850 kg/h
Reflux	1,500 kg/h
Distillate	150 kg/h
Steam consumption	490 kg/h

The sampling point was in the liquid phase at the 45th plate, i.e. 10 plates above the feed inlet. The mixture distilled consisted of 5 components *A* to *E*. The components *B* and *E*, which were low- and high-boiling, respectively, were analysed every 10 minutes.

Figure 3 shows the increase in the concentration of the low-boiling component *B* with time. At t_0, the reflux ratio was altered suddenly to infinity; at the same time the inlet and the outlet were closed and the steam supply reduced, so that the column operated on a closed cycle. The column attained its new stationary state after 100 minutes. The measured step response obtained with the gas chromatograph conformed closely to a calculated 15th order step response with an approximate time constant of 4·5 minutes for each plate.

The curve for the measured step response can be explained most readily if we assume the lag to be between 20 and 30 minutes and the delay time to be approximately 20 minutes. It is further assumed that the real dead time to the 45th plate is less than 5 minutes when a signal produced by variation of the reflux ratio passes from the head of the column over 15 plates to the 45th plate.

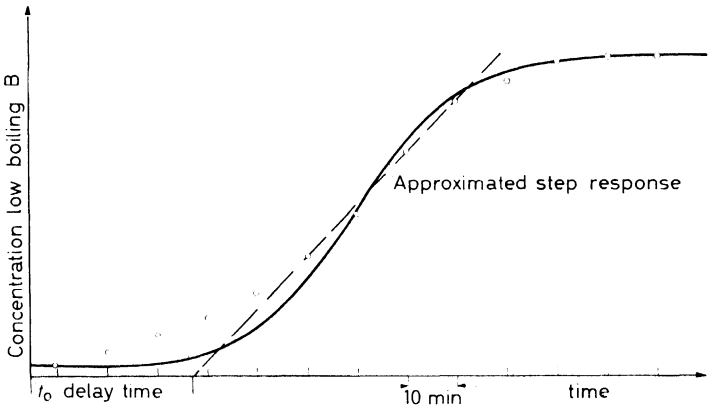


Figure 3. Measured step response and approximate 15th order step response
Real dead time: 4–5 min. Delay time (not real dead time): 20 min. Lag: 20–30 min.
Time constant: 4·5 min for one plate

It was impossible to measure accurately the smallest dead time, as the dead time of the circuit between the sampling point and the gas chromatograph was 3 minutes; and, as the sampling period was 10 minutes, changes in concentration 5 minutes after a change of reflux ratio from 1:10 to 1:infinity could only be determined by chance.

It will be seen from the values for the real dead time, delay time and lag that the sampling period for a process gas chromatograph in the control of distillation should under no circumstances exceed 10 minutes but need not necessarily be less than 3 minutes. Similarly, the actual dead time of the gas chromatograph, measured as the time required for the product to pass from the sampling point through the pump, pressure regulator, filter and vaporizer to the injection device, should not exceed 5 minutes. These conditions are difficult to satisfy without complicated equipment. In some cases the sum of this dead time and the sampling period may interfere with the control process. This occurs when the control instrument is used to regulate the composition

of the feed to the column, and the signal thus obtained, representing a disturbance variable, acts directly upon the controller regulating the distillation process. This method requires sampling periods as small as possible.

Peinke[6] has investigated the influence of periodically operating instruments with fairly large sampling periods on the efficiency of the control process in circuits of different lengths. He has established an approximate formula which applies very well when the lag is not too small, as in the case under discussion. According to this formula, the real dead time is equal to the sum of the real instrument dead time plus the sampling period, divided by 2.

Peinke showed that instruments of this type provide satisfactory control quality in circuits with proportional plus reset controllers.

Processes with characteristics as described are difficult to control and a reduction in the quality of the control may result when temperature and pressure data and signals from the gas chromatographic analyser act simultaneously on the controller. A distillation column fed with high-boiling and highly polar substances showed a surprisingly high reactivity.

Recent investigations into the dynamic behaviour of very large distillation columns by means of gas chromatography have indicated that we must abandon the view that such columns show great inertia. Changes in concentration, with a considerable effect on the distillation behaviour, are transmitted within a few minutes from plate to plate and can be detected within a few minutes over the whole length of the column. Variations in the feed concentration are not always significant in relation to the column volume so that sampling periods of 5–10 minutes are perfectly satisfactory. The position of the sampling point has a decisive effect on the efficiency of the gas chromatograph when used as a controller.

It is impossible to give any general rules concerning the optimum position for the sampling point, as this will vary with the composition of the mixture involved. Certain broad principles can, however, be established. The position of the sampling point will be determined by the nature of the distillation process. Thus, if the offtake is required to be substantially free from high-boiling fractions and the feed concentration is constant, then one sampling point at the top of the column is sufficient. It should be at the highest level at which the high-boiling components can still be detected and yield a satisfactory signal in the control device. The concentration in the column will vary if the heat supply and the temperature of the feed vary. If the sampling point is too close to the feed, then there is the risk that the values obtained will be affected excessively by periodic variations in the column.

The sampling period of the gas chromatograph and the periodic variations referred to may combine together and cause unstable behaviour. Effects of this type should be investigated and their cause eliminated.

We may also consider the case in which maximum yield of the overhead product is required and small variations in the content of the high-boiling impurity are of minor importance. Under these conditions, a second sampling point in the lower quarter of the column will ensure that the concentration of the overhead product does not exceed a given maximum.

A sample should be taken at the feed inlet if the feed shows substantial variations in concentration. Whether or not the signals from this point act only as auxiliary signals or directly will depend on the conditions involved.

The procedure discussed is particularly useful for the control of several distillation units coupled together.

Summarizing, we may say that optimum results are obtained with a sampling period between 10 and 5 minutes for one sampling point or $10/n$–$5/n$ minutes for n sampling points. The dead time of the sample feed lines should not exceed 3–5 minutes. This condition can be readily fulfilled with gases but is difficult to attain with liquids. The following rough approximation can be used to determine the dead time of sample feed lines:

$$t_D = \frac{1}{F}\left(\frac{\pi d^2}{4} \cdot L + V_F + V_D + V_V\right)$$

t_D = dead time in minutes
F = flow in millilitres per minute
d = internal diameter of the line in millimetres
L = length of the line in metres
V_F = internal volume of the filter in millilitres and of the pump in millilitres
V_D = internal volume of the pressure regulator and the separator, etc., in millilitres
V_V = volume of the vaporizer chamber and filter in the vaporizer in millilitres

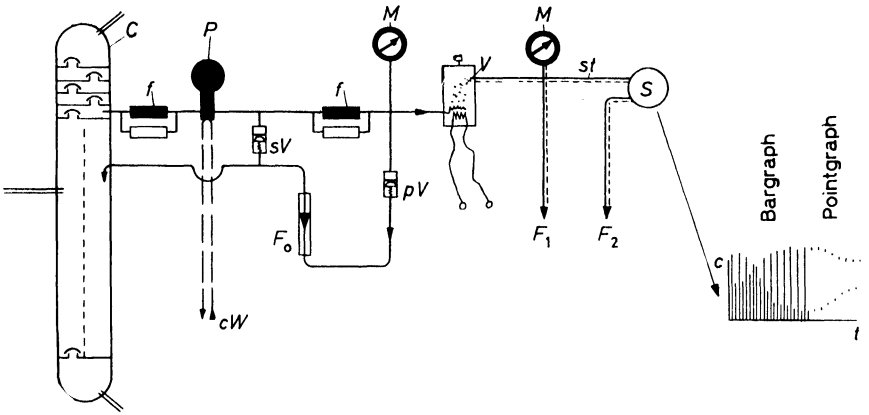


Figure 4. Simplified sample flow diagram
C column, *f* filter, *P* pump, *cW* filtered cooling water, *sV* safety valve (operates above 3·5 atm), *pV* constant pressure regulator (*p* liquid = 1·5 atm const.), F_0 rate of flow (liquid sample) = 3,000 ml/h, F_1 bypass sample flow (vaporized sample) = 20,000 ml/h (vapour), F_2 real sample flow through sampling device = 20,000 ml/h (vapour), *S* sampling device, *V* Consolidated Phillips Vaporizer regulator 38-001 MA, *st* steam-traced sample (vapour) line, *M* manometer

Figure 4 shows a suitable arrangement for sampling substances with boiling points up to 100°C. The vaporized samples pass through an automatic gas sampling loop as used in the Perkin-Elmer Process Fractometer model 184.

The authors wish to express their thanks to Dr T. Ankel, A. Meier, M. Strohmeyer and L. Weber for useful suggestions and discussions.

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Discussion

F. Sjenitzer (*prepared contribution*): In connection with page 234 at the very beginning of the paper, I should like to know whether the very short pay-out times mentioned were the results of using the GLC equipment only for finding better operating conditions, that is, merely as a tool for analysing the process; or whether it was really the result of using it later on as control equipment for the process.

My second question concerns a statement on page 240. Would the authors please give more detailed information, under what conditions changes of flow, composition, pressure or temperature are, as they say, 'transmitted within a few minutes' through 'very large distillation columns'?

R. Kaiser: The very short pay-out times we mentioned in our paper refer to an apparatus which was used to control a process for butane–propane separation. There, both the yield and the quality of the products could be considerably improved.

According to calculations over a period of one year, made by the plant where the work was done, the annual gain amounted to the enormous sum of DM 2½ million. This one can only say; I didn't dare write it down.

Concerning the rapid changes in the distillation column: the column has 60 plates; it was fed in the middle, and the product was taken off at the 43rd plate.

Figure 3 is a plot of the composition of the bottom product. The reflux conditions were suddenly altered at t_0, and after a few minutes we see a change in the composition of the distillate. This 'dead time' is of the order of 5–7 min. Obviously, such a strong disturbance is transmitted immediately through all the plates in the column.

D. Jentzsch: Manufacturers of process chromatographs have been cited so often that a remark from this side may be in order. The reason why so many process chromatographs end with just a tube is really very simple. The users of this equipment can be very secretive about what they want to do with it, and the manufacturer often has no other choice than to let his equipment end with a tube.

On the presentation of data we also have some experience. We can, of course, offer machines which print beautiful symbols in all colours of the rainbow; but cases are also known where the user of the chromatograph cannot even raise the money to buy anything more elegant than the bar graph presentation. Unfortunately, the whole problem of process chromatography is often solved too late, when such nice figures as DM 2½ million savings per year can be presented. More often the buyer is much less easy to convince when the equipment is being sold; certainly money is often saved at the wrong spot.

H. Boer: I have just a few remarks to make. We certainly agree with Dr Kaiser on the usefulness of these gas chromatographs and the short pay-out time and all

you can do with it. I should like to repeat once more what I said in the panel discussion (page 188); that we have devised a computing integrator which presents the true percentages of the components, and we also have a version of this instrument which does it in the way which Dr Kaiser advocates—printing out the data on a printing recorder. That works very well.

There is one more point I want to stress about this apparatus. The difficulty of sampling is greatly diminished, because the instrument normalizes to 100 per cent; or, if you want to omit a certain component, you may have it normalized to any desired percentage; and thus you are more or less independent of the sample size.

R. Kaiser: Let me first say that I fully agree with the remarks by Dr Jentzsch. I also agree with the last remark by Dr Boer, but his first comment is a bit dangerous. That must reach the right ear, and there are so many wrong ears. When you say that percentages must be printed, the manufacturers will be swamped with questions like 'How accurately can you give percentages?'

This is not the crucial question. The important aspect in process gas chromatography is its reproducibility, and the question should be 'How good is the reproducibility?' Whether some value is 17·9 or 17·95 per cent is not important; the trend is a much better indication.

'Sampling Problems' should of course be written with capital letters; there lies the main difficulty in process gas chromatography.

H. Boer: I quite agree with the remarks by Dr Kaiser. I should like to say that the instrument I was talking about has a very good reproducibility, so it is all right in that respect.

SECTION III

APPLICATIONS

Chairmen:

G. SCHAY

C. S. G. PHILLIPS

PANEL DISCUSSION

QUALITATIVE ASPECTS OF GAS CHROMATOGRAPHY

Chairman: J. F. K. HUBER

19

A STATISTICAL INVESTIGATION OF FACTORS AFFECTING COLUMN PERFORMANCE IN THE CHROMATOGRAPHY OF INORGANIC GASES

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THE PRESENT state of chromatographic theory rarely allows the prediction of the best operating conditions for any particular system. The influence of some operating variables on column efficiency is fairly well understood but thermodynamic data are often not available for the calculation of the resolving power of a column. For many commonly used systems, sufficient data are published to allow selection of conditions ensuring adequate performance, without the need for optimization of conditions. For new systems or when the separations obtained are barely adequate, optimum conditions must be experimentally determined. Alteration of each variable independently requires an excessive number of experiments (x^n if n variables are examined at x levels), but similar information on the effect of each variable, together with some information on the effects of the variables upon one another, may be obtained in much less time by the use of a statistical block experiment.

This paper is a report of the application of this technique to the separation of halogen and interhalogen compounds by Kel-F oils (polytrifluoromonochlorethylene). Firstly the experiments were made to determine whether the theory established for conventional columns could be applied to obtain maximum column efficiency, in terms of number of theoretical plates, N. Secondly, the effects of the variables on the separating efficiency, S, of columns, as defined by Purnell[6], was investigated and the results compared with the results for N.

Experimental design and measurements

The column materials for these separations are restricted by chemical considerations to different grades of Kel-F oils dispersed on a support of Kel-F Grade 300 low-density moulding powder. With this limitation the eight parameters listed in *Table 1* were thought to merit investigation at the two levels shown.

Column efficiency for each set of operating conditions was judged in two ways:

1. the number of theoretical plates, calculated according to the formula

$$N = 16\left(\frac{V_R + V_d}{w}\right)^2$$

Table 1

	Factor	*Parameter*	*High level*	*Low level*
Column parameter	*A*	Grade of Kel-F oil	10/200	40
	B	Loading of oil	80%	20%
	C	Mesh size of support	178–211 μ	211–295 μ
	D	Column length	14 ft.	10 ft.
Operating parameter	*E*	Sample size	5 ml at 50 mm Hg	1 ml at 50 mm Hg
	F	Temperature	90°C	60°C
	G	Flow rate of carrier gas	40 ml/min	10 ml/min
	H	Carrier gas	Helium	Nitrogen

2. the separation factor, S, proposed by Purnell, calculated according to the formula

$$S = 16\left(\frac{V_R}{w}\right)^2$$

where V_d is the dead volume, measured as the retention of the air peak
V_R is the retention volume of an eluted component, measured from the air peak
w is the peak width at the base.

The design chosen was a quarter replicate of a two-level factorial experiment outlined by Brownlee[1]. This reduced the 256 possible experiments to the 64 contained in one of the four equivalent blocks selected by application of a standard procedure known as 'confounding unwanted interactions'[2].

Although all the information obtainable from 256 experiments cannot be extracted from a quarter of the total, the use of this method allows the experimenter to decide which information is discarded. In general it is desirable to ensure that any confusion is restricted to high-order interactions. This involves a certain amount of compromise, and the most satisfactory arrangement for an eight factor experiment (factors A–H, *Table 1*) results when the interactions *ABCDE* (i.e. the interaction between *A*,*B*,*C*,*D* and *E*), *ABFGH* and *CDEFGH* are confounded[1].

The required pattern of experiments can be conveniently constructed if each experiment is denoted by a code in which each factor occurring at a high level is represented by a small letter and each factor at a low level omitted. Thus an experiment in which factors *A*,*D* and *F* (*Table 1*) were high and the remaining factors low would be designated *adf*. The experiments to be performed are those with codes containing an even number of letters in common with the confounded interactions, zero being regarded as an even number. For example *ab* has two letters in common with *ABCDE*, *ABFGH* and none in common with *CDEFGH*. This experiment is therefore included. The final distribution of experiments is shown in *Table 2*.

Apparatus and technique

Sixteen chromatographic columns, corresponding to the various combinations of factors *A*–*D* in *Table 1*, were prepared. Kel-F 300 low-density

Table 2. Results for N and S with the various combinations of factors. N result at top; S result below
(Plain type: H = Nitrogen. Bold type: H = Helium)

			A	40								10/200							
			B	20				80				20				80			
			C	211–295		178–211		211–295		178–211		211–295		178–211		211–295		178–211	
			D	10	14	10	14	10	14	10	14	10	14	10	14	10	14	10	14
E	F	G	H																
1	60	10	N_2 or He	377 147			593 255		**282** **172**	**199** **119**			**340** **132**	**213** **88**		347 202			646 346
		40	N_2 or He	**610** **269**			**548** **174**		240 118	229 141			998 226	619 302		**179** **102**			**325** **131**
	90	10	N_2 or He	**529** **195**			**461** **167**		750 383	702 353			748 228	541 197		**241** **111**			**384** **178**
		40	N_2 or He	1262 458			1166 289		**490** **192**	**400** **225**			**1024** **164**	**602** **273**		366 185			762 243
5	60	10	N_2 or He		524 227	353 171		**186** **110**			**227** **182**	**188** **76**			**339** **157**		318 188	239 138	
		40	N_2 or He		**661** **204**	**446** **253**		115 67			276 154	468 200			455 155		**185** **89**	**149** **85**	
	90	10	N_2 or He		**345** **132**	**198** **93**		319 157			601 302	355 136			522 210		**335** **170**	**224** **108**	
		40	N_2 or He		873 198	454 259		**283** **140**			**595** **279**	**468** **162**			**648** **189**		309 111	198 93	

moulding powder was sieved to the required particle size, washed in 5M hydrochloric acid, extracted with Arcton 113 and dried. The Kel-F oils were applied to the supports as solutions in Arcton 113; after evaporation of the solvent and thorough drying the material was packed in ¼ in. nominal bore tubes.

The gas chromatograph used was designed for work with inorganic halides and interhalogen compounds and was similar to the instrument utilizing a katharometer detector and described by Ellis and Iveson[3]. The technique described by these authors was employed, care being taken to maintain anhydrous conditions within the chromatograph. For each experiment the appropriate amount of chlorine was injected into the carrier gas, and the resulting trace on the recorder chart was evaluated. V_d was measured with a small air sample.

Calculation of results

Table 2 shows the results obtained for N and S. These results make possible a calculation of the mean effect of a change from low to high level of a variable and the mean effect of first order interactions, and also allow a decision to be made which effects are significant in comparison with experimental errors. As it is only necessary to calculate significant effects, work is reduced if the significance of effects is estimated first. This is done by a process known as 'analysis of variance'.

Every main factor effect and interaction determined gives rise to a certain variance. The sum of these variances plus the 'residual' variance, which includes that due to all the undetermined causes, i.e. the error, is equal to the total experimental variance. The 'residual' variance may be calculated as the difference between the sum of the known variances and the total variance.

In practice, it is only possible to estimate each variance; these estimates are known as 'sum of squares' and are calculated as follows:

$$\sum \text{Squares due to } A = I_A = \frac{\{\sum(\text{results with } A \text{ 'high'}) - \sum(\text{results with } A \text{ 'low'})\}^2}{\text{No. of observations } (=64)} \quad (1)$$

$$\sum \text{Squares due to interaction } AB = II_{AB} = \frac{\left\{\sum\begin{pmatrix}\text{results for } A \text{ and } B \\ \text{both high or both low}\end{pmatrix} - \sum\begin{pmatrix}\text{results for either} \\ A \text{ or } B \text{ high}\end{pmatrix}\right\}^2}{\text{No. of observations } (=64)} \quad (2)$$

The total sum of squares is given by:

$$\sum \text{all squares} = III = \sum(\text{all results})^2 - \frac{(\sum \text{all results})^2}{\text{No. of observations}} \quad (3)$$

The 'residual' sum of squares is equal to $III - \sum I_A - \sum II_{AB}$.

The results of such calculations are presented in *Table 3*. The mean square of each term may be obtained by division of each sum of squares by its appropriate number of degrees of freedom. A comparison of the ratio of each mean square to that of the residual with tables of variance ratios[4]

Table 3. Analyses of variance of N and S

Source of Variance	N		S	
	Sum of squares	*Confidence level of mean squares*†	*Sum of squares*	*Confidence level of mean squares*†
A	37,976	*	22,877	***
B	728,248	***	10,302	*
C	2,513		6,765	*
D	376,843	***	8,327	*
E	441,726	***	38,514	***
F	435,765	***	22,500	***
G	222,902	***	1,406	
H	305,394	***	47,118	***
AB	535		743	
AC	2,438		420	
AD	14,732		552	
AE	4,778		196	
AF	43,073	*	13,168	**
AG	1,805		689	
AH	1,671		462	
BC	124,521	***	3,938	
BD	709		18,023	**
BE	37,349	*	116	
BF	1,947		5,112	
BG	485,635	***	64,262	***
BH	14,250		315	
CD	6,663		1,369	
CE	2,162		1,089	
CF	93		3	
CG	13,139		60	
CH	2,197		144	
DE	819		7,014	*
DF	10,790		352	
DG	3,953		27,473	***
DH	9,096		240	
EF	67,925	**	6,280	*
EG	20,916		298	
EH	107,011	**	17,030	**
FG	35,768		2,256	
FH	15,037		1,702	
GH	66,758	*	21,830	***
Residual	240,805		37,422	
Total	3,886,828		390,367	

Confidence levels: *** = 99·9 per cent; ** = 99·0 per cent; * = 95 per cent.

† Mean squares values are equal to sum of squares, divided by number of degrees of freedom. All sources of variance have one degree of freedom, except the residual, which has 27. Total number of degrees of freedom is 63 (number of experiments − 1).

affords an estimate of the confidence of each result, the confidence representing the chance that a variance of a particular size represents a real effect on the performance of the column.

The mean values of N and S at each level of each significant factor can then be calculated as in *Table 4*, e.g.

$$\text{Mean for } A \text{ high} = \frac{\sum \text{All results with } A \text{ high}}{32}, \text{ etc.}$$

Table 4. Means for main effects

		N		
*A**	40 oil	478	10/200 oil	430
*B****	20%	560	80%	347
C	211–295 μ	460	178–211 μ	448
*D****	10 ft.	377	14 ft.	530
*E****	1 ml	537	5 ml	371
*F****	60°	371	90°	536
*G****	10 ml/min	395	40 ml/min	513
*H****	N_2	523	He	385
		S		
*A****	40 oil	206	10/200 oil	168
*B**	20%	200	80%	174
*C**	211–295 μ	177	178–211 μ	197
*D**	10 ft.	175	14 ft.	198
*E****	1 ml	211	5 ml	162
*F****	60°	168	90°	206
G	10 ml/min	182	40 ml/min	192
*H****	N_2	214	He	160

Precision

Confidence levels are indicated as in *Table 3*.

	N	*S*
Main effects: 95 per cent confidence level for mean 32 results	34	14
Idem for difference of two such means	48	20

Similarly, means for significant interactions can be calculated as in *Tables 5* and *6*.

It should be emphasized that the change in the mean observed for a main effect is an *average* value and the interactions may show considerable differences not disclosed by the means.

For example, the main effect means indicate that optimum values of *B* and *G* are 20 per cent and 40 ml/min. The *BG* interaction in *Table 5* shows that at 80 per cent loading the optimum flow rate is 10 ml/min, but on average, because of the very large increase for the 20 per cent level, the optimum flow is 40 ml/min. We have denoted this effect as a 'reversing' interaction.

Many of the interactions, however, show a simple 'augmenting' effect, such as interaction *EF* in *Table 5*.

Discussion of results

Correlation of the effects on N with theory[5]

The effects of column length *D* and sample size *E* are those expected from theory: *N* is proportional to column length and a small sample volume is preferred. Likewise the effects of loading *B* and carrier gas *H* follow the usually observed pattern, with optimum performance at 20 per cent loading and with nitrogen carrier gas. The interactions in which these main effects occur,

Table 5. First order interactions affecting *N*

*AF**		*A*		
	F	40	10/200	
	60°	367	376	+9
	90°	589	483	−106
		+222	+107	

*BC****		*B*		
	C	20%	80%	
	211–295 μ	611	309	−302
	178–211 μ	510	385	−125
		−101	+76	

*BE**		*B*		
	E	20%	80%	
	1 ml	664	409	−255
	5 ml	456	285	−171
		−208	−124	

*BG****		*B*		
	G	20%	80%	
	10 ml/min	414	375	−39
	40 ml/min	706	319	−387
		+292	−56	

*EF***		*E*		
	F	1 ml	5 ml	
	60°	422	321	−101
	90°	652	420	−232
		+230	+99	

*EH***		*E*		
	H	1 ml	5 ml	
	N_2	647	399	−248
	He	429	342	−85
		−220	−57	

*GH**		*G*		
	H	10 ml/min	40 ml/min	
	N_2	496	549	+53
	He	293	476	+183
		−203	−73	

Precision

Confidence levels are indicated as in *Table 3*.

First order interactions for *N*:

95 per cent confidence level for mean of 16 results = 48

Idem for difference of two such means = 68

Table 6. First order interactions affecting *S*

*AF****

	A		
F	40	10/200	
60°	172	164	−8
90°	239	172	−67
	+67	+8	

*BD****

	B		
D	20%	80%	
10 ft	205	146	−59
14 ft	194	202	+8
	−11	+56	

*BG****

	B		
G	20%	80%	
10 ml/min	163	201	+38
40 ml/min	236	147	−89
	+73	−54	

*DE**

	D		
E	10 ft.	14 ft.	
1 ml	210	206	−4
5 ml	141	184	+43
	−69	−22	

*DG****

	D		
G	10 ft.	14 ft.	
10 ml/min	150	214	+64
40 ml/min	201	182	−19
	+51	−32	

*EF**

	E		
F	1 ml	5 ml	
60°	183	154	−29
90°	240	171	−69
	+57	+17	

*EH***

	E		
H	1 ml	5 ml	
N_2	255	173	−82
He	168	152	−16
	−87	−21	

*GH****

	G		
H	10 ml/min	40 ml/min	
N_2	228	200	−28
He	137	183	+46
	−91	−17	

Precision

Confidence levels are indicated as in *Table 3*.

First order interactions for *S*:

95 per cent confidence level for mean of 16 results = 18

Idem for difference of two such means = 26

EF, *EH*, *BC*, *BE*, *BG* and *GH*, are all simple augmenting interactions and do not indicate any exceptions to the main effects (*Tables 4* and *5*).

Particle size *C* and flow rate *G* have anomalous effects. The absence of a main effect for *C* implies that in general, altering *C* may equally well improve or worsen column performance. The existence of an interaction with loading *B*, however, indicates that at 20 per cent loading better column performance is obtained with 211–295 μ material, whereas at 80 per cent loading better performance is obtained with 178–211 μ material. This divergence from theory is not surprising when it is considered that the support is chemically the same as the liquid phase and cannot be regarded (as assumed in the theory) as an inert particle surrounded by a film of stationary phase.

The main effect of flow rate *G*, namely that 40 ml/min gives higher values of *N*, is modified when considered with the interactions *GH* and *BG*. These show that improved performance can only be expected if helium is used as carrier gas and also if a 20 per cent loading is employed.

The effects of the two factors stationary phase *A* and temperature *F* are not predictable. Experimentally, 90° is preferable to 60°. At the lower temperature there is no preferred choice between the oils, but at 90° the 40 oil is markedly preferable. There would appear therefore to be a correlation with the oil viscosity, which would increase the interdiffusion coefficient in the liquid phase to give better column performance at the higher temperature.

In general the results indicate close agreement with theory, the major exception being the unusual effects of particle size.

Correlation between N and S

There is qualitative agreement on the effect of sample size *E*, temperature *F* and carrier gas *H* in both systems. The oil *A* can also be included with these parameters though the preference for the 40 oil is not so great in the *N* experiments. Consideration of the interactions involving these variables does not disclose any exceptions to the trends of the main effects.

With the variables loading *B* and column length *D*, although the main effects appear to follow the same trends, considerable differences are seen if the effects are considered in conjunction with the first order interactions *BC*, *GD* and *ED*, which only occur in measurements of *S*.

Flow rate *G* and particle size *C* show differences both in the main effects and when their interactions are considered.

Loading B

20 per cent loading results in the higher value of *N*, irrespective of the *BE* and *BG* interactions. For *S* the interactions *BD* and *BG* indicate that there are exceptions to this preference; for when column length is 14 ft., or when the flow rate is 10 ml/min, there is no significant difference between the two loadings.

Particle size C

For *N*, there is a preference for coarse particles when the loading is 20 per cent, but the finer particles are better at 80 per cent. The overall effect is negligible. For *S*, the overall effect indicates that finer particles are preferable in all cases.

Column length D

The difference between the effects of column length on N and S is the most surprising of all, as well as being the most complex. There is a direct proportionality between length and N for all combinations of other factors. In the case of S, however, there is only a small overall effect of length, and interactions with loading B, sample size E and flow rate G are observed. For 20 per cent loading (BD), 1 ml sample size (DE) and 40 ml/min flow rate, (DG) the improvement in performance with change from 10 to 14 ft. column length is much smaller than for other values of the above variables. This does not necessarily imply that with the above conditions it does not matter which length is used, but rather that the information available is not sufficient for selection of an unequivocable 'best column' where these factors are concerned. The unexpected complexity of the problem indicates, however, that where S measurements are concerned it is important to consider the effect of increasing column length on dead volume as well as on peak shape.

Flow rate G

Again there is a complex dependence of the flow rate effect on the value of other parameters. For both N and S, the interactions with loading B and carrier gas H show that the optimum flow rate depends to some extent on the value of these variables. For S, moreover, an interaction with column length DG indicates that the improvement with high flow is much greater for a 10 ft. column than for a 14 ft. column.

The complexity of these interactions is again reflected in confidence of the main effect: for N, 40 ml/min is the predominant main effect, but for S no preference exists when only mean main effects are considered.

Conclusions

Measurement of N shows that our system fits in with the established theory in most respects. The main exception to this is in the influence of particle size, which is found to depend on the loading of the stationary phase.

The analyses for N and S show a rough correlation but there are wide divergences. In particular, the effect of column length on S is very complex in comparison with the simple relationship found for N. This result is in accord with others obtained previously in our laboratory.

The statistical approach has provided a wealth of detail on this system and has brought out several complexities which were completely unexpected and could easily have been overlooked in any superficial examination. It indicates very forcefully that further effort may best be devoted to resolving the complexities of the interactions of column length and flow rate.

We are grateful to the Managing Director of the Production Group of the United Kingdom Atomic Energy Authority for permission to publish this paper.

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DISCUSSION

Authors' Additional Comments

The experiments previously described give a measure of the efficiency which can be obtained from a given column used under defined conditions. To define the efficiency which is required for a particular separation, further experiments must be made in which S_R, the value of S required when the two gases are just separated, is determined. If the ratio of the adjusted retention times of these two gases is α, then $S_R = 36(\alpha/\alpha - 1)^2$ (Reference 6). This term then provides a measure by which the results of the foregoing experiment may be assessed in relation to any particular analysis.

A block experiment was performed on the separation of chlorine and chlorine trifluoride, to determine the variation of S_R. The four factors investigated were grade of oil, loading, temperature, and flow rate, as these were expected to have the greatest influence on S_R. They were investigated over the same range as previously, the other four factors being kept constant—column length = 10 ft.; particle size = 178–211 μ; sample size = 1 ml and carrier gas = nitrogen. The results are given in *Table 7*.

Table 7. The dependence of S_R on column and operating parameters

Flow	*Tempera-ture*	*Oil* = 40		*Oil* = 10/200	
		Loading 20 per cent	*Loading 80 per cent*	*Loading 20 per cent*	*Loading 80 per cent*
10	60	210	225	184	365
	90	178	304	189	378
40	60	312	273	293	200
	90	287	320	426	263

These results indicate that the least efficiency is required when a column loaded with 20 per cent of grade 40 oil is used with a flow of 10 ml/min. Comparison with *Table 4* shows that, with the exception of the flow rate (which in any case is without influence on S), these values give a high value S. Combining the results of the two experiments, and selecting preferred values of the other variables by reference to *Tables 4* and *6*, one concludes that the following column and operating parameters would give good results:

Oil—40 grade
Loading—20 per cent
Mesh size of support—178–211 μ
Column length—14 ft.
Sample size—1 ml
Temperature—90°C
Flow rate of carrier gas—10 ml/min
Carrier gas—nitrogen

Because of the unexpected absence of any effect of particle size on N (*Table 4*), a brief examination of the particle size distribution of the two grades of Kel-F powder has been made, and the results are shown in *Table 8*.

Table 8. Particle size distribution of solid support

Nominal particle size	*Weight percentage found*				
	< 30 μ	30–178 μ	178–211 μ	211–295 μ	295–400 μ
211–295 μ	2	5	16	52	25
178–211 μ	0	10	81	9	0

The much wider spread of particle sizes found in the coarse material undoubtedly has some bearing on the unexpected effect of particle size on N, though this point has not been followed up further.

L. Rohrschneider: In the statistical investigation on two levels an error can be made, when the curve is convex to the horizontal axis. One could, for instance, measure two points on either side of the minimum which would have the same vertical co-ordinate. Thus no effect would be noted on the two levels, although the parameter does affect the quantity measured, e.g. the separation efficiency.

T. R. Phillips: I agree with Dr Rohrschneider that the method of analysis described is only applicable when the quantity measured is a continuously increasing or decreasing function of each variable parameter. If this is not the case, one must either take several values of the parameter, or restrict the range of the values to a region where it is known that no discontinuities occur. The latter method was adopted with the flow rate parameter in our experiments, the values selected being greater than that giving a minimum value for HETP in the HETP-flow rate curve.

A. Goldup: This may well account for the difficulty you are having with the lack of correlation between linear gas velocity and particle size. When you have a very small particle size you will find that the optimum linear gas velocity goes down to very low values. If you have assumed this to be fairly high this may lead to a certain amount of trouble.

T. R. Phillips: On a completely different field, now that I have seen Dr Goldup stand up, I would heartily endorse his use of S, rather than N, to measure column efficiencies; because experiment has shown that, although we might get beautifully sharp peaks, the columns need not necessarily separate anything at all.

M. A. Khan: Regarding factor S, I am not happy about the use of the simple equation which was derived by Dr Purnell on the assumption that the standard deviation of one peak is equal to the standard deviation of the other peak. Obviously, a substance which remains in the column for a longer period of time will suffer more axial broadening, and this is borne out by the fact that the standard deviation (σ), when plotted against the retention time (t_R), gives a straight line in most cases. The proportionality constant between the two quantities is $\sqrt{N}$, where N is the number of theoretical plates. The use of the assumption $\sigma_1 = \sigma_2$, instead of $N_1 = N_2$, can make a difference of a factor of 10 to 100 in the value of the minimum number of theoretical plates (N_{min}) required to separate the two peaks, depending on the value of the relative volatility factor (α).

A. Goldup: What I am talking about is that you wait 20 minutes for one peak to come out, and that the second peak comes out in 21 minutes. There is only a small fractional increase in the peak width. Frankly, I cannot see where you are getting this difference from 10 to 100.

M. A. Khan: If you work it out properly for the case when one peak comes out after 20 minutes and the other after 21 minutes, you will notice the difference in calculations. It is a question of getting the correct formula. You cannot really argue that this peak is coming out after so many seconds and the other one coming out after so many seconds, etc. I am afraid the minimum number of plates required

to achieve a given separation is not linearly related to the relative volatility factor (α). I would again stress the use of a correct expression. You cannot draw a conclusion for any particular case as such. As I said already, the standard deviation is proportional to the retention time, and the constant of proportionality between the two is the square root of the number of theoretical plates. Therefore, it would be more advisable to put $N_1 = N_2$, rather than $\sigma_1 = \sigma_2$. I have derived a different expression for the calculation of N_{min} on the basis of the assumption $N_1 = N_2$, and this work is published in *Laboratory Practice* (*1961-2*)—a Journal which unfortunately has not a wide circulation among gas chromatographers. In fact, I discussed this business of separation factor with Dr Purnell some time ago. Anybody interested in the correct use of the separation factor is recommended to consult the articles I published in *Laboratory Practice*.

T. R. Phillips: Could Dr Khan perhaps publish in more widely published journals in the future?

A. Goldup: I think I agree with Dr Khan's comment on the fact that in the derivation of S we do assume that the two peaks have the same width, but in practice we generally are dealing with peaks which have separation factors very close to unity. These peaks come out of the column very close together, and the actual difference in peak width is extremely small. I think that, practically speaking, you can make the assumption that they have same width. By doing that, you certainly get a very simple formula of a few terms. I should like to ask Dr Khan how many terms there are in his equation.

M. A. Khan: It is not a very complicated expression I have derived. The expression reads:

$$N_{min} = 9\left[1+\frac{2}{\alpha-1}\left(1+\frac{V_G}{V_R}\right)\right]^2 \qquad (1)$$

whereas Dr Purnell[7] derives:

$$N_{min} = 36\left[\frac{\alpha}{\alpha-1}\left(1+\frac{V_G}{V_R}\right)\right]^2 \qquad (2)$$

where V_G is the free or dead volume of the column and V_R is the true retention volume.

I leave it to you to make calculations for the special case you were mentioning, or for the three different cases which may arise in packed or capillary columns, viz:

$$\frac{V_R}{V_G} \geqslant 1, \quad \frac{V_R}{V_G} \approx 1 \quad \text{and} \quad \frac{V_R}{V_G} < 1$$

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DETERMINATION OF SEPARATION FACTORS FROM UNRESOLVED TWO-COMPONENT CHROMATOGRAPHIC PEAKS

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A method has been developed for the determination of separation factors from unresolved two-component peaks.

The only experimental data required are the concentrations of the two components in two fractions of the emerging combined peak.

By utilizing the Gaussian distribution function which closely approximates part or all of the experimental chromatogram one may calculate the separation factor for symmetric as well as asymmetric peaks. A special case where the chromatogram has a very sharp front and a 'normal' tail is also considered.

The method has been applied to a study of nitrogen isotope enrichment by gas–liquid chromatography. The necessary isotope ratio data were obtained by mass spectrometry. A numerical example based on this work is given in an Appendix.

IN ADDITION to the ever-widening application to chemical analysis and kinetic studies, gas chromatography is now being used as a tool for the determination of data for engineering purposes, e.g. for extractive distillation.

The use of extractive distillation requires a knowledge of vapour–liquid equilibria for ternary and multi-component systems. Such data are scarce, owing to the tedious and complex experimental procedures involved. Gas chromatography has proved to be a simple experimental technique capable of providing the desired data.

