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# QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF SILICATES

# QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF SILICATES

A scheme of quantitative
DC arc analysis of the silicate minerals,
rocks, soils and meteorites

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# PREFACE

This is a small book. It does not aspire to be either a treatise or a fully fledged laboratory manual on the use of the DC arc. It merely describes a series of quantitative methods which have been developed and used from time to time by the author and co-workers for the analysis of naturally-occurring silicates, and which it seemed, could be co-ordinated into a fairly coherent whole—an analytical scheme.

The methods have been developed mainly for the analysis of silicate rocks (igneous, sedimentary and metamorphic), individual silicate minerals and silicate meteorites. Some of the methods may be of use also for the analysis of soil, some ceramic materials and furnace slag.

Although the book is written primarily for the silicate analyst, it is addressed also to those who wish to have some idea about the accuracy and application of spectrochemical methods of silicate analysis.

The scope of spectrochemical methods of analysis can be extended indefinitely when combined with chemical methods of pre-enrichment. Such combined procedures are, however, considered beyond the scope of this book which will restrict itself to methods of direct excitation of powders.

A chapter on spectrochemical error distribution and calculation has been included because it has become evident that the usual statistical methods of presenting precision are based on a false assumption which can sometimes lead to wholly inaccurate predictions.

No attempt has been made to review the literature except in Chapter 9 and the serious reader interested in a bibliographical coverage of the spectrochemical analysis of minerals, rocks, soils and related materials should consult MITCHELL (1948), AHRENS (1950) and the Index to the Literature on Spectrochemical Analysis, Part I (MEGGERS and SCRIBNER, 1941), Part II (SCRIBNER and MEGGERS, 1947) and Part III (in press).

*Cambridge, Mass.,*
*Nov.*, 1958

## ACKNOWLEDGMENTS

A major proportion of the material described in this book is based on the co-operative investigations of the author and co-workers who at one time or another were either students, assistants or visitors. The research contributions of the following have been particularly significant: F. C. CANNEY, Ph.D.; W. H. DENNEN, Ph.D.; H. P. EUGSTER, Ph.D.; W. HOLYK, Ph.D.; W. H. PINSON, Ph.D.; R. H. SERAPHIM, Ph.D. In addition, SYLVIA BATEMAN, C. K. BELL, Ph.D., R. W. EDIE, Ph.D., LORRAINE G. GORFINKLE, MARGARET M. KEARNS, G. R. WEBBER, C. W. WELBY, Ph.D., F. B. WHITING, Ph.D. and E. YOUNG, Ph.D., have made useful contributions, either in the form of measurements, independent investigations or suggestions: indeed, it would be a difficult task to acknowledge fully the efforts of all of those who in one way or another participated in the investigations on which most of this book is based.

The initiative and interest of Prof. H. W. FAIRBAIRN is also acknowledged. Although not an analyst, his general interest in the accuracy of silicate rock analysis was a prime factor which led to a large-scale investigation on the accuracy and precision of chemical and spectrochemical methods, the results of which—distressing in some respects but nevertheless illuminating—have been published as a Bulletin (No. 980) of the U.S. Geological Survey and are discussed here. This investigation as well as the research on some of the methods of silicate analysis described in this book has had support from the Office of Naval Research, Washington.

Thanks are due to Drs. D. M. SHAW and K. H. WEDEPOHL for kindly supplying enlargements from which Plates 3 and 4 were prepared and to the Pergamon Press for their permission to reproduce them here.

# CONTENTS

CHAPTER 1

# INTRODUCTION

THE DC arc is a simple, inexpensive and easily operated source of excitation. It is ideally adapted to the qualitative analysis of almost all inorganic substances, including the naturally-occurring silicates. For some time the opinion has been held by many that accurate quantitative determinations could not be made with this source and that, therefore, its use should be restricted to qualitative and semiquantitative determinations. Although this still is the firm opinion of a few who write about spectrochemical methods of analysis there is, in any case, some confusion because of differing connotations given to the terms quantitative and semiquantitative. One analyst might for example regard determinations which can be made to within $\times \frac{1}{2}$ to $\times 2$ or so of the correct amount as semiquantitative and those that can be made to within 10% or less as quantitative; another might class the 10% or so limit as semiquantitative and restrict the use of the term, quantitative, to methods which are usually capable of determining elements to within 2–3% or less of the correct amount.

Although the accuracy of the DC arc is rarely capable of matching the best accuracy which may be achieved by means of some other sources, the stigma of semiquantitativeness is unwarranted—that is, if we are satisfied to refer to determinations which may be made to within 2·5–10% of the correct amount as quantitative. The relative deviation* of most quantitative DC arc methods which utilize an internal standard, including those described in this book, fall within the 2·5–10% range.

DC arc methods can, as a rule, be grouped into one of two categories: first, those which describe general methods by means of which many elements may be determined semiquantitatively in one or perhaps two operations, and second, those which describe methods that are truly quantitative but are specific for one or a limited number of elements.

* For definition see page 89.

The general methods are attractive because they are rapid and are valuable for some purposes, but often a much higher standard of accuracy is demanded than they are capable of giving. By using specific methods, and particularly if so-called ideal internal standards are used—for example, Ag for Cu, Fe for Co, Hf for Zr, K for Rb, one rare earth for another, and so on—excellent accuracy may be obtained. A complete quantitative silicate analysis using specific methods would, however, lose much of the attractiveness usually associated with spectrochemical methods because of the tedium of such a series of operations. In addition to speed and accuracy, sensitivity is a further prime consideration. A method which is to be used for the analysis of silicate minerals, rocks and meteorites should as a rule be as sensitive as possible. Although no perfectly general statement can be made, it is unfortunate that a gain in either speed or accuracy, or both, is often made at the expense of sensitivity.

In this book an attempt is made to reach an effective compromise between speed, accuracy and sensitivity. A scheme of analysis is described in which the complete quantitative spectrochemical analysis of a silicate mineral, rock or meteorite involves a small number of separate operations, and may therefore be regarded as rapid, but which at the same time is accurate and sensitive.

In developing this analytical scheme, these items have been borne in mind:

1. Almost all naturally-occurring silicates contain a significantly high total concentration of the alkali metals ($>0{\cdot}5$–$1\%$).

2. These elements are among the first to distil completely from the electrode cavity and the time at which they complete their distillation may usually be determined accurately.

3. Several other elements complete their distillation during the alkali metal phase of distillation.

4. CN emission may be reduced to an insignificant minimum in the presence of alkali metal vapour.

5. Differences in the distillation rates of the involatile elements are reduced significantly in the presence of admixed carbon powder.

6. Similarity between the distillation rates of internal standard and analysis elements is considered to be a prime requisite for a good internal standard when using the DC arc.

TABLE 1–1

ANALYTICAL SCHEME FOR NATURALLY-OCCURRING SILICATES

| Element | Detection limit (ppm) | | |
|---|---|---|---|
| Na | 0·3 | Volatile elements | "Rare" elements plus Na and K |
| K | 2 | | |
| Li | 0·3 | | |
| Rb | 1 | | |
| Cs | 2 | | |
| Ga | 2 | | |
| Pb | 5 | | |
| Ag | 0·5 | | |
| Cu | 1 | | |
| Tl | 1 | | |
| In | 1 | | |
| Sn | 10 | | |
| Zn | 100 | | |
| Ge | 5 | | |
| V | 3 | Involatile elements | |
| Ni | 3 | | |
| Co | 3 | | |
| Zr | 10 | | |
| Cr | 1 | | |
| Sc | 2 | | |
| Y | 10 | | |
| Nd | 10 | | |
| La | 10 | | |
| Sr | 3 | | |
| Ba | 3 | | |
| Mo | 3 | | |
| (Ti) | 10 | | |
| F | 50 | | |
| Al | 2 | | Common elements |
| Ca | 2 | | |
| Mg | 2 | | |
| Fe | 5 | | |
| Mn | 3 | | |
| Si | 20 | | |

Elements which are discussed in the analytical scheme are given in Table 1–1. Elements of each group are determined in a single operation. Approximate detection limits concentrations (ppm) are given. For a few of the volatile elements, lower detection limits may be reached by using one of the special methods described in Sec. 6–5.

Most elements listed in Table 1–1 are detectable in one or another of the common silicate minerals or rocks. Other elements are sometimes detected; boron is an example and is discussed separately in Sec. 7–5.

A separate internal standard is used for each group of elements. The internal standard may, however, be omitted. Although this will usually result in some lowering of accuracy, the speed of all and the scope of some of the methods described in this book is increased by leaving out the internal standard and the analyst may prefer to do this unless the highest accuracy is required.

The reader's attention is drawn to the investigations of HEGEMANN and co-workers at Münich (see for example, HEGEMANN and ZOELLNER, 1952) who describe quantitative procedures for the fairly complete analysis of silicates. One useful feature about these methods is that some constituents can apparently be determined with a high degree of accuracy; see Sec. 9–6 for further comments.

CHAPTER 2

# MISCELLANY

ONLY Sec. 2–1 and parts of some of the other sections deal specifically with the analytical scheme; the content of most of the rest of this chapter is made up chiefly with brief discussions, observations and notes on sundry items of a general nature.

## Sec. 2–1. Electrodes and their dimensions

Either of two lower electrode types is used to hold the sample: they have the same shape but differ in dimensions and are shown in Fig. 2.1. The upper electrode is sharpened to a point and has the diameter of the lower electrode, which is made the anode in all procedures except one in Sec. 9–4. The electrode gap is 4–5 mm.

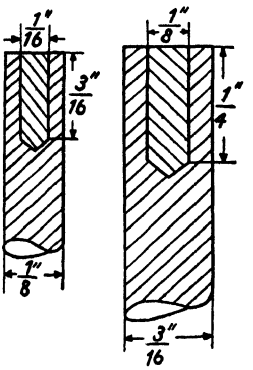



Fig. 2.1. Anode shapes. Either or both are used for all procedures of the analytical scheme except those of Sec. 9–4.

The $\frac{3}{16}$" (outside diameter) × $\frac{1}{8}$" (inside diameter) × $\frac{1}{4}$" (cavity depth) electrode is, for the sake of brevity, referred to hereafter as the $\frac{3}{16}$" electrode and the one with $\frac{1}{8}$" (outside diameter) × $\frac{1}{16}$" (inside diameter) × $\frac{3}{16}$" (cavity depth) as the $\frac{1}{8}$" electrode. About 50 mg of sample is accommodated by the $\frac{3}{16}$" electrode and about 10 mg by the $\frac{1}{8}$" electrode.

Other designs varying in complexity have been used from time to time for the analysis of the naturally occurring silicates. Although some electrode shapes might be more satisfactory for certain specific problems, it has been the general experience of the author and co-workers that nothing is gained through their use for most general procedures.

Carbon electrodes have usually been used and almost all

observations given in this book refer to such electrodes; it is quite probable, however, that graphite electrodes would serve equally well. Some observations on electrode purity are given in Sec. 2–6.

## Sec. 2–2. Power

In each method of the analytical scheme, one of two amperages, 8 amp or 7 amp, is used.

The observations on which the scheme is based have been made chiefly in two laboratories: in each, a comparatively high line voltage of 220–240 volts from a motor-generator has been used. The general consensus seems to be that a somewhat more reproducible discharge is obtained from a comparatively high line voltage—see for example BELYAKOV-BODIN and MANDELSTAM (1944). Direct comparisons of the use of various line voltages and of the relative merits of rectified AC (various) vs. motor-generator DC have not been made; neither has a systematic investigation been attempted to improve accuracy by means of stabilizing the discharge. Although the possibility of achieving some improvement this way is not overlooked, other considerations usually assume far more significance in the DC arc analysis of powders; if, however, the analyst has made provision for some form of control, so much the better. Introduction of current control may bring about a significant improvement in accuracy in the absence of an internal standard and may be found helpful for refining the precision of a method which is already highly reproducible.

## Sec. 2–3. Comments on the measurement of intensities and intensity ratios

Several elements are often determined by any one of the constituent methods of the analytical scheme and as the concentrations of elements vary considerably in the naturally-occurring silicates, extreme intensity ranges have to be measured. The use of some sectoring device is therefore usually a necessity.

The actual amount of transmission and hence the sector steps which should be used will depend upon the nature of the problem and also of course on instrument speed, slit width, emulsion speed and other pertinent items. From four to seven

steps of a sector with a transmission factor of two have been used in many of the methods described here. The unsectored exposure (100% transmission) is included if a line of an element happens to be weak and near the threshold intensity for a given photographic plate. The use of the unsectored exposure together with sectored exposures might introduce some error if the plate shows a significant intermittency effect.

As exposures are usually made through a sector, it is common practice to determine intensities and intensity ratios by means of the auto- or self-calibration method—see for example STROCK (1936) and AHRENS (1950, p. 137).

In conformity with current trends, $\log\left(\frac{d_0}{d}-1\right)$* (sometimes referred to as the Seidel function—KAISER, 1941) is usually used in place of $\log\frac{d_0}{d}$ or other measure of photographic response. The chief advantage of relating $\log\left(\frac{d_0}{d}-1\right)$ to $\log I$ is of course the fact that their extended linear relationship facilitates the accurate measurement of low photographic response—weak lines and background. Measurement of intensity (line and background) by means of the self-calibration procedure is otherwise the same except that partial Seidel curves are substituted for partial characteristic (H and D) curves. When log-log co-ordinates are employed, $\frac{d_0}{d}-1$ is plotted vs. $I$.

CANNEY (1952) has made a critical comparison of $\log\frac{d_0}{d}$ vs. $\log I$ and $\log\left(\frac{d_0}{d}-1\right)$ vs. $\log I$ curves for some Eastman plates. His conclusions corroborate those of some other workers; two of his curves are shown here (Figs. 2.2 and 2.3)

* The use of some function related to $\log\left(\frac{d_0}{d}-1\right)$ has been discussed, mainly by HONERJÄGER-SOHM and KAISER (1944) who recommend $\frac{\log\frac{d_0}{d}+\log\left(\frac{d_0}{d}-1\right)}{2}$ as a measure of photographic response. For further discussion of this general topic of extending linearity between photographic response and $I$ to low response values, see BAKER (1925), KAISER (1941: 1948), SCHMIDT (1948), FELDMAN (1949), NACHTRIEB (1950), NOAR (1950), and PRICE (1952).

for illustration. They refer to the Eastman 108-J plate (at 5850 A) developed in Kodak D-19 developer (diluted 1 : 1 with water) for 4½ minutes at 20° C. The familiar toe of the H and D curve develops at an opacity of ~2·5–3·0 (density = 0·4–0·48) whereas linearity persists in the Seidel plot to a value of $\frac{d_0}{d}$ −1 equivalent to an opacity of ~1·1–1·2 and a density of ~0·04–0·08.