Remarkable progress has been achieved in the field of gas chromatography in recent years, and extremely efficient columns producing a high degree of separation are known for many applications. Nevertheless there are still many cases where complete resolution is unobtainable. The extremely difficult separation of nitrogen isotopes may be cited as an example. Here, the two components fail to emerge as separate peaks. Although complete separation is still unobtainable with the present equipment and know-how it is important to evaluate the separation factor of the system, not only for the purpose of comparing results with other existing methods of isotope separation but also for obtaining basic data for future large-scale design and operation.

Procedures for determination of separation factors by gas chromatography

The rate of travel of a component through a chromatographic column is a function of its vapour pressure over the partitioning liquid. The following relations exist between the retention volume V_R, the partition coefficient K, and the separation factor α:

$$V_n = V_R - V_g = KV_L \tag{1}$$

where V_n is the net retention volume, V_g is the dead volume of the column and V_L is the volume of liquid.

Also:

$$\alpha = \frac{V_2}{V_1} = \frac{K_2}{K_1} = \frac{P_1^0\gamma_1}{P_2^0\gamma_2} \tag{2}$$

where P_1^0 and P_2^0 are the vapour pressures of the pure components and γ_1 and γ_2 their activity coefficients. Thus α values are usually determined from the ratios of the corrected retention volumes (or retention times). This standard procedure cannot be applied when the two components emerge as a combined peak, since the value of V_2 cannot be measured.

In a recent publication Grant and Vaughan[1] describe a peak interference method for the analysis of close-boiling isomers. The relationship between resolution and relative retention volume for the two isomers is investigated by addition of a third component. It is assumed that each component has an ideal Gaussian distribution and that the three components have identical standard deviations. It should be noted, however, that these authors calculate the relative retention volume, i.e. the relative volatility, directly from the ratio P_1^0/P_2^0, ignoring the activity coefficient ratio. This limits the applicability of the method and makes it practically useless when the vapour pressure ratio is almost unity, as is the case with isotopes.

For mixtures of radioactive isotopes, where point values of concentrations can be determined, Glueckauf[2] has proposed an elegant procedure. If the chromatogram is assumed to represent an ideal Gaussian distribution, the separation factor can be calculated for columns with a large number of theoretical plates from the following equation:

$$\ln \frac{y_1/y_2}{Y_{01}/Y_{02}} = n\lambda \frac{\bar{V} - v}{(\bar{V}v)^{\frac{1}{2}}} \tag{3}$$

Y_{01} and Y_{02} represent the original concentrations of the light resp. heavy isotopes; y_1 and y_2 are the concentrations of the isotopes at volume v; $\bar{V}$ is the geometric mean of the corrected retention volumes and $\lambda = \alpha - 1$.

In this paper a method is proposed for the determination of separation factors for non-radioactive isotopes emerging from the chromatographic column as a combined peak, corresponding to the limited separation achieved. The method is applicable to symmetrical as well as asymmetrical peaks.

Technique and apparatus used to obtain basic data

For the application of our method the concentrations of the isotopes in the original mixture and in at least two fractions of the emerging sample must be known. Suitable equipment has been developed to collect emerging

fractions of the sample[3,4,5]. It was expected that two isotopes, whose relative volatility P_1^0/P_2^0 is quite close to unity, would emerge as a combined peak, with the heavy isotope concentrated at the tail. The signal coming from a thermal conductivity cell is used to trigger a mechanism by which the desired fractions of the peak are directed into separate traps. When the components have left the column, a new sample is automatically introduced. Isotope ratios in the collected fractions are then determined with a mass spectrograph. *Figure 1a* shows the combined peak and the point of fractionation or cut point.

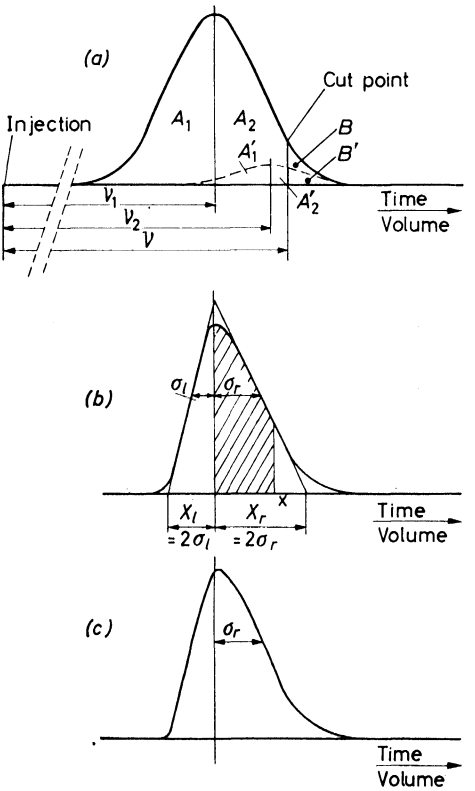


Figure 1. Unresolved two-component peaks: (*a*) Schematic diagram and nomenclature; (*b*) symmetric peak composed of two halves of Gaussian curves; (*c*) asymmetric peak composed of a triangle and one half of a Gaussian curve

General considerations and underlying assumptions

Accurate evaluation of separation factors by this method largely depends on the proper determination of peak area integrals. This may be done either by direct measurement or by integration of a suitable mathematical function representing the distribution curve. Many chromatograms can be represented by the well-known error function; we used this function whenever possible.

The method is based on the following six assumptions:

1. Carrier gas flow is constant during an experiment, so that the volume of gas passed is proportional to distance on the time axis of the chromatogram.
2. The area under a curve, beyond a distance of six standard deviations from the normal, may be neglected.
3. The area of a peak of two unresolved components is proportional to the sum of the masses of these components.
4. Peaks of isotopes are geometrically similar.
5. The distribution curves of isotopes have the same standard deviation.

As isotopes behave identically except for their partition coefficients, assumptions 3–5 are certainly justified.

One additional assumption has been made:

6. When the mass ratio of the heavy to light component is very small, as is the case with nitrogen isotopes in their natural abundance, the effect of the minor component on the shape of the experimentally recorded curve will be within the limit of experimental error (of peak width and height measurement) and may be neglected.

However, where assumption (6) does not hold a correction for the interference of the overlapping peaks can be made. A method for the determination of the true area of partially resolved chromatographic peaks is given by Bartlet and Smith[6].

Calculation of separation factors

Symmetrical peaks

When the peaks are symmetrical, each approaching a Gaussian distribution, it may be assumed that the distribution curves of both isotopes are symmetrical, with a distance $V_1 - V_2$ between their centres.

The equation for the area under the normal distribution curve is:

$$A\Big|_{-\infty}^{+\infty} = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{+\infty} e^{-t^2/2}\,dt = 1 \tag{4}$$

$t = x/\sigma$ is the normalized distance from the centre of the distribution curve, V_n, where x is the distance measured between the centre axis and a point v, on the curve. The standard deviation is σ. Thus

$$t = \frac{x}{\sigma} = \frac{v - V_n}{\sigma} \tag{5}$$

From assumption 2, the injection point may be set at $-\infty$. Hence A_1, the area under the normal curve between the injection point and the centre (or point of maximum concentration) V_1, is given by

$$A_1 = A\Big|_{-\infty}^{0} = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{0} \exp\left(\frac{-t^2}{2}\right) dt = 0{\cdot}5 \tag{6}$$

similarly, A_2, the area under the curve defined between the centre V_1 and cut point V, is

$$A_2 = A\Big|_{0}^{V} = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{0}^{V} \exp\left(\frac{-t^2}{2}\right) dt \tag{7}$$

and B, the area defined between cut point and $+\infty$ is

$$B = A\Big|_V^{+\infty} = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_V^{+\infty} \exp\left(\frac{-t^2}{2}\right) dt \tag{8}$$

The mass m_1 of the heavy isotope in the first fraction of the peak (areas A_1+A_2) is

$$m_1 = Y_1(A_1+A_2) = Y_1(0{\cdot}5+A_2) \tag{9}$$

The mass m_2 of the heavy isotope in the second fraction of the peak (area B) is then

$$m_2 = Y_2B = Y_2(0{\cdot}5-A_2) \tag{10}$$

The sum m_1+m_2 gives the total mass of the heavy isotope in the peak. Had this mass been registered separately, the area under its normalized curve would have been equal to unity (eqn 4). This curve is also cut at V into two areas. The area B' (beyond V) represents the mass m_2 of the heavy isotope in the fraction beyond the cut point.

$$B' = A'\Big|_V^{+\infty} = \frac{m_2}{m_1+m_2} = \frac{Y_2B}{Y_2B+Y_1(A_1+A_2)} \tag{11}$$

or:

$$B' = \frac{1}{1+\dfrac{Y_1(0{\cdot}5+A_2)}{Y_2(0{\cdot}5-A_2)}} \tag{11a}$$

similarly:

$$A'_1+A'_2 = A'\Big|_{-\infty}^{V} = \frac{1}{1+\dfrac{Y_2(0{\cdot}5-A_2)}{Y_1(0{\cdot}5+A_2)}} \tag{12}$$

Error function tables give the areas under the normal curves:

$$A_2 = A\Big|_0^V = \operatorname{erf}\tau = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_0^{\tau} \exp\left(\frac{-t^2}{2}\right) dt \tag{13}$$

$$A'_2 = A'\Big|_0^V = \operatorname{erf}\tau' = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_0^{\tau'} \exp\left(\frac{-t^2}{2}\right) dt \tag{14}$$

Here τ and τ' are defined as:

$$\tau = \frac{V-V_1}{\sigma}; \qquad \tau' = \frac{V-V_2}{\sigma}$$

Thus, eqns (8) and (11) can be written as

$$B = A\Big|_V^{+\infty} = A\Big|_0^{+\infty} - A\Big|_0^V = 0{\cdot}5-\operatorname{erf}\tau \tag{15}$$

$$B' = A'\Big|_V^{\infty} = A'\Big|_0^{+\infty} - A'\Big|_0^V = 0{\cdot}5-\operatorname{erf}\tau' \tag{16}$$

It should be noted that B and B' are areas under normalized curves. Eqns (15) and (16) can be rearranged:

$$\text{erf}\,\tau = 0{\cdot}5 - B = A_2 \tag{17}$$

$$\text{erf}\,\tau' = 0{\cdot}5 - B' = A'_2 \tag{18}$$

The separation factor can now be obtained as follows:

From the actual chromatogram, where V is the experimentally known cut point, $x = V - V_n$, σ and τ are determined. Area A_2 is then calculated according to eqn (13).

Area A'_2 is calculated by eqns (11a) and (18) and the value of τ' is read from the tables. Since σ is identical for both isotopes (assumption 5) the difference $\tau - \tau'$, when reconverted for the actual peaks by eqn (5), gives the distance between the centres of the peaks, $V_2 - V_1$. Finally, V_1 can be measured directly so that the separation factor α may be obtained from the equation $\alpha = V_2/V_1$.

Calculation of separation factors for unsymmetrical peaks

In many cases a chromatographic peak may be approximated by one half each of two Gaussian curves with the same height but with different standard deviations (*Figure 1b*). For these peaks the tangents at the inflection points intersect the base line at points X_1 and X_r, each at distances of twice the corresponding standard deviations from the centre of the peak, i.e. $X_l = 2\sigma_l$ and $X_r = 2\sigma_r$.

The width W of the distribution curve is thus:

$$W = X_l + X_r = 2\sigma_l + 2\sigma_r \tag{19}$$

The height h_x at a point x of a Gaussian curve is given by:

$$h_x = H \exp\left(\frac{-x^2}{2\sigma^2}\right) \tag{20}$$

At the inflection point $x = \sigma$, so that $t = 1$ and

$$h_\sigma = H \exp\left(-\tfrac{1}{2}\right) = 0{\cdot}606\,H \tag{20a}$$

In *Figure 1b*, the area under the curve between the centre and a point x_r on the curve to the right of the centre is given by:

$$A\Big|_0^{x_r} = \int_0^{x_r} H \exp\left(\frac{-x_r^2}{2\sigma_r^2}\right) \mathrm{d}x_r = H\sigma_r \int_0^{x_r} \exp\left(-t_r^2/2\right) \mathrm{d}t_r \tag{21}$$

where $$t_r = \frac{x_r}{\sigma_r}$$

When x_r has the value $$x_r = X = V - V_1$$

we can write $$\tau_r = \frac{X}{\sigma_r} = \frac{V - V_1}{\sigma_r}$$

$$A\Big|_0^{x_r} = \int_0^{x_r} \exp\left(\frac{-x_r^2}{2\sigma_r^2}\right) \mathrm{d}x_r = H\sigma_r \int_0^{\tau_r} \exp\left(\frac{-t_r^2}{2}\right) \mathrm{d}t_r \tag{21a}$$

In order that standard tables of error functions may be used, eqn (21a) is written as follows:

$$A\Big|_0^{x_r} = A_2 = H\sigma_r(2\pi)^{\frac{1}{2}} \operatorname{erf} \tau_r \tag{22}$$

The area under the left-hand side of the curve between a point $-x_1$ and the centre is

$$A\Big|_{x_l}^{0} = H\sigma_l(2\pi)^{\frac{1}{2}} \operatorname{erf} t_l; \quad A\Big|_{-\infty}^{0} = A_1 = 0{\cdot}5\, H\sigma_l(2\pi)^{\frac{1}{2}} \tag{23}$$

where

$$t_l = \frac{-x_l}{\sigma_l}$$

Because of the geometrical similarity between the peaks of the light and heavy isotopes (assumption 4), areas to the right and left of the centre V_2 of the minor peak can similarly be expressed as

$$A'\Big|_0^{x_r} = A'_2 = H'\sigma_r(2\pi)^{\frac{1}{2}} \operatorname{erf} \tau'_r \tag{24}$$

$$A'\Big|_{-x_l}^{0} = H'\sigma_l(2\pi)^{\frac{1}{2}} \operatorname{erf} t'_l; \quad A'\Big|_{-\infty}^{0} = A'_1 = 0{\cdot}5\, H'\sigma_l(2\pi)^{\frac{1}{2}} \tag{25}$$

and

$$B = A\Big|_0^{+\infty} - A_2 = H\sigma_r(2\pi)^{\frac{1}{2}}(0{\cdot}5 - \operatorname{erf} \tau_r) \tag{26}$$

$$B' = A'\Big|_0^{+\infty} - A'_2 = H'\sigma_r(2\pi)^{\frac{1}{2}}(0{\cdot}5 - \operatorname{erf} \tau'_r) \tag{27}$$

The area corresponding to the heavy isotope is given by:

$$\begin{aligned} \sum A' &= A'_1 + A'_2 + B' = Y_1(A_1 + A_2) + Y_2 B \\ &= Y_1 H(2\pi)^{\frac{1}{2}}(0{\cdot}5\sigma_l + \sigma_r \operatorname{erf} \tau_r) + Y_2\sigma_r H(2\pi)^{\frac{1}{2}}(0{\cdot}5 - \operatorname{erf} \tau_2) \end{aligned} \tag{28}$$

and also from eqns (24), (25) and (27)

$$\sum A' = 0{\cdot}5\, H'(2\pi)^{\frac{1}{2}}(\sigma_l + \sigma_r) \tag{29}$$

The values H, Y_1, Y_2, σ_l, σ_r, and $\operatorname{erf} \tau_r$ can either be directly measured or may be calculated from the experimental chromatogram. Elimination of $\sum A'$ from eqns (28) and (29) leads to an expression from which H' may be calculated. The value of B' can be obtained from eqn (28) and inserted into eqn (27), together with the value for H', to yield an expression from which $\operatorname{erf} \tau'_r$ can be calculated. The value of τ'_r is then read from a table. $V_2 - V_1$ and $\alpha = V_2/V_1$ are calculated as described before. A numerical example for this case is given in the appendix (case 1).

When the chromatographic peak has a sharp front shaped like part of a triangle and a tail conforming to half of a Gaussian distribution curve (*Figure 1c*) the calculation of the separation factor can also be carried out.

The area of the peak is:

$$A\Big|_{-\infty}^{+\infty} = A_1 + A_2 + B \tag{30}$$

A_1 can be directly measured in this case.

$$A_2 = A\Big|_0^V = H(2\pi)^{\frac{1}{2}}\sigma_r \operatorname{erf} \tau_r \tag{31}$$

$$B = A\Big|_V^\infty = H(2\pi)^{\frac{1}{2}}\sigma_r(0{\cdot}5 - \operatorname{erf} \tau_r) \tag{32}$$

The area of the minor peak is:

$$\sum A' = A'_1 + A'_2 + B' \tag{33}$$

For the calculation of A'_1 it is assumed that the concentration Y_1 of the heavy isotope in the first fraction (corresponding to the area $A_1 + A_2$) is identical with its concentration in A_1. The error introduced by this assumption is very small in this case since the concentration Y_1 is very close to the original concentration of the heavy isotope. Thus:

$$A'_1 = A_1 Y_1 \tag{34}$$

and:

$$A'_2 = A_2 Y_1 = Y_1 H(2\pi)^{\frac{1}{2}}\sigma_r \operatorname{erf} \tau_r \tag{35}$$

$$B' = B Y_2 = Y_2 H(2\pi)^{\frac{1}{2}}\sigma_r(0{\cdot}5 - \operatorname{erf} \tau_r) \tag{36}$$

Substitution in eqn (33) leads to:

$$\sum A' = A_1 Y_1 + Y_1 H(2\pi)^{\frac{1}{2}}\sigma_r \operatorname{erf} \tau_r + Y_2 H(2\pi)^{\frac{1}{2}}\sigma_r(0{\cdot}5 - \operatorname{erf} \tau_r) \tag{37}$$

The area of the minor peak is also given by

$$\sum A' = A'\Big|_{-\infty}^{+\infty} = A'_1 + 0{\cdot}5\sigma_r H'(2\pi)^{\frac{1}{2}} \tag{38}$$

H' is calculated from eqn (38) and $\operatorname{erf} \tau'_r$ is then calculated from eqn (27). The value of τ'_r is obtained, as in the preceding case, from a table. $(V_2 - V_1)$ and $\alpha = V_2/V_1$ are then determined. A numerical example is given in the Appendix (case 2).

Conclusions

A method is described for the determination of separation factors for unresolved component pairs. Its accuracy is determined by the extent to which the equations used represent the distribution curve of the emerging peak. Fortunately, in many cases in gas–liquid chromatography distribution coefficients are linear. The chromatograms may then be accurately described by a Gaussian distribution. It should be noted that where this is not the case, other ways of describing the areas under the curve can sometimes be used. Additional assumptions must then be made, as seen in case 2 of the numerical examples (see Appendix), and results are necessarily less accurate.

The method was tested on a system for which the approximate value of the separation factor could be predicted from theory. The theoretical value for the nitrogen isotopes, calculated from the vapour pressures[7], was 1·0007; a value of 1·0011 was obtained experimentally. In view of the approximations involved (such as neglecting the activity coefficient ratio) in the calculation

of the theoretical value of 1·0007, these results are satisfactory. Moreover, data obtained with other ternary systems fall within the limits of the values expected by comparison with other methods of nitrogen isotope separation.

Appendix

Numerical example

Figure 2 is an actual chromatogram recorded during an experiment concerning the enrichment of nitrogen isotopes. Basic data: mass ratio 29/28 in the first fraction (from injection point to point of fractionation, V), measured by

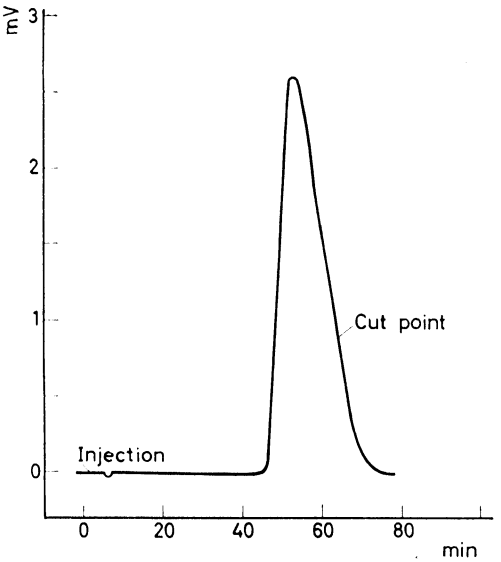


Figure 2. Experimental chromatogram, nitrogen isotopes enrichment

mass spectrograph, was 0·007285. Mass ratio in the second fraction (from cut point V to $+\infty$) was 0·008055. Enrichment ratio was 1·106. Concentrations of the heavy isotopes in the two fractions were:

$$Y_1 = \frac{0{\cdot}007285}{1{\cdot}007285} = 0{\cdot}007232 \qquad Y_2 = \frac{0{\cdot}008055}{1{\cdot}008055} = 0{\cdot}007991$$

and the concentration ratio

$$Y_1/Y_2 = 0{\cdot}9050$$

H = height of peak = 131·5 mm

h = height at cut point = 44·5 mm

X = distance between centre and cut point = 14·5 mm

V_1 = retention volume, measured in units of length (i.e. distance between injection point and centre of peak) = 70·0 mm

For demonstration purposes we will show the calculation of α for two cases:

Case 1. It is assumed that the chromatogram is made of two parts of two different Gaussian distribution curves. At the inflection points,

$$\sigma_l = 5{\cdot}1 \quad \text{and} \quad \sigma_r = 9{\cdot}0$$

Thus:

$$\tau_r = \frac{X}{\sigma_r} = \frac{14{\cdot}5}{9{\cdot}0} = 1{\cdot}611$$

from error function tables, $\operatorname{erf} \tau_r = 0{\cdot}4463$.

Substitution in eqns (29), (27) and (26) gives

$$A_1 = A\Big|_{-\infty}^{0} = 131{\cdot}5 \times 5{\cdot}1 \times (2\pi)^{\frac{1}{2}} \times 0{\cdot}5 = 840{\cdot}5 \text{ mm}^2$$

$$A_2 = A\Big|_{0}^{V} = 131{\cdot}5 \times 9{\cdot}0 \times (2\pi)^{\frac{1}{2}} \times 0{\cdot}4463 = 1323{\cdot}4 \text{ mm}^2$$

$$A_1 + A_2 = A\Big|_{-\infty}^{V} = 2163{\cdot}9 \text{ mm}^2$$

$$B = A\Big|_{V}^{+\infty} = 131{\cdot}5 \times 9{\cdot}0 \times (2\pi)^{\frac{1}{2}} \times (0{\cdot}5 - 0{\cdot}4463) = 159{\cdot}8 \text{ mm}^2$$

Substituting in eqn (28)

$$A' + A_2' = Y_1(A_1 + A_2) = 0{\cdot}007285 \times 2163{\cdot}9 = 15{\cdot}75745$$

$$B' = Y_2(B) = 0{\cdot}008055 \times 159{\cdot}8 = 1{\cdot}28315$$

$$\sum A' = 17{\cdot}04060$$

Equating eqns (28) and (29)

$$0{\cdot}5\, H'(2\pi)^{\frac{1}{2}}(\sigma_l + \sigma_r) = 17{\cdot}671 H' = 17{\cdot}0406$$

$$H' = 0{\cdot}96433$$

Now from eqn (27)

$$0{\cdot}5 - \operatorname{erf} \tau'_r = \frac{B'}{H'\sigma_r(2\pi)^{\frac{1}{2}}} = \frac{1{\cdot}28315}{0{\cdot}96433 \times 9{\cdot}0 \times 2{\cdot}5065} = 0{\cdot}058985$$

$$\operatorname{erf} \tau'_r = 0{\cdot}441015; \quad \tau'_r = 1{\cdot}564$$

We already found

$$\tau_r = 1{\cdot}6111$$

so that

$$\tau_r - \tau'_r = \Delta\tau = 0{\cdot}047$$

$$\Delta X = X - X' = V_2 - V_1 = \sigma_r \Delta\tau = 9{\cdot}0 \times 0{\cdot}047 = 0{\cdot}423$$

Since

$$V_1 = 70{\cdot}0 \text{ mm} \qquad V_2 = 70{\cdot}423 \text{ mm}$$

and finally

$$\alpha = V_2/V_1 \cong 1{\cdot}006$$

Case 2. It is assumed that the front part of the peak is half a triangle and that the back part corresponds to half of a Gaussian distribution curve, for which, as already seen in case 1, $\sigma_r = 9{\cdot}0$.

By direct measurement

$$A_1 = 684 \text{ mm}^2. \quad \text{From eqns (31) and (32)}$$

$$A_2 + B = 0{\cdot}5\, H\sigma_r(2\pi)^{\frac{1}{2}} = 1483{\cdot}2 \text{ mm}^2$$

from case 1 $\quad A_2 = 1323{\cdot}4 \quad \text{and} \quad B = 159{\cdot}8 \text{ mm}^2$

Substituting in eqn (33) or (37)

$$A'\Big|_{-\infty}^{V} = Y_1(A_1 + A_2) = 0{\cdot}007285(684 + 1323{\cdot}4) = 14{\cdot}6239 \text{ mm}^2$$

$$B' = Y_2 B = 0{\cdot}008055(159{\cdot}8) = 1{\cdot}2872 \text{ mm}^2$$

$$\sum A' = 15{\cdot}9111 \text{ mm}^2$$

Equating eqn (37) to eqn (38):

$$\sum A' = 15{\cdot}9111 = A'_1 + 0{\cdot}5\, H'\sigma_r(2\pi)^{\frac{1}{2}}$$

Now, assuming the concentration Y_1 to be the same in A_1 as in $(A_1 + A_2)$

$$A'_1 = Y_1 A_1 = 0{\cdot}007285 \times 684 = 4{\cdot}9829 \text{ mm}^2$$

From eqn (38)

$$0{\cdot}5H'\sigma_r(2\pi)^{\frac{1}{2}} = \sum A' - A'_1 = 15{\cdot}9111 - 4{\cdot}9829 = 10{\cdot}9282$$

$$H' = \frac{10{\cdot}9282}{2{\cdot}5065 \times 9{\cdot}0 \times 0{\cdot}5} = 0{\cdot}9689$$

From eqn (27)

$$B' = 1{\cdot}2872 = H'\sigma_r(2\pi)^{\frac{1}{2}}(0{\cdot}5 - \operatorname{erf}\tau'_r)$$

$$= 0{\cdot}9689 \times 9{\cdot}0 \times 2{\cdot}5065(0{\cdot}5 - \operatorname{erf}\tau'_r)$$

$$\operatorname{erf}\tau'_r = 0{\cdot}44109; \quad \tau'_r = 1{\cdot}571$$

We already know that

$$\tau_r = 1{\cdot}611$$

Since $\Delta\tau = V_2 - V_1/\sigma_r$ and $V_1 = 70{\cdot}0$ mm,

$$\alpha = V_2/V_1 = \frac{70{\cdot}36}{70{\cdot}0} \cong 1{\cdot}005$$

List of symbols

A	area of a peak (within defined boundaries)
A_1, A'_1	area of combined resp. minor peaks, from sample injection point to their centres V_1 and V_2
A_2, A'_2	area of combined resp. minor peak, from their centres to point of fractionation V
B, B'	area of combined resp. minor peaks, from point of fractionation V to infinity
h	height of peak at any point
H, H'	height of combined resp. minor peaks at point of maximum concentration V_1 resp. V_2

m_1	mass of heavy isotope in first fraction of combined peak, to cut point
m_2	mass of heavy isotope in second fraction of combined peak, from cut point to infinity
n	number of theoretical plates
P^0	vapour pressure of pure component
t, t'	distance from centre of distribution curve in units of one standard deviation
x	distance between centre axis and any point of the distribution curve
X, X'	distance from centre axis of combined resp. minor peak to cut point
y_1, y_2	concentration of light resp. heavy isotopes at any point of the peak
Y_{01}, Y_{02}	concentration of light and heavy isotopes in original sample
Y_1	concentration of heavy isotope in first fraction of the peak, up to cut point V
Y_2	concentration of heavy isotope in second fraction of the peak, from cut point to infinity
v	point on chromatographic peak
V	point of fractionation or cut point
V_1, V_2	centre of combined resp. minor peak, measured from point of injection (practically identical with V_n)
V_n	net retention volume ($= V_1$ or V_2)
$\bar{V}$	geometric average of centre of peaks
W	width of chromatogram
α	separation factor, relative volatility $= V_2/V_1$
γ	activity coefficient
λ	$\alpha - 1$
σ	standard deviation
τ, τ'	distance from centre of distribution curve to cut point for light resp. heavy isotope, in units of one standard deviation

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DISCUSSION

F. J. Spruit: I should like to ask Mr Sideman whether he can measure V_1 with sufficient accuracy, because I understand that he takes the distance up to the maximum of the first peak. Whenever there is a peak under that of the first

component the maximum of the compound peak will be moved, because of the tangent of the second peak. Can you comment on this?

S. Sideman: I am not sure I understood the question perfectly, but it seems to me that you are referring to my assumption 6, which is an answer to your question. We did assume that there was no interference of the two peaks. In other words, you can prove statistically or with an equation that there is some; but we neglected it, because the ratio of the two isotopes was some 0·3 per cent; therefore it was impossible to measure this, and there was no sense in calculating and correcting for it. In the paper I made reference to a method of correction[6] which can be applied, but this is very much trial and error if the masses are quite large. It can be calculated, but it is not easy. However, we were lucky in that we could accept our own assumption and use it as such.

A. Goldup: Dr Sideman's paper prompted me to calculate the smallest separation factor one could determine with a very high efficiency capillary column. If the peak widths of the two peaks which come out closely together are again assumed to be equal, then $\alpha_{AB} = 1 + [(\Delta t_{AB} - \Delta t_A)/t_A]$; where α_{AB} is the separation factor, Δt_A and Δt_{AB} are the peak widths for the pure component A and for the unresolved two-component pair respectively, and t_A is the retention time of the pure component A, measured from the air peak.

With a capillary column having e.g. 250,000 plates, which is possible for hydrocarbon separations, typical values for Δt_A and t_A would be 4 and 500 minutes respectively. In a carefully designed experiment one should be able to measure with a fair degree of accuracy a 10 per cent change in peak width, i.e. $\Delta t_{AB} = 4{\cdot}4$ min. Substituting this in the above eqn we find:

$$\alpha_{AB} = 1 + \frac{0{\cdot}4}{500} = 1{\cdot}0008$$

Therefore I think that on a high efficiency capillary column you can measure separation factors of this order with a fair degree of accuracy.

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QUANTITATIVE AND QUALITATIVE ANALYSIS OF FLAVOUR VOLATILES FROM EDIBLE FATS

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MICROGRAM amounts of flavour volatiles are quantitatively recovered from edible fats by vacuum distillation in a short path still. The fat is heated at 50°C in a glass retort and the distilled volatiles are collected in a U-tube trap cooled by liquid oxygen. The trap, constructed from stainless steel hypodermic tubing, is then used to inject the sample into an argon ionization gas chromatograph, volatilization being achieved by rapid ohmic heating of the tube itself. Gas connections to the chromatograph are made with the same self-heating tubing and O-ring sealed couplings of small volume. A separate pre-column can be introduced, if required, to remove water and high-boiling substances when more volatile components are being analysed. Eluted components can be condensed in similar traps cooled in liquid oxygen for direct re-chromatography on a second stationary phase or for other characterization.

Individual peaks are identified by their Kováts Retention Indices on two stationary phases (polar and non-polar) and by the determination of their carbon skeleton. For this purpose catalytic vapour phase hydrogenation is used to reduce the eluted component to the corresponding saturated hydrocarbon—oxygen, nitrogen or sulphur being eliminated. The hydrocarbon formed is identified by gas chromatography.

The difference between the retention index of a compound and that of the hydrocarbon derived from it is characteristic of its functional group and is constant within a homologous series. The determination of the carbon skeleton and of the contribution of the functional group to the retention index results in a simplification of qualitative analysis.

Accessory apparatus for the argon chromatograph

Both the flexibility of sample injection and the ease of collection of eluted components have been improved by the design of accessory apparatus which, although here applied to the chromatograph manufactured by W. G. Pye & Co. Ltd., Cambridge, can be used also with other instruments. The apparatus uses lengths of stainless steel hypodermic needle tubing (Accles & Pollock Ltd., Birmingham) for the construction of carrier gas connections and traps. This tubing has a small internal volume and may be quickly raised to, and maintained at, any desired temperature by the ohmic heating resulting when a low voltage a.c. supply is applied to the tubing itself (up to 1 V per 10 cm length). 'Speedivac' R.101 unions (Edwards High Vacuum Ltd., Crawley) which are sealed by partial compression of a silicone rubber O-ring (2·9 mm i.d. and 1·8 mm section) provide gas-tight couplings.

Table 1. Specifications of two sizes of steel hypodermic needle tubing

British s.w.g. No.	*Diameter* (mm)		*Internal volume* ml. *per 30* cm *length*	*Amps to maintain unlagged tubing at*			
	Internal	*External*		100°C	150°C	200°C	250°C
17	1·0	1·4	0·2	4·5	6	7	8
11	2·1	2·95	1	10	13	16	19

Sampling traps (*Figure 1, parts* A *and* B)

Examples of two types of trap are shown, *A* being a single U-tube trap made from a 30 cm length of No. 11 s.w.g. tubing, and *B* a 90 cm length of No. 17 s.w.g. tubing bent so that the bottoms of four loops can be immersed in liquid oxygen coolant contained in a Dewar vessel. The narrow-bore tubing is used empty; the traps made of the wider No. 11 s.w.g. tubing, however, can be packed. At present only uncoated 1 mm diameter glass ballotini have been used in these traps but a column packing containing stationary phase could also be employed, in which case absorption would assist condensation.

Collection adapter (*Figure 1, part* C)

A 30 cm length of No. 17 s.w.g. tubing, fitted at one end with a R.101 union socket and at the other with a specially designed O-ring coupling to the detector outlet nipple, provides a self-heating connection of low internal volume to the outside of the instrument case. For temperature measurement a copper/constantan thermocouple has been spot-soldered to the tubing, the entire length of which is insulated both thermally and electrically by silicone rubber.

Remote injection adapter (*Figure 1, part* D)

The design of this apparatus is more complex because the outlet end of the connecting tubing (30 cm of No. 17 s.w.g.) extends 10 cm inside the glass chromatographic column to just above the column packing. The wire conductor for the heating current also has to pass inside the glass column as a helix around the tubing, from which it is insulated by a layer of glass fibre yarn.

So that the sample emerging from the adapter during injection can be carried on to the column packing without being allowed to diffuse, the body of the adapter (part of the 'Pye closed liquid injection system') is purged with a stream of carrier gas (schematically shown in *Figure 3*). The No. 17 s.w.g. tubing passes through the injector body but is insulated from it by a Teflon (PTFE) spacer and an O-ring seal. The two gas inlets are both fitted with R.101 union sockets, through which the low voltage a.c. power is applied for ohmic heating of the adapter. Temperature measurements are again made with a thermocouple.

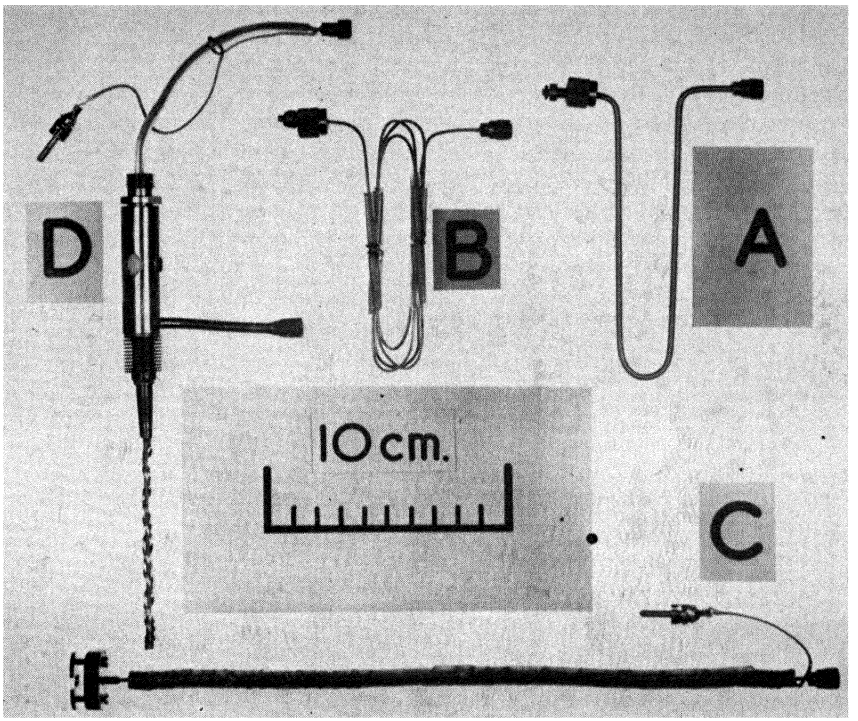


Figure 1. Accessory apparatus made of steel hypodermic tubing. *A* and *B*, sampling traps; *C*, collection adapter; *D*, remote injection adapter

Pre-column assembly (*Figure 2, parts* E *and* F)

The flexibility of the design is such that further ancillary apparatus can readily be added. Thus a short pre-column can be used to prevent water and later-running components of an injected sample from entering the analytical column[8], or for chemical characterization, if the pre-column packing is chosen to selectively delay[7] or even absorb[3] one class of compounds.

A pre-column of 3 mm bore stainless steel tubing and fitted with a R.101 union at its ends is shown in *Figure 2*, part *E*. It is packed over a length of 15 cm and is thermostated by a separate electrical heater. To allow the pre-column to be back-flushed to the atmosphere a steel T-piece is inserted in the carrier gas line (*Figure 2*, part *F*). A short length of silicone rubber tubing fitted with a spring clip connects the T-piece to the constricted glass tube which limits the gas flow when the clip is open.

Figure 3 is a schematic diagram of the two alternative carrier gas flows. A two-way valve (not illustrated) is used to switch the alternative inlets of carrier gas; the flow rate of the purge stream is controlled by a capillary restriction whose resistance to gas flow is greater than that of the pre-column.

Application of accessory apparatus

Before injection of a sample, the temperature of the trap containing it is raised by ohmic heating for up to 60 sec and the flow of carrier gas is then

started. This procedure is not only applicable to samples which have been previously collected in a trap by condensation, but is also used to volatilize inside No. 11 s.w.g. tubing liquid samples contained within a 0·1 μl capillary pipette made of 0·16 mm bore steel hypodermic needle.