Intensities and intensity ratios are determined from

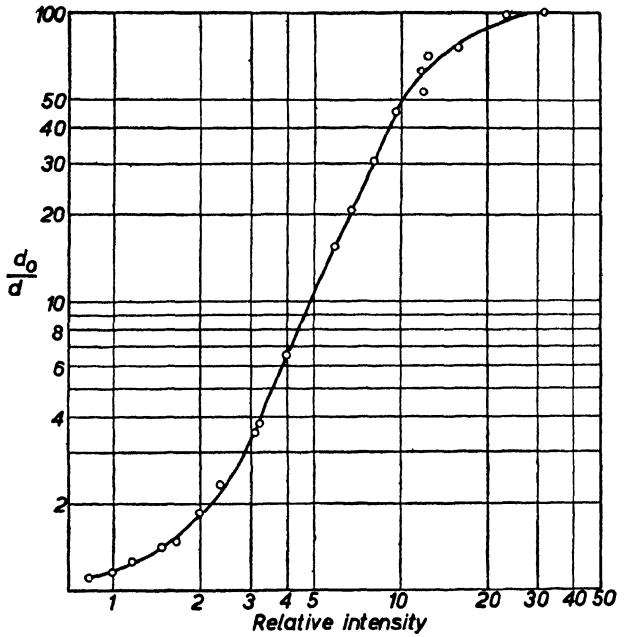



Fig. 2.2. *H* and *D* curve for 108-J plates at λ 5850 A.

separate calibration curves if a small number of sector steps are used or if the sector is omitted during the analysis exposure. Several methods have been used to construct calibration curves and the selected procedure is determined partly by the nature of the investigation. CANNEY (1952), for example, wished to determine a wide range of intensities. For this purpose he constructed a composite calibration curve (Figs. 2.2 and 2.3) by fitting several partial characteristic (or Seidel) curves for iron lines of varying intensity and of similar wavelength which had been exposed through a

seven step sector. Multiplet groups are sometimes used to prepare calibration curves. Thus, BELL (1953) investigated the geochemistry of gallium, using Ga 4172 as the analysis line and In 4101 as the internal standard line (Sec. 6–2). Spectra of at least a few potassium-bearing minerals appeared on each plate. As the intensity ratio $\left\{\frac{\text{K } 4044}{\text{K } 4047} = 2{\cdot}0\right.$ (the sum rule is obeyed implicity) and because the intensities of Ga 4172 and In 4101 and K $\left\{\begin{matrix}4044\\4047\end{matrix}\right.$ fell on the linear portion of a characteristic curve, short two-point calibration curves could be prepared and used. For this purpose, K $\left\{\begin{matrix}4044\\4047\end{matrix}\right.$ must be free from background and self-absorption. The two-line method (CHURCHILL, 1944) has sometimes been used.

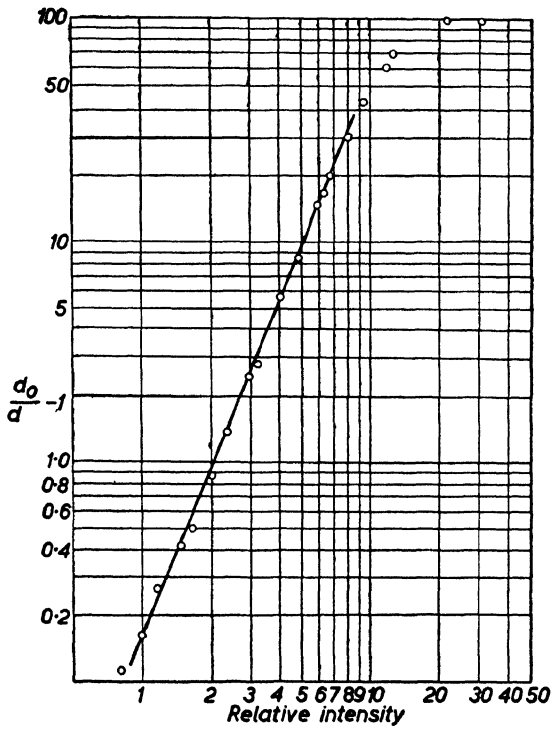



**Fig. 2.8. Plot of Seidel function versus relative intensity for 103-J plates at 5350 A.**

It is quite common practice in the Cabot Spectrographic Laboratory to carry out determinations in batches so as to reduce possible sources of error. A separate series of standards is usually run with each batch of unknowns when the internal standard is omitted. The procedure is sometimes adopted also for internal standard methods where utmost control and accuracy are desirable.

Most observations and determinations in the ultra-violet have been made on Eastman 103-O plates, developed at $4\frac{1}{2}$ minutes in Kodak D-19 developer (usually diluted 1 : 1 with water) at $20 \pm 2°$ C. Other emulsions have been used at longer wavelengths but method of development is the same.

## Sec. 2–4. Background—visible and otherwise

Background corrections have been attempted in the usual way; namely, measurement of the photographic response of line and of the adjacent background, conversion to intensities followed by the subtraction of background intensity from line plus background. Although the measurement of background response is facilitated by using the Seidel (or related) function, this does not of course solve the fundamental problem of whether the measured subtraction gives the correct relative intensity of the emitted line reaching the plate. The author's experience in this respect has been varied. When working with Ilford Ordinary plates, it seemed that valid corrections for background could be obtained this way; moreover, characteristic curves for line and for continuous radiation appeared to have equal slopes. The general experience with the Eastman 103-O plate in the Cabot Spectrographic Laboratory, has, however, indicated that the subtraction sometimes overcompensates for background. STROCK's (1936) observation appears to hold for this plate and the slopes of H and D (or Seidel) plots for line radiation usually, though not always, seem greater than those for continuous radiation. This can cause a serious error if a separate calibration curve, prepared from line radiation, is used for the determination of both line and background intensities. Significant error should, however, not exist provided intensities are measured by means of the self-calibration method in which separate characteristic or Seidel curves are drawn for both line and background.

CANNEY (1952) has emphasized the significance of invisible background—that is background intensity which by itself is not able to exceed photographic threshold but which with the aid of other radiation produces a measurable response. The significance of invisible background is easily observed by scanning a step spectrum recorded on a plate of high contrast. A step of high transmission may show a comparatively bright line on a background which is, say, 10–20% as intense as the line. A step of weaker transmission shows a weakened line on an apparently clear background. Under such conditions the analyst is tempted to regard background as zero because it is not visible, in which case his determination of the intensity of the line will be 10–20% too high. CANNEY has demonstrated that the development of a toe in some of his working curves could be attributed to invisible background. Intensity measurements had been made on a specific sector step free from visible background which, however, was quite distinct in a step of higher transmission. This was measured, reduced by an amount proportionate to the transmission ratio of the two sector steps and subtracted from line intensity.

Prefogging a plate has been suggested (FELDMAN, 1949) as a means of aiding weak radiation to exceed photographic threshold; the microphotometer deflection of a fogged area free from other radiation is regarded as $d_0$.

Plates of high contrast are popular in quantitative analysis partly because of their apparent freedom from background—" what the eye doesn't see, etc." The above observations, however, serve to remind one that in this respect plates of high contrast should be used with some caution.

## Sec. 2–5. Note on the behaviour of some silicates in the electrode cavity

Some naturally-occurring silicates are very badly: either a large proportion of the sample is lost when the discharge is started or the arc may in general behave very erratically; in either case the analysis is a failure. Biotite, serpentine, fine particle clays and some soils and other sediments, particularly those rich in organic matter or carbonates, are examples.

An entirely satisfactory burn may usually be obtained by preheating the loaded electrode, either in a muffle furnace or simply by inserting it into a gas burner flame. Heating in

the burner flame should not be carried out rapidly, otherwise material is lost in much the same way as in the arc; final heating for a few seconds at red heat is usually adequate. It is highly unlikely that such a pre-heat could cause significant loss of any element, save possibly a few very volatile ones such as arsenic and mercury when present in a volatile form—the chloride for example. These comments apply also to pre-heating in a muffle furnace unless it is carried out at a high temperature over a prolonged period. For the analysis of soil, MITCHELL (1948) recommends a pre-heat at 450° C. CANNEY (1952) analysed 324 samples of sediments (mainly shale, some rich in organic matter) and observed that a pre-heat of one hour greatly improved the arc burn; at 450° C only 5% of all arcings were regarded as poor and had to be repeated. CANNEY observed further that the background intensity emitted by the preheated sample was about one-half of that emitted by the raw sample. WELBY (1952) and YOUNG (1953) preheated as above for their investigations on the composition of marine sediments. Some sample might on rare occasions be lost despite preheating; initial arcing for a few seconds at a low amperage (2–3 amp) usually overcomes this difficulty.

Although the bulk mineralogical composition of many ultramafic rocks such as pyroxinite and dunite resembles that of the chondritic meteorites, burning properties in the arc differ widely. This is due in part to the ubiquity of some 0·5–1·0% total alkali metals in all chondrites as compared with less than 0·05% in most ultramafics. This difference is significant: whereas chondrites will arc comparatively smoothly, provided sulphur is first removed by preheating, and produce a typical alkali metal-discharge during the early arcing period, ultramafics behave far more erratically, are liable to be lost and show no alkali metal phase. HOLYK (1952) has observed that the addition of two parts of powdered carbon to an ultramafic rock not only improves the quality of the discharge but prevents loss of the ultramafic specimen which is otherwise likely to take place. Serpentine will, however, be lost in any case unless preheated.

## Sec. 2–6. Purity of carbon and graphite electrodes

Electrode purity has been the subject of much investigation and discussion; for references to the literature see

MITCHELL (1948, pp. 48–47), STRASHEIM (1948) and AHRENS (1950, pp. 48–47). Special Spectroscopic Carbon electrodes, National Carbon Company, have for the most part been used in the Cabot Spectrographic Laboratory. As the purity of these electrodes has been found satisfactory for almost all purposes, no attempts have been made to prepare them in a higher state of purity. The regular, inexpensive electrodes are used for the determination of fluorine and for elements when present at high concentrations.

K. LAQUA and A. STRASHEIM of the National Physical Laboratory, Pretoria (Union of South Africa), have recently compared the purity of several commercially available graphite and carbon electrodes before and after treatment. To test purity they employed cathode layer excitation because of its unique sensitivity for this purpose. Their results are summarized in Table 2–1. Line intensity is symbolized as follows :

(I) not always visible
I very weak, barely visible
II distinct
III strong lines
IV more than impurity.

Subscripts 1, 2, etc. indicate subdivisions; thus $I_1$ is weaker than $I_2$.

In each example, the first vertical column refers to the untreated electrode and the second, after its surface has been burnt off in the arc; the third and fourth columns (when present) refer respectively to the electrode after chemical treatment, and after combined chemical treatment and arc ignition.

The results make an interesting comparison of the purity of carbon and graphite electrodes from different sources. A and B are free from detectable boron, as is also National Special Spectroscopic *Carbon* (Sec. 7–5) which has consequently been used for the determination of boron in silicates. Neither arc ignition nor chemical treatment has removed boron from those electrodes referred to in Table 2–1 which show detectable quantities of this element.

X-ray diffraction patterns of C, D and E have been

TABLE 2–1

OBSERVATIONS ON ELECTRODE PURITY (AFTER LAQUA AND STRASHEIM)

| Element | | | Electrode description | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | A | | B | | C | | | | D | | | E | | |
| Al | 3093 | ... | (I) | (I) | $I_1$ | (I) | $III_2$ | $III_1$ | II | $I_6$ | $I_5$ | $I_4$ | $I_3$ | (I) | $I_2$ | (I) |
| B | 2498 | ... | — | — | — | — | III | III | III | III | $IV_1$ | $IV_1$ | $IV_1$ | $IV_1$ | $IV_1$ | $IV_2$ |
| Ca | 3179 | ... | — | — | — | — | IV | $III_2$ | $III_1$ | II | $I_4$ | $I_3$ | $I_3$ | $I_1$ | — | — |
| Cu | 3248 | ... | — | — | — | — | $I_4$ | $I_3$ | II | $I_2$ | — | — | III | $I_1$ | I–IV | I–II |
| Fe | 2599 | ... | $I_1$ | $I_2$ | $I_{11}$ | $I_6$ | II | $I_9$ | $I_{12}$ | $I_{12}$ | $I_8$ | $I_7$ | $I_{10}$ | $I_4$ | $I_5$ | $I_3$ |
| Mg | 2852 | ... | $II_3$ | $II_2$ | $II_9$ | $II_5$ | $III_3$ | $III_2$ | $III_4$ | $III_1$ | $II_3$ | $II_6$ | $II_{10}$ | $II_7$ | $II_4$ | $II_1$ |
| Mn | 2795 | ... | (I) | (I) | (I) | — | I | — | (I) | (I) | (I) | — | — | — | — | — |
| Si | 2516 | ... | $I_3$ | $I_2$ | $II_1$ | $I_7$ | $IV_1$ | $III_1$ | $IV_2$ | $III_2$ | $I_6$ | $I_5$ | $II_2$ | $I_3$ | $I_4$ | $I_1$ |
| Ti | 3349 | ... | — | — | — | — | III | II | (I) | (I) | (I) | (I) | (I) | (I) | (I) | (I) |
| V | 3185 | ... | — | — | — | — | $II_2$ | $II_1$ | (I) | — | (I) | — | — | — | — | — |

A Special Graphite electrodes ; National Carbon Co., Cleveland and San Francisco, U.S.A.
B Spectroscopic Graphite (Grade A) electrodes ; United Carbon Products Co. Inc., Bay City, Michigan, U.S.A.
C Carbon (regular) electrodes ; as in A.
D Purified Carbon electrodes ; C. H. Champion, National House, 60-61 Wardon Street, London, England.
E Spektralkohl RWI ; Ringsdorff-Werke G.m.b.H., Mehlem/Rhein, Germany.

prepared by J. H. VAN NIEKERK (National Physical Laboratory, Pretoria). These indicate that C has highest crystallinity and is composed of the largest crystallites whereas D has least crystallinity and is composed of the smallest crystallites. On the basis mainly of machinability D is carbon whereas C and E (together with those labelled graphite) are graphite.

CHAPTER 3

# STANDARDS

## Sec. –31. Introduction

PRACTICING spectrochemists are fully aware of the fact that quantitative spectrochemical methods of DC arc excitation of powders are liable to serious systematic error. The cause is the well-known fact that the intensity of a spectral line emitted by an element at a given concentration is not independent of the chemical composition and physical properties of the matrix material. Matrix properties will always influence line intensity to some degree; the effect may be insignificantly small or at the other extreme, excessively large. We have as a consequence the well-known golden rule for accurate quantitative determinations, that the general chemical composition and physical properties of standards and unknowns should be the same or very nearly so; or if not, some attempt should be made to compensate for possible systematic error. The general topic of the importance of matrix has been the subject of much study and the reader may refer to AHRENS (1950) for bibliographical references up to that time.

## Sec. 3–2. Two rock standards

As we are dealing with naturally-occurring silicates an attempt should be made to use such materials as standards when possible. The discussion which follows is in two parts; the first concerns the common elements and the second, the rare elements.