For collection of an eluted component a sampling trap cooled in liquid oxygen (liquid nitrogen also condenses the argon carrier gas) is attached to the outlet of the heated collection adapter. The efficiency of trapping can be determined from the diminution in peak area after re-injection of the component. A single U-tube trap of No. 17 s.w.g. tubing was found to condense

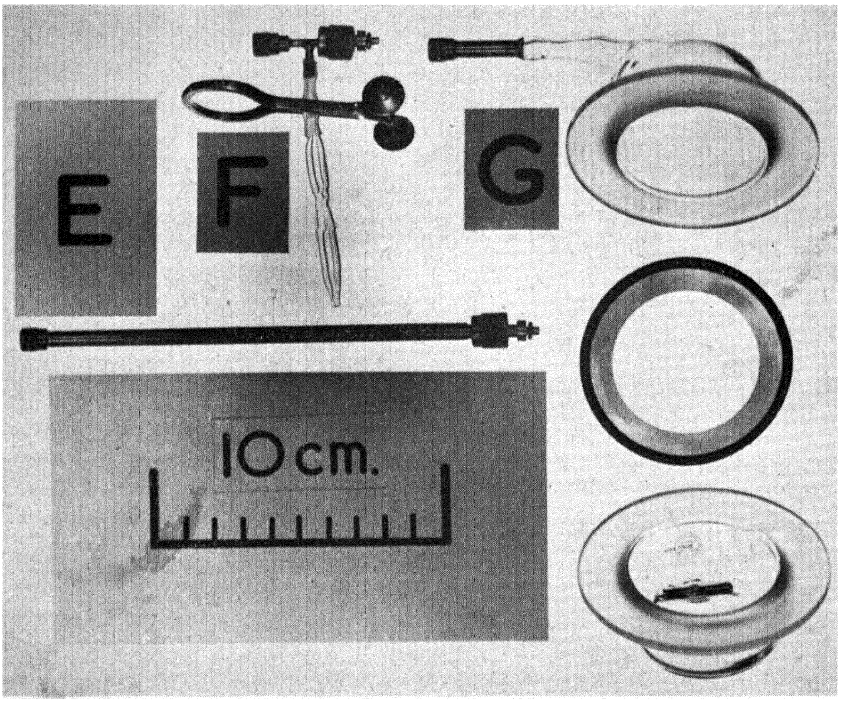


Figure 2. *E*, pre-column; *F*, back-flush assembly; *G*, retort showing top section with R.101 union, O-ring seal, and bottom section containing magnetic stirring bar

a few micrograms of n-hexane (b.p. 68°C) with only 40 per cent efficiency from an argon flow of 60 ml/min. When the 90 cm long, four-loop trap (*Figure 1*, part *B*) was used, however, the trapping efficiency for n-hexane increased to practically 100 per cent. The trapping efficiency of a single U-tube is better for higher-boiling components and when a slower flow of carrier gas is used.

Recovery of volatiles by vacuum distillation

Certain precautions have to be observed if the few micrograms of condensate applied to the gas chromatograph are to represent a quantitative recovery of the volatiles originally present in a fat. The design and operation of the

vacuum distillation apparatus must be such that secondary chemical changes are minimized and that no fractionation occurs during the isolation of the wide-boiling range of compounds that contribute to the flavour[1,5].

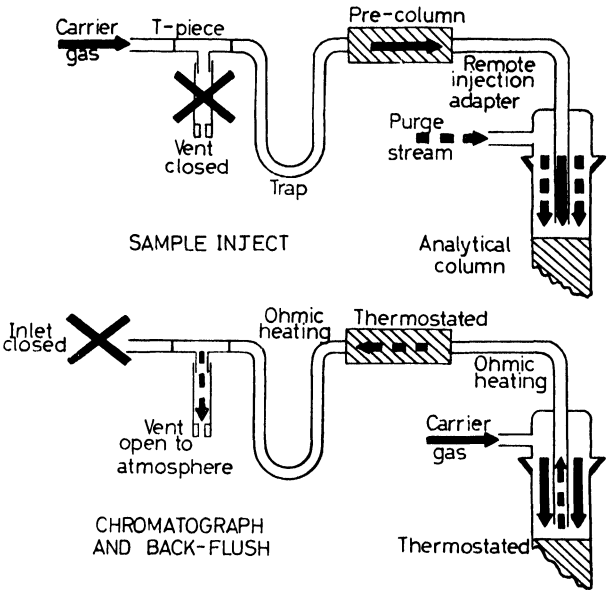


Figure 3. Schematic diagram of the two alternative carrier gas flows. The change from sample inject to chromatograph and back-flush was made after 5 min at 60 ml/min, since with the pre-column used (20 per cent diglycerol at 65°C) water emerged after 330 ml of argon

Application of the vacuum system (Figure 4)

The flavour volatiles are distilled from a retort *G* into a No. 11 s.w.g. sampling trap *A*. The retort (*Figure 2*, part *G*) consists of two flat flange glass sections which are sealed together by a large O-ring fitted around a stainless steel washer.

Before a distillation the apparatus is completely evacuated, with the fat frozen in the bottom of the retort. Then with tap *J* closed, the most volatile components and dissolved gases are allowed to distil from the fat which is now magnetically stirred and heated to 50°C. After this initial distillation in a closed system, restricted pumping is applied through the glass capillary *K*, at first with only the rotary pump and subsequently by means of the diffusion pump. Finally, argon is admitted and the sampling trap *A* transferred to the gas chromatograph for analysis.

As a test for the efficiency of the vacuum distillation technique a mixture of alcohols, ranging from ethanol to hexanol, was chromatographed, both directly from a micropipette and after recovery from solution in silicone oil at a dilution of 20 p.p.m. Chromatographic analyses were carried out with a pre-column of 20 per cent diglycerol on Celite at 65°C followed by an analytical column of 15 per cent squalane at 50°C. Direct application of the

alcohol mixture gave calibration chromatograms with normalized areas of 6 per cent C_2H_5OH, 11 per cent C_3H_7OH, 15 per cent C_4H_9OH, 24 per cent $C_5H_{11}OH$ and 44 per cent $C_6H_{13}OH$. The same alcohol mixture after recovery by vacuum distillation from silicone oil gave 6, 12, 17, 25 and 40 per cent respectively.

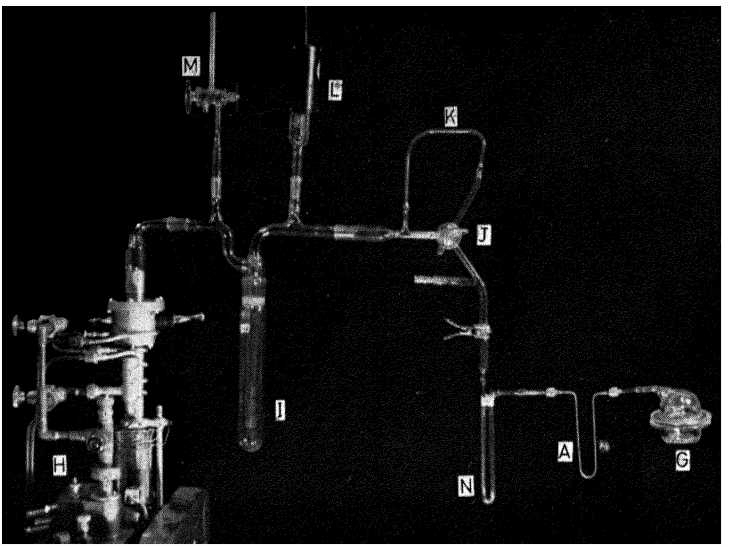


Figure 4. Vacuum system for the distillation of volatiles. *G*, retort (see also *Figure 2*); *A*, sampling trap; *H*, combined diffusion and rotary pump system; *I*, pump protection trap; *J*, two-way tap; *K*, capillary pumping restriction; *L*, Pirani gauge; *M*, argon inlet; *N*, distillation protection trap

Identification by means of retention data

The 'Retention Index' scale of Kováts

The well-documented linear relationship between the logarithm of the adjusted retention and the number of carbon atoms in a molecule of a homologous series has been utilized by Kováts, who proposed a scale of retention indices[4], the index of the n-paraffins being defined as 100 times the number of carbon atoms in the molecule.

A 'log plot' calibration from n-hexane to n-undecane is shown in *Figure 5* for a column of 15 per cent squalane on Celite at two different temperatures. Here the retention data have not been corrected for gas hold-up of the column, measurements of retention being made from the start of the chromatogram. Even so, there is only a slight deviation from linearity at low retentions. The retention of any compound run on the same column and under the same conditions can be converted to the retention index scale by interpolation on the calibration chart. The data for a homologous series of saturated aliphatic aldehydes from n-pentanal to n-decanal are also plotted on *Figure 5*. They serve to illustrate Kováts' summary of the advantages of the retention index:

(a) its dependence on temperature is very small and linear;
(b) it is independent of the column constants and of the type of chromatographic apparatus used;
(c) it provides information about the chemical nature of the substance under examination[4].

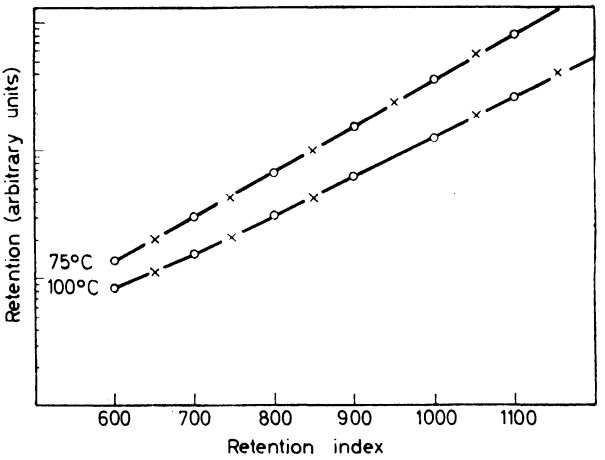


Figure 5. 'Log plot' for determination of the Retention Index on 15 per cent squalane on Celite at two temperatures. ○, calibration by n-paraffins from hexane to undecane; ×, interpolated values of aldehydes from n-pentanal to n-decanal

The concept of the Functional Retention Index

The characterization of the chemical nature of a substance can be more clearly demonstrated if, from the retention index of for example an n-alkyl derivative, the retention index of the parent n-paraffin is subtracted. The resultant difference is the contribution of the functional group and may therefore be aptly termed the Functional Retention Index (FRI).

In the series of saturated aliphatic aldehydes ranging from n-butanal to n-decanal a mean FRI value of 152 was observed on squalane at 75°C, the value at 100°C being 154. Any variation between members of the homologous series was masked by the experimental scatter of replicate determinations, which was of the order of 5 units. On dinonyl phthalate the FRI value increased with chain length, ranging from 281 to 291 at 74°C and from 289 to 296 at 100°C. *Table 2* gives the mean FRI values for four classes of n-alkyl

Table 2. The Functional Retention Index of four *n*-alkyl derivatives on two stationary phases

	Squalane at 75°C	*Dinonyl phthalate at* 74°C
n-Alkanol	230	402
n-Alkanal	152	288
n-Alk-2-enal	203	378
n-Alk-2,4-dienal	248	450

compounds; the variation among homologues containing from four to ten carbon atoms did not exceed 10 units. In general, methyl, ethyl and propyl derivatives show greater deviations and should not be included in a calculation of mean values. Tabulation of retention data in this way should greatly simplify identification of saturated and unsaturated aliphatic aldehydes, which, in complex mixture, represent the major rancid flavour constituents in autoxidized fats[2].

Catalytic vapour phase hydrogenation

The concept of the functional retention index becomes of practical significance only if the hydrocarbon skeleton of an unknown component can be experimentally determined. Just such a procedure, based on catalytic vapour phase hydrogenation, has recently been developed and applied to the identification of gas chromatographic fractions by workers at the Bartlesville Bureau of Mines Research Centre[9]. Volatile compounds containing oxygen, nitrogen or sulphur are completely reduced on being passed with hydrogen over a heated palladium on alumina catalyst, with formation of the parent saturated hydrocarbon.

We have slightly modified this procedure so that microgam samples can be efficiently hydrogenated, n-alkyl derivatives yielding the corresponding n-alkanes. For the latter, retention data have already been determined for the construction of the 'log plot' for retention index measurements.

Application of the functional retention index

Having discussed the experimental utility of the concept, we can now formally define the functional retention index (FRI). Consider the compounds $\rho \cdot \chi$ and $\rho \cdot CH_2$ which are derived from ρ by the introduction of the functional group χ and a methylene group respectively. Then on a particular stationary phase and at a certain temperature the following definition applies:

$$(FRI)_\chi = 100 \log (r_{\rho.\chi,\rho})/\log (r_{\rho.CH_2,\rho}) \quad (1)$$

where $r_{\rho.\chi,\rho}$ and $r_{\rho.CH_2,\rho}$ are the relative retentions of compounds $\rho \cdot \chi$ and $\rho \cdot CH_2$ respectively as compared with ρ. For calculation from retention index (RI) data this expression is simplified to

$$(FRI)_\chi = (RI)_{\rho.\chi} - (RI)_\rho \quad (2)$$

In the present application both ρ and $\rho \cdot CH_2$ are n-paraffins and $\rho \cdot \chi$ is an n-alkyl derivative. However, no matter what the structure of ρ, if

$$\frac{\log (r_{\rho.CH_2,\rho})}{100}$$

has the same value as the slope of the 'log plot' for n-paraffins, then both eqns (1) and (2) are valid.

The formal definition (1) can even be applied when the 'log plot' is based on a homologous series of compounds other than the n-paraffins. For example in the analysis of the methyl esters of fatty acids, the terms 'carbon

number'[10] and 'equivalent chain length'[6] have both been used for the logarithmic retention parameter that is based on the number of carbon atoms in normal saturated monocarboxylic acids.

To summarize, the Functional Retention Index is a measure of the effect of substitution by a functional group as compared with the addition of a methylene group. The parameter has the advantages claimed by Kováts for the Retention Index, and the more general application of retention parameters of this type should greatly aid the interpretation and utility of published chromatographic data.

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DISCUSSION

Author's Additional Comments

The points I wish to make are best illustrated by the diagram (*Figure 6*) of the linear relationship between the logarithm of retention volume and the number of carbon atoms of homologous compounds. The Retention Index scale of Kováts[11] is defined by the n-alkane series, and the broken lines show how the values on this scale are obtained for other compounds, in this case n-alkanals. Also shown is the R_{x9} scale[12] proposed by Smith at the last symposium, for which theoretical nonane (obtained from a 'best straight line' fit to the n-alkane results) is used as the standard for calculation of relative retentions. The two scales are derived from the same experimental determinations, and results quoted on either are interconvertible so long as the slope of the 'log plot' for the n-alkanes is defined. When the data are tabulated, however, the constant arithmetic increment of Retention Index values for a homologous series is more readily recognized than the geometric relationship of R_{x9} values.

Moreover, whereas the R_{x9} scale requires accurate correction for the gas hold-up before a 'best straight line' fit can be applied, accurate Retention Index values can even be obtained by interpolation on a curved plot, when this arises, because of consistent 'zero errors' in the measurement of retention.

I would like to suggest that Retention Index measurements could also be applied to programmed temperature chromatography. The use of a homologous series of standards for calibration directly establishes the reproducibility of the experimental procedure and, as the temperature dependence of Retention Index values is small, comparison with isothermal data might be facilitated. Instead of a 'log plot'

when the rate of rise of column temperature is uniform, a nearly linear relationship has been reported between the retention of the homologous series of n-alkanes and their carbon number (e.g. Golay, M. J. E., Ettre, L. S. and Norem, S. D., page 139).

Returning now to the diagram, I have termed the horizontal spacing between the two log plots the 'Functional Retention Index' (F.R.I.). Where the lines are parallel a mean value may be quoted for all members of a particular homologous series. A similar parameter has been proposed for the prediction of retention data from molecular formulae[13]. The value of the Retention Index of a compound is recalculated in terms of the molecular weight of a hypothetical n-alkane having the same retention. The difference between this effective molecular weight and the true formula weight is defined as the parameter 'ΔMe'. Now for an n-alkyl derivative the following relationship applies: 0·1403 (F.R.I.) = ΔMe + [Substituent Atomic Weight]. Thus, whereas the F.R.I. represents directly the order of elution of different compounds on the chromatogram, the ΔMe value is affected by the atomic weight of the functional group.

	Squalane		*Dinonyl phthalate*		
	F.R.I.	*ΔMe*	*F.R.I.*	*ΔMe*	
n-alkane thiol	292	8·9	371	20·0	(Evans and Smith, 1961)
n-alkanol	230	16·3	402	40·3	(Swoboda, 1962)

On the two stationary phases, squalane and dinonyl phthalate, the ΔMe values of thiols are about half that of alcohols because of the large difference in molecular weight. However, when the data are recalculated as F.R.I. values the true order of retention is revealed, an alcohol emerging earlier than the corresponding thiol on squalane but later on dinonyl phthalate.

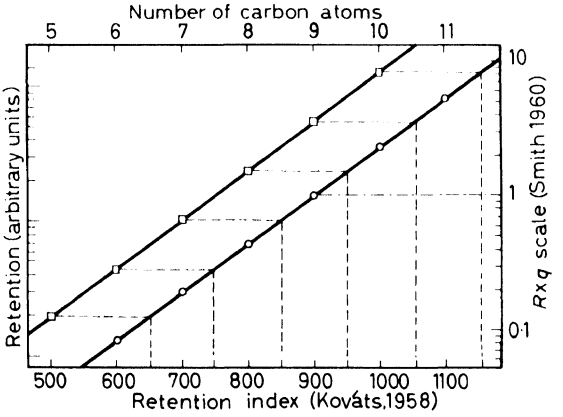


Figure 6. 'Log plot' of retention on squalane at 75° versus number of carbon atoms for two homologous series: ○, n-alkanes; □, n-alkanals

Moreover, the concept of the functional retention index is of practical significance for a compound of unknown structure, for the technique of vapour phase hydrogenation can be applied to gas chromatographic fractions to determine the hydrocarbon structure from which the compound is derived.

J. F. Smith (*prepared contribution*): Although the technique of GLC before and

after micro-hydrogenation is useful, the original work in this field (Reference 9) covered a much wider range of compounds than reported in this paper and recorded a number of anomalies. Thus β-branched compounds (or any others with weak C—C bonds) undergo skeletal cleavage, aromatic compounds give a mixture of the corresponding cyclo-alkanes and aromatic hydrocarbons, and carboxylic acids give both the corresponding cyclo-alkane and methyl-cyclo-alkane. No doubt other anomalies would come to light on further investigation.

Multivalent functional groups could give very misleading values for the F.R.I. as defined in this paper, unless the stoichiometry of the hydrogenation is known or measured by the quantitative yield of hydrocarbon.

Methyl, ethyl, propyl and to a lesser degree butyl groups attached to a functional group present difficulties in trapping and resolution, owing to the volatility and short retentions of the corresponding n-alkanes. These materials also give a very low response with the argon detector.

Mixtures must first be separated and trapped by preparative-scale GLC, or the results would be unintelligible, owing to 'peak scrambling', and, such being the case, it seems irrational not to use spectroscopic methods of identification, especially since only semi-micro quantities are required and suitable spectrometers are now relatively cheap. Spectrometric analysis used intelligently can generally provide far more structural information on the functional groups in a pure compound than the technique used in this paper and in consequence is the preferred approach in our laboratories.

Positional isomerism and multifunctional compounds present serious difficulties in the hydrogenation technique. Thus there are 78 mono-unsaturated alcohols based on the 2-methyl heptane skeleton which give the same hydrocarbon on hydrogenation. The range of retentions as well as the change of retention with hydrogenation is quite large for members of this series, which includes compounds with primary, secondary and tertiary alcohol groups in combination with allylic and non-allylic double bonds of the vinyl, vinylidene, cis- and trans-dialkyl ethylene, and cis- and trans-trialkyl ethylene type.

Infra-red spectroscopy can considerably narrow the field in such an example as this without requiring any authentic compounds and have a fair chance of uniquely defining the structure.

By contrast the technique described by Dr Swoboda would require synthesis and calibration of his method for most if not all of the possible structures, in which case spectroscopic identification would be quite unambiguous anyway. The range of F.R.I.'s within this series would, moreover, be so wide as to overlap those of many other functional groups; it would therefore be of little diagnostic value.

Nevertheless, there is considerable value in the general technique of instrumental analysis before and after chemical treatment of the sample, but the full benefit is usually realized only by the use of complementary techniques. Moreover, less drastic treatment than hydrogenation is usually more informative, as many features of the original structural group may then be preserved to allow further structural confirmation by spectroscopy. A paper by N.R.P.R.A. workers, illustrating the economy of this approach, will shortly appear in the *Journal of the Chemical Society*.

In our view the most useful feature of the hydrogenation technique is its ability to produce authentic hydrocarbons from known compounds, which would be difficult to obtain in any other way. With unknown pure compounds the value of hydrogenation lies more with the identification of the hydrocarbon skeleton than with the identification of the functional group. For the identification of the hydrocarbon skeleton the use of complementary techniques again may well be more informative than the application of GLC alone.

Correlations of retention data and structure are useful in distinguishing between a very limited number of alternative structures, but they become progressively less useful as this number increases and, in general, a practical upper limit will be reached at four or five possible alternative structures, even in favourable cases.

J. Pypker (*prepared contribution*): In between the fields covered by the methods described by Dr Swoboda, who works in the microgram range, and the so-called preparative-scale chromatography, which involves grams of starting material, a

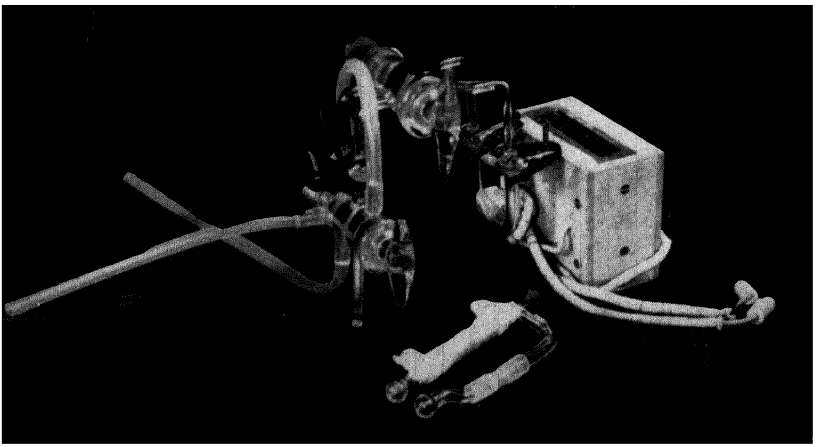


Figure 7. Photograph of the trapping and sample injection system

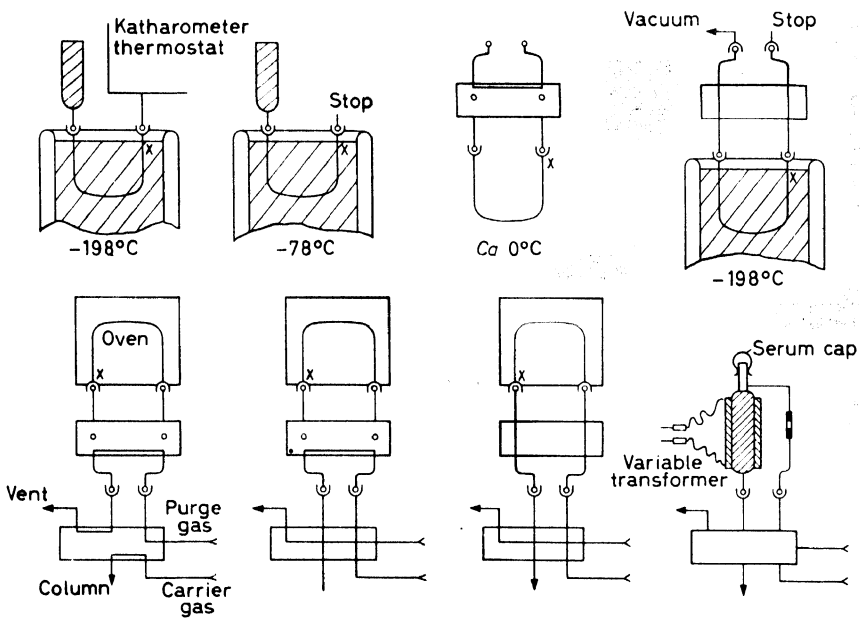


Figure 8. Schematic diagram of the trapping and sample injection system

semi-preparative method, used for some years now at the Central Institute for Nutrition and Food Research T.N.O. (Utrecht, the Netherlands), was found valuable in flavour research. The mixtures under investigation were very complicated and little was known of the chemical structure of components.

To get retention data on different columns and to isolate purified components in a sufficient quantity for (I.R.) spectrometry or chemical (spot) tests, a trapping and sample injection system was developed, as shown in *Figures 7* and *8*. The hot laminar stream of carrier gas leaving the detector is directed on to a very cold surface in a simple glass U tube (i.d. 5 mm). Complete trapping occurs when the gas flow (at 50–150°C) does not exceed 200 ml/min. This restricts the column diameter to 10 mm, which is sufficient for sample sizes up to 100 μg per component. Liquid samples are first injected on to a short top column mounted on the lower valve. Purging of high-boiling material may be accomplished by turning this valve at a predetermined time after injection.

The material represented by a peak is trapped after leaving the detector and rechromatographed on a different column. It will then often be found that this material contains more than one component. When these components are trapped

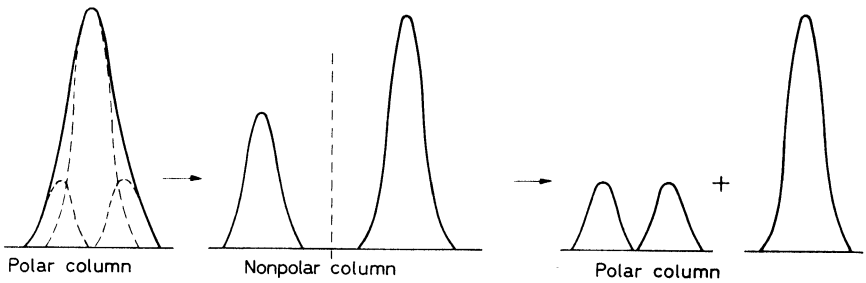


Figure 9. Isolation of pure components by repeated chromatography on two different columns

and run again on the first column used (alternatively on a third one or at a different temperature), often an apparently 'pure peak' is again shown to be complex (*Figure 9*).

Figure 10 shows how two partly separated components can be rechromatographed without substantial loss of material on the best-resolving column to yield two condensates, each contaminated with only a small amount of the other. Absorption bands of these impurities can easily be recognized from a comparison of the I.R.-spectra of the two fractions.

In this way mixtures containing more than 50 components were investigated and identification of single components representing more than 1 per cent of the total was generally possible from the combined data.

M. B. Evans (*prepared contribution*): The certainty with which a substance can be identified by its retention is obviously dependent upon the precision with which the retention data have been obtained. The procedure for determination of retention indices described by Dr Swoboda is not capable of giving the optimum accuracy, as indicated by the scatter for replicate determinations. These errors may be attributed to three factors:

(*1*) The fact that no corrections are made for the dead volume of the column, which will give rise to nonlinear 'log plots' for the n-alkanes[12].

(*2*) The inaccuracy inherent in the use of separate chromatograms for unknown and standard in the calculation of relative retentions (*loc. cit.*).

(*3*) The use of squalane for the chromatography of polar materials such as alcohols and aldehydes.

Accurate retention indices can be obtained by means of the expression:

$$I = 100\left\{\frac{\log R_{x9}}{b} + 9\right\}$$

where R_{x9} is the retention relative to n-nonane as determined by our standard procedure, and b the slope of the 'log plot' for the n-alkanes. Clearly, the error in I will be dependent upon the precision with which b can be determined. A precise value of b can be obtained when the widest possible range of n-alkanes is used for the calibration procedure, as in our latest method for determination

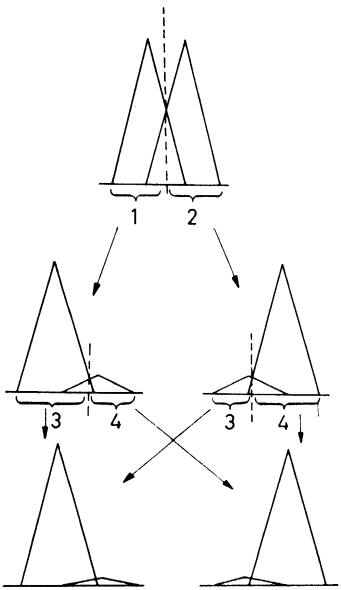


Figure 10. Purification of badly resolved components by repeated chromatography on a single column. Cuts are made at the broken lines; numbers represent trapping vessels

of R_{N9} values[14]. This calibration procedure also gives the true dead volume of the column. The value of b should be quoted with all data published in R_{x9} and I units in order that the two forms may be interconverted. This conversion is not possible when retention is measured from a point other than the dead volume point. Incidentally, b also gives an indication of the retentive character of the column.

The functional retention index is a concept similar to our ΔMe parameter which we have defined as

$$\Delta Me = Me - M$$

where M is the true molecular weight and Me the effective molecular weight given by

$$Me = 14{\cdot}026\,\frac{\log R_{x9}}{b} + 128{\cdot}25.$$

We have found that ΔMe is constant within a homologous series, except for methyl, ethyl and possibly propyl derivatives. The standard deviations on our

results over a much wider range of materials are equivalent to an error of ±0·5 per cent on retention, whereas the data Dr Swoboda reports are equivalent to a 4–5 per cent error. I would suggest that his greater scatter is due to adsorption troubles, alcohols and aldehydes being known to tail badly on pure squalane. The variation of F.R.I. with chain length is almost certainly a consequence of the fact that no correction is made for the column dead volume.

ΔMe has a slight temperature dependence, so that $\Delta Me_\theta = \Delta Me_0 + \mu\theta$, where ΔMe_θ and ΔMe_0 are the values at $\theta°$ and 0°C respectively, and μ is the temperature coefficient. Thus the retentions of all members of a homologous series can be defined by one simple equation, on one particular stationary phase. To illustrate the precision of the method I should like to quote some results obtained with polyethylene glycol-400 as stationary phase. ΔMe_0 and μ values were computed for suitable mono-substituted n-alkanes.

I should like to make one last point which Dr Swoboda has not made clear. The particular attraction of both ΔMe and FRI is that they can be utilized for the prediction of compounds which cannot be unambiguously synthesized, and that is very useful to the organic chemist.

Table 3. Values of ΔMe_0 and μ for mono-substituted n-alkanes

Homologous series	Me_0	μ
I-Iodoalkanes	−34·55	$+10{\cdot}44 \times 10^{-2}$
α-Alkenes	+8·47	$+1{\cdot}44 \times 10^{-2}$
n-Alkane thiols	+44·95	$+8{\cdot}20 \times 10^{-2}$
β-Alkanones	+58·45	$+9{\cdot}70 \times 10^{-2}$

Table 4. Calculated and observed R_{x9} values at 138°C

Compound	*b*	R_{x9}	
		Observed	*Calculated*
n-decane thiol	0·1872	23·18	23·25
hexadecene-1	0·1868	26·34	26·31
Undecanone-2	0·1877	33·11	33·62
1-iododecane	0·1877	40·75	40·11
Nonanol-1	0·1872	48·13	48·95
Octadecene-1	0·1868	62·42	62·19
Decanol-1	0·1872	75·33	75·30

Retention time of n-nonane ($R_{x9} = 1{\cdot}0$) ~ 30 sec.

The data represent a standard deviation of 1 per cent between the observed and calculated values of R_{x9}.

P. G. Dodsworth: We became very interested in the potential usefulness of retention indices when faced with the problem of identifying the components of various mixtures of polychloromononitrobenzenes. Fortunately we were able to obtain reference samples of all twenty compounds from nitrobenzene to pentachloronitrobenzene, but there were obvious advantages to be gained if retention indices could be predicted from structure. We therefore measured retention indices, on the polar column we had chosen, for quite a wide range of substituted benzenes, and certain encouraging regularities soon became obvious.

Three of the pairs in *Table 5* do not fit the pattern quite as well as the others; these are marked with an asterisk. Perhaps it is significant that they all have three adjacent positions substituted.

Table 5. Retention indices of substituted nitrobenzenes and anilines at 125°C on 1 per cent w/w 10- -(2-hydroxyethyl)polyoxyethylphenothiazine coated on Celite

	Halogen positions	*Retention indices*			*Differences*	
		Cl	Br	I	Cl-Br	Cl-I
Nitrobenzenes	2	1,824	1,949	2,140	125	191
	3	1,753	1,883	2,074	130	191
	4	1,783		2,100		317
	2,5	1,926	2,184		258	
	2,3	1,989	2,212		223*	
	3,4,5-Cl_3	2,022			379*	
	3,5-Cl_2-4-I			2,401		
Anilines	2,4	2,023	2,275		252	
	2,5	2,039	2,288		249	
	2,6	1,774	2,003		229*	

Table 6. Retention indices of chloronitrobenzenes on 1 per cent (125°C) and 5 per cent (150°C) columns

Cl *positions*	I_n (1 *per cent*)		I_p (1 *per cent*)		I_n (5 *per cent*)	
	Observed	*Calculated*	*Observed*	*Calculated*	*Observed*	*Calculated*
—	1,140	1,185	1,540	1,642	1,095	1,118
2	1,291	1,296	1,824	1,838	1,237	1,244
3	1,269	1,265	1,753	1,731	1,220	1,218
4	1,297	1,265	1,783	1,731	1,227	1,218
2,3	1,421	1,401	1,989	1,950	1,374	1,365
2,4	1,383	1,377	1,936	1,927	1,351	1,343
2,5	1,382	1,377	1,926	1,927	1,346	1,343
2,6	1,363	1,353	1,930	1,887	1,337	1,327
3,4	1,408	1,387	1,929	1,893	1,369	1,358
3,5	1,337	1,346	1,810	1,820	1,316	1,317
2,3,4	1,533	1,514	2,133	2,077	1,510	1,493
2,3,5	1,460	1,482	2,007	2,040	1,453	1,465
2,3,6	1,473	1,458	2,042	2,000	1,462	1,449
2,4,5	1,481	1,499	2,042	2,089	1,471	1,484
2,4,6	1,425	1,433	1,949	1,976	1,418	1,426
3,4,5	1,497	1,500	2,022	2,019	1,488	1,486
2,3,4,5	1,622	1,627	2,195	2,203	1,616	1,621
2,3,4,6	1,563	1,571	2,107	2,126	1,569	1,576
2,3,5,6	1,553	1,563	2,081	2,112	1,563	1,570
2,3,4,5,6	1,700	1,699	2,232	2,240	1,712	1,713

We then measured our complete set of chloronitrobenzenes on a non-polar column (1 per cent SE-30 on Celite) and examined the two sets of retention indices, I_p and I_n, and their differences, as was done by Kováts. We were not able to find additive constants related to structure which would represent the data satisfactorily, but the I_n values could be fitted, by a suitable choice of 7 constants, by what we call the 'adjacent substituent method', in which one tries to calculate the retention index from a series of values, each related to a set of three adjacent substituents

around the ring. The mean error was 13 units, but a maximum error of 45 was found for nitrobenzene. The I_p values were rather worse, with a mean error of 30 units, and a maximum error of 102, again for nitrobenzene. It seemed likely that adsorption on the Celite could be making the problem more difficult, so we decided to repeat the measurements on columns with 5 per cent stationary phase, at a temperature of 150°C. Unfortunately this work is not yet complete; but the I_n values are now represented rather better by 7 adjacent substituent constants: the mean error has decreased from 13 to 8 units, and the maximum error has been halved. Again, the maximum error is found for nitrobenzene. Possibly this means that with 10 per cent or more stationary phase the fit might be acceptable, although we might still have to use more than 7 constants.

P. A. T. Swoboda: In taste panel testing of flavours, personal preferences inevitably complicate what should be an objective evaluation. From the criticisms we have just heard it seems that a similar difficulty can sometimes arise even in gas chromatography. The prepared contributions of Dr P. G. Dodsworth and Dr J. Pypker require no answer. They are both reports of a great amount of careful research in two very difficult fields. I shall therefore limit myself to a few of the points raised by the workers from the Natural Rubber Producers Research Association.

Dr H. J. Coleman, one of the originators of the technique of catalytic vapour phase hydrogenation, is present here at Hamburg. I have discussed Dr J. F. Smith's criticism with him and therefore this reply also reflects his views. The application of several independent methods of analysis to the identification of gas chromatographic fractions will lead to a greater certainty of correct identification. At the Bartlesville Bureau of Mines Research Center these techniques are regarded as complementary; each with its own advantages and limitations.

The most important difference between micro-hydrogenation and infra-red is in the sample size that can be conveniently handled. Whereas microgram samples can be used in the former (and for this purpose my paper describes apparatus whereby the Pye Chromatograph may be converted into a micro-preparative instrument), the present-day instrumentation of infra-red spectrophotometers makes the latter method of analysis increasingly difficult with sub-milligram amounts. Moreover, as gas chromatographic identification relies on the separation of components, results obtained with impure or mixed samples may be more easily interpreted than infra-red spectra. Quantitative analysis of the products of micro-hydrogenation is helpful when side reactions occur or when multivalent functional groups are present, and the problem of trapping the lower hydrocarbons is avoided if vapour samples are analysed with the flame ionization detector.

The contribution of Mr M. B. Evans is mainly concerned with the precision of retention data. The 'R_{x9}' and 'Retention Index' procedures are only alternative ways of calculation of experimental results which utilize the same homologous series of standards. For interconversion of the two scales the slope b of the 'log plot' is needed and I agree that this should always be given. The mean value and standard deviation of the slope of the 'log plot' graphs used in my determination of the Functional Retention Indices were:

for squalane at 75°: $b = 0{\cdot}360 \pm 0{\cdot}003$ (16 observations)
and, for dinonyl phthalate at 74°: $b = 0{\cdot}346 \pm 0{\cdot}003$ (13 observations)

The use of the statistical 'best straight line' in obtaining the retention of theoretical nonane results in a minimizing of random errors in R_{x9}, and will therefore have the same effect on Retention Indices. Although it is desirable to use adjusted retention measurements to ensure a truly linear 'log plot', this is not essential. Accurate Retention Index values can even be obtained by graphical

interpolation on a curved 'log plot'. The diagram (*Figure 11*) illustrates this for two hypothetical homologous series and for the case where the correction for the dead volume of the column is equal in magnitude to the smallest retention volume.

Similarly a systematic error in the slope b, as can arise from a change in column temperature, has in general a smaller effect on Retention Index than on R_{x9} values because the former is obtained by an interpolation procedure. As a trivial example, the retention of decane may be considered. This, by definition, is always 1,000 on the Retention Index scale, whatever the temperature. The expression quoted by Mr M. B. Evans then gives the R_{x9} value of decane as the antilogarithm of b, which is temperature dependent.