Several of the common elements can usually be determined chemically with satisfactory accuracy and as a result carefully analysed rocks may be used as rock standards. The FAIRBAIRN *et al.* (1951) study had this in mind. Two common rocks, one a granite from Westerly, Rhode Island, and referred to hereafter as G-1, and one a diabase from Center-

ville, Virginia, and referred to hereafter as W-1, were analysed by 84 chemists from 25 laboratories of repute from different countries. The principal object for having such a large number of determinations was to obtain a thoroughly accurate value for each common constituent. A second object was an attempt to determine the accuracy of single routine chemical determinations of the common constituents in silicate rocks. The statistical conclusions of the investigation and the full details of each chemical analysis are discussed and given by FAIRBAIRN *et al.* (1951).

Table 3–1 (p. 24), gives the value recommended by FAIRBAIRN (1953) of each chemically determined constituent. Recommended values usually represent the arithmetic means ($\bar{x}$) of all or nearly all the individual chemical determinations. The relative deviation (C) is included.

The value of C varies enormously; from 0·5% for $SiO_2$ in granite to 39% for $P_2O_5$ in the same rock. In general, C decreases with increase in concentration. This characteristic of chemical but not of spectrochemical methods of analysis is illustrated in Fig. 9.1 and discussed further in Sec. 9–2. Because of this relationship the recommended values of the commonest constituents in G-1 and W-1 are likely to be more accurate than those which are present at comparatively low concentrations.

Calculations of C assume a normal (Gaussian) distribution of chemical error. Actually chemical error distribution is often complex: it is occasionally normal or nearly so, sometimes it is *lognormal*, as is usual in spectrochemical analysis (see page 39). A special type of reciprocal skewness develops in the frequency distribution curves in constituent elements of such pairs as Si-Al and Ca-Mg where incomplete removal of silicon and calcium may influence the determinations of aluminium and magnesium respectively. FAIRBAIRN and SCHAIRER (1952) examined 12 careful chemical anlayses of a synthetic silicate glass of known composition and were able to relate an excess in some of the alumina determinations with a deficiency in the corresponding silica determinations. Allowance for such behaviour gives the underscored values for $SiO_2$ and $Al_2O_3$ in Table 3–1 which are recommended. Although C is rarely a true measure of error dispersion it is nevertheless a satisfactory guide for most general purposes

including those at hand and the values given in Table 8–1 may be used as indicators of precision.

Only a comparatively small number of analysts have determined the rare elements. This has been due mainly to a lack of spectrochemists adequately experienced with the quantitative analysis of the naturally-occurring silicates; a few who agreed to participate were in the end unfortunately unable to do so because of lack of time. The investigation was, however, not restricted to spectrochemical methods and the co-operation from chemists has been valuable. Despite the fact that the total number of analysts is comparatively small and that the accuracy of the determinations is usually inferior to the chemical determinations of the common constituents, the results are nevertheless of much value. Four spectrochemists (R. L. MITCHELL, Macaulay Institute of Soils Research, Aberdeen; K. J. MURATA, U.S. Geological Survey, and L. G. GORFINKLE and L. H. AHRENS, Department of Geology and Geophysics, M. I. T.) participated in the investigation in its earlier stages and their results have already appeared in the literature (FAIRBAIRN *et al.*, 1951). S. R. NOCKOLDS (Department of Petrology and Mineralogy, Cambridge University) and D. M. SHAW and G. R. WEBBER, (Department of Geology, McMaster University, Hamilton), have subsequently analysed G-1 and W-1 and their results are included here. Each of the spectrochemists used more or less general methods. Those used by MITCHELL, and by GORFINKLE and AHRENS have been described in the literature (MITCHELL, 1948, and AHRENS, this book). A. KVALHEIM, Statens Råstofflaboratorium, Trondheim, determined scandium only, using a spectrochemical method described by KVALHEIM and STROCK (1939).

H. W. LAKIN, H. ALMOND, F. WARD, and LAURA REICHEN (U.S. Geological Survey) determined Co, Cu, Mo, Ni, and Pb colorimetrically using field methods which have been developed at the U.S. Geological Survey, whereas H. BLOOM, also of the U.S. Geological Survey, determined Co, Cu, Pb and Zn using laboratory methods. M. H. HEY (British Museum) has made a comparatively complete chemical analysis and determined Ba, Cr, Cu, F, Ga, Ni, Pb, Sr, V, Y + Ce + La, etc., and Zr. This contribution is of considerable value and the following remarks about procedure are quoted from a letter.

" Our technique for V, Cr, Mo, Ni, Cu, Zn, Pb, Cd, Ga is that of E. B. SANDELL, but if there is much Ni or Cu we check by the gravimetric method of HARWOOD and THEOBALD for Ni, and the alternative colorimetric method of A. W. GROVES for Cu. For Ba we usually obtain two figures, one with S, Zr and rare earths by HILLEBRAND'S method and one on the insoluble from the Mn determination after GROVES (1951, page 165). Sr is determined by RAWSON'S method on the CaO. In rocks where the Sr or Ba may be of special interest, we often obtain a second Sr and a second or third Ba figure on a special portion after GROVES (1951, p. 165)." For further information about individual determinations, see footnote entries to Tables 3–2(A) and 3–2(B).

All available determinations of the rare constituents are given in Tables 3–2(A) and 3–2(B).*

When consideration is taken of the fact that a number of different procedures have been used, that several of the methods are general and are not claimed to be highly accurate, and that the concentrations of a few elements sometimes border on detection limits, the conclusion may be made that, taken as a whole agreement is satisfactory : occasionally it is excellent and occasionally very poor. A discussion of the recommended value for each constituent follows.

It will be impossible to apply a strictly rigorous statistical treatment to the data because the nature of the distribution of the observations about the true concentrations is not known. If we were confined to several determinations by a

* Some semi-quantitative determinations (C. O. HARVEY, Geological Survey and Museum, South Kensington, London) came to hand after preparation of Table 3–2; they are as follows:

| | G-1 | W-1 |
|---|---|---|
| | (ppm) | |
| Ba | 1000 | 100 |
| Cr | 30 | 120 |
| Co | <5 | 26 |
| Ga | 10 | 20 |
| La | 100 | <5 |
| Mn | 340 | 1300 |
| Ni | <10 | 60 |
| Sc | <10 | 70 |
| Sr | 220 | 180 |
| V | <20 | 250 |
| Y | <20 | 30 |
| Zr | 300 | 80 |

single spectrochemical method the solution would be comparatively simple; as distribution is lognormal, or at least nearly so (Chap. 4), we would be obliged to choose the geometric mean as the most favoured result. Provided dispersion is small, however, the arithmetic mean or average may in any case be used irrespective of whether the distribution is normal, lognormal or of some other type, complex or simple. The arithmetic mean will therefore be used here to calculate the recommended values for those elements which show a small or moderate dispersion; these are in the majority. As

TABLE 3-1

RECOMMENDED VALUES FOR EACH CHEMICALLY DETERMINED COMMON CONSTITUENT IN STANDARD GRANITE G-1 AND STANDARD DIABASE W-1* (AFTER FAIRBAIRN, 1953)

| Constituent | G-1 ($\bar{x}$) | G-1 C (%) | W-1 ($\bar{x}$) | W-1 C (%) |
|---|---|---|---|---|
| $Na_2O$ | 3·25 | 5·2 | 2·0 | 9·8 |
| $K_2O$ | 5·4 | 6·8 | 0·63 | 23 |
| $SiO_2$ | 72·4 → 72·9 | 0·5 | 52·3 → 52·7 | 0·6 |
| $TiO_2$ | 0·25 | 17 | 1·10 | 14 |
| $Al_2O_3$ | 14·4 → 18·9 | 2·2 | 15·1 → 14·7 | 3·3 |
| $Fe_2O_3$ | 0·93 | 37 | 1·50 | 30 |
| FeO | 0·99 | 13·5 | 8·7 | 4·7 |
| MnO | 0·027 | 28 | 0·17 | 21 |
| MgO | 0·39 | 27 | 6·6 | 4·2 |
| CaO | 1·4 | 8·2 | 11·0 | 1·8 |
| $P_2O_5$ | 0·09 | 39 | 0·18 | 33 |

the overall distribution of observations is more likely to approach a lognormal rather than a normal distribution, the geometric mean will usually be used in those few examples where dispersion is large and only a few determinations have been made. No hard and fast rule is used, however.

The use of the geometric mean in place of the arithmetic mean may be illustrated by taking the example of vanadium in granite discussed on page 46.

Recommended values will be given in bold print; values

* Small quantities of each rock powder may be obtained from the U.S. Geological Survey (Geochemical Section), Washington.

TABLE 3–2 (A)

DETERMINATIONS OF SEVERAL OF THE MINOR CONSTITUENT ELEMENTS IN GRANITE G-1

| Analyst | B[a] | Ba | Be | Co | Cr | Cs | Cu | Fe | Ga | La | Li |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | — | 3000 | n.d. | n.d. | 10 | — | <8 | — | 20 | 430 | 19 |
| 2 | n.d. | 1300 | 2 | 3 | 30 | — | 15 | — | 18 | 190 | — |
| 3 | — | 1300 | — | n.d. | 25 | 2·5[b] | 5 | 900[d] | 19 | 130 | 23 |
| 4 | — | 1300 | — | — | 20 | — | — | 800 | 15 | 60 | 25 |
| 5 | — | — | <15 | <2 | 8 | — | 6 | — | 18 | — | <25 |
| 6 | — | 1100 | — | — | 27 | — | tr. | 450 | 15 | — | — |
| 7 | — | — | — | 10 | — | — | 10 | — | — | — | — |
| 8 | — | — | — | 3 | — | — | 20 | — | — | — | — |

| Analyst | Mo[e] | Nd | Ni | Pb | Rb | Sc | Sr | V | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 6 | — | 5 | 25 | 590 | n.d. | 900 | 17 | 30 | — | 200 |
| 2 | 6 | — | n.d. | 22 | — | 2 | 120 | 26 | n.d. | — | 190 |
| 3 | — | 80 | — | 23 | 550[f] | 4 | 250 | 18 | 24 | — | 280 |
| 4 | 5 | — | n.d. | 50 | 250 | — | 280 | 20 | 10 | — | 180 |
| 5 | <4 | — | <2·5 | 37 | — | <3 | — | 8 | 20 | — | 130 |
| 6 | — | — | — | 28 | — | — | 450 | 20 | 270[g] | — | 200 |
| 7 | 14 | — | 60 | 15 | — | — | — | — | — | — | — |
| 8 | — | — | — | 14 | — | — | — | — | — | 55 | — |

*Analysts:* 1. MITCHELL; 2. MURATA; 3. GORFINKLE and AHRENS; 4. NOCKOLDS; 5. SHAW and WEBBER; 6. HEY; 7. LAKIN *et al.*; 8. BLOOM. [a] 1 ppm reported by H. P. EUGSTER. [b] F. C. CANNEY (1952). [c] L. PECK (U.S. Geol. Survey, Denver), E. H. OSLUND (Minnesota Geological Survey), W. SUNKEL (Div. Chem. Services, Pretoria) and J. H. SCOON (Dept. of Mineral. and Petrology, Cambridge University) report 900, 900, 400 and 800 ppm, respectively. [d] R. H. SERAPHIM (1951). [e] E. B. SANDELL (1953), Dept. of Chemistry, University of Minnesota, reports 6·6 ppm. [f] Mean of three separate determinations by three different analysts in Cabot Spectrographic Laboratory. [g] Total rare earths (Ce, Y, La, Nd, etc.). n.d. = not detected.

## TABLE 3-2 (B)

DETERMINATIONS OF SEVERAL OF THE MINOR CONSTITUENT ELEMENTS IN DIABASE W-1

| Analyst | B[a] | Ba | Be | Co | Cr | Cs | Cu | F | Ga | La | Li |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | — | 250 | n.d. | 35 | 120 | — | 130 | — | 15 | 32 | 9 |
| 2 | 10 | 390 | n.d. | 25 | 130 | — | 90 | — | 12 | n.d. | — |
| 3 | — | 270 | — | 30 | 110 | — | 44 | 200 | 13 | n.d. | 9 |
| 4 | — | 150 | — | 50 | 150 | — | — | — | 20 | — | 20 |
| 5 | — | — | <15 | 55 | 150 | — | 140 | — | 11 | — | <25 |
| 6 | — | 270 | — | — | 100 | — | 100 | — | 15 | — | — |
| 7 | — | — | — | 20 | — | — | 80 | — | — | — | — |
| 8 | — | — | — | 40 | — | — | 130 | — | — | — | — |

| Analyst | Mo[b] | Nd | Ni | Pb | Rb | Sc[d] | Sr | V | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | n.d. | — | 47 | n.d. | 15 | 15 | 420 | 220 | n.d. | — | 50 |
| 2 | n.d. | — | 80 | n.d. | — | 34 | 120 | 220 | — | — | 90 |
| 3 | — | n.d. | — | 7 | 64[c] | 51 | 250 | 340 | n.d. | — | 90 |
| 4 | — | — | 80 | — | 20 | 50 | 180 | 250 | — | — | 100 |
| 5 | <4 | — | 140 | 20[c] | — | 35 | — | 170 | 35[e] | — | 150 |
| 6 | — | — | 70 | 10 | — | — | 450 | 220 | — | — | 70 |
| 7 | 5 | — | 150 | 5 | — | — | — | — | — | — | — |
| 8 | — | — | 80 | 5 | — | — | — | — | — | 90 | — |

[a] 2·6 ppm reported by H. P. EUGSTER. [b] E. B. SANDELL (1953) reports 0·5 ppm. [c] Average of three, as in G-1. [d] 36 ppm reported by A. KVALHEIM. [e] Analyst No. 5 employed Y 4374 and this possible high value is probably due to interference from Mn 4374. Analyst No. 2 had also reported high yttrium in the diabase, but has since recognized Mn interference.

which are based on inadequate data and which indicate magnitudes only, are parenthesized.

*Barium*—Agreement between Nos. 2, 3, 4 and 6 is close in G-1 and their average of **1300 ppm** is recommended. In W-1 the recommended value is **270 ppm**, the average of Nos. 1, 2, 3, 4 and 6.

*Boron*—In W-1 the geometric mean (5 ppm) of the two spectrochemical determinations, 10 ppm and 2·6 ppm, may be regarded as a magnitude.

*Beryllium*—The value of (2 ppm) reported by No. 2 in G-1 may be taken as a magnitude.

*Cobalt*—The data on G-1 are not satisfactory for recommending an accurate value; the geometric mean of Nos. 2, 7 and 8 (4 ppm) should be a good magnitude. In W-1 the average of **36 ppm** for all determinations is recommended.

*Cesium*—Data inadequate partly because the concentration of cesium is exceptionally low in G-1 and hence not easily detectable. (See page 31 for further discussion of Cs in G-1.)

*Chromium*—Nos. 1, 2, 3, 4, 5 and 6 average at **20 ppm** in G-1 and this value will be used. Agreement is excellent in W-1 and the average of all determinations, **130 ppm**, is recommended.

*Copper*—The average of Nos. 2, 3, 5, 7 and 8 is **11 ppm** in G-1. Although this value is recommended, it may be subject to considerable revision because of rather poor agreement. Except for No. 3 agreement is better in W-1, probably because of its higher copper concentration; the average of Nos. 1, 2, 5, 6, 7 and 8, **110 ppm**, is recommended.

*Fluorine*—Several chemists and two spectrochemists have determined fluorine in G-1. Agreement is not particularly good even when restricted to the chemical determinations which range from 400 to 900 ppm. The average of all determinations, **740 ppm**, is recommended. The value of (200 ppm) reported by No. 3 in W-1 may be regarded as a general magnitude.

*Gallium*—The five spectrochemical determinations agree satisfactorily in both G-1 and W-1, and these in turn agree

well with the chemical determinations of No. 6. The average of all determinations, **17·5 ppm** for G-1 and **14·5 ppm** for W-1 is recommended.

*Lanthanum*—Agreement is poor in G-1. The geometric mean of **160 ppm** will be used; this value is close to the average of the two determinations (No. 2 and No. 8) which are in agreement.

*Lithium*—The recommended value for G-1 is **22 ppm**, the average of Nos. 1, 3 and 4. For W-1 the average of Nos. 1 and 3, **9 ppm** will be used. Repeated observations in the Cabot Spectrographic Laboratory, particularly by WELBY (1952), show that the lithium concentration in W-1 is considerably lower than in G-1; hence the use of Nos. 1 and 3 only.

*Molybdenum*—Nos. 1, 2, 4 and the determination of Sandell (see footnote entry [e]) agree well in G-1; their average of **6·6 ppm** is recommended. Information on W-1 is unsatisfactory: (0·5 ppm) will be considered as a magnitude; see SANDELL (1953) in this respect.

*Neodymium*—Data inadequate. The value (80 ppm) reported by No. 3 for G-1 may be regarded as a general magnitude.

*Nickel*—Available data for G-1 unsatisfactory. No. 1 gives a value of 5 ppm whereas that reported by No. 7 is 60 ppm. It is probable that the lower value is closer to the true concentration because analysts No. 2 and 4 would otherwise have indicated nickel; moreover, No. 5 reports <2·5 ppm. Agreement is moderate in W-1 for which the average **90 ppm** of Nos. 1, 2, 4, 5, 6, 7 and 8 is recommended.

*Lead*—All eight analysts determined lead in G-1 and their average of **27 ppm** is recommended. Agreement is much poorer at the lower concentration in W-1. No. 5 has stated (private communication) that his determination is probably unreliable because of manganese interference and will therefore be omitted. The average of Nos. 3, 6, 7 and 8 is **7 ppm** and is recommended.

*Rubidium*—The average of Nos. 1 and 3 in G-1, **570 ppm** is recommended. The value given by No. 3 is an average of three determinations made by three different analysts using different methods. Despite agreement between Nos. 1 and 4 the value of **64 ppm** will be recommended

for W-1. As in G-1 this is an average of three determinations. The general validity of the magnitude has been substantiated further by (1) subsequent investigations in the Cabot Spectrographic Laboratory using G-1 as a standard and sodium and potassium as variable internal standards, and (2) general investigations on igneous, metamorphic and sedimentary rocks using G-1 and W-1 as standards ; each investigator found that the magnitudes reported here for G-1 and W-1 provided the most satisfactory fit to their intensity measurements.

*Scandium*—The concentration of scandium in G-1 borders on the detection limit of most spectrochemical methods. The average of Nos. 2 and 3, (3 ppm), may be regarded as a reasonable magnitude. For W-1, **37 ppm** is the average of Nos. 1, 2, 3, 4, 5 and the value reported by KVALHEIM (see Table 3–2(B)), and is recommended.

*Strontium*—Agreement in G-1 is poor as values range from 120 to 900 ppm. Analyst No. 1 has reported occasional difficulty (private communication) with strontium determinations and this value will be omitted. The average of Nos. 2, 3, 4 and 6 is **280 ppm** and is recommended. (The geometric mean for all determinations is 350 ppm and the arithmetic mean, 400 ppm.) Agreement is a little better in W-1 and the average, **290 ppm**, of Nos. 1, 2, 3, 4 and 6 is recommended.

*Vanadium*—Agreement is reasonable in G-1 and the average of **18 ppm** for Nos. 1, 2, 3, 4, 5 and 6 is recommended. Values for W-1 are in very satisfactory agreement and the average of **240 ppm** for Nos. 1, 2, 3, 4, 5 and 6 is recommended.

*Yttrium*—Nos. 1, 3, 4 and 5 average at **21 ppm** in G-1 and this value is recommended. No value will be recommended for W-1. (See comments in Table 3–2(B).)

*Zinc*—A single determination only, No. 8, is available for both G-1 and W-1 ; the respective values (55 ppm) and (90 ppm) may be regarded as magnitudes.

*Zirconium*—Agreement is very satisfactory in G-1. The average of Nos. 1, 2, 3, 4, 5 and 6 is **200 ppm** and is recommended. Agreement in W-1 is not as satisfactory ; the average **90 ppm** for Nos. 1, 2, 3, 4, 5 and 6 is recommended.

All recommended values, common elements and rare elements are given in Table 8–3.

TABLE 8–3

RECOMMENDED VALUES OF COMMON AND RARE CONSTITUENTS IN G-1 AND W-1 ; GIVEN AS ELEMENT AND AS OXIDE

| | G-1 | W-1 | | G-1 | W-1 | |
|---|---|---|---|---|---|---|
| Na | 2·4 | 1·5 | $Na_2O$ | 3·25 | 2·00 | % |
| K | 4·5 | 0·58 | $K_2O$ | 5·4 | 0·68 | % |
| Si | 33·7 | 24·4 | $SiO_2$ | 72·4 | 52·3 | % |
| Ti | 0·15 | 0·67 | $TiO_2$ | 0·25 | 1·1 | % |
| Al | 7·9 | 8·3 | $Al_2O_3$ | 14·4 | 15·1 | % |
| Fe | 1·42 | 7·9 | $Fe_2O_3$ | 0·98 | 1·5 | % |
| | | | FeO | 0·99 | 8·7 | % |
| Mn | 0·021 | 0·18 | MnO | 0·027 | 0·17 | % |
| Mg | 0·24 | 4·0 | MgO | 0·39 | 6·6 | % |
| Ca | 1·0 | 7·9 | CaO | 1·4 | 11·0 | % |
| P | 0·089 | 0·57 | $P_2O_5$ | 0·09 | 0·18 | % |
| Ba | 1300 | 270 | BaO | 1500 | 300 | ppm |
| B | —— | (5) | $B_2O_3$ | —— | (15) | ppm |
| Be | (2) | —— | BeO | (6) | —— | ppm |
| Co | (4) | 36 | CoO | (5) | 46 | ppm |
| Cr | 20 | 130 | $Cr_2O_3$ | 29 | 190 | ppm |
| Cs | (2·5) | —— | $Cs_2O$ | (3) | —— | ppm |
| Cu | 11 | 110 | CuO | 14 | 140 | ppm |
| F | 740 | (20) | | | | ppm |
| Ga | 17·5 | 14·5 | $Ga_2O_3$ | 23·5 | 19·5 | ppm |
| La | 160 | (32) | $La_2O_3$ | 190 | (37) | ppm |
| Li | 22 | 9 | $Li_2O$ | 47 | 19 | ppm |
| Mo | 5·5 | (0·5) | $MoO_2$ | 8·0 | (0·6) | ppm |
| Nd | (80) | —— | $Nd_2O_3$ | (93) | —— | ppm |
| Ni | (5) | 90 | NiO | (6·5) | 115 | ppm |
| Pb | 27 | 7 | PbO | 29 | 7·5 | ppm |
| Rb | 570 | 64 | $Rb_2O$ | 620 | 70 | ppm |
| Sc | (3) | 37 | $Sc_2O_3$ | (4·5) | 57 | ppm |
| Sr | 280 | 290 | SrO | 330 | 340 | ppm |
| V | 18 | 240 | $V_2O_3$ | 26 | 350 | ppm |
| Y | 21 | —— | $Y_2O_3$ | 27 | —— | ppm |
| Zn | (55) | (90) | ZnO | (67) | (110) | ppm |
| Zr | 200 | 90 | $ZrO_2$ | 244 | 122 | ppm |

## Sec. 3–3. Some comments on the use of G-1, W-1 and other silicate standards

As granite G-1 and diabase W-1 represent two rather distinct compositional types, they and their mixtures may be

used as standards for the analysis of a comparatively wide variety of materials, namely: the common igneous rocks granite, syenite, diorite, basalt, diabase and gabbro; metamorphic rocks and silicate meteorites of similar composition; and also some sediments. A few typical working curves prepared from G-1 and W-1 and used for the determination of some elements in sediments appear in Fig. 7.1.

Some extrapolation of the working curves prepared from G-1 and W-1 may be necessary but if not excessive, is not likely to introduce serious error. Cesium is an extreme example. Its concentration in G-1 is quite abnormally low, as shown in Fig. 3.1, a frequency distribution plot of cesium in New England granite (AHRENS, 1954), and even if the use of a single-point working curve were attempted, as described below, extrapolation would be far too great. When such a problem arises a primary synthetic standard containing, say, 1000 ppm of cesium (or other element) should first be prepared by mixing a suitable compound (the Cs mineral, pollucite, for example) with one of the synthetic silicate bases discussed on page 36. Final standards are prepared by mixing different proportions of the primary standard with G-1, W-1 or any other silicate rock which happens to be low in cesium (or other element). Equivalence in composition of the matrix material of standards and unknowns is thus insured. A correction for the presence of cesium (or other element) in the rock used as matrix material is made by means of an addition plot (page 38). Molybdenum contrasts strongly with cesium: its concentration in G-1 is far higher than in a very high proportion of granites (see SANDELL and KURODA, 1952, and frequency distribution plots of AHRENS, 1954)—and many other igneous rocks for that matter—and as a result, G-1 is a particularly valuable standard for molybdenum.

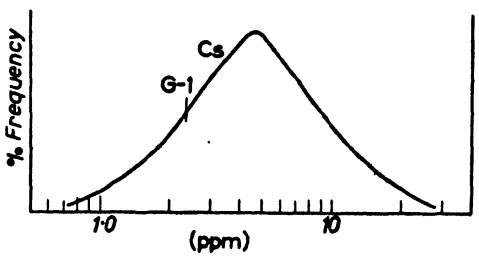



Fig. 3.1. Frequency distribution curve for Cs in New England granite. Note location of G-1.

If an investigation happens to be restricted either to

granite, or to diabase, basalt or gabbro, single-point working curves (AHRENS, 1950), may be prepared from either G-1 or W-1 and used for the analysis of the unknowns. FAIRBAIRN, AHRENS and GORFINKLE (1952), for example, used W-1 in this way to determine potassium and rubidium in many specimens of Columbia river basalt. The single plotted point must be accurately located and the standard should therefore be arced at least in quadruplicate. The analysis line must be

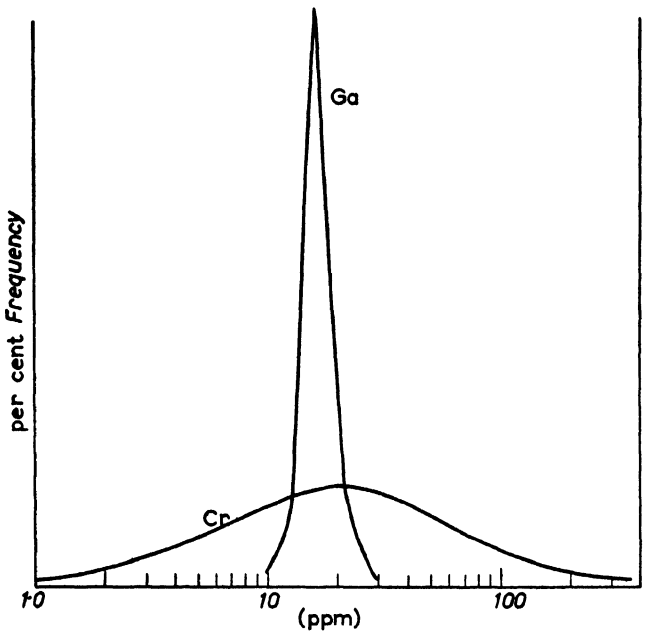



Fig. 3.2. Frequency distribution plots for Ga (extremely small dispersion) and Cr (large dispersion) in Canadian granite.

free from self-absorption and if background is present an accurate correction must be made. Whether or not the use of such a single-point working curve is permissible depends mainly on the geochemical dispersion of the element in the particular rock type. A single-point working curve may be used very satisfactorily to determine gallium, for example, in granite because dispersion is extremely small, but not chromium in the same rock type because dispersion is extremely large. Fig. 3.2 illustrates this point. Further information of this type may be obtained from AHRENS (1954).

The use of G-1 and W-1 is not restricted to rocks having the general chemical composition of either granite, diabase, basalt and gabbro, or intermediate types. The determination of the alkali metals in dunite, serpentine, other ultramafics, chondrites and quartz are examples (Chap. 5). The concentrations of the alkali metals in quartz and these silicates is much less than in either G-1 or W-1 and as a result standards may be prepared by mixing either of the standard rocks with one or other of these materials—preferably a specimen that reconnaissance has shown to have a comparatively low concentration of alkali metals. When preparing such standards, allowance must naturally be made for the amount of element present in the dunite or similar base material; the addition method, as described below, may be used for this purpose.

It has become rather common practice of the author and his co-workers to use the addition method when direct use cannot be made of standards as in the above examples. In so doing the use of purely synthetic standards may usually be avoided. This general procedure is perhaps not as widely known and in as common use as it ought to be. This applies particularly to the analysis of the naturally-occurring silicates where the addition method may be used effectively for many purposes. The general principles of the method have been discussed by OERTEL (1944), HARVEY (1950) and AHRENS (1950). Many examples of its use are given in this book; two will be given here in some detail: (1) the determination of calcium in lepidolite mica, and (2) the determination of rubidium in chrondritic meteorites (Sec. 5–6).

HOLYK (1952) has determined calcium as a minor constituent in a suite of lepidolite micas. Standards were prepared by mixing diabase W-1 (7·9% Ca) with a lepidolite from San Diego, California, which reconnaisance analysis had shown to contain an abnormally low concentration of calcium. A preliminary standard containing 1% Ca was first prepared and this was mixed with further proportions of San Diego lepidolite to give a series of addition standards containing 630, 313, 160, 78, 39 and 19 ppm of added calcium. Fig. 3.3(a) shows an addition plot of ppm calcium added vs. the intensity of Ca 3968. The amount (32 ppm) of calcium in the San Diego lepidolite is given by the intersection of the extra-

polated curve and the abscissal scale. Fig. 3.3(b) shows a working curve prepared by relating the intensity of Ca 3968 to the amount (32 ppm + amount added) of calcium in each standard. The arcing procedure (Chap. 7) happens to be particularly satisfactory and consequently the plotted points in Figs. 3.3(a) and 3.3(b) are closely spaced about the addition and normal working curves.