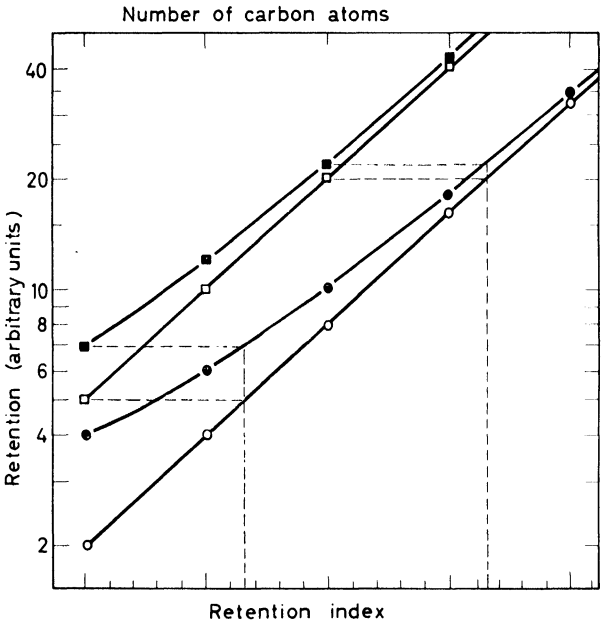


Figure 11. The interpolated value of Retention Index is unaffected by curvature of the 'log-plot' observed when no correction is made for the gas hold-up

Adjusted Retentions: ○, 2, 4, 8, 16, 32; □, 5, 10, 20, 40
Uncorrected Retentions: ●, 4, 6, 10, 18, 34; ■, 7, 12, 22, 42

To consider the relation between errors on the two scales we need only differentiate the equation:

$$\delta(\mathrm{RI}) = \frac{100\delta(R_{x9})}{2{\cdot}303b(R_{x9})} = \frac{\text{per cent } \delta(R_{x9})}{2{\cdot}303b}$$

Thus my value of 5 units for the scatter in Retention Index is equivalent to a 4 per cent error in relative retention on squalane at 75°C. This must not be compared with a standard deviation of $\sigma = \pm 0{\cdot}5$ per cent, but rather with 4σ, the range within which 94 per cent of the replicate determinations fall. The difference in precision between my results and those published by M. B. Evans and J. F. Smith is not so extreme after all.

All retention measurements are susceptible to the influence of the solid support and to changes in the character of the stationary phase. With careful pre-heating

of the column packing I find no undue tailing of alcohols or aldehydes on squalane. Indeed some difficulty was at first experienced with alcohols on dinonyl phthalate, and this is confirmed by the paper of E. R. Adlard, M. A. Khan and B. T. Whitham presented at this Symposium (page 84). Precise data are now being obtained by M. B. Evans and J. F. Smith on polyethylene glycol 400, a stationary phase which in a previous publication they described as readily changing its character. This stresses the caution that has to be used when data from different laboratories are compared. Nevertheless, the publication of precise relative retention data is always of value to the analyst, particularly when sufficient details are given to enable the results to be recalculated in any desired form.

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22

THE IMPORTANCE OF GAS CHROMATOGRAPHIC METHODS FOR THE CHEMISTRY OF BORON ALKYLS AND HYDRIDES

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IMPORTANT progress has been possible in the chemistry of boron compounds thanks to the use of gas chromatography. The chemical properties of boron compounds, in particular their sensitivity to oxygen and water, necessitate special methods and techniques. This is exemplified with compounds such as trialkylboranes, boron heterocyclics and alkyldiboranes and also with bisborolanes. Compounds separated by gas chromatography were identified by their retention times, which reflect structure and size of the molecule, and by mass and infra-red spectrometry.

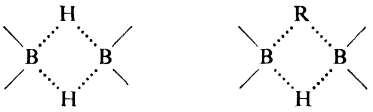
This work represents an example of an unusually close combination of a physical method of separation and a special field of chemistry. In this field gas chromatography not only supplies analytical information of a qualitative and quantitative nature, but also makes possible the purification of substances on a preparative scale. However, a knowledge of the reactions and properties of the compounds under test is indispensable if the gas chromatographic results are to be correctly evaluated and put to good use. The organo-boron compounds which are being studied in the Mülheim Institute by R. Köster and his colleagues are characterized by a great sensitivity to oxygen and in some cases to water as well. (For further details of the particular handling techniques required, see refs 1, 2.) These are a consequence of the reactivity of B—C and B—H bonds which, together with the acceptor nature of the trivalent boron, influences the chemical reactions between these compounds themselves and with other substances. The reactivity of the two types of boron compounds enhances their chemical interest but also increases the difficulty of analysing the many reactions which occur in mixtures of boron alkyls and hydrides. Distillation techniques are often too slow to allow the isolation of individual components. Furthermore, exposure to heat during distillation frequently leads to a change in composition which makes the isolation of pure compounds even more difficult.

Gas chromatography is also of considerable importance in the preparation of the pure samples required for analytical techniques such as infra-red and mass spectroscopy, which can contribute significantly to the elucidation of structure. Both techniques, particularly mass spectrometry, were used for the identification of gas chromatographic fractions; infra-red spectroscopy proved particularly useful with boron hydrides and their alkyl derivatives, owing to their characteristic and intense B—H bands.

A few features of the chemical behaviour of this class of compounds will be

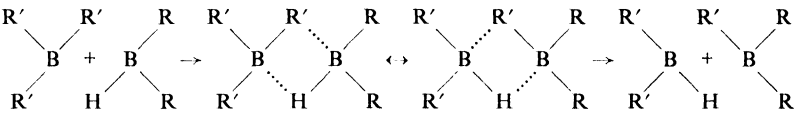
presented first, since they will facilitate the understanding of the problems and procedures involved.

1. Boron hydrides and alkylborohydrides are capable of association:



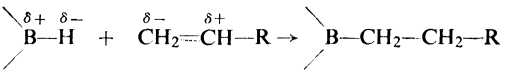
The bonds between boron atoms are known as 'electron deficient bonds'.

2. Owing to the high polarity and polarizability of the B—C and B—H bonds, alkyl groups and hydride hydrogen are capable of switching from one boron atom to another if these are bridged as shown[3]:

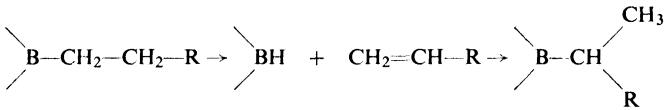


As will be shown below, one must postulate bridges in which the alkyl groups are simultaneously stabilized by hydrogen bonding. In general alkyl bridges between trialkylboranes cannot exist; for the latter are not associated. On the other hand mixed association products are formed from boron and aluminium trialkyls[4]. Thus both boron hydrides and aluminium alkyls act as catalysts for the transfer of alkyl groups amongst boron trialkyls. This exchange of alkyl groups between BR_3 and BR'_3 may be recognized by the formation of two new boron trialkyls, BR_2R' and BRR'_2.

3. Hydroboration takes place by addition of the B—H dipole to a polarized double bond[5,6], e.g.



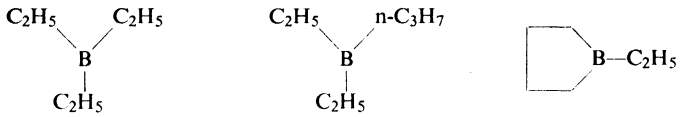
The reverse reaction, i.e. the removal of an olefin from trialkylboranes, is the first reaction to occur on thermal treatment[7,8]. Since the addition of the B—H dipole to an asymmetrical olefin can take place in two directions, the isomerization of alkyl groups, such as isopropyl and t-butyl, attached to boron can be readily explained:



The following selected examples demonstrate the contributions which gas chromatography can make to the elucidation of these reactions of alkyl boranes.

Alkyl boranes

Trialkylboranes may have identical or different alkyl groups attached to boron or they may be cyclic compounds (boron heterocyclics), e.g.



Appreciable elimination of olefins at 150°C precludes the handling of trialkylboranes beyond $B(C_5H_{11})_3$, because of the excessive temperatures required. Since the first step toward isomerization is the elimination of an olefin and attendant formation of the boron hydride catalysing the exchange reaction, isomerization may be neglected as well below the temperature mentioned.

Mixed boron trialkyls are readily formed from mixtures of the pure trialkyl boranes by catalytic or thermal transalkylation, as shown by *Figure 1* for the transalkylation of $B(C_2H_5)_3$ and $B(C_3H_7)_3$ catalysed by boron hydrides. By means of gas chromatography the equilibrium concentrations may be determined rapidly and accurately. The occurrence of this exchange was recognized some time ago by Köster and Bruno[4]. However, the separation of the exchange products by distillation was complicated by retro-reactions.

Thermal exchange may be regarded as a particular case of hydride catalysis; for alkylborohydrides are formed from trialkyl boranes at 150°C by olefin elimination.

The top of *Figure 1* shows the chromatogram of the initial mixture which also contains a small amount of $B(n\text{-}C_3H_7)_2(i\text{-}C_3H_7)$ accounted for below. The middle chromatogram was recorded a few seconds after addition of the catalyst ($R_4B_2H_2$) to the mixture, and the lower one represents the mixture after several hours. Equilibration ceases in the chromatographic column, the most likely reasons being that:

(a) the reaction partners are rapidly separated owing to the great difference in volatility;
(b) the stationary phase will hinder the formation of the electron deficient bond in those cases where donor-acceptor complex formation occurs between the stationary phase and the trialkylborane or the boron hydride.
(c) In addition one cannot exclude the possibility that the highly reactive catalyst may be destroyed even in thoroughly conditioned columns.

No differences in exchange rate could be observed for other alkyl groups such as methyl, isobutyl or n-butyl, which have no branching on the α-C-atom. Appreciably smaller exchange rates are found on the other hand for isopropyl and other secondary alkyl groups attached to boron. Thus the exchange between tri-n-propyl- and tri-isopropylborane only reaches equilibrium after a few days. Over a period of minutes, only traces of the mixed boranes are formed[1]. Conversely, this result may be taken as direct evidence for the formation of an alkyl bridge through the intermediary of a BH_2B bridge. Steric hindrance may be looked upon as the reason for the sluggish exchange of isopropyl groups. Inductive effects of substituents likewise affect the bridging tendency and the B—C bond strength. This will

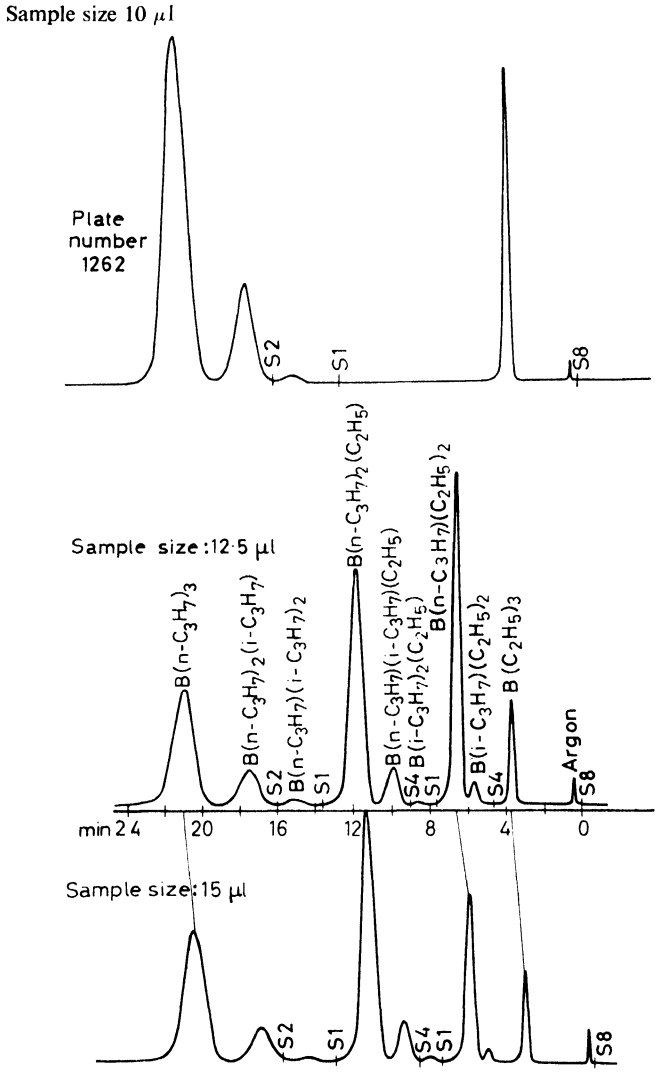
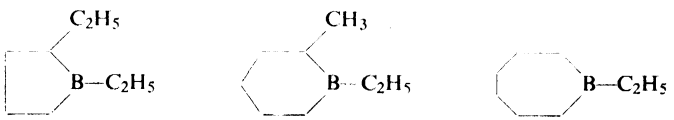
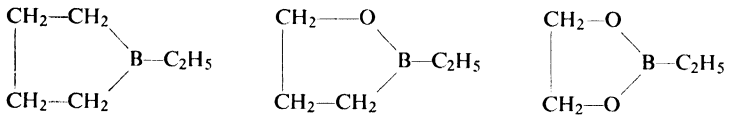


Figure 1. Exchange of alkyl groups between $B(C_2H_5)_3$ and $B(C_3H_7)_3$
Stationary phase: Apiezon
Column length: 2 m
Carrier gas: helium, 151 ml/min
Inlet pressure: 0·8 atg
Temperature: 91°C

again entail a modification of exchange rate between alkyl groups. Measurements of this type were carried out with boracyclanes. When compounds such as



are treated with $B(n—C_3H_7)_3$ under transalkylation conditions, only the ethyl attached to the boron is substituted by propyl whilst the heterocyclic moiety does not participate in the reaction. This means that it does not contribute to the electron deficient bond either[3]. *Figure 2* shows that the ratios of 5-, 6- and 7- membered rings are not altered by the exchange. The influence of inductive effects on exchange rate was determined gas chromatographically with $B(nC_3H_7)_3$ and the following compounds:



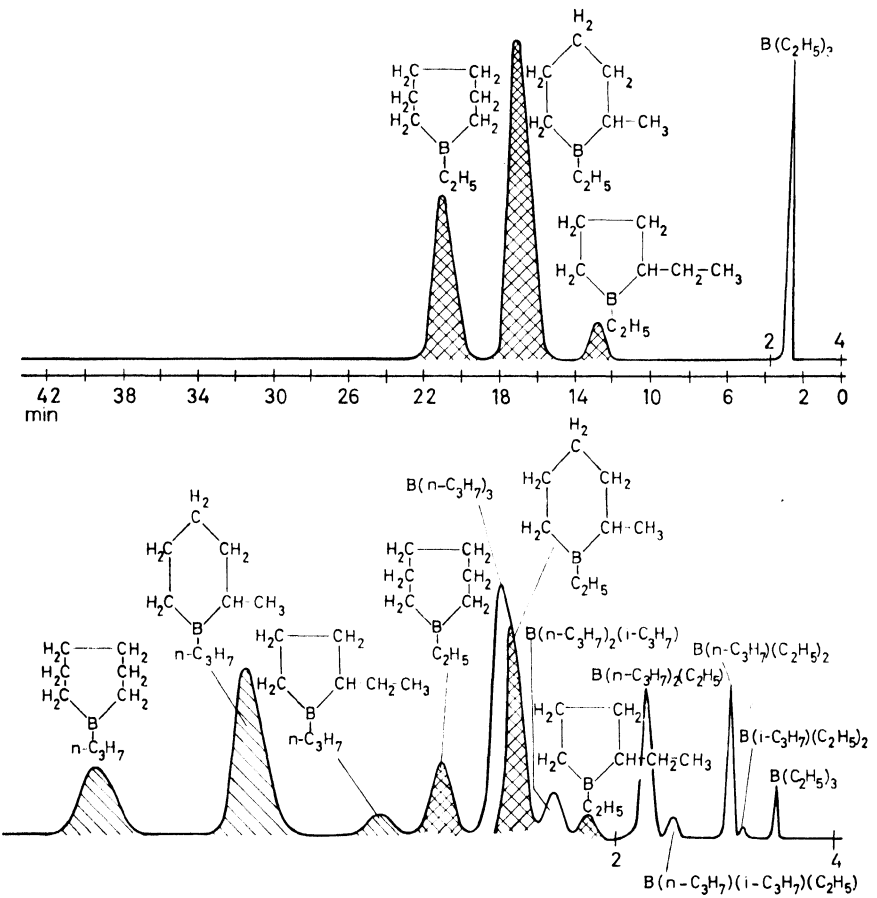


Figure 2. Exchange of alkyl groups between B-alkylboracylanes with 5-, 6- and 7-membered rings

Column: 2 m, squalane on Chromosorb 0·3–0·4 mm
Carrier gas: helium, 100 ml/min
Inlet pressure: 0·7 atg
Temperature: 100°C
Sample size: 10–15 μl

It is found that the inductive effect of the oxygen atom leads to a retardation of the rate of exchange ranging from seconds to hours to days. Once again the heterocycle does not participate in the electron deficient bond.

Identification of new trialkylboranes

The identification of numerous compounds, obtained pure for the first time by means of gas chromatography, was necessary in order to correlate them with the associated peaks. The pure substances were separated from the eluate in a specially constructed cold trap from which the condensate could be transferred to the inlet of a mass spectrometer without coming into contact with air or water[9]. Generally such compounds may be identified mass-spectroscopically by their parent peaks with B^{10} and B^{11}. There are, however, other characteristic masses which may also be utilized for identification. The mass spectroscopic data required for such an identification have been presented by Henneberg, Damen and Köster[9], and are based on spectra of alkylboranes purified by gas chromatography. Complex mixtures of trialkylboranes may be analysed by combination of these mass spectral data with the relationships between retention volumes and molecular size and structure discussed below. These relationships may be in the form of Kováts indices. Hydrocarbons present in the alkylborane mixtures are readily distinguished on emerging from the chromatograph if the effluent is fed to a small hydrogen flame. Unlike boron compounds, the hydrocarbons do not impart an intense green colour to the flame. The same result may naturally be obtained by continuous monitoring of the effluent with a mass spectrometer set to a mass characteristic of boron compounds.

Isomerization of alkyl groups attached to boron

In all n-propylboranes small amounts of the isomeric isopropyl compounds can be detected by gas chromatography. Because the equilibrium reaction:

$$\text{b-n-}C_3H_7 \rightleftharpoons \text{bH} + CH_2{=}CH{-}CH_3 \rightleftharpoons \text{b-i}C_3H_7 \qquad (\text{b} = \tfrac{1}{3}\text{B})$$

is shifted to the left, isopropylboranes are extensively isomerized to n-propyl compounds at temperatures only slightly in excess of 100°C. Isomerization of the individual isopropyl groups in tri-isopropylborane leads to the formation of three new compounds, iin, inn and nnn (i = isopropyl, n = n-propyl). Thus $B(i\text{-}C_3H_7)_3$, prepared by a Grignard reaction, was distilled at atmospheric pressure at about 150°C; the distillate contained the following proportions of the four possible isomers:

iii: 39·6 per cent iin: 31·7 per cent inn: 22·3 per cent nnn: 6·4 per cent

Figure 3 depicts the composition when the isomerization has reached equilibrium. Both pure iii as well as nnn were heated. After 24 hours at 159°C, pure nnn was converted to the equilibrium mixture, which contains 15 per cent of nni and about 1 per cent of nii in addition to nnn. On heating iii the same mixture is eventually formed, corresponding to an almost complete isomerization of the isopropyl groups. This rearrangement had already been described by McCusker[10], who was not able to prove it directly but only by the degradation products (alcohols) of the alkylboranes. It was in fact a

genuine equilibrium since isomerization of nnn yielded the same final mixture. The identity of the four propylborane peaks was established mass-spectroscopically[1,2].

Similarly it could be shown that $B(t\text{-butyl})_3$ cannot exist, which is in agreement with the work of McCusker[10].

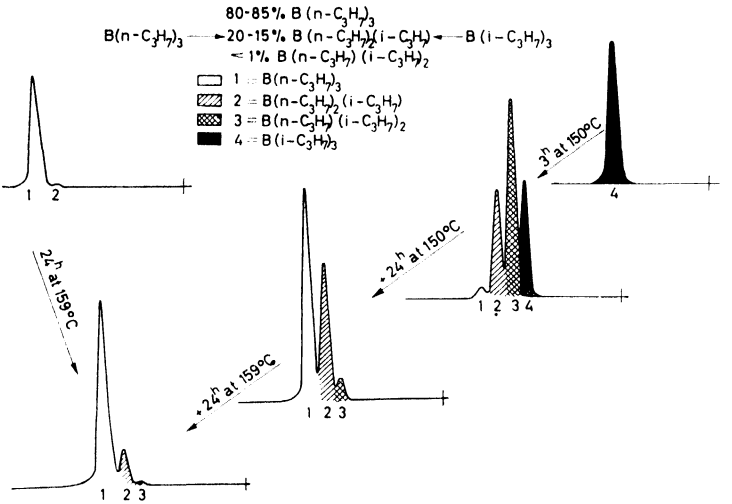
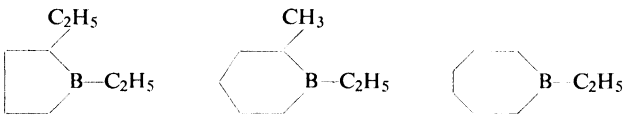


Figure 3. Isomerization of tripropylborane
Column: silicone oil DC 710* on Chromosorb 0·3–0·4 mm
Carrier gas: helium 105 ml/min
Sample size: 5 µl

*Dow Corning Corp., Midland, Mich., U.S.A.

A temperature dependent equilibrium is established for the following three compounds:



and at temperatures of about 160°C the equilibrium lies almost completely towards the six-membered ring[3]. The chromatograms of *Figure 2* indicate the position of this equilibrium. These equilibria are very similar to those for side chain isomerization.

From even these few examples it will be clear that the chemistry of alkylboranes is governed to a large extent by exchange and isomerization reactions. The qualitative and above all the quantitative interpretation of these equilibria has become possible almost exclusively through the use of gas chromatography in combination with mass spectroscopic identification. Alkylboranes may also be identified directly from gas chromatographic data.

Retention volumes of trialkylboranes

In their relation to structure, retention volumes are governed by the same rules as those applying to hydrocarbons. In *Figure 4* the retention volumes

of a few trialkylboranes with straight, branched and cyclic alkyl groups are plotted logarithmically against C-number. From this graph the following rules may be deduced.

1. If for example the ethyl groups of $B(C_2H_5)_3$ are replaced successively by another alkyl group, the retention volumes of the four possible boranes of the series fit fairly well on a straight line. This is true even when the C-number increases by more than one unit for each new substituent.
2. A cyclopropyl group attached to boron[11] influences the trialkylborane in such a way that its retention volume corresponds to that of a compound with one more C-atom. Thus the retention volumes of cee and nne are virtually identical although the first has a total of 7 C-atoms whilst the latter has 8 C-atoms (c = cyclopropyl).

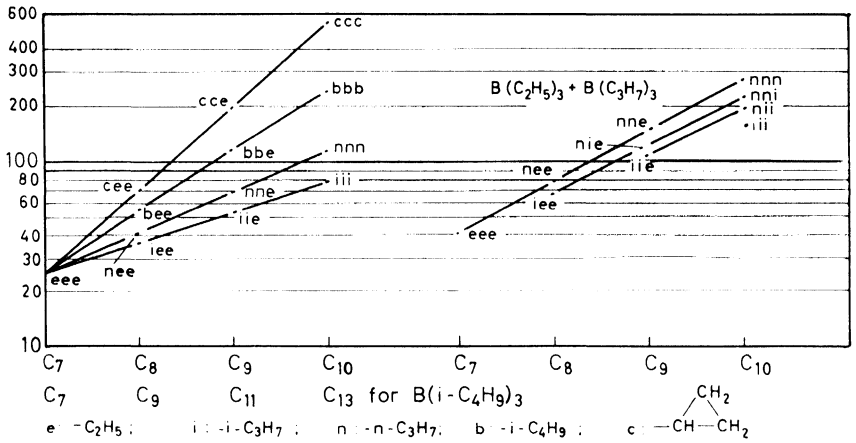


Figure 4. Retention volumes of mixed alkylboranes

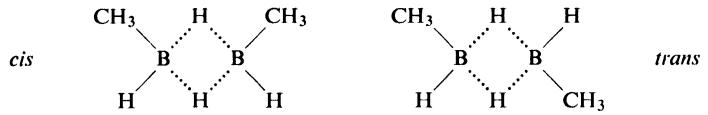
Stationary phase:	silicone oil DC 710	Apiezon
Column length:	2 m	2 m
Carrier gas:	helium, 151 ml/min	helium, 176 ml/min
Inlet pressure:	0·7 atg	0·8 atg
Temperature:	114°C	91°C

3. Trialkylboranes of equal C-number and containing one or more branched alkyl groups lie on a straight line, the slope of which is approximately equal to that of the trialkylboranes with unbranched alkyl groups. The effect of the first branched group is greater than that of the second. When a stationary phase with a more pronounced donor character is used, these differences may be increased owing to greater differences in steric hindrance to complex formation. This occurs, for example, with 7,8-benzoquinoline.

Gas chromatographic study of alkyl derivatives of diborane

When trimethylborane and diborane are mixed, a slow reaction produces five different methyldiboranes[12]: monomethyl-diborane, 1,1- and 1,2-dimethyldiborane, trimethyldiborane and tetramethyldiborane. The 1,2-dimethyldiborane[13] could occur in two different forms if *cis-trans* isomerism

around the BH_2B-bridge were possible, as suggested by Lehmann, Wilson and Shapiro[14].



In the search for these two isomers by gas chromatography a stationary phase must be selected with caution. It should not have a too high donor activity because the interaction of the unpaired electrons with the electron deficiency of the trivalent boron present at its equilibrium concentration might give rise to rupture of the bridge followed by complex formation. The boranes would

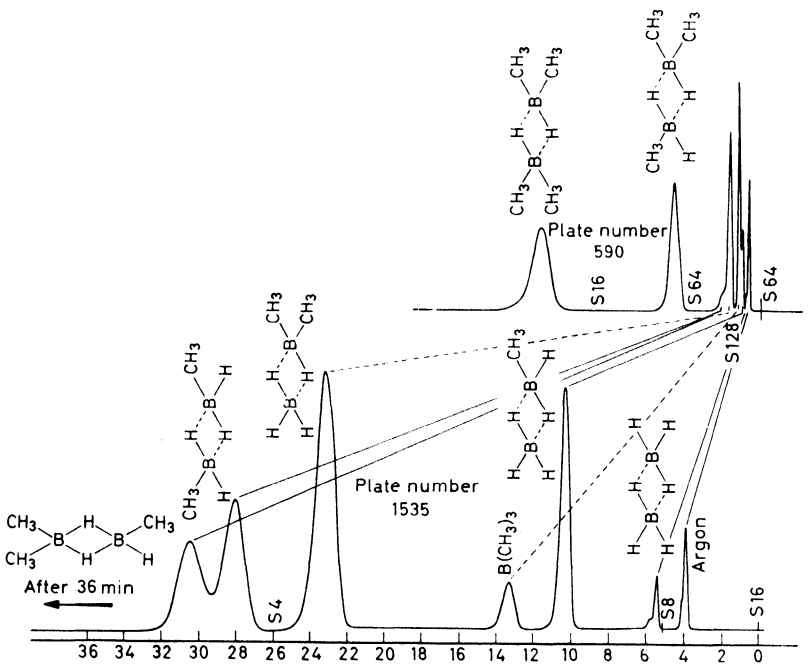
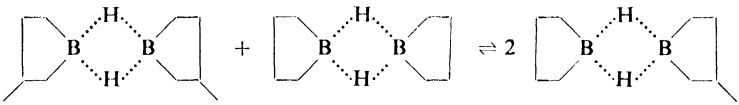


Figure 5. Separation of methyldiboranes
Stationary phase: silicone oil DC 710
Carrier gas: helium
Temperature: 22°C
Column length: 1 m (top); 10 m (bottom)
Inlet pressure: 0·07 atm (top); 2·0 atm (bottom)

then be retained entirely in their monomeric form in the column. Non-polar stationary phases such as squalane, the Apiezons and silicone oils should be suitable. The top half of *Figure 5* shows a chromatogram of a methyldiborane mixture. The lower half of *Figure 5* shows the chromatogram of a similar mixture of methylboranes with an improved separation. All the peaks with one exception correspond to methyldiboranes which Lehmann,

Wilson and Shapiro[14] had already prepared in pure form using standard equipment. With the help of gas chromatographic separation all these components may be isolated from a single reaction mixture. The identification of the several peaks is not difficult since mono-, di-, tri- and tetramethyldiborane differ from each other by single C-number units. It is true that the logarithmic plot of retention volumes against C-number does not give a straight line but identification is readily achieved by infra-red spectroscopy. The separation of the three dimethyldiborane isomers shown in the chromatogram of *Figure 5* was of particular interest. The existence of both *cis-trans* isomers of 1,2-dimethyldiborane allows one to draw important conclusions concerning the stability of the BH_2B bridge. We have isolated samples corresponding to both peaks from the eluate and found that they had almost identical infra-red spectra which coincided with the spectrum recorded for the mixture of the two isomers by the authors named above[14]. More particularly, there was no splitting of the B—H vibration band into the symmetrical and antisymmetrical type characteristic of all diborane derivatives with two hydrogens on a single boron atom not participating in a bridge. Surprisingly, on repeated chromatography both the alleged *cis* and *trans* isomers of 1,2-dimethyldiborane again gave two peaks with retention times identical to those of the original isomer mixture. This phenomenon may be explained by assumption of an isomerization catalysed by electron donors which can rupture the bridge partially or even completely. New configurations are then formed by recombination of the fragments. Such an isomerization could not have occurred in the column, since in that case one would not have obtained two peaks. It is, however, possible that isomerization may have taken place in the cold trap or in the cells. Thermodynamically 1,2-dimethyldiborane is less stable than 1,1-dimethyldiborane, but nevertheless the former is stable. Lehmann, Wilson and Shapiro found that 1,2-dimethyldiborane was stable for two weeks at room temperature and that none of the 1,1-isomer was formed. The isomerization of the *cis* and *trans* forms of 1,2-dimethyldiborane requires at least a partial rupture of the bridge. The conversion of either symmetrical dimethyldiborane into the asymmetrical dimethyldiborane or other methyldiboranes would require, in addition, methyl-hydride exchange across the bridge. It is in fact surprising that this isomerism was detected for the relatively weakly associated methylboranes. It appeared far more promising to look for similar *cis* and *trans* isomers amongst the stable alkyldiboranes. The bis-borolanes, a class of compounds first prepared by Köster[15], represent such a case. These bis-borolanes are outstanding by the great stability of their BH_2B bridges. In the absence of catalytic effects appreciable dissociation of the bridge only starts at temperatures above 100°C. Evidence for this may be found in the course of the thermal exchange reaction between bis-(3-methylborolane) and bis-borolane:



which may readily be followed by gas chromatography, as shown in *Figure 6*[16]. Even at 150°C it takes several hours for the equilibrium concentration

of the 'mixed' bis-borolane to be formed. This reaction is only conceivable if one assumes an intermediate dissociation of the bridge. It may be shown that the addition of a small amount of a relatively strong donor[16] will allow

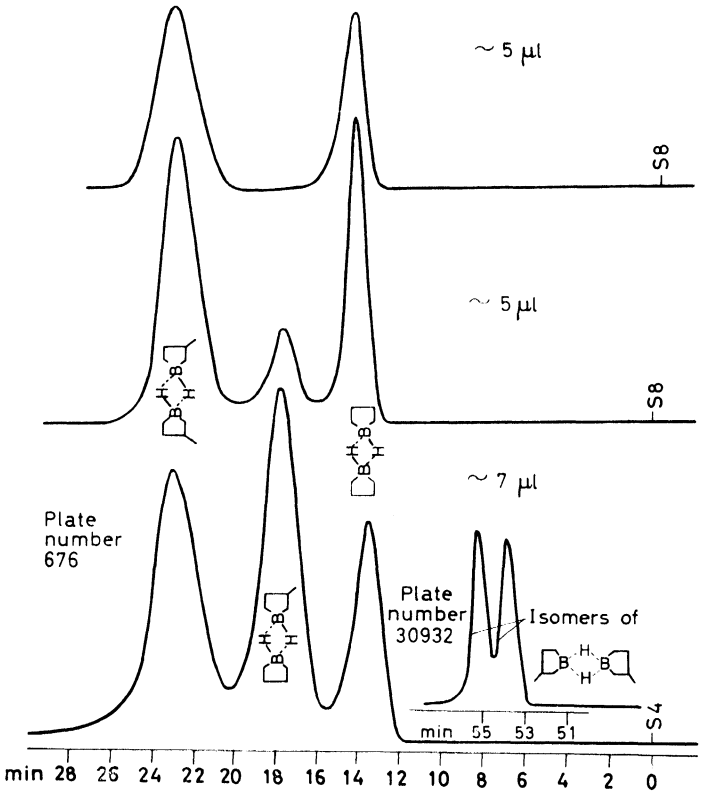


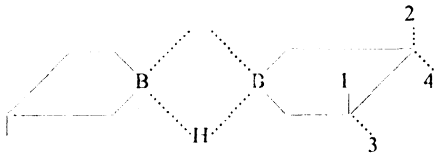
Figure 6. Dissociation-association equilibria of bis-borolanes

		Insert:
Stationary phase:	silicone oil DC 710	methyl silicone rubber SE 30*
Carrier gas:	helium, 105 ml/min	argon
Inlet pressure:	0·5 atg	0·7 atg
Column:	1 m	40 m × 0·25 mm i.d.
Temperature:	116°C	105°C
Sample size:	5, 5 and 7 µl	1 γ

* Scientific Laboratories, Inc., Pennsylvania, U.S.A.

this exchange to proceed even at room temperature. This evidence supports the assumption of a catalytic isomerization of *cis*- and *trans*-1,2-dimethyl-diborane. The peak with the longest retention time in the chromatogram of *Figure 6* must be ascribed to the bis-(3-methyl-borolane). This peak is too wide in relation to its retention time and we therefore believed that it would be possible to separate the isomers of bis-(3-methyl-borolane) with the greater number of plates of a capillary column. Since each half of the molecule contains an asymmetric C-atom, a total of four isomers is possible

if the planes of the two five-membered rings are spatially fixed by the bridge.



The position of the methyl group in 1, 2, 3 or 4 corresponds to four distinct isomers: *trans*-syn (1), *trans*-anti (2), *cis*-syn (3) and *cis*-anti (4). Gas chromatography, however, only gave two peaks as shown in the capillary chromatogram of *Figure 6*. One may assume that the syn- and anti-forms of both *cis* and *trans* isomers differ only slightly and that only the separation of the two *cis*-(3 and 4) forms from the two *trans*-(1 and 2) forms was achieved.

For analysis of alkylboranes and borohydrides by capillary chromatography flame ionization detectors can be used. In the long run, however, difficulties are caused by deposits of boron oxides and carbides on electrode, jet and electrical insulation. With flame ionization detectors the response factors for the alkylboranes appear to be appreciably smaller than for hydrocarbons of the same molecular weight.

Quantitative analysis

Alkylboranes show some deviation from the weight per cent approximation used with hydrocarbons in gas chromatography, and response factors had to be determined. By comparison with mass spectrometric analyses of alkylborane mixtures, calibration factors can also be obtained for gas chromatographic analysis. The required calibration spectra must be obtained with small samples (5 μl) isolated from the eluate during gas chromatographic separation.

One could imagine a simpler method based on a Martin gas density balance, which has a response depending only on molecular weight. The latter is generally known or may be determined by mass spectroscopy with great ease. In practice the gas chromatographic column is followed by a thermal conductivity cell in combination with a gas density balance. The determination of the response factors for a thermal conductivity cell by means of the respective molecular weights is independent of the quantity injected as well as of the concentration of the individual components.

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DISCUSSION

A. Kopenetz: I should like to ask you how, in practice, you handle the samples?

G. Schomburg: Sample containers can only be opened under an inert atmosphere, and the needle of the syringe must also be held in an inert atmosphere during transfer to the chromatograph. Otherwise injection is carried out in the normal manner. The sample introduction system of Tenney and Harris may also be used, and this makes it somewhat easier to introduce the sample in an inert atmosphere. Obviously the carrier gas must be free of oxygen and water.

The greatest difficulties are encountered in removing active hydroxyl groups from the support, as these can interfere with the chromatographic separation of these compounds. We have attempted to do this by pre-treatment with the compounds being analysed as well as by treatment with trimethylchlorosilane. These are some of the precautions that must be taken in practice.

H. Kelker: Dr Schomburg has drawn our attention to the fact that equilibria are, or may be, established relatively rapidly. Have you ever observed any signs of further equilibration during elution, particularly of single late peaks which are moving in relatively pure form in the carrier gas after one or the other reaction product has already been eluted?

G. Schomburg: This can only occur to a negligible extent if at all. You may remember the upper chromatogram of *Figure 1*, showing triethylborane and tripropylborane, and you will have observed that no mixed alkylboranes could be seen. This is the first indication that no further exchange occurs between these two, which are rapidly separated at the beginning of the column. Indeed, one would not expect such an exchange since the catalyst, a borohydride, is readily decomposed on the column, much more easily than the trialkylboranes. This again impedes any exchange. The third factor is that the stationary phase acts as donor and neutralizes the electron deficient bonds, thereby making any further exchange impossible, since the deficiency on the boron is occupied by the donor.

There are many reasons for believing that this does not occur and the measurable effects are very small.

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THE ANALYSIS OF COMPLEX PHENOLIC MIXTURES BY CAPILLARY COLUMN GLC AFTER SILYLATION

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The use of a high resolution glass capillary column for the analysis of phenols boiling in the range 190–300°C is described. The effects of non-linear adsorption and intermolecular condensation are overcome by silylation of the mixture by a simple procedure which also results in an improved separation of *meta-* and *para-* isomers. The conditions for the separation of the resulting trimethyl silyl ethers (TMSE) of phenol, all the cresols, xylenols and ethyl phenols are given and retention data are presented for the ethers of 66 phenols for the purpose of wide-range analysis. The application of the technique to quantitative analysis is discussed and is illustrated by the results from two test mixtures.