PINSON, AHRENS and FRANCK (1953) and AHRENS, PINSON and KEARNS (1952) have investigated the abundances of Li, Sr, Ba, Sc and Zr, and Rb and K, respectively, in chrondites. Addition plots using G-1 and W-1 were made in each case; see PINSON (1951) for examples. We will consider the example of rubidium (Sec. 5–6). Varying proportions of G-1 (570 ppm Rb) and the Homestead chondrite were mixed to give a series of addition standards. Fig. 3.4(a) relates the intensity of Rb 7800 to the amount of added rubidium. The intercept in Fig. 3.4(a) shows the Homestead chondrite to contain 14 ppm of $Rb_2O$. Fig. 3.4(b) shows a working curve prepared as in the example of calcium in lepidolite. In this example, however, the concentrations of the unknowns vary to an extremely small extent—a characteristic of chondrites—and hover around 10 ppm. This curve could be used for the determination of rubidium in various rocks as well, varying in composition all the way from mica- and feldspar-bearing peridotites*, to various varieties of basalt, diabase and gabbro, to granite and syenite.

The rock or mineral used as a base may sometimes contain such low concentrations of the analysis element(s) that its most sensitive line is not detectable. An addition plot is unnecessary and a working curve is prepared on the assumption that the base material is free from analysis element(s). This assumption is, of course, not strictly valid and although residual impurity by itself may not emit sufficient line intensity to exceed photographic threshold, it may make a noticeable contribution in the low concentration standards and produce a toe to the working curve—compare the effect of invisible background (Sec. 2–4).

Considerable care has been taken to prepare homogeneous powders of G-1 and W-1 (FAIRBAIRN *et al.*, 1951, pp. 3–4). G-1

* Rubidium is never detectable in ultramafics free from mica and feldspar because its concentration is invariably $<0{\cdot}1$ ppm.

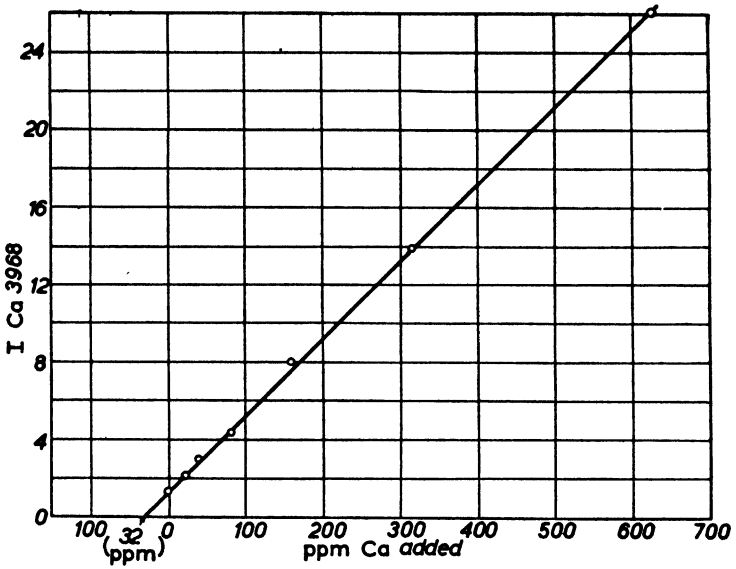



Fig. 8.3(*a*). Additional plot for Ca in lepidolite. San Diego lepidolite as base.

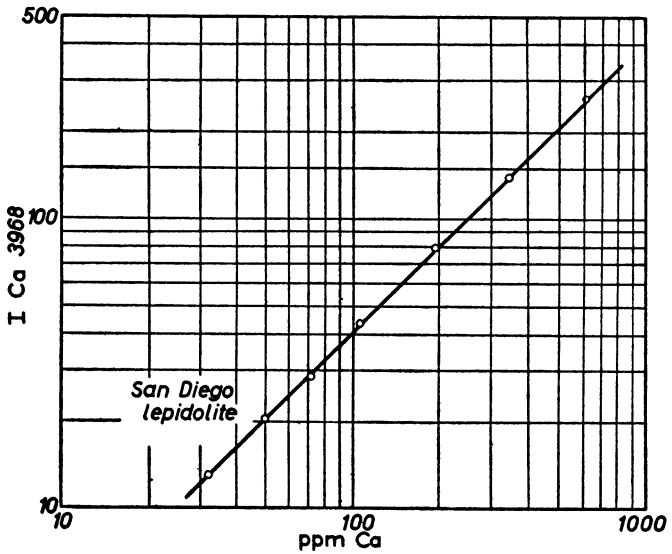



Fig. 8.3(*b*). Working curve for Ca in lepidolite. Each point average of three determinations.

however, is a comparatively coarse powder and if only a few milligrams or so are used for analysis, as is required for cathode layer excitation for example, discrepant results may be found. It may therefore be advisable to first grind larger quantities of G-1 in an agate mortar so as to reduce particle size.

Silicate standards other than G-1 and W-1 are available for investigations which are restricted to the common elements. U.S. Bureau of Standards samples Nos. 70 and 99, potash and soda feldspar respectively, may be used in conjunction with G-1 and W-1 for some purposes (see Sec. 5–4 for example). The two standard clays (Nos. 97 and 98—flint clay and plastic clay) are also useful. In general, the analyst will find it of value to assemble a large variety of accurately analysed silicate minerals, rocks and meteorites.

Occasions arise when the analyst may wish to use synthetic standards, either by themselves or mixed with W-1 and G-1. In some problems it is virtually impossible to use the available naturally-occurring standards and in any case a whole lot of preliminary reconnaissance work must invariably be performed with the aid of synthetic standards.

It is not the purpose here to go into the general problem of preparing synthetic standards and the reader may refer to several of the general texts for information. A few typical examples of silicate base materials will, however, be given.

The principal ingredients of most synthetic silicates are alumina, silica and a compound of an alkali metal. An example of a composition of a simple base is, 15% $Na_2CO_3$, 30% $Al_2O_3$ and 55% $SiO_2$. Varying amounts of CaO, MgO and $Fe_2O_3$ are sometimes added, as for example in the base material used by CANNEY (1952) which had the composition 60% $SiO_2$, 15% $Al_2O_3$, 5% $Fe_2O_3$, 10% $Na_2CO_3$, 5% CaO and 5% MgO. A slightly more complex mixture has been used by MITCHELL (1948, p. 81) for the analysis of soil. It has the composition: 68% $SiO_2$, 20% $Al_2O_3$, 5% $Fe_2O_3$, 2% CaO, 2% MgO, 3·5% $Na_2CO_3$, 3·5% $K_2SO_4$ and 1% $TiO_2$. SHAW and WEBBER (1952) have used two synthetic bases; one composed of 64% $SiO_2$, 24% $Al_2O_3$, 8% nepheline syenite, 5% pyroxene and 5% KCl, and the other 77% $SiO_2$, 5% pyroxene and 5% KCl. Innumerable other base materials have been used for the analysis of silicates. STROCK (1936) lists several and the

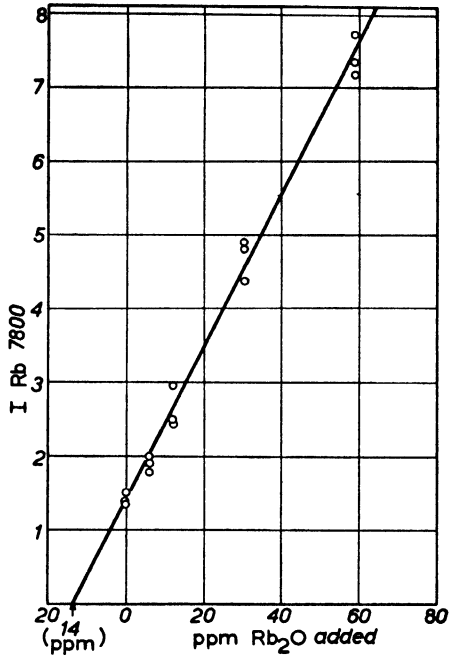



Fig. 3.4(*a*). Addition plot for Rb in chondrites.

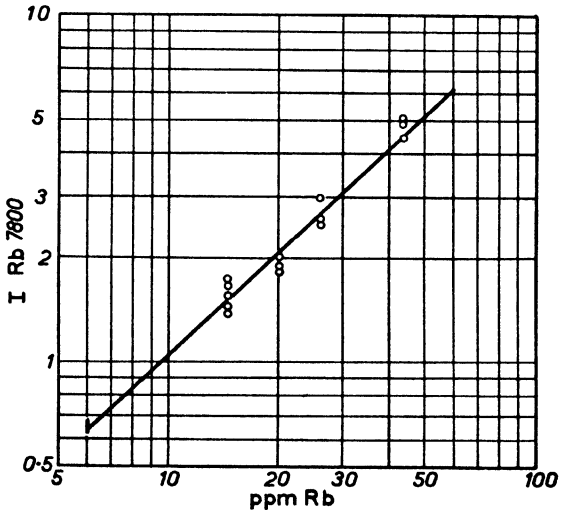



Fig. 3.4(*b*). Working curve for determination of Rb in chondrites. The amount of extrapolation which was required for the investigation is indicated.

reader may refer to MITCHELL (1948) and AHRENS (1950) for further general information in this respect. MITCHELL (1948, p. 228) gives a useful description of methods for preparing in pure form each of the ingredients likely to be used for synthetic standards.

Synthetic silicate mixtures should be sintered for several hours in a muffle furnace at temperatures from 900 to 1300° C. The burning quality of the sintered base is far superior to the raw mixture; not only is the reproducibility of the discharge much improved, but systematic error is likely to be smaller.

If the analyst prefers in any case to use synthetic standards in place of G-1 and W-1, he might find it helpful to analyse these two rocks together with a batch of unknowns so as to determine to what extent his determination may deviate from those recommended in this chapter.

CHAPTER 4

# LOGNORMAL DISTRIBUTION OF SPECTROCHEMICAL ERROR

AN analyst usually attempts to provide a reliable statement about the accuracy and precision (reproducibility) of a new method. Although spectrochemists are sometimes not able to evaluate the magnitude of systematic error and hence may have difficulty in expressing accuracy, they are always able to carry out many replicate determinations from which it should be possible to calculate precision.

Precision is usually expressed in terms of the standard deviation ($s$) and the relative deviation ($C$), both of which are calculated from the familiar relationship,

$$s = \sqrt{\frac{\Sigma d^2}{n-1}} \quad \ldots . \quad (4\text{–}1)$$

which assumes a normal (Gaussian) distribution of the observations. $n$ is number of observations and $d$ the deviation of each observation from the arithmetic mean ($\bar{x}$) or average of all observations. The relative deviation, $C$, (the standard deviation expressed as a per cent) $= \frac{s}{\bar{x}} \times 100$. Relative deviation is synonymous with coefficient of variation, per cent spread, root mean square error; occasionally the term, standard deviation, is used for both $s$ and $C$. It will be recalled that calculations made on this basis predict that two-thirds of all observations should fall within one $s$ or one $C$ of the true value and that 95% of all observations within $2s$ or $2C$ of this value.

Statisticians and some analytical chemists have gone to great lengths to explain in detail the mathematics of statistics; yet extraordinarily enough, they rarely question the nature of the distribution and the tacit assumption is all too often

made that distribution is normal*—or at least that calculations can be made on the basis of this assumption. As it happens, the general nature of a distribution is of little consequence provided dispersion is small. As dispersion increases, however, the nature of the distribution becomes increasingly important, and unless some cognizance is taken of this fact, wholly false predictions about reproducibility may be made. In the discussion which follows, extreme examples are purposely chosen to emphasize this point.

On rare occasions we find, for example, a statement in the literature which refers to a *very* approximate method for which $C = \pm \sim 200\%$. From this we conclude that about two-thirds of all determinations can be made to within 200% of the correct amount. Moreover, it is implied that it is equally likely to have a result 200% too high as one 200% too low. If the correct amount is, say, 1%, we follow quite clearly that a +200% error means that 3% of the constituent has been reported but it requires an impossible stretch of the imagination to conceive what the equally likely value of −200% of 1% is supposed to be. What the statement might intend to convey is that about two-thirds of all determinations can be made to within $\times$ 3 (+ 200%) and $\times \frac{1}{3}$ (− 67%) of the correct amount. It is quite common to find the reproducibility of a semiquantitative method given as $C =$ about 50%. Normal law predicts that two-thirds of all observations fall within $\pm$ 50% of the correct amount and that 95% of all observations fall within $2C$ ($\pm$ 100%) of this amount; the remaining 5%, equally divided between plus and minus, are predicted to have deviations of >100%: thus $2\frac{1}{2}$% of all determinations are negative and unreal. However, it is not merely the fact that completely unreal values are sometimes predicted on the basis of assumed normal distribution but in addition, the whole error probability distribution may be severely distorted. In the above example we might presume that the analyst intended to convey that most determinations could be made to within + 50% ($\times$ 3/2) and − 30% ($\times$ 2/3) of the true amount. Indeed, error distribution is occasionally given this way (HEGEMANN and ZOELLNER, 1952). Conversa-

* SCHLECHT (1949) has discussed and emphasized the misuse of statistics in analytical chemistry; some of his bibliographical quotations are most appropriate.

tions with many spectrochemists leave little doubt that many of them intuitively *think* in terms of such a distribution based on a geometric rather than a linear scale; in other words, a *lognormal* type distribution.*

GADDUM (1945) draws attention to the fact that lognormal distributions are much more common than is usually thought. He gives many examples and the author (AHRENS, 1954) has added another one; namely, the lognormal distribution of elements in specific rock types. We have, however, no rigorous statistical *proof* that the error distribution in spectrochemical analysis is lognormal because no large-scale statistical investigations have been made on *approximate* procedures. Nevertheless, the facts that (1) experienced spectrochemists are aware that error distribution in approximate procedures appears to follow the double or half, triple or one-third and so on geometric type distribution, and that (2) completely false and unreal predictions are sometimes made on the basis of assumed normal distribution leaves little doubt that distribution is either lognormal or at least closely approaches it. Some further support is given from the fairly complete data used for Fig. 4.2 below.

We may now proceed to examine three sets of observations, each having totally different dispersion; namely, $C = 3{\cdot}5\%$, 21% and 170% respectively. The principal object is to observe how skewness and hence deviation from *apparently* normal behaviour becomes progressively greater with increase in the magnitude of the dispersion. The data which we are to consider are given in Table 4–1. The first column gives a series of replicate determinations of the ratio $\frac{\text{I Si } 2528}{\text{I Be } 2494}$ (AHRENS, 1950, Chap. 23), the second, replicate determinations of the ratio $\frac{\text{I Ca (I) } 4227}{\text{I Ca (II) } 3934}$ in an erratic discharge (AHRENS, 1950, Chap. 7) and the third, the amount of vanadium in several specimens of North American granite. This example is chosen because no adequate data are available for extremely erratic spectrochemical procedures. However, as the distribution of vanadium in granite is lognormal, these data may serve for illustration.

* The distribution of $x$ is lognormal when the distribution of $\log x$ is normal (GADDUM, 1945). The term *reciprocal* is in some respects more descriptive than *lognormal* for indicating the nature of the distribution.