THE ANALYSIS of complex phenolic mixtures presents an important problem from the viewpoint of assessing the quality of tar acid fractions derived from coal tars. This applies particularly to the lower-boiling range, viz. 180–230°, which includes phenol, cresols and xylenols, many of which are of industrial importance. Although fractions containing these compounds are now frequently tested by GLC, difficulties are often experienced in the separation of those isomers which have very similar physical properties; the use of either selective stationary phases or columns of high resolving power is then essential.

Brooks[1] has recommended the use of 2:4-trixylenyl phosphate for the selective separation of *meta-* and *para*-cresols, *meta-* and *para*-ethyl phenols and of 2:4- and 2:5-xylenols on packed columns of relatively low efficiency. This technique is useful for the analysis of low-boiling mixtures, particularly when the number of components is limited, but in the case of more complex mixtures a much higher degree of resolution is required. This problem arises in the analysis of the higher-boiling phenolic fractions derived from coal tar, many of which have a potential commercial value. The number of possible isomers these fractions may contain increases rapidly with increasing molecular weight, but in general certain preferred structures have been found to exist. Thus, the C_9 and C_{10} isomers largely consist of the ten possible methyl ethyl phenols, the two indanols and the twelve possible methyl indanols. Capillary column GLC has been applied to this problem, owing to the ease with which the necessary resolution can be attained. However, attempts to chromatograph phenols on capillary columns constructed from various materials were not successful, since tailing peaks were produced, which indicated the existence of non-linear adsorption effects on the capillary wall. Further troubles were experienced in the presence of dihydric phenols, where

some intermolecular condensation appeared to occur, which resulted in elution of only a small proportion of the original sample from the column.

These phenomena were not experienced with hydrocarbons; hence the need to remove the effect of the phenolic —OH group is apparent. Langer *et al.*[2] have proposed such a method, which involves the prior quantitative conversion of the phenols to their trimethyl silyl ethers (TMSE). A double advantage is said to be gained, viz. the adsorptive —OH groups are replaced by a non-adsorptive —$OSi(CH_3)_3$ group, and also the boiling point difference for *meta*- and *para*-isomers is increased. These facts are illustrated by *Figure 1*,

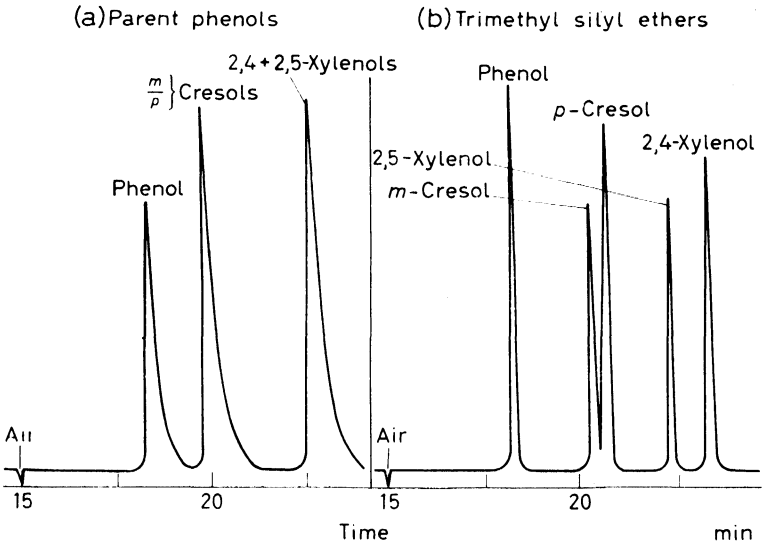


Figure 1. Effect of silylation on GLC of phenols. 6,000 cm × 0·02 cm diameter glass capillary, coated with silicone oil MS 500. Micro argon detector at 1,000 V

in which, for a mixture of low-boiling phenols, chromatograms of (*a*) parent phenols and (*b*) their TMSEs are compared.

This technique was therefore utilized in the proposed method for the analysis of complex phenolic mixtures.

Glass capillary columns of the type first described by Desty[3] were employed to separate the products, as these were found to give far less adsorption than metal columns.

Conversion of phenols to their TMSEs

The trimethyl silyl ethers of phenols can be produced by two basic methods:
(a) By reaction with trimethyl silyl chloride:

$$ROH + (CH_3)_3SiCl = ROSi(CH_3)_3 + HCl$$

(b) By reaction with hexamethyldisilazane:

$$2ROH + (CH_3)_3SiNHSi(CH_3)_3 = 2ROSi(CH_3)_3 + NH_3$$

In the procedure originally proposed the reaction in both cases is carried out in pyridine solution with a trace of HCl added as a catalyst. For the present purposes, however, a modified procedure based on method (b) was evolved, without the use of pyridine, which could interfere with the separation. In addition, the reagent hexamethyldisilazane is readily available; it is a relatively non-toxic, colourless liquid boiling at 120°C which is therefore more suitable for the purposes of routine analysis than the highly corrosive trimethyl silyl chloride. The modified procedure is as follows:

0·5 ml hexamethyldisilazane is added to 0·1 g of the phenolic sample contained in a small sample phial. A trace of gaseous HCl is introduced from a small glass capillary tube containing concentrated HCl and held in the space immediately above the mixture for a few seconds. The contents are then shaken and the phial is placed in an oven maintained at 100°C for 60 min, to allow the reaction to proceed to completion. A sample of the reaction mixture is then withdrawn and chromatographed on a suitable capillary column. The excess reagent acts as a diluting medium and causes no interference with the phenolic ethers during the separation.

Numerous test mixtures have been silylated by this technique, each containing a variety of both monohydric and dihydric phenols. With few exceptions no trace of unreacted sample has been detected by chromatographic analysis of the products; in fact, a close examination of this reaction has shown that the majority of phenols are converted quantitatively to their TMSE within a few minutes. The exceptions occurred in the case of compounds substituted in both *ortho* positions to the —OH group; the extent of the reaction under the conditions described depends on the size of these groups. Thus a 50 per cent conversion is obtained for 2:6-xylenol, decreasing to negligible conversion for 2:6-ditertiary butyl phenol. However, in the case of 2:6-xylenol, a conversion of between 95 and 100 per cent can be obtained by extension of the reaction time. The effect of di-*ortho* substitution on the reaction could be a disadvantage in cases where the concentrations of di-*ortho* substituted phenols are significant. Most coal tar fractions, however, contain these compounds in only very low concentrations and no trace of unchanged phenols has yet been detected in practice.

Apparatus

A glass capillary column, produced on a machine of the type described by Desty[4], is suspended within an electrically heated air jacket whose temperature is controlled by means of a variable transformer. A Lovelock micro argon detector[5], containing a radium D source, is used to detect the eluted components; it is also contained in the air jacket to form a compact arrangement.

Dry batteries are used to supply E.H.T. to the detector, the output of which is fed to a conventional impedance converter comprising an electrometer valve in the input circuit. A 2·5 mV, 1 second response potentiometric recorder is connected to the output circuit via an attenuater, so that the maximum impedance presented to the recorder is 100 ohms. Argon carrier gas is supplied to the column through a pressure control valve and several fine control needle valves. A diagram of the injection system is given in *Figure 2*. The sample is introduced into the preheater region from the micropipette

shown. This is simply a small glass capillary tube attached to the lower end of a stiff platinum wire. The upper end of the wire is sealed into a B.7 Q and Q cone which closes the system as the sample is introduced, to avoid sample losses. The argon gas stream is turned off during the addition of sample to the column to ensure complete vaporization before the sample is carried to the stream splitter. The fraction which enters the column then depends on the ratio of the column flow rate to that of the by-pass, which can be controlled within wide limits.

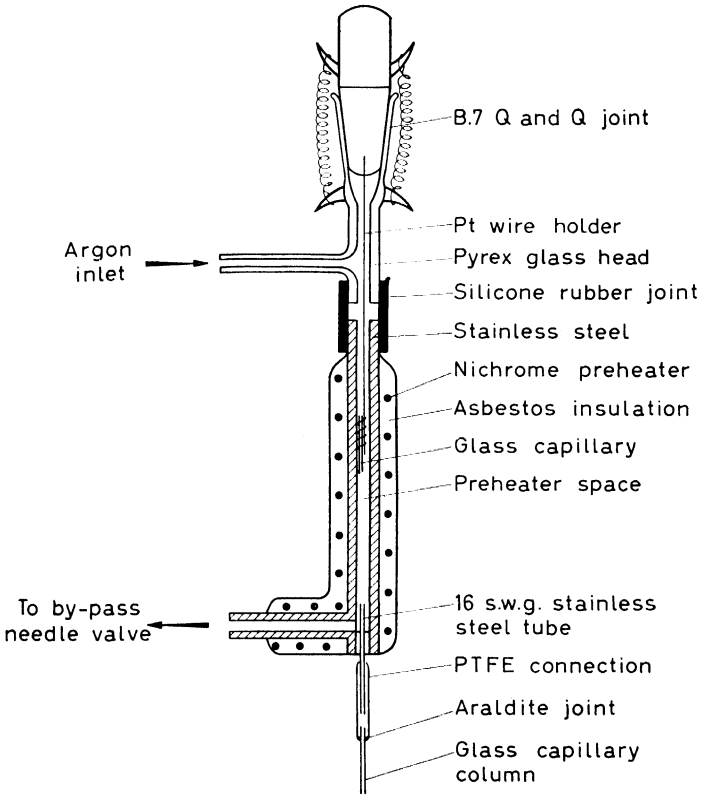


Figure 2. Sample injection system

Retention characteristics of TMSEs of low-boiling phenols

Test mixtures containing phenol, cresol, ethyl phenols and xylenols were silylated by the method previously described and analysed under the following conditions:

Column: 6,000 cm × 0·02 cm i.d. soda-glass capillary coated with silicone oil MS 550[a]
Film thickness: 0·1 μ
Detector: Micro argon at 1,000 V

Column inlet pressure: 60 cm Hg
Column flow rate: 0.3 ml argon/minute
Column temperature: 50°C to 130°C
By-pass flow rate: 50 ml argon/minute
Quantity chromatographed: $\sim 0{\cdot}1\ \gamma$
Column efficiency (phenol) = 100,000 theoretical plates
a value (= Ratio of mobile to stationary phase) = 494

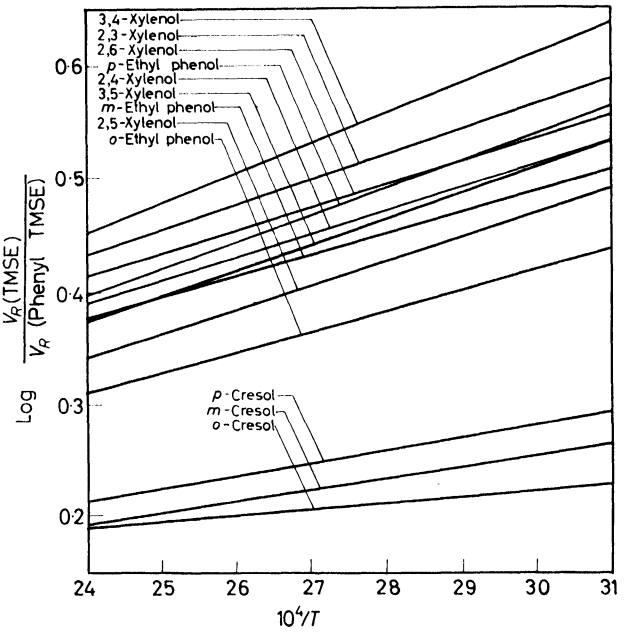


Figure 3. Effect of temperature on the retention characteristics of low-boiling trimethyl silyl ethers. T = column temperature in °K

Relative retention volumes (phenol = 1), corrected for column hold-up, were plotted against the reciprocal of the absolute column temperature. *Figure 3* shows the form of the graphs obtained. Several interesting features are noted:

1. The line for 2:6-xylenol TMSE intersects that for *p*-ethyl phenol TMSE at a point corresponding to a column temperature of 77°C. Thus on the capillary column the 2:6-xylenol ether emerges before the *p*-ethyl phenol ether at temperatures below 77°C and after the *p*-ethyl phenol ether at higher temperatures. At the extremes of temperature used, viz. 50°C and 130°C, a peak separation is obtained for the two compounds under the above conditions.
2. The line for 3:5-xylenol TMSE intersects both the 2:4-xylenol TMSE and *m*-ethyl phenol TMSE lines at points corresponding to temperatures of 50°C and 130°C respectively. Thus the ethers of *m*-ethyl phenol and 3:5-xylenol emerge together at 130°C, separated from the 2:4-xylenol

ether, which comes after them. At 50°C the ethers of 2:4-xylenol and 3:5-xylenol emerge together but are completely separated from the ether of *m*-ethyl phenol.

3. The slope of the line for *o*-cresol TMSE is smaller than the slopes for the *m*- and *p*-cresol ethers, which are almost equal. Thus, changes in column temperature over the wide range used do not critically affect the separation between *m*- and *p*-cresol ethers. The *o*-cresol ether, however, merges rapidly into the *m*-cresol ether as the temperature is raised.

Examination of *Figure 3* indicates that the optimum temperature for separation of all thirteen components, from the viewpoint of retention data, lies in the range 90 to 100°C. Under the conditions described separate peaks were obtained for all the components at 92°C. Relative retention data at this temperature are given in *Table 1*.

Table 1. Relative retention volumes for trimethyl silyl ethers at 92°C on silicone oil MS 550

Compound	*Relative retention volume*
Phenol TMSE	1·00
o-Cresol TMSE	1·58
m-Cresol TMSE	1·63
p-Cresol TMSE	1·75
o-Ethyl phenol TMSE	2·25
2:5-Xylenol TMSE	2·42
m-Ethyl phenol TMSE	2·54
3:5-Xylenol TMSE	2·57
2:4-Xylenol TMSE	2·62
p-Ethyl phenol TMSE	2·73
2:6-Xylenol TMSE	2·80
2:3-Xylenol TMSE	2·97
3:4-Xylenol TMSE	3·08

V_g° (phenol) at 92°C = 525 ml argon
t_R (phenol) at 92°C = 9·4 min

Analysis of wide boiling range phenolic mixtures

In order to attain a quantitative separation between any two components *A* and *B* the following condition, derived from the properties of symmetrical elution curves, must be fulfilled:

$$\frac{n^{\frac{1}{2}}}{4}\left[\frac{K_B/K_A - 1}{a/K + 1}\right] > 1 \qquad (1)$$

where n = column efficiency calculated from peak *A* or *B*

K_A, K_B = partition coefficients of compounds *A* and *B* respectively

K = average partition coefficient = $(K_A + K_B)/2$

$$a = \frac{\text{Hold-up of column}}{\text{Volume of stationary phase on column}}$$

The efficiency of glass capillary columns of the type used in the present

work was found to decrease with increasing retention volume. This is due to the predominant effect of the mass transfer factor in the gas phase predicted by the Golay equation[6] for high values of a and K. The value of a/K, however, also decreases with increasing retention volume and this has an effect opposite to that of n on the resolution. A region therefore exists on the chromatogram, in which the column has a maximum resolving power, corresponding to a/K values lying between 1 and $\frac{1}{3}$ for glass capillaries with

Table 2. Retention values of phenyl trimethyl silyl ethers relative to 5-indanyl trimethyl silyl ether at 100°C

t_R 5-indanyl TMSE = 23·2 min
V_g° 5-indanyl TMSE = 2,630 ml

TMSE of compound	*R.R.V.*	*PK. No.*	*TMSE of compound*	*R.R.V.*	*PK. No.*
Phenol	0·108	1	3-Methyl-5-isopropyl phenol	0·600	22
o-Cresol	0·164	2	3-Methyl-4-ethyl phenol	0·603	22
m-Cresol	0·177	3	4-Methyl-2-*n*-propyl phenol	0·613	23
p-Cresol	0·190	4	2:3:6-Trimethyl phenol	0·645	24
o-Ethyl phenol	0·242	5	2:4-Diethyl phenol	0·661	25
2:5-Xylenol	0·257	6	4-*sec*-Butyl phenol	0·693	26
2:4-Xylenol	0·289	7	3:5-Diethyl phenol	0·726	27
3:5-Xylenol	0·289	7	Resorcinol	0·740	28
m-Ethyl phenol	0·289	7	3:4:5-Trimethyl phenol	0·762	29
2-Isopropyl phenol	0·314	8	2:3:4-Trimethyl phenol	0·762	29
2:6-Xylenol	0·319	8	4-Methyl catechol	0·768	30
Guaiacol	0·319	8	3-Methyl catechol	0·826	31
p-Ethyl phenol	0·319	8	4-Indanol	0·831	31
2:3-Xylenol	0·344	9	4-n-Butyl phenol	0·955	32
3:4-Xylenol	0·376	10	2-Methyl-4-indanol	0·960	32
3-Methyl-6-ethyl phenol	0·381	10	5-Indanol	1·00	33
2-n-Propyl phenol	0·386	10	1-Methyl-4-indanol	1·01	34
3-Isopropyl phenol	0·386	10	4-Methyl resorcinol	1·08	35
2-Methyl-5-ethyl phenol	0·415	11	5-Methyl resorcinol	1·10	36
4-Isopropyl phenol	0·438	12	2-Methyl resorcinol	1·16	37
3-Methyl-2-ethyl phenol	0·445	13	1-Methyl-5-indanol	1·22	38
2-Methyl-6-ethyl phenol	0·456	14	6-Methyl-4-indanol	1·28	39
3-Methyl-5-ethyl phenol	0·470	15	2:3:5-Tetramethylphenol	1·36	40
3-n-Propyl phenol	0·479	16	2:3:4:5-Tetramethylphenol	1·40	41
2-Methyl-4-ethyl phenol	0·483	17	6-Methyl-5-indanol	1·45	42
Catechol	0·494	17	5-Methyl-4-indanol	1·48	43
2-Methyl-5-isopropyl phenol	0·521	18	7-Methyl-4-indanol	1·55	44
2-Methyl-3-ethyl phenol	0·541	19	4-Methyl-5-indanol	1·69	45
4-n-Propyl phenol	0·550	19	7-Methyl-5-indanol	1·77	45
2:3:5-Trimethyl phenol	0·550	19	α-Naphthol	2·38	46
2:4:5-Trimethyl phenol	0·550	19	β-Naphthol	2·70	47
2:4:6-Trimethyl phenol	0·554	20	Pentamethyl phenol	3·09	48
4-Methyl-3-ethyl phenol	0·583	21	*o*-Phenyl phenol	3·22	49

various a values. This rule was found to hold at different column temperatures, hence the optimum temperature for the separation of mixtures of wide boiling range was considered to be that temperature at which the main components were eluted within the range $a/K = 1$ to $a/K = \frac{1}{3}$. With the column described previously, however, a temperature of 160°C was necessary to elute the TMSEs of phenols boiling in the range 190–300°C. This is too high from the viewpoint of prolonged usage since a slight loss of stationary

phase occurred, which caused some detector instability. A further column was therefore prepared and operated as follows:

Column: 7,600 cm × 0·02 cm. i.d., coated with silicone oil MS 550
Film thickness: 0·02 μ
Detector: micro-argon at 1,250 V
Column inlet pressure: 70 cm Hg
Column flow rate: 0·133 ml/min
Column temperature: 100°C
By-pass flow rate: 50 ml argon/minute
Quantity chromatographed: approx. 0·1 γ
Column efficiency (5-indanol TMSE) = 160,000 theoretical plates
a value = 2,900

Under these conditions the ethers of phenols boiling between 4-indanol and *o*-phenyl phenol were eluted in the range $a/K = 1$ and $a/K = \frac{1}{3}$. Thus maximum overall resolution was obtained for these compounds, which constitute the bulk of the boiling range 230 to 300°C. Relative retention volumes for a number of phenyl trimethyl silyl ethers are given in *Table 2*. Each compound has been characterized by a peak number in order to show the extent of the resolution which could be obtained under the above conditions. Thus compounds with the same peak number are eluted together to give a single peak.

By applying condition (1) to the column for the region of maximum resolution, we may see that pairs of compounds having a value of $K_B/K_A > 1{\cdot}013$ will be resolved.

Quantitative analysis

Quantitative analysis of phenolic mixtures was carried out by internal normalization of the peak areas after application of a suitable correction factor. This correction factor was found to be approximately equal to the molecular weight of the parent phenol; hence calculated values of this could be used for most purposes:

$$\% \text{ w/w R'OH} = \frac{\text{Peak area R'OSi(CH}_3)_3 \times \text{m.wt. R'OH}}{\Sigma[\text{Peak areas ROSi(CH}_3)_3 \times \text{m.wt. ROH}]}$$

Table 3. Results from the analysis of low-boiling phenolic isomers

Compound	% w/w *Added*	% w/w *Determined*	
		Run 1	*Run 2*
o-Cresol	9·1	9·0	9·0
m-Cresol	40·7	40·5	40·8
p-Cresol	21·4	22·5	22·6
2:5-Xylenol	16·2	15·8	15·5
2:4-Xylenol	12·5	12·3	12·0

Tables 3 and *4* show the results obtained with the internal normalization method for two test mixtures: the first consisting of a simple mixture of

Table 4. Results from the analysis of wide boiling range phenols

Compound	% w/w *Added*	% w/w *Determined*	
		Run 1	*Run 2*
Phenol	3·3	3·0	3·4
m-Cresol	2·9	2·7	3·0
p-Cresol	4·0	4·2	4·6
3:4-Xylenol	4·4	5·0	5·1
4-Indanol	11·2	11·3	11·5
5-Indanol	13·7	14·2	14·3
α-Naphthol	27·6	27·7	27·2
β-Naphthol	32·8	32·0	31·0

cresols and two xylenols and the second consisting of typical phenols from the entire boiling range which has been considered. The techniques described in this paper have been applied with considerable success to the analysis of tar acid fractions boiling in the range 190° to 300°C. In nearly every case all major components have been identified. Numerous minor peaks have also been detected which cannot yet be positively identified, although most of these almost certainly correspond to dimethyl indanols.

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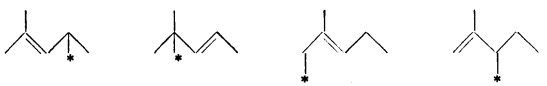
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DISCUSSION

M. B. Evans: The principle of applying chemical reactions to substantiate GLC retention data for identification purposes has recently proved to be of value in the analysis of the complex mixtures resulting from the oxidation and sulphuration of olefins.

The sulphuration of 2-methyl pentene-2 in the presence of accelerators such as MBT and TMTD gives rise to complex mixtures of mono- and disulphides containing the groups:



A1 A2 B1 B2

(* = point of attachment).

The G.L.C. assignments of the disulphides were confirmed by examination of the thiols obtained by treatment with $LiAlH_4$, which selectively attacks S–S bonds.

Assignments of the monosulphides were facilitated by the application of the ingenious silver ion degradation technique of Dr B. Saville[7], which is specific to the groups marked A. Thus all sulphides other than those of the type BSB were removed. Since the silver mercaptides of the groups formerly attached to A groups could be isolated, it was possible to confirm further assignments by GLC examination of the thiols obtained by hydrolysis of these mercaptides.

I should like to emphasize that the spectroscopic methods also used were invaluable in the analysis of these sulphides.

Lastly we have recently proved chromatographically that cyclo-hexenyl hydroperoxide occurs in an oxidized sample of cyclo-hexene. Chromatography on a column of 5 per cent DNP on Celite at 65°C revealed the presence of a number of peaks with relatively short retentions, and one late peak which disappeared on treatment of the sample with triphenyl phosphine. At the same time a peak for the expected cyclo-hexenol appeared, so that we could confidently assign the late peak in the parent sample to cyclo-hexenyl hydroperoxide.

G. Schomburg: I should like to ask Mr Grant if it is possible to silylate other types of compounds. I think this will depend on the acidity of the hydrogen in the hydroxyl group. Could you please tell me if there are any possibilities of applying your method to other hydroxyl compounds?

D. W. Grant: Of course, the silylating reagent which we used, $(CH_3)_3SiNH\ Si(CH_3)_3$, is very reactive towards OH groups in general. We have only applied it to phenols, but I believe it can be applied to a number of other hydroxyl compounds.

H. B. Hass: I should like to point out that silylation is becoming a common technique in carbohydrate chemistry. About four years ago Chang and I published a paper[8] in which we pointed out that even such an involved compound as sucrose can be treated with $(CH_3)_3SiCl$ and converted into a perfectly distillable material. This has also been done with dextrose and other carbohydrates.

A. Prox: We have found that the hydroxy groups of aliphatic hydroxy amino acids (serine and threonine) can also be protected by silylation with $(CH_3)_3SiNH\ Si(CH_3)_3$. After N-acetylation and esterification of the remaining hydrogens these compounds can be easily chromatographed. We think that these compounds would be destroyed in the column if the hydroxyl group was not protected.

D. W. Grant: I fully agree with these remarks.

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PANEL DISCUSSION

QUALITATIVE ASPECTS OF GAS CHROMATOGRAPHY

Chairman: J. F. K. HUBER
Panel: H. BOER and K. P. HUPE
Report by: A. B. LITTLEWOOD

Papers were presented by Dr K. P. Hupe on 'Retention data and Gas Chromatography', and by Dr H. Boer on the application of specific chemical and physical methods of identifying vapours emerging from the chromatographic column. Dr Hupe spoke first as summarized below.

In the identification of an unknown substance by gas chromatographic retention data, there are two principal questions to be answered:

(*1*) With what degree of certainty can one identify a substance from retention values alone?

(*2*) Which parameters of the chromatogram are the most accurate, the most practical, and have the best reproducibility?

The first of these questions is easily answered; retention data simply provide one characteristic number for each chemical species, and such data are therefore no better at identification than, for example, a single determination of a melting point. In the general case, gas chromatography is valuable because of its separating power. Pure components separated thereby can then be effectively identified by other means, such as those described by Dr Boer. One common problem, however, in which gas chromatography is effective at unambiguous identification is when the mixture of interest contains but few compounds, about which some information is already available.

Even for simple substances, retention data may be inadequate, e.g. ethyl formate and methyl acetate have similar retentions on both polar and non-polar stationary liquids. For more complex substances of higher molecular weight, for which there are many possible isomers, the problem is still harder.

The answer to the second question lies, above all, in the collection and publication of important retention data. At present there are four methods of presenting retention data:

(1) the specific retention volume;
(2) the relative retention;
(3) the retention index of Kováts;
(4) the theoretical nonane number of Evans and Smith.

The specific retention volume is necessary for determination of physico-chemical data from gas chromatography; but for qualitative identification it is cumbersome, and it cannot be determined with sufficient precision on most commercial apparatus.

The inaccuracy in the measurement of column parameters is eliminated if retentions relative to a similar substance are determined; in such determinations, a correction for dead volume should be made, and relative retentions should not exceed 3 or 4. Relative retentions do not depend on flow rate or pressure drop; and if the reference substance is of the same chemical class as the substances being compared, relative retentions are not very dependent on temperature. In theory relative retentions are also independent of the proportion of stationary liquid and the nature of the carrier gas, but this may not be so with polar substances. Again, the reproducibility of the retention data of polar substances is best if retentions are compared with those of a reference substance of similar class.

A drawback to the use of simple relative retention data is that there is no real

standardization of substances used for reference purposes by different workers, which limits the utility of the data and increases the possibility of error.

Kováts, and Evans and Smith, have each introduced retention parameters of greater generality. Kováts, in his retention index[1], uses the whole range of n-alkanes as reference substances, whereas Evans and Smith recommend reference to their so-called 'Theoretical Nonane Value'[2] (as R_{x9} values). Both methods are clear and uniform; and though at first sight the retention index appears to involve more calculation, it proves simple if the calculation is properly laid out. Of the two schemes, the R_{x9} method may be liable to greater error for substances with retentions differing very much from that of nonane. A further advantage of the Retention Index is its small and usually linear variation with temperature.

We leave for discussion the question as to whether retention data should be expressed relative to n-alkanes in either of the above ways. The question, whether or not such a procedure is thermodynamically justified, especially with strongly polar substances, cannot yet be properly answered.

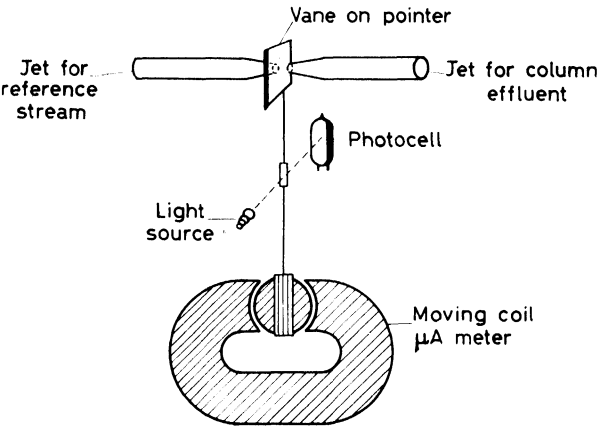


Figure 1. Jet stream detector of V. N. Smith, described by H. Boer. Unbalance of the jet streams causes displacement of the pointer. The photocell acts as a sensor for a feedback loop which controls the current through the coil to bring the pointer back to its original position. The feedback current is recorded

Most of Dr Boer's talk was integrated with a chart on the blackboard which summarized the many ways in which gas chromatography and ancillary techniques used with it could be used for qualitative identification. This chart, in which some of Dr Boer's further remarks are incorporated, is shown in *Table 1*. Dr Boer's thesis was that the information obtainable could be classified roughly into the five classes which form the headings to the five columns of the chart. Most of the entries are self-explanatory. We add the following notes:

(a) It is not commonly realized that halogen may be detected in a flame ionization detector if a thin copper wire is placed in the flame. The flame goes green in the presence of halogen.

(b) In many cases, particularly with hydrocarbons, the boiling point of a substance is obtained by running it in a linear temperature programmed chromatogram on a non-polar stationary phase. Under such circumstances, the boiling point is an approximately linear function of emergence time.

(c) The 'Jet Stream Detector' is a simple apparatus developed by V. N. Smith at Shell Laboratory, Emeryville. The flows from two columns (see *Figure 1*) are

directed on to the sides of a little vane attached to the needle of a moving coil meter, which is held in an equilibrium position by the passage of a current through the coil. When a vapour appears in one jet stream, the force on that side of the vane increases, thus moving the coil, and a change in the current is required to restore equilibrium. Movement of the coil is detected by a photo-electric device, and by means of suitable electronics the current necessary to maintain equilibrium is recorded. The record forms a chromatogram.

(d) Dr Boer pointed out that one could very often obtain a great deal of diagnostic information by using two detectors, one of which responds proportionally to mass, and one of which responds to some specific property. The ionization cross-section detector is very suitable as a detector which responds to mass. A selection of suitable specific properties of interest, all of which have been used in gas chromatographic detectors, are included in the table under 'Specific Detection, (d)'.

The discussion was organized under the headings given below.

(a) *Measurement of Retention Data*

Dr J. F. Smith said that standards and specifications for the measurement of retention data were at present under review by a sub-committee of the Gas Chromatography Discussion Group. He suggested that the series of n-alkanes should be used as standard substances; and that other compounds should be related to these, via either retention indices or R_{x9} values. He emphasized the well-known fact that all retention parameters involve measurement from the air peak, not from the start of the chromatogram; and suggested that for precise data, flow should be controlled to within about $\frac{1}{2}$–1 per cent, and temperature to within 0·1 or 0·2°C.

Dr. H. Kelker raised the point that carrier gas or sample reaching the column from the sample injector may not be at the column temperature, and asked how long a tube is required before the flowing gas has come to thermal equilibrium. Dr G. W. A. Rijnders suggested that the temperature of the liquid phase alone was important, and that the first part of the column was not cooled by the passage of cooler carrier gas. This suggestion was echoed by Dr G. Dijkstra, who referred to a similar discussion at the last symposium, and said that there is no heat exchange with the liquid phase.

Finally, Dr Kelker asked if there were any commercial apparatus on which specific retention volumes could be measured, to which question he received no answer; maybe this implies that the correct answer would be 'None'.

There was then a short discussion on the relevance of the proportion of stationary phase in packed columns on retention data. Dr J. F. Smith suggested that in accurate work the ratio of area to volume of stationary liquid should be quoted; and also two experiments should preferably be performed, with different proportions of stationary liquid. Dr D. M. Ottenstein said that the effect of the proportion of stationary phase both on retention and on column performance depended in a complex way on the problem being treated, and also on the medium supporting the liquid. He illustrated this thesis by comparing the performances of Celite and Firebrick coated with various proportions of stationary liquid.

(b) *Presentation of Retention Data*

Dr G. Schomburg said that measurement of absolute retention data was required for equilibrium studies only, but that relative retention data were suitable for practical purposes. Dr R. Kaiser said that in his experience the retention index of Kováts was very useful for routine presentation of retention data; and that, though it seems a rather complicated expression, it is easily taught to unskilled staff, who

Table 1. Diagnostic Methods for Vapours Emerging from a Gas Chromatographic Column

Elemental Analysis

Carbon

1. Flame ionization detector—molar response approximately proportional to number of non-oxygenated carbon atoms
2. Use of infra-red detection of CO_2
3. Isotopic exchange

Hydrogen

1. $H_2O + Fe \rightarrow H_2$
2. $H_2O + CaC_2 \rightarrow C_2H_2$

} Reactions in a reactor after the column

Halogen

1. Beilstein test[a]
2. Coulometric identification of halogen
3. Prof. Cremer's detector [see page 189]

Sulphur

1. Smell in flame
2. Coulometry of SO_2 or H_2S

Physical constants

Molecular weight

1. Gas density meter
2. Jet stream detector[c]

Boiling point

1. Temperature-programmed GLC[b]

Heat of combustion

1. Flame detector
2. Catalytic combustion detector (p. 178).

Functional groups

Diagnosis from column by retention data

Diagnosis from column by means of physical/chemical absorption

1. Molecular sieves—retain straight chains
2. $>C=C<$ + H_2SO_4
3. $>C=C<$ + Silver aluminium silicate
4. $>C=C<$ + $Hg(ClO_4)_2$
5. $R\text{-}CH_2OH$ + acid substrate, dehydrate to olefin

Specific detection[d]

(a) One detector for mass, one for specific property:

1. Cross-section detector + . . .
2. Combustion detector + . . .
3. . . . + emissivity
4. . . . + flame ionization detector
5. . . . + surface potential detector
6. . . . + dielectric constant detector

Structural analysis

'*External*' *methods*: i.e. simple organic reactions carried out independently of GC, in which GC is used to identify the products

1. Ozonolysis of olefins
2. Hydrogenation and dehydrogenation
3. Methylene insertion
4. Oxidative breakdown

Pulse reactor: i.e. a reactor placed immediately ahead of a chromatographic column. An unknown substance, being injected, first passes through the reactor, after which identifiable and characteristic products are separated by the column

1. Hydrogenation and dehydrogenation
2. Pyrolysis

		7. . . . + argon detector family 8. .. . + mass spectrometer family 9. . . . + UV-detector 10. . . . + IR-detector (b) Chemical detectors 1. Titration 2. Electrical conductivity 3. Coulometry 4. Colorimetry '*External*': i.e. separate diagnostic instruments which are used to study each pure component separated by GC MS, UV, IR, NMR, etc.	
Radiochemistry			
1. Liquid scintillation 2. Scintillation crystal 3. Combustion + gas counter 4. Hydrocracking + gas counter 5. Gas counter as such			

can then use it easily and effectively. Dr. J. F. Smith agreed, and emphasized the importance of using n-alkanes as standard substances.

(c) *Qualitative use of Detectors*

Mr P. L. Timms described some elegant work in which unknown silicon–germanium hydrides could be completely characterized by gas chromatographic separation in combination with qualitatively selective detectors. The molecular weight of an unknown compound was determined within about 1 per cent by means of a gas density meter. A less precise molecular weight of a smaller sample could be obtained from katharometer measurements on the vapour in hydrogen carrier gas, and with a gas density meter with nitrogen used as carrier gas. Finally, the silicon–germanium ratio could be obtained by gas chromatographic analysis of $SiCl_4$, $SiCl_3H$, and $GeCl_4$ produced when the unknown compound was passed over gold chloride, again in combination with a gas density meter as detector.

On the use of mass spectrometers, Dr D. Henneburg pointed out first, that for identification purposes it is necessary to use a good mass spectrometer; and second, that, though this is expensive, it may not prove more expensive than the total cost of the several other types of diagnostic detector that might otherwise be necessary.

Dr H. Boer then described the jet stream detector already mentioned; and in connection with this, Mr G. F. Oldham referred to the fact that the gas velocity in a detector increases as a vapour is emerging from the column, and asked what effect this might have. Mr E. R. Adlard confirmed Mr Oldham's observation. Dr Boer agreed with the observation, but said that it had not been recognized as a perturbing influence on the operation of the detector.

(d) *Gas Chromatography and Other Methods of Analysis*

Mr M. B. Evans pointed out, that in his experience the combination of GLC and infra-red spectrophotometry has proved to be one of the strongest analytical tools; in this connection Dr Boer referred to commercial infra-red micro-cells suitable for taking spectra of the quantities of material normally encountered in GLC. Finally Dr H. J. Coleman illustrated the power of the technique with an example in which particular peaks on a chromatogram were identified as cyclic sulphides, and by hydrogenation or de-sulphurization the hydrocarbon structure was identified. The analysis was confirmed by comparison of infra-red spectra of the peaks with those of synthetic products, which were identical.

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24

ANALYSIS OF MILLI-MICROLITRE QUANTITIES OF PERMANENT GAS MIXTURES

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A chromatographic method is described for the determination of milli-microlitre (10^{-6} ml s.t.p.) quantities of hydrogen, nitrogen, oxygen, neon, argon, krypton, xenon, carbon monoxide, methane and carbon dioxide.

The technique is based on the use of high purity helium (+99·999 per cent) carrier gas, a column of molecular sieve or silica gel adsorbent for separation of the gases and a radioactive type ionization detector. With this detector the above gases are ionized while the helium is unaffected. The apparatus for the purification of helium is described and the necessity for retaining this high purity discussed. The performance characteristics of the detector as a function of temperature, pressure, gas flow and electrode setting and voltage are reported.

A method of calibration for various gases is described, the additions ranging from 10^{-7} ml to 10^{-3} ml (s.t.p.). Column performance for these low levels is illustrated. Reproducibility data and detection limits for the different gases are given.

MANY present-day methods for the analysis of volatile multi-component mixtures are based on a chromatographic separation. The availability of sensitive detectors has led to rapid advances in the organic chemistry field, but it is only recently that such detectors have been developed for the analysis of permanent gases.

The work reported in this paper deals with the application of the 'Penning effect' to detection of permanent gases in helium after chromatographic separation.

Apparatus

The chromatograph consists of a purification train for the carrier gas, a gas sample handling system, a chromatographic column and an ionization detector with the appropriate electronic equipment.

Helium purification system

Cylinder helium (commercial grade) is first passed through traps of Linde molecular sieve 5A (calcium alumino-silicate) at 20°C and −196°C to remove the bulk of the impurities. The molecular sieve is activated by pre-heating in air at 400°C for several hours. This part of the apparatus is duplicated so that one set of traps is always operative. The helium then passes through tubes containing titanium sponge at 800–1000°C and Hopcalite[a] granules at 300–400°C to remove remaining traces of oxygen, nitrogen and hydrogen.

The final treatment consists of two more molecular sieve 5A traps at 20°C and −196°C to remove moisture formed in the oxidation of hydrogen by the Hopcalite. The apparatus can be constructed in stainless steel or silica and is capable of purifying helium at flow rates of up to 200 ml/min.

The primary low temperature trap is regenerated by removal of the refrigerant, which allows desorption of the permanent gases at room temperature. With higher purity cylinder helium, particularly if low in argon, the low temperature traps can be omitted.

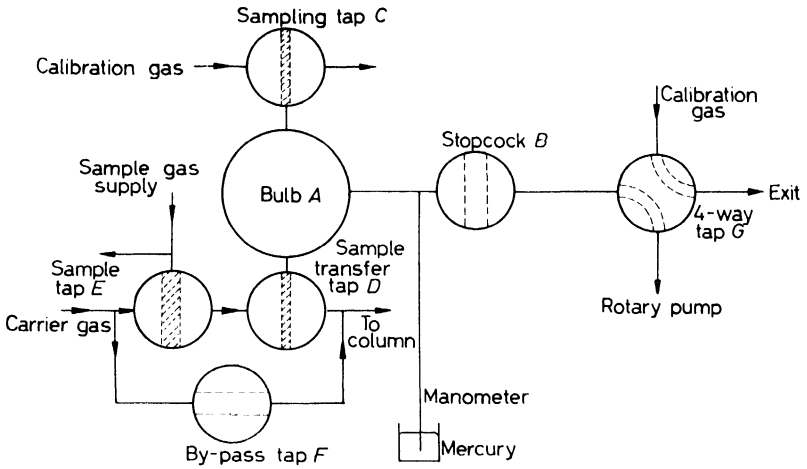


Figure 1. Gas sample handling system

Gas sample handling system

The glass system illustrated in *Figure 1* is designed for the introduction of gas samples and standards at any pressure up to 1 atm; the volumes can be as small as 10^{-5} ml or as great as 1 ml (s.t.p.).

The volume of bulb *A* is approximately 100 ml; it can be evacuated to a pressure of a few microns Hg by a two-stage rotary pump via the stopcock *B* and four-way tap *G*. The gas used for calibration (or the sample) is allowed to flow from the cylinder through the tap *C* to the atmosphere. When the barrel is turned through 90°, the volume of the trapped portion, i.e. 30 μl, is transferred into bulb *A*. In this way the size of the sample transferred to the column is dependent on the number of additions made by turning the tap *C*. The bore in the sample introduction tap *D* also has a capacity of 30 μl, which effectively transfers to the chromatographic column 0·008 μl (8×10^{-6} ml at s.t.p.) of sample per turn of tap *C*. Alternatively, the pressure in bulb *A* can be set at various values up to atmospheric by introduction of gas through tap *G*, allowing tap *D* to transfer up to 30 μl of gas at s.t.p. Tap *E* has a bore of capacity 0·70 ml and is used to sample gases containing trace impurities.

Chromatographic column

The column normally used consists of a 120 cm long 5 mm bore stainless steel tube packed with 36–60 mesh molecular sieve 5A initially activated at

400°C. The column is electrically heated with thermostatic control for the range 50–250°C, but is normally operated at 100°C. Other columns of molecular sieve 5A, ranging from 30 to 60 cm with a diameter of 3 mm, have been successfully used for separations at room temperature and −80°C. Reactivation is carried out *in situ* by heating at 250°C for several hours in a stream of helium. For determination of carbon dioxide the molecular sieve 5A is replaced by a column of 36–60 mesh silica gel, 60 cm long by 3 mm diameter for use at 20°C, or 120 cm long by 5 mm diameter for operation at 100°C.

Detector

The detector is similar to that described by Lovelock [1] except for the absence of the scavenge gas supply. The gas issuing from the chromatographic column passes down the anode into the ionization chamber, where it is bombarded with beta particles from either a 10 mc strontium-90 or a 100 mc tritium source. The radioactive foil seated in close contact with the brass body of the chamber acts as the earth electrode. The anode is supported co-axially within the chamber by a PTFE insulator. The E.H.T. and amplifier unit for use with the detector is of the type used in the Pye argon chromatograph; the output from the amplifier is fed to a 10 mV 1 sec response recorder.

Carrier gas purity

The purity of the helium carrier gas determines the magnitude and nature of the signal when a sample passes through the apparatus. High sensitivity combined with reproducibility can only be satisfactorily obtained by the use of high purity gas. Such helium can be readily obtained by the purification method already described.

Original experiments with only molecular sieve 5A low temperature traps (−196°C) showed that the required purity of helium, at flow rates up to 100 ml/min, could be maintained for only a few hours. However, it is possible to maintain a flow of pure helium over a period of several months if the chemical purification system is incorporated. Titanium at 800–1000°C is most efficient for operation over long periods in removing oxygen and nitrogen (below 1 v.p.m.). It is essential to put the Hopcalite (300°C) after the titanium to ensure oxidation of hydrogen diffusing out of the titanium in addition to 'break through' gas from the initial traps.

With this high purity helium (total impurities less than 10 v.p.m.) all peaks are positive, owing to an increase in ionization current as the eluted components pass through the detector. However, when less pure carrier gas is used a negative peak is first obtained for oxygen, owing to a decrease in the ionization current. Further contamination of the helium results in negative peaks for all the eluted components. *Table 1* gives the level of impurity for maximum ionization current and shows large differences between one component and another. The effect of water is particularly marked; helium containing above 10 v.p.m. water results in oxygen giving negative signals, and at 50 v.p.m. water all components give negative response. The closer the impurity concentration in the carrier gas approaches the limiting value, the smaller is the usable range of the apparatus for analysis of samples.

Table 1. Maximum impurity levels

Impurity	*Limiting concentration* in helium (% by vol.)*
Hydrogen	0·15
Oxygen	0·04
Nitrogen	0·08
Argon	0·10
Methane	0·05
Carbon monoxide	0·03
Carbon dioxide	0·01
Water	<0·005

* The effect is additive so that combination of impurities will reduce the individual values.

Even with high purity helium saturation of the system occurs if too large a sample is analysed, resulting in peak inversion (*Figure 2*).

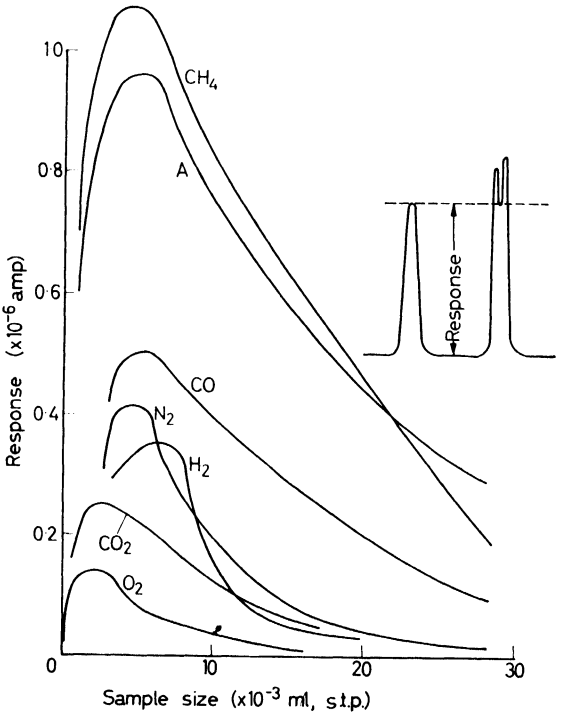


Figure 2. Effect of large sample additions. Detector volts, 1,000 V; flow rate, 75 ml/min

Factors influencing operation

For the molecular sieve 5A column of 120 cm × 5 mm diameter at 100°C, and with response for components based on peak height measurements, the following conditions were studied.

Detector temperature

Under normal conditions a 1°C rise in detector temperature within the range 20–40°C results in a positive error of 0·5 per cent. When the detector is operated at very low temperatures, the sensitivity is appreciably reduced and higher operating voltages are required. For instance, in the present apparatus the response at 1,750 V and −80°C is equal to that at 1,250 V and 20°C.

Flow rate

The behaviour of the detector is influenced by the velocity of the gas issuing from the anode. Under normal conditions the response falls by 10 per cent when the helium flow is increased from 50 to 100 ml/min.

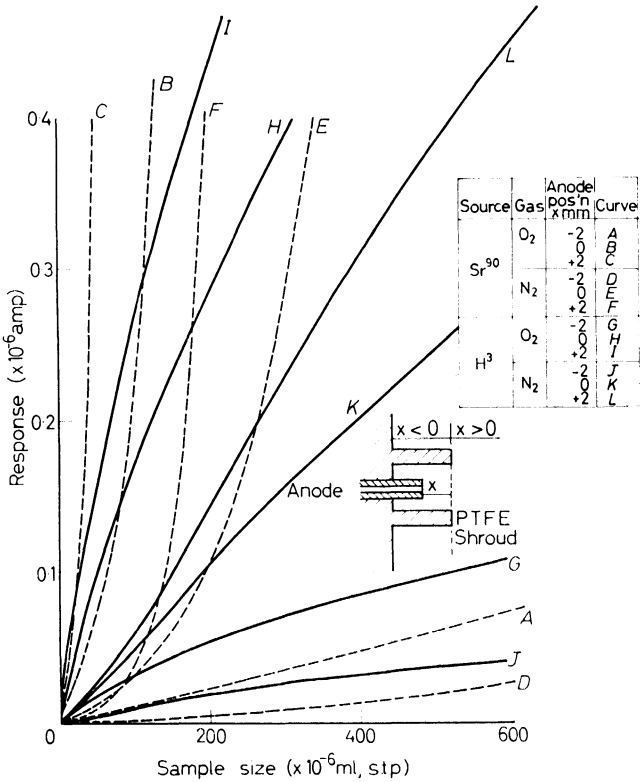


Figure 3. Effect of anode position

Pressure

The ionization current for helium or helium containing impurities decreases with rise in pressure. Under normal operating pressures, i.e. 760 ± 20 mm Hg, the average loss in response for an eluted component is 4 per cent per 10 mm Hg rise in pressure. Up to 90 per cent loss in response can occur if a detector is used which is designed to operate at high voltage and low primary current.

Position of anode within the detector

The position of the anode is primarily governed by the average range of the beta particles. It is found to be more critical with strontium-90 than with a tritium source (*Figure 3*). With the anode well in the shroud the efficiency rapidly falls off with increasing concentration. When the anode protrudes beyond the shroud the efficiency increases rapidly with increasing concentration. It is difficult to obtain one particular anode setting which will give a linear response for all gases. For example, at any fixed anode position and voltage, the response for increasing sample size rises much more sharply for nitrogen than for oxygen. The optimum anode position is 1–2 mm inside the PTFE shroud with strontium-90 and 2–3 mm beyond the shroud with a tritium source.

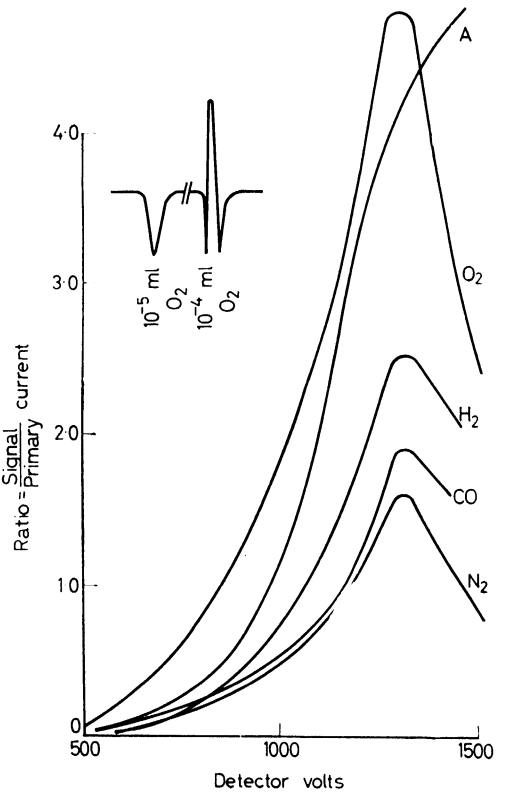


Figure 4. Effect of voltage on detector performance

Primary current

A detector with tritium sources of different strength was used to determine the effect of primary current on the response. The primary current varied between 10^{-6} and 10^{-8} amp at applied potentials of 750, 1,000 and 1,250 V. It was found that the value of the primary current at a particular voltage critically affects the shape of the response curve. The nonlinearity of this

curve increases with higher voltages and smaller primary currents, the effect being most noticeable in nitrogen response.

Detector voltage

At any particular concentration of a permanent gas in helium the response increases with voltage, whereas the ratio of sample response (signal) to primary current has a maximum limiting value (*Figure 4*). The applied voltage also has a limiting value beyond which the electrical field becomes unstable. This results in negative peaks for small samples but positive peaks with negative fronts and tails for larger samples. Hydrogen is the first gas to give a negative signal under these conditions, especially in the presence of water vapour.

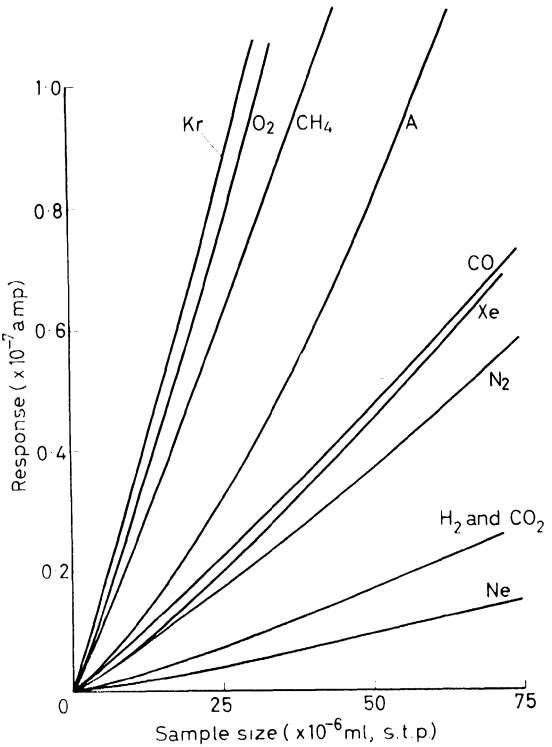


Figure 5. Response for various gases. Detector volts, 1,250 V; flow rate, 75 ml/min

Results

Response of various gases

Calibration curves (*Figure 5*) were obtained with the strontium-90 detector at 1,250 V and with a helium flow of 75 ml/min. Similar results are obtained at 750 V with the tritium detector. In the range covered by the graph (10^{-7} to 10^{-4} ml approximately) the efficiency increases with quantity of sample. Above this range, however, the efficiency falls off with increasing quantities of sample, as shown previously by the saturation curves (*Figure 2*). Under

the above conditions peak heights equivalent to 5×10^{-10} amp (10 times the noise level) can be measured. The limits of detection range from 5×10^{-8} ml for the gases detected with high sensitivity, such as oxygen, krypton and methane, to 5×10^{-7} ml for neon and hydrogen. A chromatogram of $1{\cdot}6 \times 10^{-5}$ ml coal gas–air mixture (*Figure 6*) illustrates the quality of separation (see also *Table 2*) and noise level at low concentrations.

Table 2. Relative retention volumes

(Linde Molecular sieve 5A; 100°C)

Neon	1·0
Hydrogen	1·1
Oxygen	2·0
Argon	2·0
Nitrogen	3·4
Krypton	4·0
Methane	5·0
Carbon monoxide	10·0
Xenon	13·8

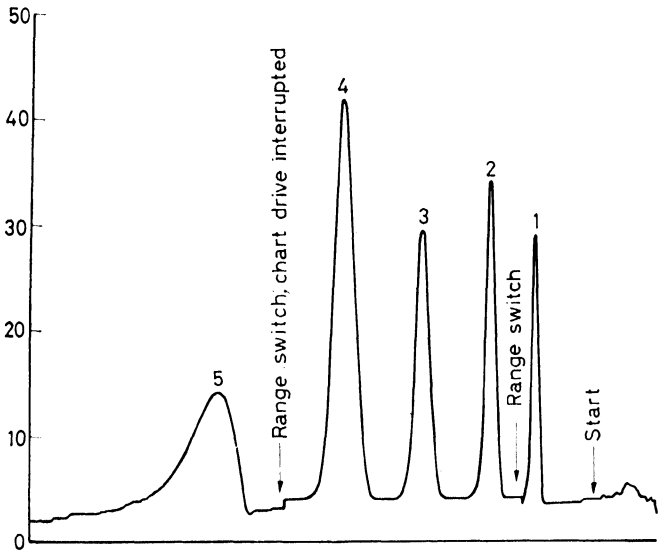


Figure 6. Chromatogram of coal gas–air mixture. Tritium detector at 750 V. Flow rate 65 ml/min. Temperature 100°C. Column 120 cm × 5 mm Linde molecular sieve 5A. Chart drive interrupted between peaks 4 and 5

Peak number	*Compound*	*Amount* (ml)	*Sensitivity*
1	Hydrogen	3×10^{-6}	max
2	Oxygen	2	1/3 max
3	Nitrogen	8	1/3 max
4	Methane	2	1/3 max
5	Carbon monoxide	1	max

Equally satisfactory results are obtained for the analysis of trace impurities in helium or carbon dioxide. Samples in this case are admitted, without pre-concentration, via tap *E*.

Reproducibility

Reproducibility tests were carried out on several gases in the range 10^{-6} to 10^{-4} ml. Twenty determinations were carried out on each gas over a 1 hour period. The results, based on peak height measurements, which provide a check on the reliability of detector response and sample transfer by tap *D* are given in *Table 3*.

Table 3. Reproducibility data

Component	*Volume chromatographed* (ml)	*Standard deviation* (ml)
Hydrogen	32×10^{-6}	$\pm0{\cdot}8\times10^{-6}$
Oxygen	3×10^{-6}	$0{\cdot}03\times10^{-6}$
Nitrogen	13×10^{-6}	$0{\cdot}2\times10^{-6}$
Methane	4×10^{-6}	$0{\cdot}03\times10^{-6}$
Carbon monoxide	12×10^{-6}	$0{\cdot}2\times10^{-6}$

Discussion

The purity of the helium carrier gas determines whether elastic collision, excitation, electron capture or ionization processes predominate when a gas sample is analysed. If we consider the analysis of a sample, using the highest purity helium, the following principal processes occur:

$$\underset{\text{(ionizing source)}}{\text{He} + \bar{e}} \rightarrow \underset{\text{(metastable)}}{\text{He}^*} + \underset{\text{(less } V_{m\text{He}})}{\bar{e}} \qquad (1)$$

where $V_{m\text{He}}$ is the metastable potential of helium, and

$$\underset{\text{(sample)}}{\text{He}^* + \text{A}} \rightarrow \text{He} + \text{A}^+ + \bar{e} \qquad (2)$$

The passage of the beta particles through the helium results in the formation of both metastable and ionized helium atoms. The metastable (2^3S) helium atoms predominate under the conditions described and have energies of 19·8 eV; on collision they ionize any impurity gas whose ionization potential is lower than this. The ejected electrons are themselves accelerated by the electrical field and acquire enough energy ($E > V_{m\text{He}}$) to excite further helium atoms. Under these conditions the concentration of metastable helium atoms will greatly exceed the total impurity concentration, giving a linear response for ionization current versus quantity of component being determined. An alternative mechanism must be predominating when neon (ionization potential 21·5 eV) is the added impurity. It is most improbable that the observed high ionization current (*Figure 5*) could be obtained at the low concentrations of neon by direct electron impact with the few high energy electrons in the helium. A more plausible explanation is found when we consider a two-stage process of ionization. The neon is first excited to a metastable state ($V_{m\text{Ne}} = 16{\cdot}5$) by collision with a metastable helium atom. The metastable neon (lifetime 10^{-5} sec) further collides with another (2^3S) helium atom or an electron (> 5 V) to yield a neon ion. The purity of the helium plays an important role in this process, since the lifetime of the metastable neon atom is considerably reduced by the presence of impurities.

When all the impurities have not been removed from the helium carrier gas the probability of electron capture, competing with the ionization process, is increased. The high ionization current from the helium carrier gas before a sample is injected is due to ionization of these impurities according to eqn (2). If an electron-capturing molecule, such as oxygen, now enters the detector the process described by eqn (3) can occur, resulting in a decrease in ionization. For this reason certain chromatograms show a negative peak for oxygen although all the other component peaks are positive.

$$O_2 + \bar{e} \rightarrow O_2^- \qquad (3)$$

At still higher impurity concentrations in the helium supply, the lifetime and concentration of the helium metastable atoms is reduced. Under these conditions the mean free path of the electron and the energy per collision is small, which results in energy losses to processes not producing excited helium atoms. Thus the ionization current is reduced when the eluted sample passes into the detector, as shown by the shape of the saturation curves (*Figure 2*). Further contamination of the helium results in no response, owing to the absence of any metastable helium atoms.

One peculiarity is the anomalous behaviour observed at low sample concentrations with high detector voltages when traces of water vapour are present in the carrier gas (see Detector Voltage). The reduction in ionization current cannot be explained in terms of electron capture, since *inter alia* there is no evidence in the literature for the existence of negative nitrogen ions; neither would an electron capture mechanism readily explain why, on further increases in impurity concentration, the ionization current starts to rise.

Provided that contamination of the radioactive foil can be avoided, tritium is more suitable than strontium-90. The anode setting is not as critical, neither is there a marked change in the shape of the calibration curves with voltage. Also the value of the primary current can be kept high owing to the use of stronger sources, and loss in linearity is minimized.

Conclusion

A technique has been described for the determination of milli-microlitre quantities of permanent gases by the application of an ionization process to the detection of the components eluted from a chromatographic column. Close control of detector temperature, gas pressure and flow rate is necessary for reproducible analysis. It is essential that high purity helium is used to maintain this precision and every effort should be made to avoid contamination by air leaks or moisture desorbed from the apparatus.

The apparatus is capable of handling larger quantities of gas in which trace impurities have to be determined. The method is particularly successful for analysis of the reactor coolant gases carbon dioxide and helium, where the impurities at the v.p.m. level can be determined within five minutes following sampling.

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[1] LOVELOCK, J. E. *Gas Chromatography 1960*, (Ed. R. P. W. Scott), pp. 16–25, Butterworths, London, 1960

[a] Hopkins & Williams Ltd., Chadwell Heath, Essex, Great Britain

DISCUSSION

J. Serpinet (*As Dr Serpinet was unable to attend the session, the contribution was read by the Chairman*): We are using a metastable helium detector in combination with a molecular sieve column for the analysis of simple organic gases such as oxygen and carbon monoxide as described by Berry, but with a purely physical process of purification of the carrier gas.

An 8 m long column filled with Linde 5A molecular sieve and cooled in liquid nitrogen serves adequately to purify commercial 99·95 per cent helium, if three conditions are fulfilled:

(*1*) Contamination of the purified helium should be avoided by the use of metal tubing.

(*2*) The purifying column should be activated *in situ*, without contact with the atmosphere.

(*3*) The flow of carrier gas should be rapid, to prevent back diffusion of atmospheric moisture.

At first we get negative peaks, then W-shaped peaks, and finally well-shaped positive peaks after one or two days.

Since our publication on this subject[2] we tried with success the use of mixtures of helium and nitrogen-free neon, and the sensitivity was increased by a factor of three. We are not suggesting an explanation of this phenomenon.

We are now able to detect 0·2 p.p.m. of oxygen or carbon monoxide in catalytic cracking gases. Contamination of the sieves by the main component of the mixture is the main problem, but this can be overcome by the use of a by-pass or back-flushing system.

Over a period of a few weeks, the heights of the peaks are a linear function of the concentration of the permanent gases over a range of about 0·2–100 p.p.m., depending on the gas.

Perhaps the response would be higher with helium of higher purity, as prepared by the technique described by Berry, or with the geometry of the apparatus adapted to the use of helium, but our solution is simple and it is already commonly used for the purification of argon for the Lovelock detection system. The only difference lies in the use of liquid nitrogen to cool the molecular sieve.

M. A. Khan: I have four questions:

(*1*) May I know what is the energy associated with these β particles?

(*2*) I wonder whether you have made any calculations on the collision efficiency of these excited atoms in your system. There are certain well-known formulae based on the Maxwell-Boltzmann distribution.

(*3*) What are the chances for multiple ionization in the particular system you have studied?

(*4*) Could you give me an idea of the life and the mean free path of the excited atoms in the system you have investigated?

R. Berry: That is quite a tall order you have put to me. In many cases the things we have done have been purely for the purpose of giving the analyst a tool to do permanent gas analysis, rather than getting lost on a lot of fundamental studies which lead us nowhere. We have done practical work in terms of the best geometry for the detector, and we gave some illustrations on this work.

A. F. Williams: This may be an appropriate place to raise the question of purity. Mr Berry has actually taken care of this, because he has gone to extreme precautions. We have found that, unless extreme precautions are taken, water cannot be quantitatively removed from carrier gases by most normal drying agents, such as silica gel and even molecular sieves. We have checked this by taking compounds such as $SiHCl_3$ or $SiCl_4$, and injecting these on to a column under extremely dry

conditions. We then used carrier gases treated with various drying agents, and were able to detect HCl in all cases, which is an indication that hydrolysis occurs. Only by using concentrated sulphuric acid have we been able to get a continuous stream of dry carrier gas without taking extreme precautions.

R. Berry: There are quite a lot of people who readily talk of gas dried to a few p.p.m., but when you examine their systems critically you find that they are operating at 300–400 p.p.m. The molecular sieve is the only adsorbent I have found satisfactory for drying gases at room temperature, and molecular sieve 5A will definitely get your system down to one volume per million, if you are prepared to give time for equilibration. You must always remember that the pipe-work after the drier is just like a sponge, and it will readily give off moisture; so that, although the gas immediately issuing from your purifier is one volume per million, a few feet along your capillary pipe-work you have probably got a couple of hundred p.p.m. for several hours to come, or even days.

E. R. Adlard: I wonder if Mr Berry would comment upon the information which Mr Phillips read out from Dr Serpinet, about the necessity for using metal tubing. Do you use nylon tubing in your apparatus at all? I know that the United Kingdom Atomic Energy Authority have published some information on the permeability of various plastic materials.

R. Berry: Nylon really is the worst plastic you could think of, as regards moisture. We did various moisture experiments with different plastic materials and metals, and we would put materials in the following order, with regard to desorption of moisture: stainless steel, nickel, PTFE, polythene, copper, nylon. We found in the case of nylon that if you first deliberately saturate the internal surfaces of the nylon tubing, so that you have a really wet surface, and then connect this to a dry gas stream and constantly monitor the moisture coming off with, e.g., an electrolytic moisture meter, it is very difficult to get your nylon tubing much below a few hundred p.p.m. In some cases this could indeed be actual diffusion through the nylon, because it was not a particularly thick wall we used, but with comparable thicknesses of Teflon and polythene the moisture readily came down from about 1,000 to 3 or 4 p.p.m. in three or four hours. After that it tailed off and seemed to keep at this 3–4 p.p.m. level, as though this was the true diffusion of moisture through the material.

M. M. Wirth: When you put on fairly large samples for trace analysis, do you find any poisoning effect in your system? If, for instance, you put on a large sample of moist air for trace analysis, do you find you have to wait subsequently for several hours to get a stable system again?

R. Berry: Generally you don't have to wait, because the maximum sample size we take is well below 1 ml. On your analytical column you have several grams of molecular sieve, which is dry to start with, and you can put up to 4 per cent loading by weight on molecular sieve before the equilibrium vapour pressure of water over the molecular sieve starts to rise appreciably. Therefore, you do not see much change in your standing current, and your sensitivity in general does not alter, but there is no doubt that if you keep on using a very wet gas, or if someone inadvertently puts through a water sample instead of a gas sample—as has occurred—then re-activation of the analytical column becomes necessary. This is easily done by heating the molecular sieve *in situ* to 230°C, with the helium carrier gas going through. If you do this for 24 hours and then cool the column to, say, 100°C, your operating temperature, the system is back to normal.

G. R. Primavesi: You made the remark that no one had reported carbon monoxide in carbon dioxide above the level of six p.p.m. We have done this with an ordinary thermal conductivity cell, using a 1½ litre sample. We used a large amount of silica gel and the sample sits down on the silica gel, and the carbon

monoxide comes out considerably more concentrated than it went in. You can actually see half a p.p.m. You do not have to be frightened of using a 1½ litre sample because it does actually sit down on the silica gel, and leaves all the permanent gases in quite high concentrations. It is possible, without a fancy apparatus like this, and without much trouble, to obtain purification.

R. Berry: I must admit that I am unaware of what you have done on this question, but that is neither here nor there. On your last point about fancy apparatus: these particular instruments have been in routine operation for quite a long time now, with quite junior grades of people operating them without much trouble; we have found that they can operate this chromatograph a lot easier than they can handle many of the conventional ones which we buy through the suppliers. It probably looks like a nightmarish purifier, but when you study it, it is quite a simple one really and it does operate without any trouble.

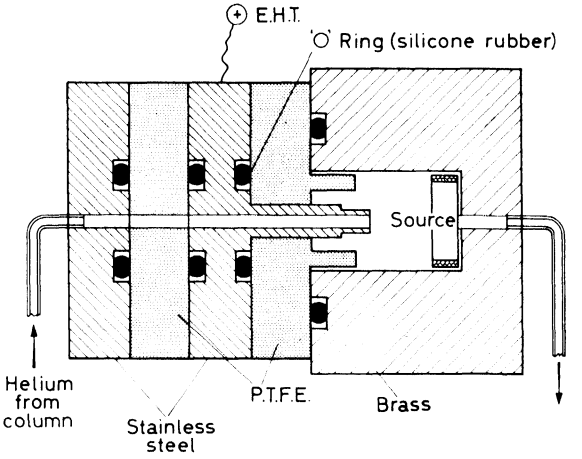


Figure 7. Schematic diagram of helium ionization detector

J. C. Sternberg: We have used a related type of detector with helium, and found that operation of the detector at elevated pressure was helpful. Desorption of water from the tubing gives rise to a fixed vapour pressure at any one temperature; since the detector is a concentration-sensing device, we found that by increasing the pressure we could change the characteristics from those described by Mr Berry for impure helium to those found with pure helium.

R. Berry: I think the point here is the question of leakage in the detectors themselves. Your remark on the desorption from the tubing is quite true. It is the old comment I made: once having purified the helium you should keep it pure.

As you can see from *Figure 7*, the gas from the column comes in straight through the Teflon insulation piece, through another stainless steel probe leading into the ionization chamber, and then out via capillary tubing. The main thing here is that silicone rubber O-ring seals are used at every stage; because we have found with the conventionally-designed argon micro-detectors, that you are wasting your time trying to use them. The amount of diffusion which occurs across the face between the atmosphere and the helium is fantastic. We have used this type of detector with O-rings at low pressure, high pressure and at temperatures down to −80°C without any trouble whatsoever; I would point out here that to avoid

back-diffusion you might need about a metre of stainless steel capillary downstream. The connections are, of course, silver-soldered. I suggest that with a detector like this you might find that you do not need to go to high pressures to get over the trouble.

J. C. Sternberg: The instrument we used had all-metal seals and was leak-tight. The effect was demonstrated not to be due to back-diffusion.

A. F. Williams: Regarding the problems created by adsorption on various materials which might be used for sealing devices or connecting tubes we have some experience from an investigation in a somewhat different direction on some organic compounds. We found that materials may be divided into two classes:

(*1*) Those which absorb the vapours (e.g. certain rubbers) and release them into the gas stream after a certain induction period.

(*2*) Those which act as membranes and continuously permit the passage of the vapour to different degrees (e.g. polythene and polypropylene).

It is thus important to give careful thought to the choice of the various materials which may be considered for use in gas chromatographic apparatus.

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[2] SERPINET, J. *Anal. Chim. Acta* 1961 **25** 505

25

TRACE ANALYSES BY MEANS OF GAS–SOLID CHROMATOGRAPHY

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In gas–liquid chromatography the irregularities in the base line are to a large extent determined by the vapour pressure of the partitioning liquid. The detection limit obtainable in gas–solid chromatography should therefore in principle be better than in gas–liquid chromatography.

The paper describes the results obtained in the trace analyses of the lower-boiling hydrocarbons (up to C_6) in air and hydrogen in concentrations ranging from 100 to 0·010 p.p.m., with deactivated alumina as partitioning agent. The analyses were carried out without preconcentration steps, with equipment utilizing the very sensitive flame ionization detector.

The various factors determining the quantitative behaviour and the limit of detection attainable are discussed and optimum working conditions are given. For the preparation of test mixtures a dynamic dilution apparatus has been used which allows a dilution of $1:10^8$ to be attained reproducibly.

For acetylene, difficulties were encountered owing to irreversibility of adsorption. Pretreatment of the column with acetylene was found to be sufficient to eliminate these effects. The experimental set-up and a special burner construction allowed the use of different carrier gases including air, which was found to be especially interesting for air pollution problems. The separation characteristics of the columns could be kept constant over a long period by moistening of the carrier gas with water.

Quantitative analyses of dilute mixtures of hydrocarbons in hydrogen and air can be performed at room temperature with time of analysis ranging from 10 to 30 minutes and with a detection limit of a few thousandths of a p.p.m.

GAS CHROMATOGRAPHY offers a convenient tool for determination and identification of trace components in gases, even when many of these are simultaneously present. Concentrations down to about 100 p.p.m. in the sample can be detected by direct analysis if heat conductivity is used for detection. Up to a few years ago, however, problems involving still lower concentrations in gas mixtures had to be solved by means of concentration techniques. In these, a large volume of gas is cooled in traps and a portion of the concentrated sample is analysed. In favourable cases the detection limit under these conditions may well be below 0·1 p.p.m. in the sample[1,2].

The development of the ultra-sensitive ionization detectors with a detection limit of 0·001 p.p.m. or lower has enabled analyses in this concentration region to be performed without preconcentration steps[3,4]. A major limitation for this procedure when used in gas–liquid chromatography is the instability of the base line of the recorder, owing to liquid phase being stripped irregularly from the column and reaching the detector.

This prompts the use of gas–solid chromatography for the analyses of these very low concentrations. The paper describes the results obtained in direct

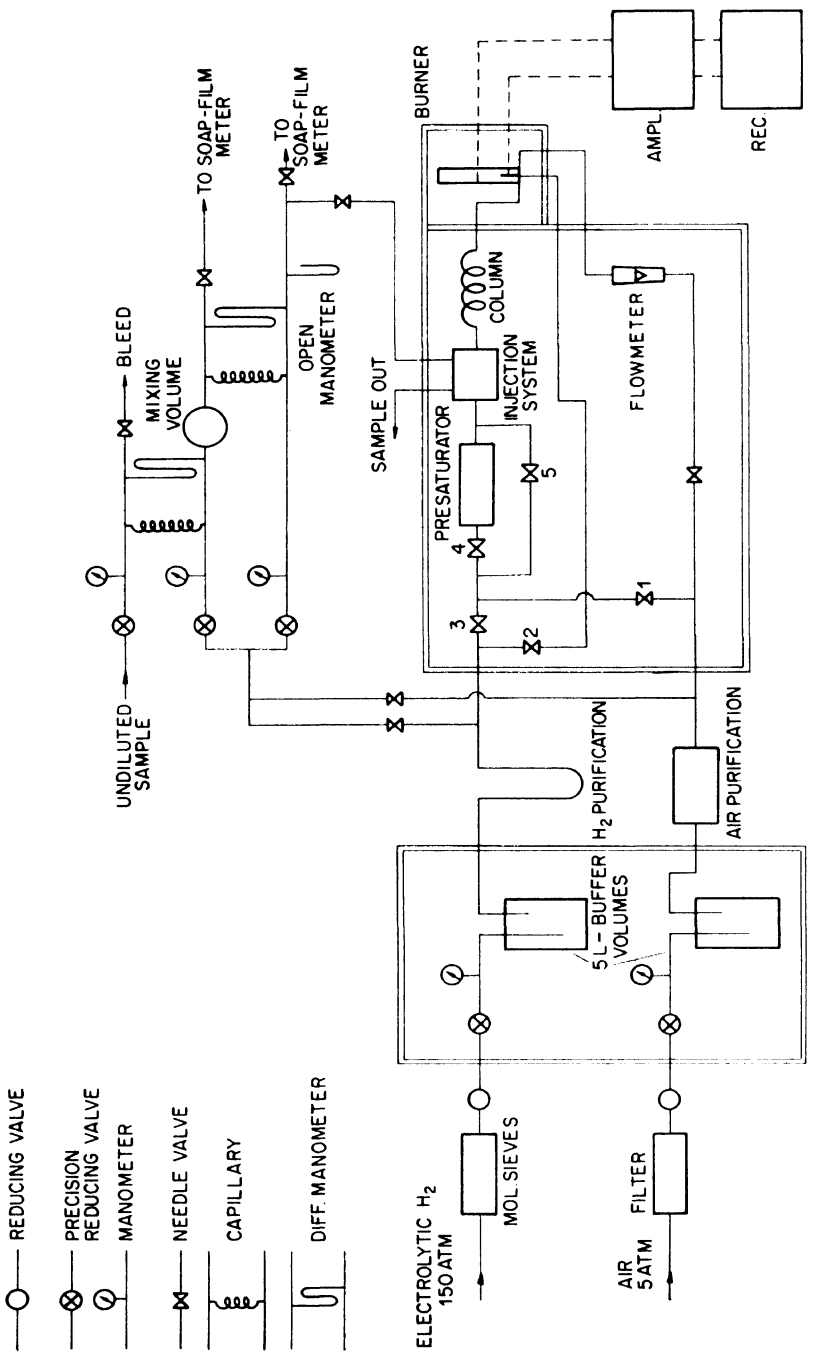


Figure 1. Apparatus for trace analysis

trace analyses with alumina as adsorbent and detection by flame ionization. The samples analysed were air and hydrogen containing hydrocarbons up to C_6 in concentrations ranging from 0·003 to 100 p.p.m.