## TABLE 4–1

THREE SETS OF OBSERVATIONS, EACH HAVING A TOTALLY DIFFERENT AMOUNT OF DISPERSION

| Observation No. | $\frac{\text{Si 2528}}{\text{Be 2494}} \times 10$ | $\log \frac{\text{Si 2528}}{\text{Be 2494}}$ | $\frac{\text{Ca 4227}}{\text{Ca 3934}}$ | $\log \frac{\text{Ca 4227}}{\text{Ca 3934}}$ | Sample No. | V (ppm) | log V |
|---|---|---|---|---|---|---|---|
| 1 | 8·1 | 0·91 | 3·0 | 0·48 | G– 1 | 21 | 1·32 |
| 2 | 8·9 | 0·95 | 4·0 | 0·60 | KB– 1 | 75 | 1·87 |
| 3 | 7·8 | 0·89 | 3·4 | 0·53 | 2 | 48 | 1·68 |
| 4 | 7·9 | 0·90 | 3·9 | 0·59 | 3 | 201 | 2·30 |
| 5 | 9·0 | 0·95 | 3·4 | 0·53 | 4 | 50 | 1·70 |
| 6 | 8·2 | 0·92 | 4·3 | 0·63 | 5 | 7·5 | 0·87 |
| 7 | 8·7 | 0·94 | 4·1 | 0·49 | 6 | 30 | 1·47 |
| 8 | 8·6 | 0·93 | 4·9 | 0·69 | 7 | 33 | 1·52 |
| 9 | 8·3 | 0·92 | 4·2 | 0·62 | 8 | 27 | 1·43 |
| 10 | 7·6 | 0·88 | 5·0 | 0·70 | 9 | 34 | 1·53 |
| 11 | 8·7 | 0·94 | 5·3 | 0·72 | 10 | 42 | 1·62 |
| 12 | 8·5 | 0·93 | 3·1 | 0·49 | 11 | 10 | 1·00 |
| 13 | 8·9 | 0·95 | 3·9 | 0·59 | 12 | 52 | 1·72 |
| 14 | 8·4 | 0·92 | 3·0 | 0·47 | 13 | 51 | 1·71 |
| 15 | 8·5 | 0·93 | 3·8 | 0·58 | 14 | 82 | 1·91 |
| 16 | 8·7 | 0·94 | 4·3 | 0·63 | 15 | 630 | 2·80 |
| 17 | 9·0 | 0·95 | 2·8 | 0·45 | 16 | 144 | 2·15 |
| 18 | 8·5 | 0·93 | 4·1 | 0·61 | 17 | 94 | 1·98 |
| 19 | 7·9 | 0·90 | 5·3 | 0·72 | 18 | 94 | 1·98 |
| 20 | 7·4 | 0·87 | 5·2 | 0·71 | 19 | 29 | 1·45 |
| 21 | 7·1 | 0·85 | 3·9 | 0·59 | 48– 63 | 8 | 0·92 |
| 22 | 8·0 | 0·90 | 4·2 | 0·62 | 48–115 | 11 | 1·04 |
| 23 | 8·8 | 0·94 | 4·0 | 0·60 | 48–158 | 5·5 | 0·74 |
| 24 | 9·0 | 0·95 | 3·4 | 0·53 | 48–188 | 23 | 1·36 |
| 25 | 8·8 | 0·94 | 4·3 | 0·63 | 48–485 | 19 | 1·28 |
| 26 | 9·0 | 0·95 | 6·1 | 0·81 | 48–489 | 7 | 0·84 |
| 27 | 8·3 | 0·92 | 6·0 | 0·80 | 48–490 | 6 | 0·75 |
| 28 | 8·3 | 0·92 | 3·3 | 0·52 | | | |
| 29 | 8·3 | 0·92 | 4·0 | 0·60 | | | |
| 30 | 8·8 | 0·94 | 3·5 | 0·54 | | | |
| 31 | 8·4 | 0·92 | 4·2 | 0·62 | | | |
| 32 | 9·2 | 0·97 | 4·6 | 0·66 | | | |
| 33 | 8·4 | 0·92 | | | | | |
| 34 | 8·0 | 0·90 | | | | | |
| 35 | 8·3 | 0·92 | | | | | |
| 36 | 8·2 | 0·91 | | | | | |
| 37 | 7·8 | 0·89 | | | | | |
| 38 | 8·7 | 0·94 | | | | | |
| Av. (arithmetic mean) | 8·4 | 0·925 | ·40 | 0·60 | | 67 | 1·50 |
| C | 8·5% | | 21% | | | 170% | |

Figs. 4.1, 4.2 and 4.3 have been prepared from the data in Table 4–1. Each shows two frequency distribution plots ; one is of the usual type, but in the other the logarithm (base 10) of each observation has been used. Logarithms may be avoided by using semilog paper in which case, however, some power factor, for example $\times$ 1·6, must be chosen to give the interval. Intervals for all plots in Figs. 4.1, 4.2 and 4.3 vary and are so chosen that observations occur in at least five, but not in an excessively large number of intervals.

Both plots in Fig. 4.1 and the log plots in Figs. 4.2 and 4.3 are symmetrical and appear, or at least quite closely

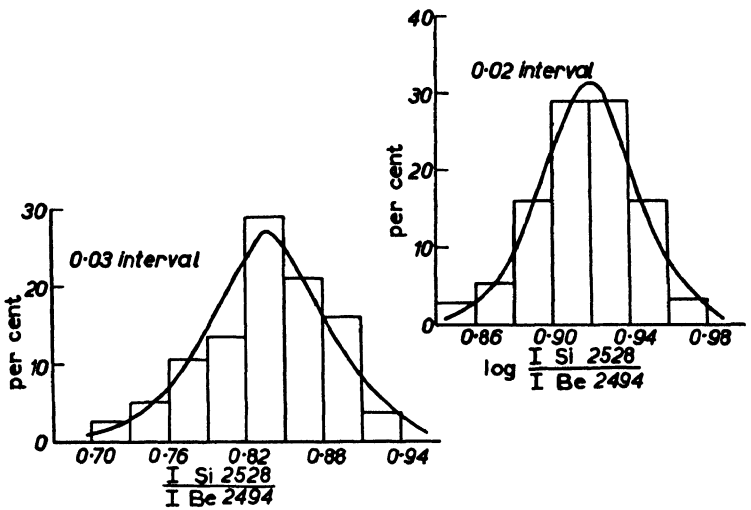



Fig. 4.1. Frequency distribution plots of $\frac{\text{I Si 2528}}{\text{I Be 2494}}$ and the logarithm of this ratio.

approach, being normal. The linear plot in Fig. 4.2 shows some skewness whereas that in Fig. 4.3 is so extreme that completely false predictions would be made if a normal distribution were to be assumed. One may conclude from the above three examples, a discussion by COCHRAN (1938) and an inspection of a large number of distribution curves (AHRENS, 1954), that in lognormal distributions, it is safe for practical purposes to assume a normal distribution provided $C < \sim 15\%$ ; above $C = \sim 15\%$, calculations and predictions should be based on assumed lognormal distribution.

As normal and lognormal curves are identical in shape the expression for a normal curve (see any book on statistics) applies also to the lognormal curve; hence for a lognormal distribution use may be made of the relationship,

$$\lambda = \sqrt{\frac{\Sigma d_l^2}{n-1}} \quad \ldots . \quad (4\text{–}2)$$

where, however, $\lambda$ (GADDUM, 1945) replaces $s$, and $d_l$ refers to the deviation of the log of an observation from the log of the true value. Values of $\lambda$ for the three distributions in Figs. 4.1, 4.2 and 4.3 calculate at 0·015, 0·091 and 1·50, respectively.

If distribution is normal, the arithmetic mean ($\bar{x}$) of a series of observations gives a close approximation to the correct value; indeed, the arithmetic mean is often used also in an attempt to achieve the same purpose even if distribution is not normal as in spectrochemical analysis. Figs. 4.1, 4.2 and 4.3 show that when dispersion is small, mode and arithmetic mean (Table 4–1) coincide, but that when dispersion is large the arithmetic mean becomes positively displaced with respect to the mode. The mode (the most frequent observation) should presumably be the closest approach to the true value which, in a lognormal distribution, is given by the

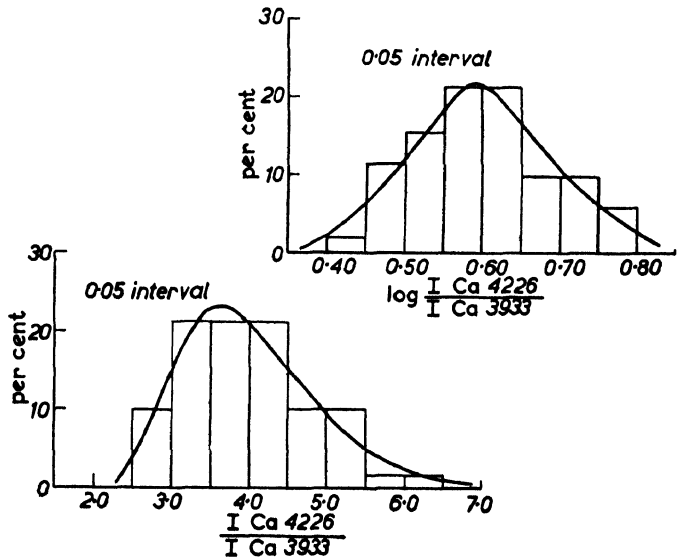



Fig. 4.2. Frequency distribution plots of I Ca 4226/I Ca 3933 and the logarithm of this ratio.

geometric mean, the $n$th root of the product of $n$ observations. In the example of vanadium, the arithmetic mean is 67 ppm whereas the geometric mean (82 ppm) is barely half this value. For a discussion of the relationship between arithmetic mean and geometric mean in lognormal distributions, see AHRENS (1954).

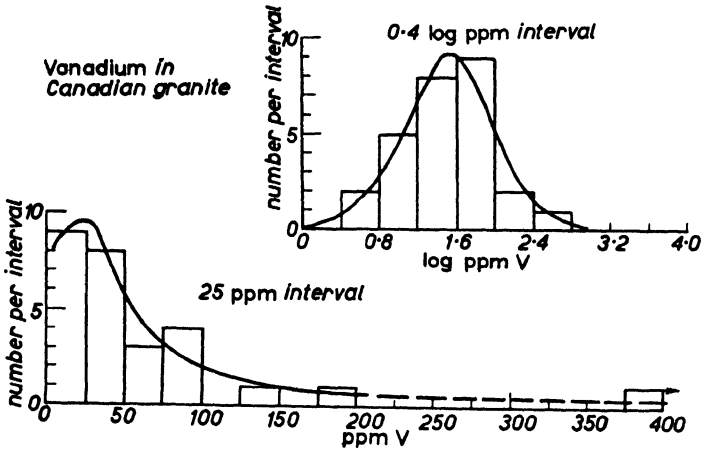



Fig. 4.8. Frequency distribution plots of $V$ and log $V$ in Canadian granite.

All statistical data on the three sets of observations discussed in this chapter are assembled in Table 4–2.

TABLE 4–2

STATISTICAL DATA ON INTENSITY RATIOS AND VANADIUM ABUNDANCE

| | $\frac{Si}{Be}$ | $\log \frac{Si}{Be}$ | $\frac{Ca}{Ca}$ | $\log \frac{Ca}{Ca}$ | V | log V |
|---|---|---|---|---|---|---|
| am (x) | 8·4 | 0·925 | 4·0 | 0·60 | 67 | 1·50 |
| gm | 8·4 | — | 4·0 | — | 82 | — |
| s | 0·29 | — | 0·8 | — | 60 | — |
| 2 s | 0·58 | — | 1·6 | — | 120 | — |
| C | 3·5% | — | 21% | — | 90% | — |
| 2 C | 7·0% | — | 42% | — | 180% | — |
| $\lambda$ | — | 0·015 | — | 0·091 | — | 0·50 |
| 2 $\lambda$ | — | 0·030 | — | 0·18 | — | 1·00 |
| $\lambda'$ | 1·085 | — | 1·24 | — | 3·2 | — |
| $\lambda''$ | 1·070 | — | 1·52 | — | 10·0 | — |

The example of vanadium in granite will be used to illustrate some calculations based on a lognormal distribution.

The arithmetic mean ($\bar{x}$) of the log vanadium values in Table 4–1 is 1·50; the antilog of this value, 32 ppm, is the geometric mean of the vanadium determinations. The deviation, $d$, of each observation from 1·50 is calculated, squared and summated, whence substitution in Eq. 4–2 gives $\lambda = 0{\cdot}50$. Hence, the limits within which two-thirds of all observations should fall are; $1{\cdot}50 + 0{\cdot}50 = 2{\cdot}00$, and $1{\cdot}50 - 0{\cdot}50 = 1{\cdot}00$, respectively. From the antilogs we find $32^* \times 3{\cdot}2^* = 100$ ppm and $32 \times \frac{1}{3.2} = 10$ ppm, as the limits. Ninety-five per cent of all observations should fall within $1{\cdot}50 + 2\lambda$ and $1{\cdot}50 - 2\lambda$, namely (antilogs) $32 \times 10 = 320$ ppm and $32 \times \frac{1}{10} = 3{\cdot}2$ ppm, respectively.

Although logarithms and hence $\lambda$ must in any case be used in lognormal distributions, it may be convenient to use the antilog of $\lambda$ as well, as has been done above. The antilog of $\lambda$ and $2\lambda$ will be designated as $\lambda'$ and $\lambda''$, and instead of giving the reciprocal as the lower limit this could for convenience be taken as understood, and omitted. Thus given that $\lambda'$ and $\lambda''$, are 3·2 and 10, respectively, we understand that two-thirds of all observations should fall within $\frac{1}{3{\cdot}2}$ and $\times$ 3·2 of the correct amount (the geometric mean) and that 95% of all observations should fall within $\frac{1}{10}$ and $\times$ 10 of the correct amount.

The principal conclusions which may be drawn from the discussions in this chapter are summarized as follows.

Spectrochemical error distribution is of the lognormal type, but provided dispersion is small ($C < \sim 15\%$) a normal distribution may be safely assumed. A lognormal distribution should be assumed at greater dispersions; in which case, the geometric mean of a series of replicate determinations replaces the arithmetic mean for the calculation of the "correct" line intensity (or intensity ratio): the ability of a method to reproduce this value is expressed in terms of $\lambda$ and $2\lambda$; $\lambda'$ and $\lambda''$ may be used as well.

* The fact that the geometric mean and the antilog of $\lambda$ each have integers 3 and 2 is purely fortuitous.

CHAPTER 5

# THE ALKALI METALS

## Sec. 5–1. Introduction

THE common alkali metals sodium and potassium are usually determined separately in a chemical analysis of silicates, usually by means of the Lawrence-Smith fusion procedure. Flame-photometric procedures have fairly recently come into use and will undoubtedly be used to an increasing extent because of their ability to determine the alkali metals accurately over a fairly wide concentration range. Spectrochemical methods offer advantages of speed, a very high sensitivity and the ability to determine all alkali metals in one general operation over a very wide concentration range with an accuracy that is satisfactory for many purposes.

The accuracy of a spectrochemical method is comparable with that of the Lawrence-Smith fusion procedure at concentrations as high as 4–5%, and below this becomes superior: at concentrations of the magnitude of 0·1% it is far superior; moreover, whereas the fusion procedure cannot be used at concentrations much less than this magnitude, spectrochemical methods may be used down to 1–10 ppm and sometimes even less. For potassium, this is of particular geophysical significance (Sec. 5–5).