Description of the apparatus

Figure 1 represents the flow scheme of the apparatus used.

To reduce the basic ionization current as far as possible the hydrogen and air are carefully purified and the valves, manometers and tubing are freed from all traces of oil. Electrolytic hydrogen is passed through Linde molecular sieves 5A at 150 atm. This purification is followed by cooling in liquid nitrogen over the same adsorbent at low pressure to remove the last traces of contaminants.

Air is supplied by a 5 atm laboratory line and is first filtered to free it from oil and dust particles. Final purification is achieved by passing it through an oven with CuO at 850°C. Both the hydrogen and the air lines contain buffer volumes of 5 litres for flow stabilization.

The purified hydrogen and air streams can be used for two purposes: as diluent gas for the preparation of test samples of low concentration from hydrocarbon mixtures of known composition and as carrier and burner gas for the analyses proper.

Both purified hydrogen and purified air can be used as carrier gas: for hydrogen valves 1 and 2 are closed; for air valves 1 and 2 are opened and valve 3 closed. Before entering the injection system and the column, the carrier gas passes through a short column of Silocel loaded with water. This compensates for the loss of water of the alumina column due to the stripping by the carrier gas. The water content of the alumina is kept constant at the desired value by adjustment of a by-pass to the presaturator (by means of valves 4 and 5).

The chromatographic columns (length 2 to 3 m, inner diameter 3 mm) and all parts in contact with the sample are made of stainless steel. The apparatus was used at room temperature without a thermostat but all main parts were placed in insulating containers to protect them from draughts and temperature fluctuations.

Details of the burner construction are shown in *Figure 2*. Except for the capillaries for column gas, additional hydrogen supply and air, which are made of stainless steel, the construction material used is brass. The burner tip has two channels for gas introduction: a centre hole of 0·2 mm diameter for column gas and an outer ring for additional hydrogen supply. Air is introduced by a 1·0 mm capillary and is distributed around the burner tip by means of a sintered metal disc. Normal working conditions for hydrogen as column gas are: 2·5 l/h H_2 and 65 l/h air and for air: 1·2 l/h air as column gas, 3·8 l/h additional H_2 and 65 l/h air as burner gas.

The burner tip is electrically insulated from earth by means of a block of PTFE in which channels are drilled for the connection of the capillaries. It is also insulated from the chimney by means of a thin sleeve of PTFE. The tip is kept at -90 V with respect to earth potential. The upper electrode is formed by a 1·5 cm diameter platinum gauze, 2 cm above the electrode tip. The chimney, which has a diameter of 2·5 cm, is insulated from both electrodes

and from the earth and is connected to the guard terminal of a Vibron 33B amplifier[a]. The input circuit for the amplifier is shown in *Figure 3*. Measuring resistances of 10^{10}, $3 \cdot 10^{10}$ and $10^{11}\Omega$ are used. To increase the speed of response the shielding for the high terminal lead, the resistance box and the

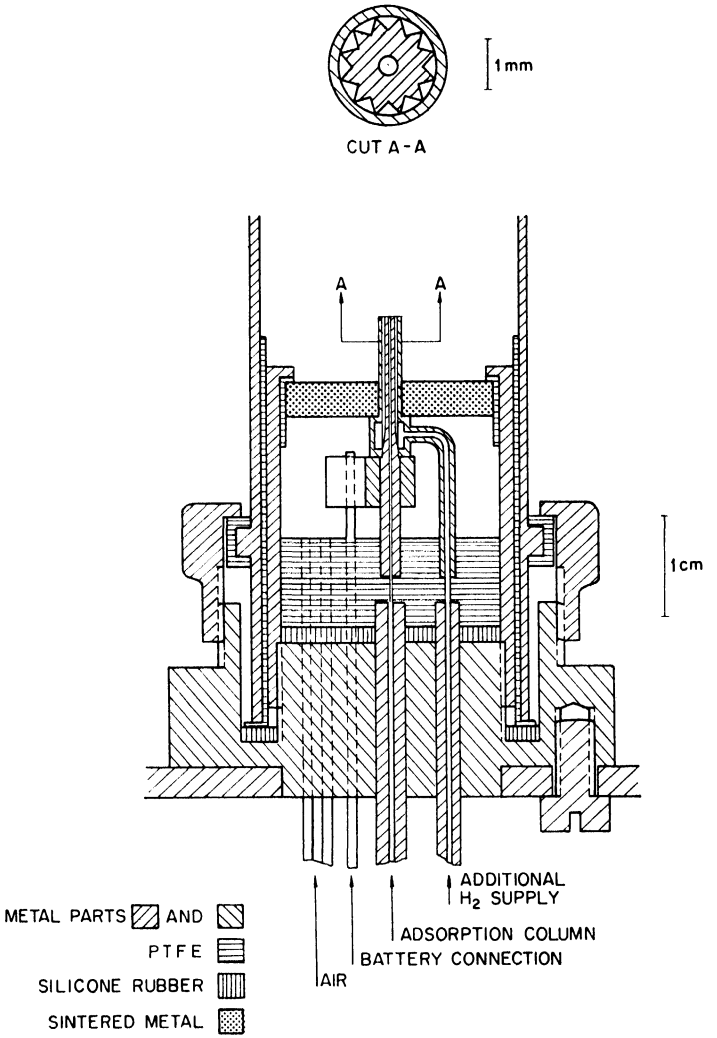


Figure 2. Burner construction

chimney are kept at a guard potential whereas the batteries, the compensation circuit and the shielding of the low terminal are earthed. The output of the amplifier is fed to a recording millivoltmeter (2·5 mV full scale).

Under normal working conditions the noise was about $2 \cdot 5 \times 10^{-15}$ amp,

equal to the noise with the flame extinguished, and the basic ionization current was $2{\cdot}7 \times 10^{-12}$ amp for H_2 as carrier gas and $2{\cdot}6 \times 10^{-12}$ amp for air as carrier gas. The responses (peak heights) for 0·001 p.p.m. n-C_4 in a 5 ml sample were 3×10^{-15} and 2×10^{-15} amp, respectively.

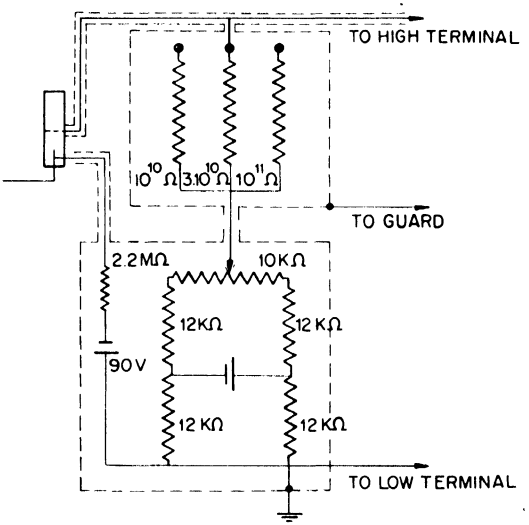


Figure 3. Input circuit for Vibron 33B electrometer

The injection system consists of a combination of two stainless steel sliding taps with O-ring seals. The sample volume was 5 ml. For the preparation of test samples of known composition a system of three parallel flow lines with reducing and needle valves for flow regulation was used, the lines being mutually connected by silver capillaries of 0·127 mm inner diameter. The undiluted sample flowing through the first line can thus be injected into the flow of diluent gas in the second line and thence into the third line. Thus, for instance, a dilution of $1:10^6$ can be achieved in two steps if flow rates of 5 ml/h are choosen for both capillaries and 5 l/h for the lines. Even dilution of $1:10^8$ could be obtained reproducibly by using two capillaries of 25 m length. The precise dilution ratio follows from the flow rates measured in the second and third line and from the manometer readings which show the pressure drop over the calibrated capillaries. Less strongly diluted samples (dilution ratios down to $1:10^4$) can be taken directly from the second line.

Separations

It has been shown by Scott[5] that good separations for the lower hydrocarbons can be obtained with alumina as solid adsorbent. A 100–200 mesh fraction of aluminium oxide[b] (basic, activity grade 1, for chromatographic analysis) served our purpose very well.

Separation proved to depend very strongly on the pre-treatment of the alumina. Heated aluminas gave high retention times and poor separations

with a pronounced tailing of the components and these effects became worse the higher the heating temperature. If symmetrical peaks and sharp separations are to be obtained, the sites of highest activity apparently should be covered. Water is well suited for this deactivation as it is not detected by the flame ionization detector. The results obtained after addition of various percentages of water to the alumina (after two hours' drying at 100°C) showed that 1 to 2 per cent by weight on alumina gives the best separations. For amounts of water over 2 per cent the differences in retention times became too small, especially for the early-eluted components. For all types of treatment it was found that the logarithm of the specific retention volume depends linearly on the carbon number of the molecule. (This could not be accurately checked for the CH_4 peak, which practically coincides with the air peak.) As expected, the position of the unsaturates especially is influenced by the water treatment; for acetylene and propene even a reversal in elution order is observed, acetylene coming after propene for dry alumina.

The time of analysis is quite short; with a 2 m column containing alumina with 2 per cent water, 14 components including n-pentane can be analysed within 8 minutes. Isopentane and butadiene-1,3 are completely separated; *trans*-butene-2 and isobutane peaks coincide.

The water content of the alumina must be kept constant by presaturation of the carrier gas.

Quantitative results and discussion

The applicability of the method for the quantitative analysis of trace components was evaluated by analysis of a standard mixture of saturated and unsaturated hydrocarbons at various concentration levels. The mixture was diluted for this purpose with hydrogen and air by means of the dilution apparatus described.

For correct dilution of the standard to a concentration of the order of 0·001 p.p.m. the diluent gases must necessarily be extremely pure and contain an even lower concentration of any of the components. It was impossible, however, to purify the gases to this extent. To overcome this difficulty the same purified gas was used as diluent and as carrier gas (*Figure 1*); introduction of a sample of the diluent gas into the column should not then give rise to any peaks pertaining to the impurities. Analysis of purified hydrogen with hydrogen as carrier gas still gives a blank of about 0·002 p.p.m. on the CH_4 and C_2H_6 place, and for purified air with air as carrier gas a blank of about 0·010 p.p.m. is found. Where necessary a correction has been made for these blanks.

In successive runs the concentration was increased stepwise from 0·070 to 100 p.p.m. per component and on each concentration level a number of identical analyses were carried out, one directly after the other. Thereupon followed a series of experiments with decreasing concentration. After a change of concentration the sample gas was passed through the sample loop for at least 15 hours before an analysis was made.

With repeated analyses at one concentration the relative peak heights remained practically constant except for the acetylene peak, which increased in the beginning and approached a constant value after a few analyses. At the

next higher concentration the acetylene values were again too low initially. This behaviour was observed with both carrier gases but only for runs at increasing concentrations. After a decrease of concentration the acetylene peak had the same size for all runs.

The surface of the alumina must evidently be saturated with acetylene before reversible adsorption takes place. Apparently, the acetylene first adsorbed is very strongly attached to the surface, as the saturation effect is not observed during a series of experiments with decreasing concentration. This behaviour suggests that presaturation of the alumina column might solve this problem. Indeed, columns treated with acetylene before use gave perfectly normal acetylene analyses over a period of several months.

When in a logarithmic plot of recorder deflection versus concentration (calculated from dilution) a straight line is drawn between calibration points at various concentration levels (ranging from 0·01 to 100 p.p.m.), slopes of about 0·95 and almost 1·00 are found for all components, with hydrogen, respectively air, as carrier gas. Accordingly it can be said that the response is linear.

Table 1. Quantitative analyses of hydrocarbons with gas-solid chromatography

Component	*Carrier gas:* H_2 *Concentration**, 0·001 p.p.m.		*Carrier gas: air Concentration**, 0·001 p.p.m.	
	Found	*Calc.**	*Found*	*Calc.**
Methane	10	5	57	83
Ethane	5	6	92	88
Ethene	6	6	97	93
Propane	6	6	97	88
Acetylene	3	7	109	103
Propene	5	6	91	91
n-Butane	7	6	94	97
1,3-Butadiene	7	6	87	94

* Obtained by multiplication of the concentration in the standard mixture by the dilution factor.

Table 1 shows the results of analyses in the region of 0·01 and 0·1 p.p.m. The experimental values were derived from peak heights and an absolute calibration at 100 p.p.m., under the assumption that response is linear for the various components. Except for methane determined with air as carrier gas, the deviations are only a few times 0·001 p.p.m. The discrepancies between experimental and calculated values for methane in air shown in the table are probably due to the contribution of the blank at the place of the CH_4 peak, which was not reproducible. These discrepancies also indicate that the error introduced by the assumption of linearity is not of prime importance for the accuracy of analysis.

If the absolute calibration is to be valid, the conditions during analysis must be kept rigorously constant. The relative response factors for the hydrogen burner were in agreement with those cited in the literature; but for

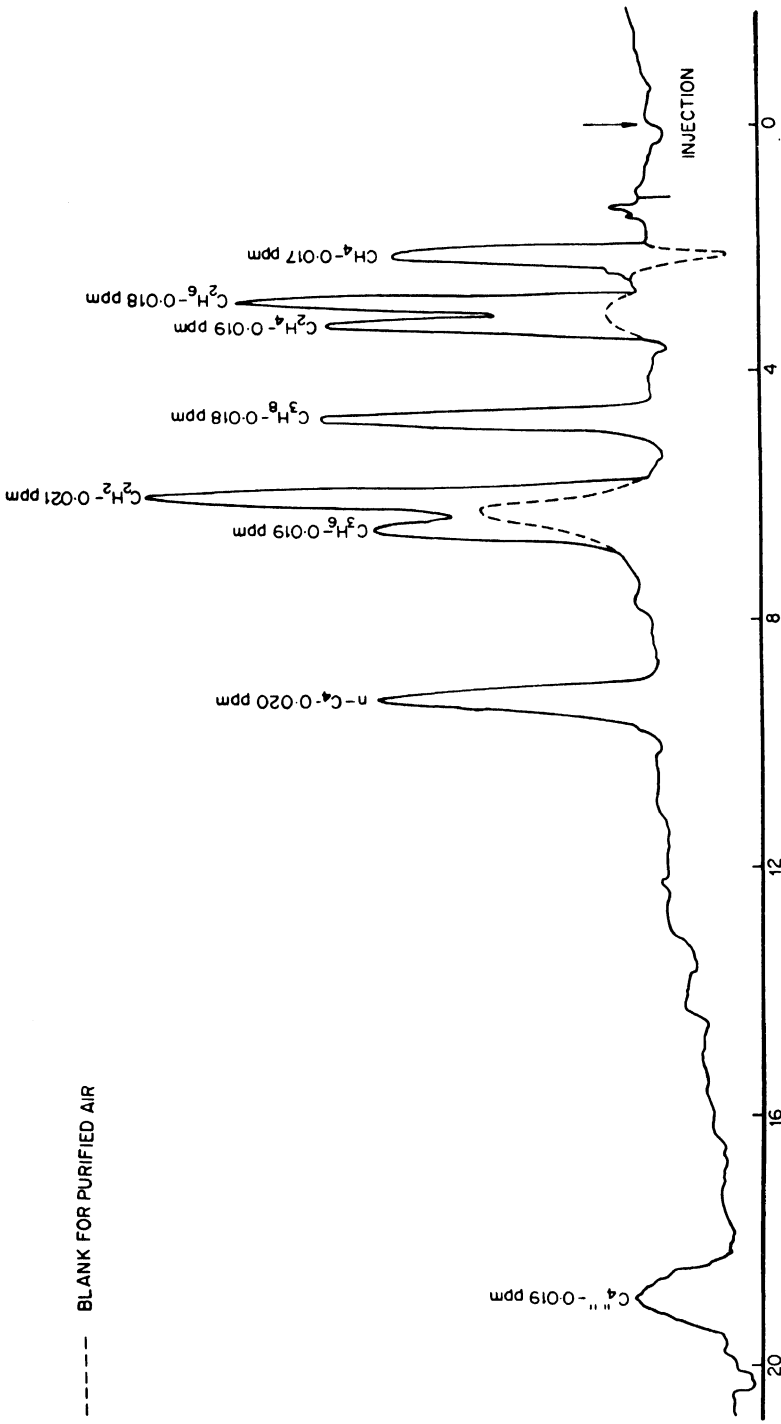


Figure 4. Analysis of hydrocarbon mixture with air as carrier gas
Column length: 2 m. *Column diameter:* 3 mm. *Adsorbent:* alumina with 2% w water. *Temperature:* 20°C. *Inlet pressure:* 3 atg.

the air burner they were quite different: acetylene especially gave a very large signal.

Two chromatograms, for air containing 0·02 p.p.m. of each component (*Figure 4*) and for hydrogen containing 0·035 p.p.m. of the same components (*Figure 5*), show the irregularity of the base line, the pattern of the blank, and the noise level.

For optimum results (sharp peaks) at the lowest concentration level the time of analysis should be as short as possible. This requirement, together with the characteristics of the components to be separated, determines the column length and linear carrier gas velocity. In this study 2 and 3 m columns were used with an inlet pressure of 3 atg. The choice of the column diameter depends especially on the flow rate at which the optimum signal-to-noise ratio is obtained. This was found to be about 3 l/h for the hydrogen burner, which corresponds to a column diameter of 3 mm; a sample volume of 5 ml was allowable for this diameter. For the air burner the optimum lies somewhat higher.

An electrode distance of 2 cm gave the best signal-to-noise ratio, shorter distances gave rise to too much noise and larger distances resulted in a decrease in signal. The amount of burner air was not critical; a large excess, however, resulted in a high noise level, especially when air was the column gas. A flow of 65 l/h was used in all experiments.

The major difficulties encountered were base line instability and, with samples at low concentrations, the appearance of unexpected peaks. During some analyses a severe drift of the base line was observed, the causes of which could not be traced; probably slight temperature variations in the surroundings of the detector were involved. The extra peaks in the blank occurred in the beginning of the chromatogram and corresponded to hydrocarbon concentrations of the order of 0·010–0·001 p.p.m. They proved to be due to the O-rings in the injection system: with different rings other peaks were found.

The response of the electrical equipment was quite slow, despite the precaution mentioned above; peaks with a width of less than 10 sec were not recorded correctly. Most probably the slow response contributes to the low noise level, because measurements with fast-responding amplifiers connected to an oscilloscope showed that the flame alone generated much more noise in the region 1–10 c/sec.

Conclusions

This investigation shows that direct quantitative trace analysis of hydrocarbons in concentrations down to $\sim$0·003 p.p.m. in air or hydrogen is possible with a reasonable accuracy. The noise (of the order of 10^{-15} amp) is equal to that of the electrical equipment. With amplifiers giving off less noise a detection limit even lower than 0·001 p.p.m. may be expected if the difficulty of base line instability can be overcome.

Air used as column gas offers attractive possibilities, as acetylene detection is three times as sensitive with air as with hydrogen. For hydrocarbons in air and especially in oxygen it may also be used to advantage as there are fewer difficulties with the oxygen peak, which interferes with the registration of the early-eluted components when hydrogen is used as carrier gas.

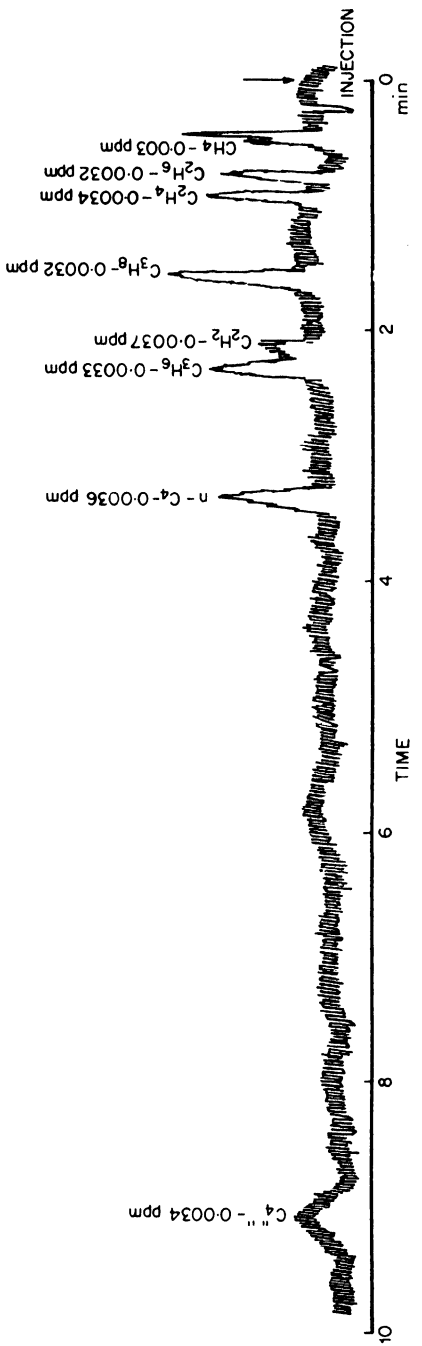


Figure 5. Analysis of hydrocarbon mixture with hydrogen as carrier gas (conditions as in *Figure 4*)

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[b] M. Woelm, Eschwege, DBR

DISCUSSION

J. Janak: I should like to congratulate the authors on their results in the trace analysis of gaseous hydrocarbons in air and in hydrogen. At this point I should like to state that it is possible to detect different volatile materials very simply down to 10^{-2} p.p.b., or perhaps less. Our way is, of course, not direct; in principle it is a concentration method. However, the usefulness of concentration methods described so far is related not so much to the problem of using large samples as to the difficulty of sampling sufficiently quickly in chromatographic columns or directly in the detector. We have now applied high-frequency heating of some adsorbents and supports for liquid phases, to desorb the sorbed concentrates practically instantaneously. Only about 100 W of 40–50 MHz energy is necessary to heat 1–2 g of silicate-type material to 300 °C in one to two seconds. In this way it is possible to detect, for example, down to 2×10^{-3} p.p.b. of some fluorated hydrocarbons in a gas sample of only 1 l. I must apologize that I am not able to demonstrate the full scheme of the apparatus at the moment, but details will be published in the near future.

J. C. Winters: The electrode spacing seems to be much larger than the distance between the electrode and the earth wall of the detector. Does this not seriously affect the linearity of response?

F. H. Huyten: Indeed, the spacing between the electrode and the burner tip is quite large. We first began with an electrode distance of about 1 cm, which is the normal distance used for this type of work. However, when we began to optimize our results it appeared that the signal-to-noise ratio was better for the present spacing of 2 cm.

Regarding the linearity of response, we have checked this by means of the dilution apparatus described, and we found that from 100 p.p.m. to about 1 p.p.b. there was quite a linear range. If you make a logarithmic plot of the peak height versus the concentration calculated from the dilution apparatus, you find quite straight lines, with a slope of 0·95–1, which means that the deviation may be only about 80 per cent for 5 decades.

T. R. Phillips: In the analysis of hydrogen isotopes on modified alumina columns we observed an effect similar to the 'conditioning' necessary for the analysis of acetylene. Our alumina was modified by deposition of ferric oxide on the surface, as proposed by Moore and Ward. We found that the column must be conditioned with a large sample of hydrogen before the analysis, so that the active sites are blocked. The column then remains conditioned for about 30 minutes. The effect is greater for hydrogen than for deuterium.

F. H. Huyten: Concerning the adsorption of acetylene at the gas–solid surface, I am not quite sure whether it is a chemical or a physical process. We observed that the pre-saturation with acetylene was sufficient for several months.

D. Roberts: In the field of gas–liquid chromatography we have observed a

similar effect with naphthalene. We are using 2½ per cent polyethylene glycol on Celite, and we find that the sensitivity increases over 4 injections of about 1 μl. The final sensitivity is about 80 or 90 per cent greater than at the beginning.

K. G. Berger: I am not quite clear where this trouble with the rubber ring arises, but it is possible to design injection systems with metal-to-metal connections, where there is no possibility of such absorption effects. One particular type of coupling which I have used is the Ermeto coupling, which is of American manufacture. It can be obtained in stainless steel and gives you pressure-type connections up to very high pressure.

F. H. Huyten: The system we have used is a Kel-F plug which is a valve in a stainless steel housing. Initially we used a copper housing, and we had difficulties with the leakage. With the stainless steel we also had difficulties, but I now think we are beginning to overcome them.

J. Mawson: This paper is of considerable interest to people who want to have measurements on oxygen plants. Our experience is very similar to that of the authors. We have also used alumina columns and we have two instruments running, one of which has run for about three years and was reported on briefly two years ago. We have an instrument with a full-scale deflection of 3 p.p.m. acetylene and with a stability of ± 1 per cent on the base line. We use an Argon detector.

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REACTION GAS CHROMATOGRAPHY

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Fatty acids may be determined quantitatively as esters, if boron trifluoride/methanol is used as esterifying agent and the esterification is completed in a reactor under reproducible conditions.

For the analysis of ^{14}C-labelled compounds some methods are described which may find use mainly for the examination of biological material with low specific activity.

IT IS interesting to note that modern gas chromatography originated from problems connected with biochemical considerations. As a result of work which was widely publicized, for example by James and Martin[1] on the quantitative and qualitative gas-chromatographic determination of mixtures of fatty acids, and by Hesse, Eilbracht and Reicheneder[2] on Calotropis resin, future possibilities were pointed out to the biochemist for, e.g., dealing successfully with the problem of the material background of dynamic equilibria, a question which is becoming of much interest and often requires numerous analyses to be carried out within brief periods of time. Associated with this is the desire for reliable analysis of aqueous solutions and high-boiling natural substances.

For many problems a combination of the gas-chromatographic system with reaction units for the transformation of given substances or mixtures of substances appeared to be very suitable. Some examples will make this clear.

Quantitative gas chromatographic determination of fatty acids of low volatility

In connection with the problem whether fatty acids of low volatility are formed in the first part of the stomach of Colobinae monkeys, as in the case of ruminants, the preserved stomach contents were distilled in order to obtain the acids; the distillate was titrated and freeze-dried. For the subsequent esterification, samples of the freeze-dried potassium salts of the fatty acids were treated with sulphuric acid and boron trifluoride/methanol reagent[3]. The esterified fractions obtained under definite conditions were then injected into a reactor after the insoluble components had been removed. In earlier investigations with reaction gas chromatography[4], it had been shown that esters pass unchanged through calcium hydride zones mounted in front of analytical separating columns for removal of water and acids. Accordingly, the ester fractions could be injected directly into a reactor without previous isolation of the esters, the purpose of the reactor now being to complete the esterification. The experimental arrangement is clear from *Figure 1*.

Before and after each series of determinations, calibration is carried out with test mixtures esterified under the same conditions. The mean values from several calibrations fluctuated by ± 1–4 per cent per component. As *Figure 2* shows, sharp peaks were obtained at a column temperature of 110°C for formic, acetic, propionic and n-butyric acids. Quantitative evaluation was carried out in accordance with the recommendations made by Janák[5].

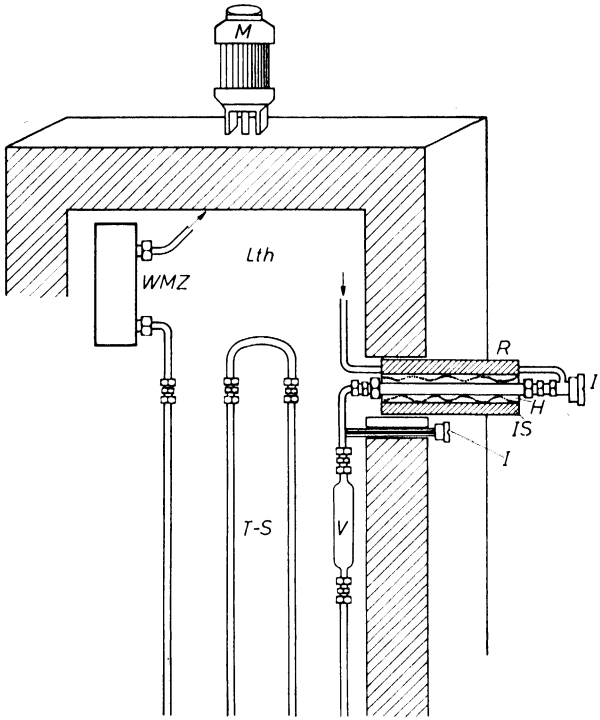


Figure 1. Gas Chromatograph with reactor. *Lth* = air thermostat; *M* = motor with fan; *TS* = separating column; *WMZ* = thermal conductivity cell (Siemens); *I* = injection points; *R* = reactor, with *H* = heating and *IS* = insulation; *V* = fore-cell

In the stomach contents of several animals, formic (0·7–3·7), acetic (54·2–70·5), n-propionic (19·0–34·7), n-butyric (7·6–9·9), iso-valeric (0·4–2·0) and n-valeric acids (0·6–2·5 mol. per cent) were found, and these findings are in accord with those for ruminants.

Analysis of ^{14}C-labelled compounds

For the gas chromatographic analysis of weakly active ^{14}C-labelled fractions from biological material, it was desirable to combine the methods of reaction gas chromatography with a sensitive measurement of the ^{14}C activity. According to data of Curran[6], Wolfgang and Rowlands[7], Ache, Thiemann and Herr[8], James and Piper[9], and Scharpenseel[10], counting tubes operated in the proportional region should be particularly suitable for this purpose.

A discussion of one problem will serve to describe an experimental arrangement which has proved satisfactory.

^{14}C-barium carbide was prepared by melting $BaCO_3$, $Ba^{14}CO_3$ and magnesium in a bomb tube[11]. After pulverization of the bomb tube with its contents, the powder, containing $Ba^{14}C_2$ and BaC_2, is put into a reactor (*Figure 3*). Acetylene, produced by the injection of water, passes through a

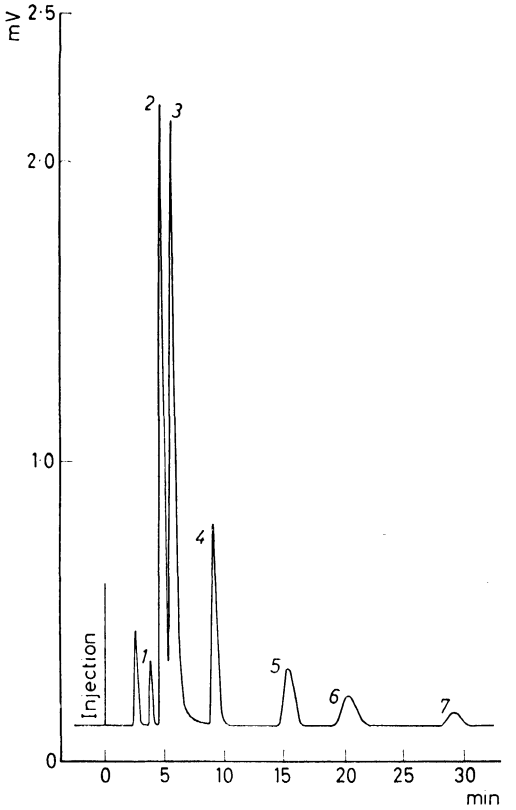


Figure 2. Gas chromatogram of methyl esters of fatty acids. Methyl ester of formic acid (1), acetic acid (3), n-propionic acid (4), n-butyric acid (5), isovaleric acid (6), and n-valeric acid (7); 2 = methanol. Separating column: 6·4 m tube 6 mm diameter, dimethyl phthalate/Kieselguhr (30:100); $T = 110°C$; flow rate 100 ml H_2/min. Reactor: Quartz wool, 170°C. Fore-cell: calcium hydride/Kieselguhr (1:1)

second reactor, or a second reactor zone, containing a hydrogenation catalyst. Particularly in work involving high specific activities, or when it is necessary to avoid the use of a hydrogenation zone, the barium carbide is decomposed outside the gas chromatographic system. The hydrogenation properties of catalysts towards acetylene at various temperatures were tested, in order to allow this compound or its hydrogenation products to react further, forming definite products, in reactors mounted before or after a separating column.

In this context, the interesting experimental arrangements of Emmett and

his co-workers[12], of Keulemans and Rijnders[13] and of Scharfe[14] should be specially mentioned. Emmett and his co-workers used ^{14}C-labelled compounds to examine cracking and isomerization reactions on catalysts; Keulemans examined the reactivity of naphthenes, using a micro-reactor; Scharfe used a fore-column for the hydrogenation of unsaturated hydrocarbons. Catalytic syntheses of ^{14}C-labelled unsaturated hydrocarbons in conjunction with gas chromatography were carried out also by a group of Russian workers[15]. Finally, reference should also be made to preparation of ^{14}C-labelled compounds from $Ba^{14}C_2$[16].

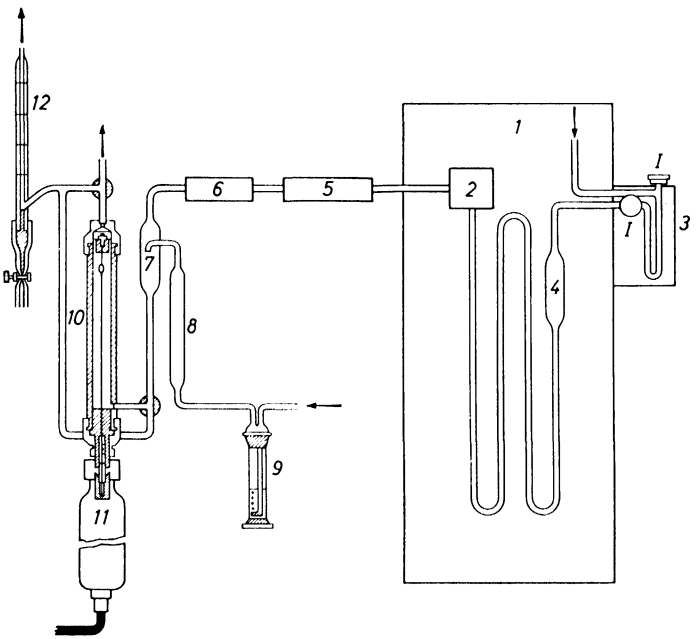


Figure 3. Apparatus for gas chromatography and measurement of radioactivity. *1*, air thermostat; *2*, thermal conductivity cell; *3*, reactor (*1*, injection points); *4*, fore-cell; *5*, Raney nickel or copper oxide furnace; *6*, drying cell; *7*, mixing cell; *8*, purifying column (molecular sieve) for methane; *9*, wash bottle; *10*, through-flow proportional counting tube; *11*, pre-amplifier in combination with measuring device FH 49 and 5 kV high tension unit[a]; *12*, bubble counter

With a sufficiently high sensitivity of the radiation detector, it should be possible to extend the separating system to a semi-preparative scale and to perform the analysis in a by-pass system. In *Figure 3*, only the experimental arrangement on the analytical scale is shown.

In agreement with the findings of James and Piper[9] and of Zlatkis and Ridgway[17], combustion of the emerging fractions to CO_2, or cracking to CH_4, is recommended for satisfactory analysis and good, reproducible counting rates. As may be inferred from *Table 1*, quantitative cracking to methane takes place at 410°C in a reactor packed with Raney nickel. Accordingly, an operating temperature of 420°C for the Raney nickel furnace (*5*) ensures complete conversion of a fraction into methane, which is directly (without

drying cell *6*) swept into the mixing vessel *7* by the carrier gas (H_2), where it is mixed with methane in a ratio of 1:1 (50 ml H_2/min + 50 ml CH_4/min). The gas mixture then passes through the counting chamber of the proportional counting tube (*10*). The favourable geometry of the counting tube, with an internal volume of 62·8 ml, ensures a relatively long residence time, which is a prerequisite for high counting efficiency. However, as

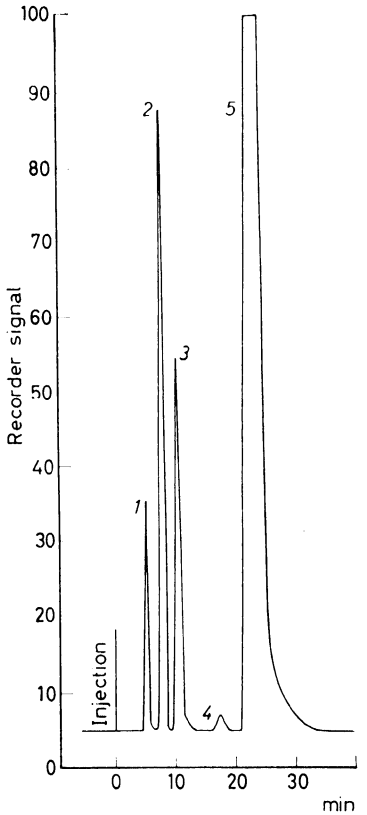


Figure 4. Radiochromatogram of gas chromatographic fractions (counted after cracking to methane). *1*, methane; *2*, ethane; *3*, ethylene; *4*, propane; *5*, acetylene. Separating column: 1·60 m Blaugel (90 mesh) + 6·4 m dimethylsulfolane/Kielselguhr (20:100) + 1·6 m dinonyl phthalate/Kieselguhr (30:100); $T = 20°C$; flow rate 50 ml H_2/min. Recorder: FH 585[a] with potentiometric recorder

Figure 4 shows, the purging time is sufficiently short to enable sharp activity peaks to be produced. In addition, the three-way cocks at the inlet and outlet of the counting tube permit the measurement of stationary fractions. The counting tube used had the following characteristics: operating potential 3·6 kV, plateau width 200 V, gradient 7·5 per cent, background counting rate 50–60 c.p.m., sensitivity of detection better than 2×10^{-10}C.

The activity peaks of *Figure 4* were obtained after injection of 1 ml of a mixture of approximately 98 per cent hydrogen and about 2 per cent acetylene

with a ^{14}C-content of approximately 0·0002 per cent. The retention times of the individual compounds were measured with inactive acetylene. *Table 1* shows the results of some hydrogenation experiments.

Table 1. Hydrogenation of ^{14}C-acetylene

Catalyst	*T*, °C	*% Total activity*				
		Methane	*Ethane*	*Ethylene*	*Propane*	*Acetylene*
None		2·9–3·7	0·2–0·6	1·7–2·6	—	93·2–95·4
I (Palladium)	1	2·8–3·6	1·9–2·5	2·4–2·8	—	92·3–93·5
	14	2·9–3·4	1·4–1·5	2·2–2·6	—	92·0–93·2
	20	1·9–3·1	2·9–6·1	3·5–4·1	0·2–0·4	87·6–90·0
	75	2·7	64·6	29·6	1·0	1·8
	130	3·1	91·5	3·0	2·1	—
II (Raney nickel)	100	4·8–5·4	80–85		2·9–3·4	0–0·4*
	270	> 50	< 50			
	410	100				
III (Grünkontakt)	185	1·7	62	7	22†	7

* 10·8–12·5 per cent with higher retention times (not identified).
† Propane + 2 compounds with higher retention times (not identified).
Catalyst I: palladium on kieselguhr (10 per cent Pd)[b]. Carrier: pumice.
Catalyst II: Raney nickel, prepared from Raney alloy: 50 per cent Ni, 50 per cent Al (Schuchardt). Carrier: pumice.
Catalyst III: Grünkontakt[b] (nickel/pumice catalyst).

^{14}C-labelled alcohols, obtained from fermentations with ^{14}C-glutamic acid, were analysed by gas chromatography, partly from aqueous solution and partly after extraction. As has already been described on numerous occasions[4], alcohols are dehydrated to olefins on heated acidic surfaces. This method, when applied to aqueous solutions of ^{14}C-alcohols, led to ^{14}C-olefins, which could be analysed directly in the gas flow counter by their counting rates. ^{14}C-alcohols, enriched by extraction, were separated by gas chromatography in a current of helium, and the fractions burnt to CO_2 in a copper oxide combustion furnace (*5*, *Figure 3*). The CO_2 from the combustion can then be dried with magnesium perchlorate (*6*, *Figure 3*) and measured for activity with the gas flow counter, after which it may be absorbed on soda lime. Decomposition of the soda lime in a vacuum apparatus, described by Simon[18], and transference of the CO_2 into a gas counting tube, allows a control analysis to be made.

Special thanks are due to the Bundesministerium für Atomenergie and to the Deutsche Forschungsgemeinschaft for their support of this work. I am greatly obliged to Professor B. Husfeld for his constant help; I thank the Degussa concern for the provision of catalysts; and I am very grateful in particular to my co-workers A. Rapp and O. Bachmann.

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DISCUSSION

Author's Additional Comments

The advantages of chemical reaction prior to the separation process are clearly illustrated in the analysis of blood alcohol. Experience has shown that blood cannot be injected directly into a vaporizer, because at the required high temperature (*ca* 400°C) a significant fraction of the alcohol would be dehydrated in the presence of the catalytically active components of the blood. If whole blood is injected into a reactor consisting of vaporizer, dehydrating zone and calcium hydride zone[19], blood alcohol can be quantitatively determined as ethylene in a separating column connected to the reactor. The results are comparable to those obtained by the alcohol-dehydrogenase method. No more than 0·1 ml whole blood is required for the analysis, which can be done in 10 minutes or less. The arguments applying to the complex blood–alcohol mixture, namely that significant rearrangement and decomposition is observed at high vaporization temperatures, would also be valid for other samples of a complex nature.

A. Thiemann: I have a question for Dr Drawert. If I understand correctly, you determine the alcohol by dehydrating it, then converting the water to hydrogen on calcium hydride, and determining the hydrogen.

As far as I know, blood also contains free water. Isn't this zero signal so large that it interferes with the measurement of the alcohol?

F. Drawert: We measure ethylene, not hydrogen. The conditions were carefully checked, and I think I can say that, except for alcohol, no compounds occur in blood which give a significant concentration of ethylene.

V. Braun: Under some pathological conditions the concentrations of acetone in the blood is abnormally high. Wouldn't this interfere?

F. Drawert: I cannot give an unqualified answer to the question of Dr Braun. In our research we did not raise the question whether acetone interferes or not. I can only say: probably not.

V. Braun: In forensic medicine, acetone can be eliminated by the ADH method. With the Widmark method acetone would be determined with the alcohol.

F. Drawert: I am no criminologist; we were interested in this problem for other reasons. After all, we work at the Forschungsinstitut für Rebenzüchtung, and we don't want to cut our own fingers!

F. L. Gager: One of my colleagues (E. W. Robb) has also used a method for the esterification of acids for gas chromatography. The tetramethyl ammonium salts are prepared by titration of the free acids with $(CH_3)_4NOH$ in methanol, or by elution of the acids from an anion exchange resin with $(CH_3)_4NCl$ in methanol. The tetramethyl ammonium salts are injected into a pre-heater at 220–270°C, and the resulting methyl esters are separated on the column. Trimethyl amine is the other product.

Yields of 95 per cent have been obtained for aromatics; aliphatic, hydroxy- and dicarboxylic acids are converted for about 90 per cent. Pyrolysis occurs if the pre-heater temperature is above 270°C. The reaction seems to be quite applicable to mixtures of acids. We hope to publish this work in the near future.

H. Pauschmann: How many blood analyses can you do in one run, before the decomposition products of the organic components in the blood clog the equipment, and how fast can you clean the apparatus?

F. Drawert: When the reaction tube has a uniform inside diameter of 10 mm (the forthcoming publication in *Zeitschrift für physiologische Chemie* contains a detailed description) you could do 35–50 blood analyses. Then you could remove the whole system, insert a new one, and wait an hour to reach equilibrium for the next analysis.

H. Pauschmann: 50 analyses per hour?

F. Drawert: No; after you have connected the new system you have to wait an hour before equilibrium is reached again; then you can continue with the analyses.

H. Pauschmann: That means that if you duplicate the system and use a change-over valve, you could operate continuously?

F. Drawert: Yes.

E. M. Emery: The method given in the paper for the analysis of animal rumen fluid seems rather elaborate. As we showed in two publications last year[20], we can analyse rumen fluid by direct injection of the fluid on to a column of 20 per cent Tween 80 and 2 per cent phosphoric acid on Chromosorb-W. We use a flame ionization detector, which is insensitive to the large amount of water in the sample. Symmetrical peaks are obtained for the low levels of organic acids present, and we have analysed up to 100 samples per day with this method.

F. Drawert: Is your procedure quantitative, and what is the average error and the scatter for the complete procedure and for each component?

E. M. Emery: I cannot recall the exact figures, since most of the work was done by my biochemist associates. I would have to look up the papers published last year; but we do the quantitative analysis by direct comparison with known mixtures of the low acids in water, and all the acids are down in the range of less than 1 per cent. I think each of the acids can be determined to within about 0·1 per cent.

V. Braun: Dr Drawert, how high is the average error for your technique? A method can only be admitted in court if the average error is smaller than 0·008–0·01 per cent absolute.

F. Drawert: I will read you a few data from our paper which is in the press now.

Accuracy of ethanol analysis

Concentration in sample, per cent	*Found*	
	Average, per cent	*Average error, per cent*
0·10	0·099	0·004
0·15	0·152	0·001
0·20	0·200	0·004
0·25	0·250	0·006

V. Braun: This would be fully adequate for a good method!

F. Drawert: I should say so.

P. Jungmann: What materials have you used for dehydration, and at what temperature?

F. Drawert: You can use a 1:1 mixture of P_2O_5/pumice at about 300°C.

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27

IDENTIFICATION OF HYDROCARBONS BY THERMAL CRACKING

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A simple, non-catalytic system has been designed for the partial thermal decomposition of organic molecules and the identification and approximate estimation of the products by gas chromatography. Samples weighing up to 1 mg are injected into a nitrogen gas stream, and pass through a quartz reactor heated to about 500°C. The products are carried directly on to an analytical gas chromatographic column and the separated components are detected with a hydrogen flame ionization device of conventional design. The cracking patterns obtained show a satisfactory repeatability and the original substance can be identified by the identity and quantity of the fragments. Recombination effects can be eliminated by correct choice of operating conditions.

The cracking patterns of some representative hydrocarbons up to C_{10} are presented and interpreted in terms of the structure of the parent molecule. The thermal stability of carbon rings, especially those of aromatic character, and of unsaturated linkages is evident from the results.

Extensions, improvements and limitations of the technique are discussed and applications in both analysis and synthesis indicated.

GAS CHROMATOGRAPHY is perhaps the most powerful separating technique available[1] and is used in many laboratories for the routine quantitative analysis of mixtures of known components. Frequently, however, the identification of separated components gives rise to difficulties. These may sometimes be solved by reference to relationships between retention time and carbon number or to the rather similar 'retention indices' of Kováts[2], although these methods are of limited value in the region above about C_{10}. Optical or mass spectrometry[3,4] has been used for identification of substances separated by gas chromatography. The high initial cost of mass spectrometers precludes their widespread use, and infra-red and ultra-violet spectra give only limited structural information about hydrocarbons.

A simple and inexpensive system with which considerable structural detail can be obtained might be based on the thermal decomposition of separated components, with subsequent analysis of the products. Such techniques have been applied to polymers[5] and high-melting solids[6]; extensions to some lower molecular weight substances have recently been described briefly[7,8].

The feasibility of such a system for hydrocarbon analysis has been investigated and the potentialities of the technique are demonstrated, not only for identification, but also for process research.

Apparatus and materials

The essentials of the flow system are shown in *Figure 1*. Samples of the material to be identified are injected into the carrier gas stream at the point indicated, the vapours pass through the heated cracker, and products are swept directly on to the analytical column.

Since the performance of the cracking unit ultimately controls the success of the process, the design and operating conditions of the cracker are the most important factors in the whole system. The cracker should meet three

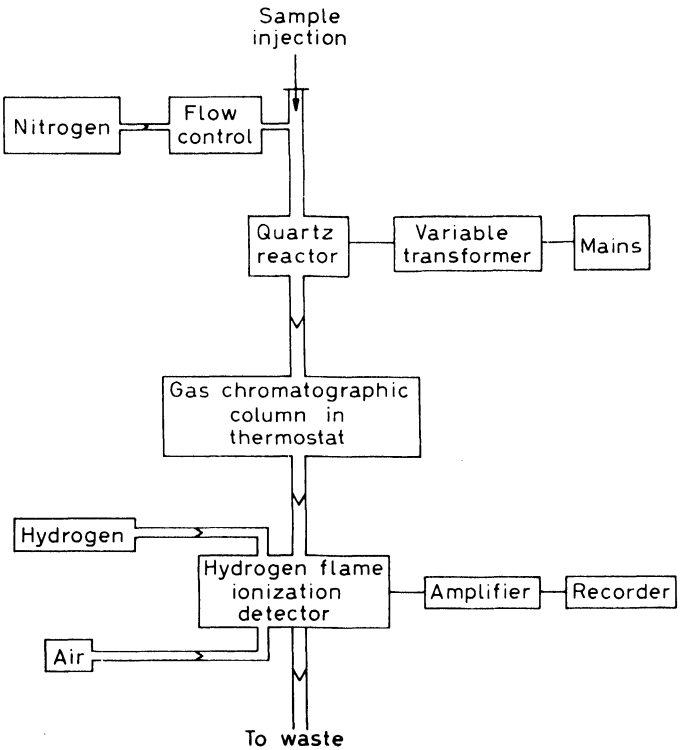


Figure 1. Experimental arrangement for thermal cracking product studies

requirements: the construction should be simple, the cracker should not possess catalytic activity and it should be able to withstand high temperatures. A straight quartz tube, wound with a nichrome heating coil, satisfies these needs adequately. The cracker used in this investigation is sketched in *Figure 2* and consists of an open quartz tube 32 cm long and 10 mm i.d. The 25 s.w.g. nichrome coil is wound over the middle 14 cm of the tube and has a resistance of about 31 ohms. The spring-loaded steel-to-quartz conical joints are completely gas tight and sufficiently cool under operating conditions, so that no problems arise from the unequal expansions of the different materials.

The GC system comprises a 3 m 4 mm i.d. copper column packed with

10 per cent w/w squalane on 50–60 mesh Sil-o-cel, a hydrogen flame ionization detector very similar to that described by Desty[9], a Vibron[a] amplifier (type 56A) and Philips 5 mV f.s.d. recorder. Nitrogen, first passed over hot copper turnings, is the carrier gas; hydrogen and air are fed separately to the detector.

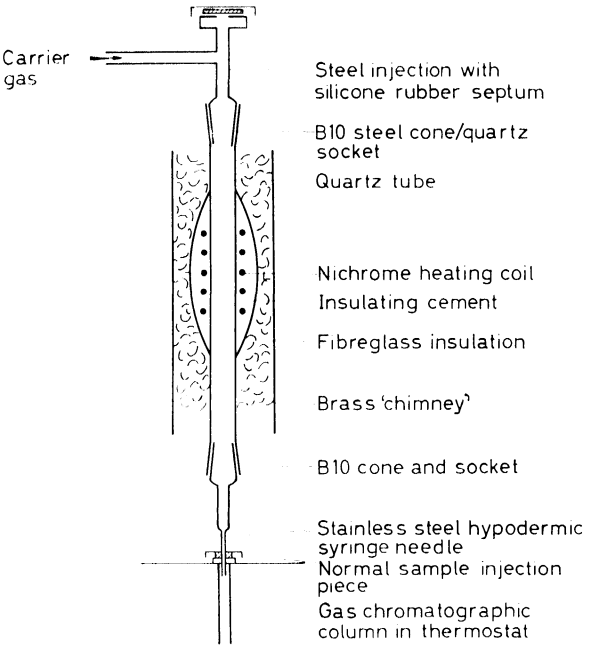


Figure 2. Quartz reactor for thermal decomposition

Hydrocarbons (Phillips Petroleum Co., generally 'research grade') are injected into the reactor with a 10 μl Hamilton syringe.

Operating conditions and technique

The reactor temperature was controlled by means of a variable transformer; temperatures were measured with an iron–constantan thermocouple with the hot junction approximately at the centre of the heated zone, while nitrogen flowed through the reactor at a rate of about 30 ml/min to simulate actual operating conditions. A temperature of about 500°C was used in most of the work described here.

The choice of operating conditions not only affects the separating efficiency of the analytical column, but also the residence time of the sample in the cracker. Since column permeabilities may vary between wide limits for different columns, the choice of a suitable inlet pressure depends on the particular column in use; the information in *Table 1* applies to the cracker and column employed in the present work.

For the determination of the cracking pattern of a hydrocarbon a sample

Table 1. Operating conditions for cracker and analytical column

Cracker temperature	500°C
Inlet pressure of cracker	2·02 atm
Outlet pressure of column	1·00 atm
Calculated residence time in cracker	20 sec
Volumetric carrier gas flow (s.t.p.)	25 cc min^{-1}
Volumetric hydrogen flow	30 cc min^{-1}
Volumetric air flow	300 cc min^{-1}
Temperature of column	30 or 120°C

of about 1 μl is injected. The relative peak areas of the resulting chromatogram are calculated from the peak areas measured with a planimeter; they are approximately equivalent to the relative weights[10].

Results

Thermal cracking of non-aromatic hydrocarbons at 500°C leads to substantial decomposition (10–90 per cent). The major products correspond to simple fragments of the parent molecule, often with additional unsaturation; not all of the decomposition products have been identified. The cracking patterns of some 23 non-aromatics are given in *Tables 2*, *3* and *4*.

With aromatics only side-chain fragmentation is observed, even at 700°C. In *Table 5* relevant data are presented.

The repeatability of the cracking patterns has been checked for 2,4-dimethylpentane. From eleven runs, made over a 30 hour period, relative peak areas were determined; means and standard deviations of these values are listed in *Table 6*.

Influence of sample size and temperature

Reactions between fragment radicals and undecomposed molecules will complicate cracking patterns. With 2,4-dimethylpentane as test substance, a peak due to such a process appears, having a retention about twice that of the parent molecule. In *Figure 3*, the dependence of the area of this peak on

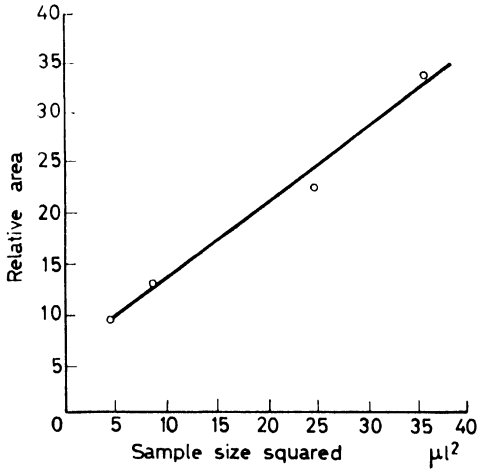


Figure 3. Dependence of 'recombination' peak area on sample size

Table 2. Thermal cracking patterns of alkanes at 500°C (20-second residence time)

Relative retention distance	*Identity of product*	*Relative peak area* × 100%						
		n-C_4	iso-C_5	neo-C_5	2,2-Dimethyl butane	2,3-Dimethyl butane	2-Methyl pentane	3-Methyl pentane
0·23	C_1	2	12	—	9	7	9	9
0·29	C_2''							
0·48	C_3''	5	9	—	1	10	10	5
1·00	C_4''-1/iso-C_4''/1,3-$''C_4''$	—	17	0·5	10	3	10	4
1·10	n-C_4	93	—	—	—	—	—	—
1·26	*trans*-C_4''-2	—	7	—	0·5 (+ *cis*)	0·5	Trace	5
1·31	neo-C_5	—	—	99·5	—	—	—	—
1·38	*cis*-C_4''-2	—	5	—	(see *trans*)	Trace	Trace	4
1·61	?	—	—	—	—	Trace	—	—
1·90	3-MeC_4''-1	—	~0·1	—	—	0·5	4	Trace
2·44	iso-C_5	—	50	—	--	Trace	4	—
2·55	C_5''-1	—	—	—	—	—	1	—
2·83	2-MeC_4''-1	—	~0·3	—	3	Trace	Trace	9
3·10	Isoprene	—	—	—	2	3	—	—
3·20	C_5''-2	—	—	—	—	—	6	4
3·74	2-MeC_4''-2	—	—	—	11	16	—	—
4·69	2,2-DiMeC_4	—	—	—	63	—	—	—
4·91	?	—	—	—	—	6	—	—
6·41	2,3-DiMeC_4	—	—	—	—	54	—	—
6·57	2-MeC_5	—	—	—	—	—	60	—
7·49	3-MeC_5	—	—	—	—	—	—	60

Table 3. Thermal cracking patterns of alkenes at 500°C (20-second residence time)

Relative retention distance	*Identity of product*	*Relative peak area* × 100%											
		C_4''-1	iso-C_4''	*trans*-C_4''-2	*cis*-C_4''-2	C_5''-2	C_5''-1	C_6''-1	2MeC_4''-2	2MeC_4''-1	3MeC_4''-1	2MeC_5''-1	*trans*-4MeC_5''-2
0·23	C_1	4	—	1	—	12	18	11	7	9	3	12	9
0·29	C_2''												
0·48	C_3''	2	1	3	Trace	8	18	14	2	3	9	4	7
0·58	($''C_3''$?)	—	—	—	—	—	—	—	0·5	2	—	—	—
1·00	C_4''-1/iso-C_4'' etc.	94	99	2	0·5	14	20	15	11	11	9	15	9
1·26	*trans*-C_4''-2	—	—	94	2·5	4	0·5	Trace	3	0·5	6	—	2
1·38	*cis*-C_4''-2	—	—	Trace	97	3	1	0·5	2	0·5	8	—	2
1·56	1,2$''C_4''$*	—	—	—	—	0·5	—	—	0·5	0·5	—	—	—
1·90	3 MeC_4''-1	—	—	—	—	3	1	0·5	1	Trace	58	—	4
2·04	($''C_5''$-1,4?)	—	—	—	—	3	2	4	—	—	—	—	—
2·12	Di MeC_2''	—	—	—	—	—			—	—	—	—	—
2·27	?	—	—	—	—	—	—	—	Trace	—	—	—	—
2·55	C_5''-1	—	—	—	—	0·5	39	5	—	—	—	—	Trace
2·83	2 MeC_4''-1	—	—	—	—	—	—	—	3	37‡	—	6	Trace
3·10	Isoprene	—	—	—	—	—	—	—	20	25‡	7	7	12
3·20	C_5''-2	—	—	—	—	39	—	2	—	—	—	—	2
3·29	?	—	—	—	—	—	—		—	—	—	—	—
3·74	2 MeC_4''-2	—	—	—	—	9†	—	4†	47	12‡	—	1	9
3·80	Cyclo $''C_5''$	—	—	—	—	—	—	—	—	—	—	—	—
3·95	?	—	—	—	—	—	—	—	—	—	—	—	6
4·10	?	—	—	—	—	5	—	1	—	—	—	—	—
4·23	?	—	—	—	—	—	—	—	3	—	—	—	—
4·40	?	—	—	—	—	—	—	—	—	—	—	0·5	—
5·10	Cyclo C_5''	—	—	—	—	—	—	—	—	—	—	—	Trace
5·32	?	—	—	—	—	—	—	1	—	—	—	—	—
5·52	*cis*-4MeC_5''-2	—	—	—	—	—	—	—	—	—	—	—	6
5·92	*trans*-4MeC_5''-2	—	—	—	—	—	—	—	—	—	—	—	32
6·28	?	—	—	—	—	—	—	3	—	—	—	—	—
7·35	2 MeC_5''-1	—	—	—	—	—	—	—	—	—	—	54	—
7·51	C_6''-1	—	—	—	—	—	—	38	—	—	—	—	—

* Or vinyl acetylene. † May include cyclo $''C_5''$. ‡ Very approximate figure.

Table 4. Thermal cracking patterns of miscellaneous hydrocarbons at 500°C (20-second residence time)

Relative retention distance	*Identity of product*	*Relative peak area* × 100%		
		Cyclopentane	*Cyclopentene*	*Isoprene*
0·23	C_1 }	1	8	4
0·29	C_2'' }			
0·48	C_3''	1	6	2
1·00	C_4''-1/iso-C_4'' etc.	Trace	4	2
1·26	*trans*-C_4''-2	—	—	0·5
1·56	1,2″C_4''/vinyl C_2'''	—	—	0·5
2·16	DiMe C_2'''	—	Trace	—
2·55	C_5''-1	1	—	—
2·83	2 MeC_4''-1	—	—	0·5
3·10	Isoprene	—	—	91
3·20	C_5''-2	7	—	—
3·80	Cyclo ″C_5''	—	29	—
4·63	?	4	—	—
5·10	Cyclo ″C_5	—	52	—
5·29	?	1	—	—
6·22	Cyclo C_5	85	—	—

sample size is shown. At low concentrations, these secondary reactions can be virtually eliminated.

The data in *Table 7* show the influence of temperature on the depth of cracking and on the extent of radical–molecule reactions for 2,4-dimethylpentane. Similar results were obtained for a number of other hydrocarbons: cyclopentene gives 61 wt % of cyclopentadiene at 600°C, compared to 29 per cent at 500°.

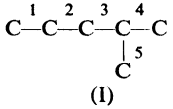
Discussion

The data presented in *Tables 2* to *5* show that the pyrolysis unit described produces reasonable amounts of primary decomposition products from a variety of hydrocarbons. As will be demonstrated later, the major products are clearly related to the parent molecule. The repeatability of the cracking patterns is not unsatisfactory, particularly in comparison with typical analytical GC repeatabilities. The conditions in the prototype reactor used here cannot easily be defined precisely, owing to the marked temperature gradient which exists; but even so 'between laboratories' agreement should be adequate for identification purposes.

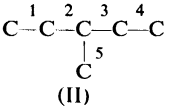
Clearly it is desirable to avoid large concentrations of reactive radicals in the cracker; use of small samples (less than 1 μl) and temperatures below about 550°C leads to cracking patterns essentially free of secondary effects.

The influence of structure on the types and amounts of fragments formed becomes apparent from a study of related groups of compounds; conversely, the nature of a parent molecule can be deduced from the fragmentation pattern. Some informative examples are given below.

2-Methyl and 3-methylpentane



(I)



(II)

Table 5. Thermal cracking of aromatic hydrocarbons at 500°C (20-second residence time)

Relative retention distance	*Identity of product*	*Relative peak area* × 100%								
		Benzene	*Toluene*	*Ethyl benzene*	*Xylenes*			*Isopropyl benzene*	*n-Butyl benzene*	*t-Butyl benzene*
					o-	*m-*	*p-*			
0·2–0·5	Mixture of light hydrocarbons	—	—	2	—	Trace	—	5.5	6	4
1·00	Benzene	100	—	4·3	—	—	—	5	1	2
1·86	Toluene	—	100	0·2	Trace	—	—	0·5	1·5	0·1
3·26	Ethyl benzene	—	—	75·5	—	—	—	1	1	1
3·64	*m*/*p*-Xylene	—	—	—	4	99	100	—	—	—
3·90	Styrene	—	—	17	—	—	—	14	7·5	2
4·21	*o*-Xylene	—	—	—	96	—	—	—	—	—
4·78	Isopropylbenzene	—	—	—	—	1	—	56	—	—
4·88	?	—	—	—	1		—	—	Trace	—
5·26	n-Propylbenzene	—	—	—	—	—	—	—	1	—
5·60	?	—	—	—	—	—	Trace	—	Trace	—
6·65	(Isopropenylbenzene)	—	—	—	—	—	—	18	—	9
7·25	t-Butylbenzene	—	—	—	—	—	—	—	—	81
10·07	n-Butylbenzene	—	—	—	—	—	—	—	82	—
12·11	?	—	—	—	—	—	—	—	—	1

Table 6. Repeatability of cracking patterns—decomposition of 2,4-dimethylpentane at 500°C

Peak number	*Mean relative area*	σ	*Mean actual peak area (arbitrary units)*	σ
1	0·122	0·010	—	—
2	0·271	0·017	—	—
3	0·272	0·019	—	—
4	0·048	0·007	—	—
5	0·156	0·017	—	—
6	1·000	—	221	8·6

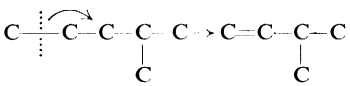
Table 7. The influence of temperature on cracking of 2,4-dimethylpentane (percentage for 1 μl samples) (peak areas)

Peak number	*Remarks*	*Temperature* °C				
		388	500	580	640	690*
1	This 'peak' consists of a group of light hydrocarbons inc. C_4	Trace	36·5	53·2	65·4	64
2	Identity not established	Nil	3	13·1	9·5	4·2
3	Identity not established	Nil	9·2	2·2	Nil	Nil
4	Undecomposed 2,4 DMP	100	51·3	29·1	2·9	Nil
5	'Recombination' peak	Nil	Nil	2·4	22·2	25·8

* For sample 0·5 μl.

From the structure of these molecules it would be predicted that little propylene would appear on cracking (II), whereas (I) should give much. Similarly linear C_4 is a simple fragment of (II) but not of (I): *Table 2* lists 9 wt % butene-2 from (II) and only a trace from (I).

The formation of 2- and 3-methylbutene-1 from these two paraffins is a further distinctive feature. Fragmentation of (I) to methylbutene involves rupture of bond 1 with unsaturation accordingly appearing at the terminal C—C bond:



3-methylbutene-1

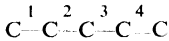
From (II) either bonds 1 or 4 may be broken, as they are equivalent:



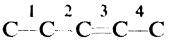
2-methylbutene-1

One would further expect this latter reaction to produce about twice as much methylbutene as the reaction (I) → 3-methylbutene. All of these expectations are borne out.

Pentene-1 and pentene-2



(III)



(IV)

Consideration of these olefins demonstrates the influence of double bond position on fragmentation. In thermal decomposition the weaker bonds break preferentially. The double bond will be the strongest in the molecule and bonds immediately adjacent to it will be relatively stronger than the rest by virtue of the higher electron density in the vicinity of the unsaturated link.

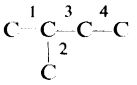
In view of these considerations one may expect the bond strengths to decrease in the order:

(III) $4 > 3 > 2 > 1$

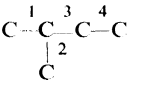
(IV) $3 > 4 \sim 2 > 1$

From (IV) less propylene and more butene-2 may be expected than from (III); this also is confirmed by the results (*Table 3*).

2-Methylbutene-1 and 2-methylbutene-2



(V)



(VI)

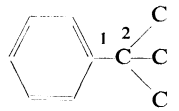
Bond 1 is the strongest and 4 the weakest in (V). Accordingly, the principal pyrolytic product expected is isobutene, together with isoprene, formed by dehydrogenation. Conversely, butene-2 is an unlikely product, since its formation requires rupture of stronger bonds. In *Table 3* yields of 11, 25 and 1 wt % are listed for these three products.

In 2-methylbutene-2 bond 3 is by far the most stable, so that propylene is an unlikely product. Fission of the identical bonds 1 and 2 leads to butene-2 or butadiene-1,3; fission of bond 4 to isobutene. Of the observed products propylene accounts for only 2 per cent, whereas 5 per cent butene-2 and 11 per cent butene-1/butadiene-1,3/isobutene are obtained. Formation of isoprene from (VI) can occur by loss of hydrogen and rearrangement to the most stable, mesomeric, system; about 20 per cent isoprene is found in the products.

Normal- and tertiary-butylbenzene

As a final example of structural influences on fragmentation, the interesting behaviour of these related aromatics is discussed (*Table 5*). It is evident from the behaviour of lighter aromatics that ring breakdown does not occur.

All of the carbon–carbon side chain bonds in n-butylbenzene break to give the four lighter homologues in comparable amounts; the main product is styrene, which is especially stable. On the other hand, the t-butyl side chain decomposes by fission of only two bonds:



Benzene (bond 1 breaks) or methyl styrene (bond 2) are the main products.

These examples show that the observed decomposition pattern is closely related to the carbon skeleton of the parent molecule; they are in accord with the observations of Voge and Greensfelder[11, 12] and their interpretation of thermal cracking mechanisms based on the Rice–Kossiakoff theory[13].

The method as applied here covers only hydrocarbons up to C_{10}, for which identification problems are not generally severe, except perhaps with olefin isomers. However, above this region, any technique which can give structural information about hydrocarbons is valuable, and thermal cracking data may well complement information obtained from infra-red, mass and nuclear resonance spectrometry. The particularly attractive feature of the technique is that by identification of actual skeletal fragments it affords direct information on the structure of the parent molecule with respect to position of double bonds and branching. To cope adequately with the range of products which would arise from pyrolysis of materials of higher molecular weight, a more complex gas chromatographic set-up is needed. The ideal would be a combination of an efficient column for the separation of gaseous products (C_5 and lighter), and temperature-programmed equipment for more speedy elution of the higher-boiling fragments and the undecomposed parent. This high-temperature column would have a non-selective stationary phase, so that in addition to information on the fragments an approximate boiling point of the parent may be obtained.

The technique involves the identification of many fragments, and it may appear that this presents a more extensive problem than the identification of a single substance of higher mass. However, the problem is by no means as difficult as this. Firstly, the most significant fragments are olefinic, and secondly it seems probable that the really useful fragments all have low molecular weights (carbon number up to C_6). Consequently, calibration requirements are considerably less extensive than at first might seem necessary.

As yet, the method has not been applied to mixtures. Provided that sample size and depth of cracking be small, there seems no reason to anticipate interference any more than with pure components. However, the information obtainable would be less clear and would lead to an average structure of the sample as a whole. Empirically, the thermal stabilities of different petroleum fractions might be compared and the influence of various additives on the thermal decomposition of such mixtures studied.

The cracking system described here provides a very simple means to investigate synthesis of particular unsaturated molecules. For example, conversion on a fairly extensive scale of cyclopentene to cyclopentadiene and of methylbutenes to isoprene was observed in this work. The influence of temperature, pressure and concentration, within limits, on numerous potentially valuable dehydrogenations can thus be rapidly deduced.

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[a] Associated Electrical Industries Ltd., Richmond, Surrey, Great Britain

DISCUSSION

F. Sjenitzer: I should like to have some more information on the experimental line shown in *Figure 3* on page 359. This line seems to indicate that the amount of re-combined molecules changes linearly with the square of the concentration, thus suggesting a reaction of second order. Surely this experimental line should run through the origin of the graph; and then it is more likely that some parabolic curve applies, if we may disregard the highest point at 35 μl^2. The result would, of course, be a reaction of lower order than two.

S. G. Perry: I should not like to use the data given in *Figure 3* to draw any kinetic conclusions. The precision of the 'relative area' figures is not high, especially for small samples, where the area of the re-combination peak was only about 4 cm^2. In addition, the method of sample introduction may lead to systematic and/or random errors. Accordingly, I do not believe that the data allow the kind of interpretation Dr Sjenitzer is seeking.

Within the indicated limits I believe that the data presented here show that a bi-molecular process does occur in the cracker, which can be eliminated by the use of small samples.

K. D. Kilburn: I should like to ask Dr Perry if he has had any experience of carrying out such a cracking reaction with hydrogen as carrier gas; in other words, carrying out the cracking in a hydrogen atmosphere.

S. G. Perry: I am afraid the short answer to that question is just 'no'.

SUMMING UP ON BEHALF OF THE TRANS-OCEANIC VISITORS

PROFESSOR W. W. BRANDT

VERY FREQUENTLY the tourist travelling in a foreign country finds that when he returns home he is criticized for having spent his time travelling in a foreign country rather than at home, and he is called upon to justify his travels. I think that those who criticize us often overlook the tremendous value which is gained from the personal contact one has with those in other countries; and the one who is nothing but a tourist, I think, receives considerable satisfaction from just observing the customs and habits and approaches to life which other people take, comparing these with his own. The scientist at an international meeting finds himself in much the same situation. 'Why not stay at home,' we are told, 'and go to the meetings in your own country, rather than bothering to travel abroad and attend meetings in a foreign country?' The benefits which are to be obtained from this type of meeting, I think, are very clear to those of us who are here. We find it very profitable to be able to listen to those of you who contribute to the discussion and to the presentations, to find out how you approach gas chromatography, what type of feeling you have about it, what type of problems you have run into, and how you solve them. I know from my own standpoint, and I am sure from that of my colleagues, that the opportunity to sit at a table and talk with you about gas chromatography, about other problems, and to talk with you out in the hall, makes a meeting such as this extremely valuable and very much worth the effort which it takes for us to manage to find some way to get across the water to attend.

We feel that we are particularly fortunate this year to have been able to come to Hamburg. Certainly those who guided the destiny of this meeting and selected this city really did us a favour; because, for those of us who enjoyed the touring, it is a beautiful city and certainly very interesting. For those of us who enjoyed the scientific aspects we certainly could not have asked for better facilities than we have had here. This auditorium certainly stands out as an example of excellence. The acoustics are superb. I think we could have done without the microphones, although the portable microphones are very nice, but several times you discovered you could hear when the microphone was not working. In addition, the close proximity of the exhibit is useful. We can walk right out of the door and see essentially the bulk of gas chromatographic equipment available in Europe. We can have ample opportunity to discuss things in the hall or in separate meeting rooms. It has certainly been an ideal situation.

I know I speak on behalf of my American colleagues, because many of them have expressed these comments to me, that they have thoroughly enjoyed this meeting. We want to thank all of you very sincerely for the part you may have had in it. I am sure I also speak for my European colleagues who

come from other parts of the Continent and are not native Germans. Certainly, I want to express for all of us who come from elsewhere our very sincere appreciation, and with a little closing attempt I might say, 'Es war ein sehr fruchtbarer Kongreß und ein Vergnügen, daran teilzunehmen. Wir danken Ihnen allen für Ihr Interesse und Ihre Mitarbeit.'

CLOSING ADDRESS

Mr C. S. G. PHILLIPS

SO, DAMEN UND HERREN, Mesdames et Messieurs, Ladies and Gentlemen, we come to the close of our Symposium. In his opening address Dr Kienitz expressed our appreciation to those many people and organizations whose efforts have made it possible to hold this meeting here in Hamburg. For me it remains only to thank all those who have worked so hard to keep it running smoothly these last few days, though I can do no more than pick out a few by name, to whom I feel we are particularly indebted.

First of all, however, I would like to thank you all on behalf of the Organizing Committee for coming to this meeting and by your interest and enthusiasm providing the essential ingredients for its success. The continuing vigour of gas chromatography has been amply demonstrated by your many and varied contributions to our discussions, both formal and informal, and perhaps I should add, most of all very informal.

Our chairmen, authors, reporters, translators and assistants have often had very difficult tasks to perform, but they have brought us through most efficiently and courteously. We owe, of course, a very special and heavy debt to our Editor and co-ordinator, Dr van Swaay. Few, I think, will realize what a heavy burden he has shouldered, and shouldered so competently and cheerfully. Hij heeft zelfs tijd gehad om ons Engels te corrigeren; een noodzakelijke maar vrij ongewone taak voor een Nederlander (please forgive my double-Dutch accent). I fear he has a further heavy burden in putting together our final Proceedings and in trying to distil (a verb for which I should perhaps apologize in this company)—to distil into them the essence of our wide-ranging discussions. I hope all contributors will assist him by filling out their discussion slips before they go. It is perhaps not necessary for me to remind you that your remarks may look a little odd in the cold light of print, if he has to rely only on the recordings.

This has been a joint effort of the Gas Chromatography Discussion Group and the Gesellschaft Deutscher Chemiker. In fact, of course, all the real work of organization has been done here in Germany. The local Committee, and especially Herr Dr Oertel, have put in an enormous effort to make our stay here so pleasant and well-ordered. He and his student assistants have always been at hand to deal with the many major and minor emergencies that necessarily arise in such a meeting as this. There are many others, too, whose work behind the scenes has been vital and yet, because of their efficiency, so little apparent; and here I would like to express our appreciation especially to Herr Kuchenbuch. Last but by no means least we are indebted to Herr Dr Fritsche of the Gesellschaft Deutscher Chemiker, who has been the central figure in all our organization. We have come so much to rely on him, that I begin to feel that I must also thank him for arranging such excellent weather for our stay here in Hamburg. I am sure he did something about that too. Not only have we had a stimulating time here in this magnificent Auditorium Maximum; my wife assures me that the ladies have also much enjoyed their time in Hamburg.

Finally, I would like to address our German friends on behalf of all my English-speaking colleagues.

Es war uns eine außerordentlich große Freude so viele unserer deutschen Kollegen, deren besonders interessante Arbeiten wir natürlich schon seit Jahren mit großem Interesse verfolgen, hier persönlich zu treffen. Ich möchte mich nun zum Sprecher aller meiner englischsprechenden Kollegen machen, und unseren deutschen Freunden sehr herzlich dafür danken, daß uns der Gebrauch unserer eigenen Sprache so ausgebreitet ermöglicht wurde. Wie wichtig dieses Entgegenkommen für uns war wird Ihnen ohne Zweifel klar werden, wenn Sie mich deutsch sprechen hören. Wenn Sie das überhaupt als deutsch anerkennen wollen.

And now, we wish you a pleasant voyage home und auf Wiedersehen.

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