Chemical and flame-photometric procedures are superior at concentrations $> \sim 5\%$ and should be used if utmost accuracy is required.

## Sec. 5–2. Distillation of the alkali metals

Sodium and potassium are common elements (2·8 and 2·6% by weight, respectively, of the earth's surface igneous rocks) and with the exception of a few ultramafics (dunite, serpentine and pyroxenite) nearly all silicate rocks and meteorites contain a significant (>0·5–1·0%) concentration of the alkali metals. At such concentrations, they exert a powerful influence on the arc discharge. They distil readily

and because their first ionization potentials (~4–5 volts) are lower than those of any other elements they lower arc temperature during the period of their distillation and in so doing " suppress " the distillation of many other elements. Not only is the time required to completely distil the alkali metals important for their determination but also for the determination of the so-called volatile elements (Chap 6). Times of complete alkali metal distillation vary widely and it will be shown that the total alkali metal concentration is a principal factor. Before doing so, however, two methods will be described for determining the " end point " of the alkali metal phase of distillation.

In the first, use is made of the fact that the colour and appearance of the arc discharge varies with change in composition of the arc gas. The flame-like appearance of the arc, usually yellow because of the ubiquity of sodium, thins as the alkali metal phase of volatilization nears completion. This " intermediate " phase may persist for some seconds, after which the arc usually alters its appearance completely. The time at which the alkali metal phase of distillation ceases is not always easily determined and some experience may be required. In any case, an error of a few seconds in determining the " end point " is usually only of little consequence. When in doubt the analyst may overexpose a little except for Na (Sec. 5–5), Li (Sec. 5–4), Rb (Sec. 5–11) and Tl (Sec. 6–4) where care must be exercised not to continue the exposure past the main phase of alkali metal distillation. Calcium imparts a yellow-orange colour to the arc and as a result, some difficulty may be experienced in determining the end point when the sample contains an appreciable concentration of this alkaline earth.

The image of the arc on the spectrograph slit may be inspected if a spherical condenser of short focal length is used in the analysis ; otherwise an image projected on to the wall or screen by means of an auxiliary condenser may be observed.

The voltage drop across the electrode gap depends in part on the composition of the arc gas and this property is used as an indicator in the second method of determining the end of the alkali metal phase of volatilization. Voltage drop is at a minimum in the presence of alkali metal vapour because first

ionization potentials of these elements are lower than those of other elements. As the alkali metal phase of distillation nears completion, the potential drop usually becomes erratic and then increases; this indicates complete distillation of the alkali metals The end point may be sharp or comparatively diffuse and the remarks above about the use of colour and appearance as an indicator apply here also.

The voltage drop vs. time relationship for microcline, granite, and diabase when arced at 3 amp as below and in Sec. 5–4 is shown in Fig. 5.1. Voltage changes from a minimum of about 40 volts to the maximum plateau of 80–85 volts, which is reached after complete volatilization of all elements. Times for complete distillation are indicated. Such $v$ vs. $t$ curves sometimes show more irregularities than those shown in Fig. 5.1.

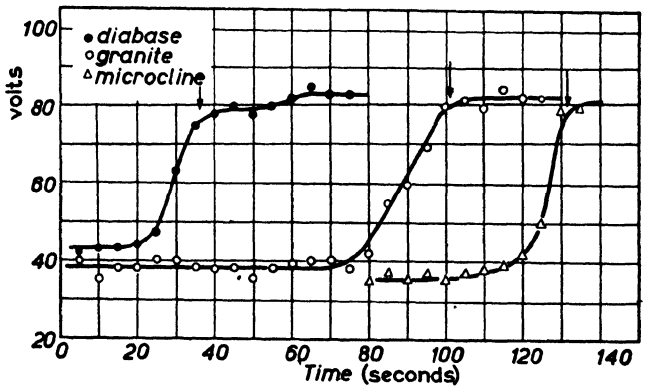



Fig. 5.1. Volta ge-time of curves for diabase (2% Na+K), granite (6·9% Na+K) and microline (12·3% Na+K).

Some observed times of complete distillation of the alkali metals from various silicates are given in Table 5–1. Total alkali metal concentration ranges from a few ppm to about 12 per cent. Times refer to volatilization from the $\frac{1}{8}''$ anode (carbon and graphite) arced at 3 amp.

The fairly well-known fact that rate of distillation from a carbon anode is more rapid than from a graphite anode is emphasized in Table 5–1. Time ratios, graphite-to-carbon, range from 1·25 to 1·75 and average at 1·40. A decrease in the total concentration of the alkali metals from 12% in

microcline to 0·85% in chrondite causes a 5–8 fold decrease in the time for their complete distillation; this regularity is brought out more clearly in Fig. 5.2. Distillation of the alkali metals from dunite is complete in a matter of a few seconds, but as alkali metal concentrations are so low, no visible effect can be measured.

TABLE 5–1

OBSERVED TIMES OF COMPLETE DISTILLATION OF THE ALKALI METALS FROM VARIOUS SILICATES

| Sample description | %K | %Na | Σ% alks. | Time (seconds) (i) | (ii) | (iii) | Av. | gr/c |
|---|---|---|---|---|---|---|---|---|
| Microcline | 10·5 | 1·8 | 12·3 | c* 130 | 140 | 135 | 135 | 1·27 |
| | | | | gr* 170 | 170 | – | 170 | |
| Albite ... | 0·84 | 6·9 | 7·2 | c 100 | 110 | – | 105 | 1·29 |
| | | | | gr 120 | 145 | 150 | 135 | |
| Granite ... | 4·5 | 2·4 | 6·9 | c 95 | 90 | – | 95 | 1·72 |
| | | | | gr 120 | 160 | – | 140 | |
| Biotite ... | 6·1 | 0·4 | 6·5 | c 90 | – | – | 90 | – |
| | | | | gr – | – | – | – | |
| Diabase ... | 0·52 | 1·5 | 2·0 | c 40 | 35 | – | 37 | 1·43 |
| | | | | gr 55 | 50 | – | 53 | |
| Chondrite... | 0·1 | 0·75 | 0·85 | c 15 | 15 | 20 | 17 | ~1·75 |
| | | | | gr ~30 | ~30 | – | ~30 | |
| Dunite ... | <·003 | <·002 | <·005 | c <10 | – | – | <10 | – |
| | | | | gr | | | | |

* c=carbon. gr=graphite.

General composition, structure and bonding also influence rate of distillation of the alkali metals in silicates and CANNEY (1952) has observed that distillation is more rapid from shale than from an igneous rock which contains an equivalent concentration of the alkali metals.

The exposure times for most methods described in this chapter and in Chap. 6 are variable as they depend on the total concentration of the alkali metals. The very first few seconds of excitation should be recorded because of the

volatility of these elements—this becomes imperative when their total concentration is low. Exposure is continued until the main phase of alkali metal distillation ceases, as determined by either or both of the methods described above.

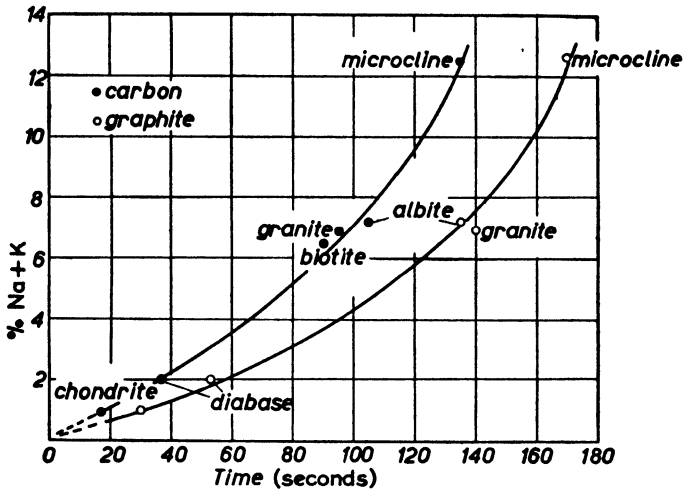



Fig. 5.2. Variation of time of complete alkali metal distillation with total alkali metal content.

## Sec. 5–3. Some lines of the alkali metals

Sensitive lines of the alkali metals may be classed into two groups ; those located in the yellow-red and those in the blue-violet. Table 5–2 (p. 53), lists several lines belonging to each group ; most are referred to in the text.

Nearly all attention will be given to the yellow-red group because the most sensitive line of each alkali metal, together with several of their weaker lines which may be used at higher concentrations, are located within this general wavelength range.

# ANALYTICAL PROCEDURES

Spectrochemical methods for determining the alkali metals have been used for a variety of purposes in the Cabot Spectrographic Laboratory. Some methods have been general,

whereas others have been specific and have demanded the utmost accuracy; large concentration ranges have been covered. The general methods (Secs. 5–4 and 5–5) will be discussed first, but it will become evident that all alkali-metal methods are basically similar and fit fairly well into the analytical scheme as a whole.

## Sec. 5–4. A general method with internal standardization

This method is applicable to most common igneous rocks such as granite, syenite, diorite, gabbro, basalt and diabase, as well as metamorphic and sedimentary equivalents, but not to the ultramafics, nor as a rule to specific minerals.

The spectroscopic properties of all alkali metals are similar. As a result, it is usually possible to achieve the highest accuracy by using one alkali metal as an internal standard for the determination of the others : this forms the basis of nearly all internal standard procedures described in this section and elsewhere in this chapter.

Two steps are required for a complete alkali metal analysis as one alkali metal is always the internal standard. In the first step, lithium added as spodumene, is used as the internal standard for the determination of sodium and occasionally potassium; in the second, sodium, and sometimes potassium, is used as a variable internal standard for the determination of the other alkali metals.

*The first step*

Spodumene has been chosen as the source for lithium because the quality of the discharge is particularly satisfactory in the presence of a large amount of this mineral. $Li_2CO_3$ and other compounds have been tried but they have been found to be distinctly inferior, mainly because the arc burn is more erratic. Spodumene does, however, always contain some sodium. A spectrochemical examination of three different specimens showed magnitudes of 0·2–0·3%. For many purposes this may be ignored as spodumene is added to both standards and unknowns; if necessary, however, the sodium content may be determined by means of an addition plot using U.S. Bureau of Standards albite (6·9%) as the

addition standard. Alternatively it might be more satisfactory to prepare a synthetic spodumene glass from ingredients which are free from disturbing amounts of sodium.

The concentration of lithium in most silicate rocks, minerals and sediments is insignificantly low compared with its concentration (~2–2·5%) in added spodumene, and hence,

TABLE 5–2

SENSITIVE LINES OF THE ALKALI METALS

| Element | UV group | | | Yellow-red group | | |
|---|---|---|---|---|---|---|
| | Wave-length A | Excit. pot. Low (volts) | high | Wave-length A | Excit. pot. Low (volts) | high |
| Cs ... | 4593·177 | 0·00 | 2·69 | 8943·50 | 0·00 | 1·38 |
| | 4555·355 | 0·00 | 2·71 | 8521·10 | 0·00 | 1·45 |
| K ... | 4047·201 | 0·00 | 3·05 | 7698·979 | 0·00 | 1·60 |
| | 4044·140 | 0·00 | 3·05 | 7664·907 | 0·00 | 1·61 |
| | | | | 6938·98 | 1·60 | 3·40 |
| | | | | 6911·3 | 1·60 | 3·40 |
| Li ... | 4971·990 | 1·84 | 4·32 | 8126·52 | 1·84 | 3·36 |
| | 4602·863 | 1·84 | 4·52 | 6707·844 | 0·00 | 1·84 |
| | 3232·61 | 0·00 | 3·82 | 6103·642 | 1·84 | 3·86 |
| Na | 3302·988 | 0·00 | 3·74 | 8194·811 | 2·10 | 3·60 |
| | 3302·323 | 0·00 | 3·74 | 8183·270 | 2·09 | 3·60 |
| | | | | 6160·760 | 2·10 | 4·10 |
| | | | | 6154·229 | 2·10 | 4·10 |
| | | | | 5688·224 | 2·10 | 4·27 |
| | | | | 5682·657 | 2·09 | 4·27 |
| | | | | 5895·923 | 0·00 | 2·09 |
| | | | | 5889·953 | 0·00 | 2·10 |
| Rb ... | 4215·556 | 0·00 | 2·93 | 7947·60 | 0·00 | 1·55 |
| | 4201·851 | 0·00 | 2·94 | 7800·227 | 0·00 | 1·58 |

with the exception of the lithium minerals and occasionally biotite and muscovite, danger from interference is absent. A method for determining Li, Rb and Cs in biotite is described in Sec. 5–10.

Details of procedure are as follows. The sample is mixed with two parts powdered spodumene. One part of the mixture is mixed with one part of carbon powder, loaded into a $\frac{1}{16}$" anode and arced at 7 amp until distillation of the alkali metals is complete. Exposure time is fairly uniform at 25–35 seconds

because the presence of a high proportion of spodumene ensures a high concentration of alkali metal in all specimens. Superimpose two exposures for each sample.

Carbon powder is added and a moderately high amperage (7 as compared with 8) is used in order to reduce the volatility difference between lithium and the other alkali metals. The rate of distillation of lithium from spodumene is otherwise distinctly slower than that of the other alkali metals from the specimen and reproducibility is consequently unsatisfactory.

The intensity ratio of the analysis pair, $\frac{\text{Na } 5682}{\text{Li } 4972}$ may be determined from partial characteristic curves. Fig. 5.8 is a working curve relating $\frac{\text{Na } 5682}{\text{Li } 4972}$ to the amount of sodium in each of a series of primary silicate standards and their mixtures. The close fit of individual points about the working curve indicates very satisfactory reproducibility. This has been borne out repeatedly and the relative deviation calculates at 2·5–3%. Such reproducibility compares very favourably with the Lawrence-Smith fusion procedure and is about as good as can be achieved by DC arc excitation of powders in general.

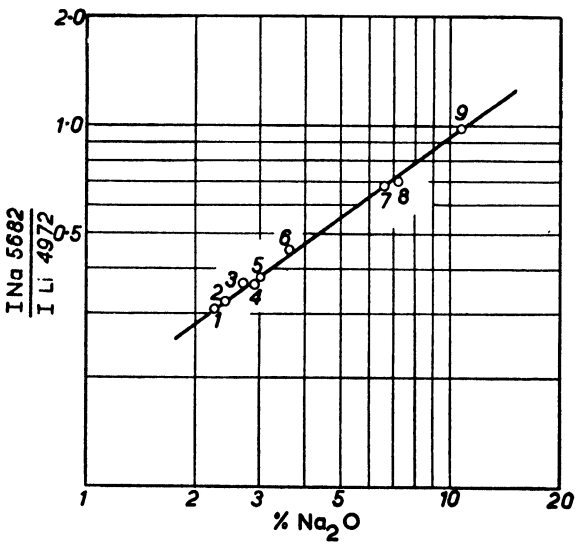



Fig. 5.8. Working curve for the determination of sodium.
(See Fig. 5.4 for description of samples labelled 1 to 7.)

The replicate determinations in Table 5–8 illustrate reproducibility. Column *a* refers to G-1 and the others to randomly chosen duplicate determinations of sodium in Canadian rocks as given by EDIE (1951).

TABLE 5–8

SOME REPLICATE DETERMINATIONS OF SODIUM IN VARIOUS CANADIAN ROCKS

| | | %Na | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
| 1. | ... ... | 2·45 | 1·65 | 1·45 | 1·45 | 3·90 | 4·80 | 1·60 | 0·33 |
| 2. | ... ... | 2·46 | 1·65 | 1·35 | 1·55 | 3·90 | 3·90 | 1·65 | 0·31 |
| 3. | ... ... | 2·40 | | | | | | | |
| 4. | ... ... | 2·51 | | | | | | | |
| 5. | ... ... | 2·55 | | | | | | | |

*a* = granite G-1
*b* = microcline granite
*c* = plagioclase amphibolite
*d* = chlorite-sericite schist
*e* = albite granite
*f* = albite granite (another sample)
*g* = diabase
*h* = quartzite

Determinations of sodium and potassium only are required for most petrological purposes, in which case potassium may be determined with sodium in the first step provided its concentration >2–3%. The pair $\frac{\text{K } 6939}{\text{Li } 4972}$ is used and provides a satisfactory precision, only slightly less than that for sodium. A lower concentration cannot be determined because background is excessive at λ 6939 A when using the arcing procedure outlined above.

*The second step*

Sodium has been chosen as a general variable internal standard in place of potassium because its concentration is far more uniformly distributed in the naturally-occurring silicates.

No material is added to the powdered specimen which is loaded into a $\frac{1}{8}$″ anode and excited at 8 amp; exposure is continued until alkali metal distillation is complete. Such times vary greatly as may be seen from an inspection of Table 5–1 which refers to the conditions of arcing given here.

Components of the Na $\begin{cases}5682\\5688\end{cases}$ and Na $\begin{cases}6160\\6154\end{cases}$ doublets

may serve as internal standard lines; Na 6160·76 is rarely usable, however, because of direct line interference from Ca 6161·29 and Ca 6162·17. Replicate determinations indicate that Na 6154 is superior to Na $\begin{cases}5682\\5688\end{cases}$. Na 6154 is, however, a comparatively weak line and is not usable at low sodium concentrations; general interference from CaO emission, always excessive in anorthosite, further restricts the use of this line. CaO emission only develops strongly when the alkali metal phase of distillation begins to wane, and interference can often, therefore, be held to an insignificant level by underexposing for a few seconds; this does not appear to introduce serious error.

Some typical replicate intensity ratio determinations are given in Table 5–4. Precision is satisfactory and calculations based on Table 5–4 and other observations indicate a relative deviation of about 4% for potassium, and a little more for lithium, rubidium and caesium.

TABLE 5–4

SOME REPLICATE INTENSITY RATIO DETERMINATIONS USING NA 5682 AS THE INTERNAL STANDARD LINE

| | $\frac{\text{Rb 7800}}{\text{Na 5682}}$ (W-1) | $\frac{\text{Rb 7800}}{\text{Na 5682}}$ (G-1) | $\frac{\text{Li 6707}}{\text{Na 5682}}$ (W-1) | $\frac{\text{K 6939}}{\text{Na 5682}}$ (G-1) |
|---|---|---|---|---|
| | ·35 | 1·12 | 2·35 | ·48 |
| | ·34 | 1·27 | 2·25 | ·58 |
| | ·30 | 1·28 | 2·20 | ·55 |
| | ·35 | 1·19 | 2·20 | ·59 |
| | ·34 | 1·22 | 2·40 | ·55 |
| | ·33 | 1·25 | 2·12 | ·54 |
| Av. | ·33 | 1·22 | 2·25 | ·55 |

The working curves in Fig. 5.4 relate the ratio, $\frac{\text{I K 6939}}{\text{I Na 5682}}$ to the concentration ratio potassium to sodium.

Potassium may be determined over the concentration

range ~0·2–>5% K. As K $\begin{cases}6939\\6911\end{cases}$ are not intense lines and as their low levels are 1·6 volts above the ground state, they show no self-absorption even at high concentrations of potassium. Although a fairly large proportion of the naturally-occurring silicates contain >0·2% K, many do not, in which case other methods must be used; see Secs. 5–6 and 5–7.

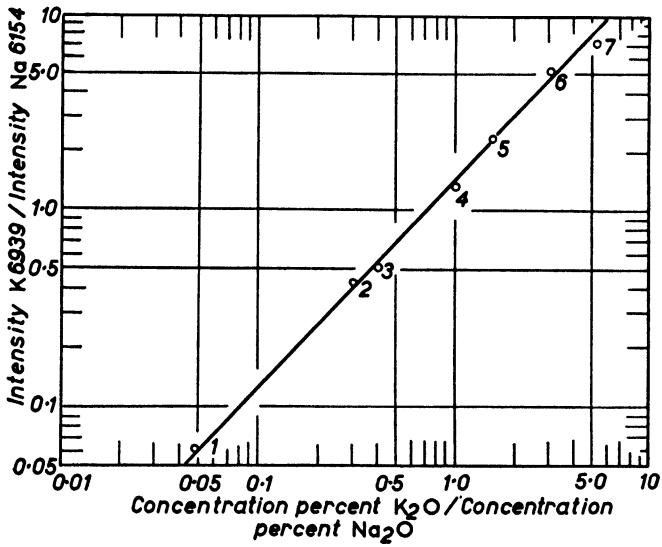



Fig. 5.4. Working curve for potassium (indirect method; sodium as variable internal standard). Applicable over a wide range of K/Na concentration ratios.
(1) Na feldspar (*U.S. Bur. Standards No.* 99).
(2) W-1.
(3) One part Na feldspar and one part G-1.
(4) One part Na feldspar and one part K feldspar.
(5) G-1.
(6) One part G-1 and one part K feldspar.
(7) K feldspar (*U.S. Bur. Standards No.* 70).

The detection limit of rubidium is about 1 ppm under favourable conditions. This is adequate for its determination in almost all naturally-occurring silicates with the exception of the ultramafic rocks. Rubidium is very closely associated with potassium in almost all the silicates, including meteorites, and in these materials the intensity of Rb $\begin{cases}7947\\7800\end{cases}$ is usually 2–8 times greater than K 6939 (Plate 1). Several sector steps

must, therefore, be used in order to determine both elements in a single operation over as wide a range of concentrations as possible. The first step (maximum exposure) is usually required for the determination of potassium in basalt, diabase and gabbro, whereas steps of very low transmission must be used to determine rubidium in rocks such as granite and shale. These general comments apply also to cesium and lithium, where Li 6707 may tend to be overexposed and Cs 8521 underexposed unless a full transmission range is used.

The abundance of cesium is about 1/50–1/100 that of rubidium and although it has a low detection limit (~2 ppm) it is not always low enough. Cesium is usually detectable in granite, shale and some intermediate rocks, occasionally in basalt, diabase and gabbro but never in chondrites and ultramafics.

Ti 8518 is often evident in the spectra emitted from silicates. Separation of Ti 8518 and Cs 8521 is considerable in grating spectrographs but may be very small in prism instruments, and although the lines are usually resolved, the author is aware of examples of misidentification.

Li 6707 is extremely sensitive (detection limit $\ll 1$ ppm) and usually free from background and is as a result detectable in virtually every silicate rock, mineral, sediment or meteorite. It is a ground state line which readily shows self-absorption (STROCK, 1936 ; AHRENS, 1950). This sometimes introduces a difficulty because Li 6103, the next most sensitive line, may not be in evidence at a concentration at which self-absorption has begun in Li 6707. Li 6707 is at least 5–10 times as intense as Li 6103. Li 6103·642 is subject to interference from Ca 6102·72 in many rocks, unless dispersion is large. Interference is definitely not evident in a mineral such as muscovite or biotite where lithium is comparatively high and calcium low. In a rock such as granite, however, interference may develop depending upon the amount of calcium and the extent to which the recommended exposure time may have been exceeded. If in doubt, the analyst should underexpose by a few seconds as calcium emission is at a minimum during the main phase of alkali metal distillation. Neighbouring calcium lines may be used as check lines in much the same way as Fe 4144 has been used with respect to interference of Fe 4202 with Rb 4202 on a prism spectrograph (AHRENS,

1950). A correction may be attempted as in the Fe-Rb example provided interference is not excessive.

Interference is usually excessive in calcium-rich rocks in which case Li 8126 may sometimes be used if Li 6707 is self-absorbing. Li 8126 is a little less intense than Li 6103 and self-absorbing Li 6707 might have to be used over at least a moderate range of concentration. Li 8126 is usually free from direct line interference but halation for Na $\begin{cases}8195\\8188\end{cases}$ can be quite troublesome (Plate 1).

## Sec. 5–5. A general method without the use of an internal standard

Although accuracy is lowered by omission of the internal standard, it is nevertheless adequate for a wide variety of purposes. Methods which do not employ an internal standard are usually simpler, less time-consuming and capable of much wider application than those that do. A critical statistical survey has not been made of the reproducibility of the simpler procedures, but available data indicate a relative deviation of about 15%. As it has been common practice to carry out determinations in triplicate, this magnitude reduces to 5–10%.

All alkali metals are determined in one operation. The arcing procedure is identical to that of the second step in Sec. 5–4, except that the internal standard is omitted. Analysis lines are the same and comments about sensitivity and interference apply equally well. For sodium, the internal standard lines Na $\begin{cases}5682\\5688\end{cases}$ (Sec. 5–4) may be used as analysis lines ; a lower detection limit may be reached with Na $\begin{cases}8183\\8195\end{cases}$ whereas the " D " lines Na $\begin{cases}5890\\5896\end{cases}$ may be used down to $\ll 1$ ppm.

Fig. 5.5 shows a typical working curve which was used by PINSON, AHRENS and FRANCK (1954) for the determination of extremely low concentrations of lithium in ultramafic rocks and chondrites. For this purpose, a mixture of G-1 (22 ppm Li) and a lithium-low peridotite served as standards.

The analyst may find it to his advantage to use a combination of procedures with and without internal

standardization when carrying out a survey of the distribution of all alkali metals in a suite of specimens. It might, for example, be desirable to know the concentration of potassium as a major constituent with utmost accuracy, in which case the internal standard procedures should be used, whereas in some specimens low in potassium the simpler procedure without internal standardization would be sufficiently accurate. The work of EUGSTER (1954) is instructive in this respect. The distribution

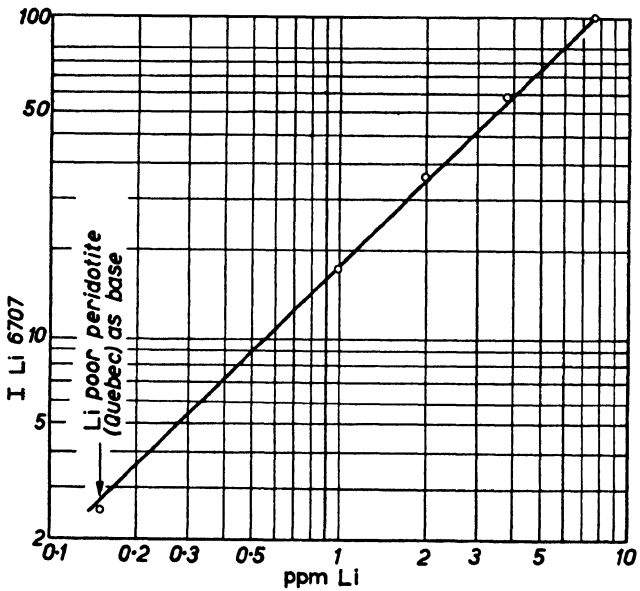



Fig. 5.5. Working curve for the determination of extremely low concentrations of Li (0·1–10 ppm) in ultramafic rocks and chondrites.

of the alkali metals in some thirty-two specimens of metamorphic rocks from Switzerland was investigated. A wide variety of specimens composed mainly of phyllite, hornfels, biotite schist and quartzite rich in organic matter were analysed ; some typical determinations are given in Table 5–5.

These determinations provide a good indication of the range of concentrations that may be handled. Several procedures were used, as follows :

No asterisk—no internal standard.

* General procedure as outlined in Sec. 5–4.

** Potassium as internal standard in place of sodium, the procedure otherwise being the same as described in Sec. 5–4. This may be compared with the use of potassium as an internal standard for the determination of the other alkali metals and thallium (Secs. 5–9 and 6–4, respectively).

TABLE 5–5

ALKALI METAL CONTENTS OF SOME SWISS METAMORPHIC ROCKS (EUGSTER, 1954)

| No. | Description | Na (%) | K (%) | Rb (ppm) | Li (ppm) | Cs (ppm) |
|---|---|---|---|---|---|---|
| BG3 | Phyllite (1) ... ... | 1·3* | 4·7* | 110** | 31** | 8 |
| 838 | Phyllite (2) ... ... | 0·18* | 0·42* | 120* | 23 | 2 |
| 545 | Quartzite rich in organic matter ... ... | 0·034 | 0·084 | 27 | 5 | — |
| 250 | Biotite schist ... ... | 0·19* | 3·9* | 570* | 43* | 4·5 |

The general methods described above usually provide satisfactory sensitivity for most purposes. A few rather specific problems, mainly associated with the accurate determination of potassium at low concentrations, have, however, arisen. An isotope ($K_{40}$) is unstable and its radioactivity is not only a significant source of earth heat but is also a principal source of the earth's argon. The accurate determination of potassium in materials such as the ultramafic rocks and chondrites is consequently of much geophysical and geochemical significance because a significant proportion of the earth's interior may be composed of these materials.

In addition to methods concerned mainly with the determination of low concentrations of potassium, others of a more or less specific nature will be described in the rest of this chapter. Most methods are merely modifications of those already described.

## Sec. 5–6. Potassium in chondrites and in ultramafic rocks containing moderately low (0·04–0·5%) amounts of potassium

The common silicate meteorites (chondrites) usually contain ~·1% K, ~·8% Na, ~10 ppm Rb, ~8 ppm Li and

$\leqslant 1$ ppm Cs. Sodium, rubidium and lithium may be determined at these concentrations using the procedure described in Secs. 5–4 (2nd step) and 5–5. The concentration of cesium is so low that it cannot be determined unless preliminary concentration is undertaken and this element will not be discussed further. K $\begin{cases}6939\\6911\end{cases}$ are not detectable at $\sim 0{\cdot}1\%$ : two alternatives may be attempted; one referred to by PINSON (1951) and AHRENS, PINSON and KEARNS (1952), and the other by HOLYK (1952) and HOLYK and AHRENS (1953). Although later research has shown the second method as more accurate and versatile, the earlier one will be outlined first mainly because this method was first to indicate the presence of serious error in the Lawrence-Smith fusion procedure when used to determine low concentrations of potassium.

PINSON (1951) replaced the $\frac{1}{8}''$ anode by one of $\frac{3}{16}''$ diameter, conditions of excitation otherwise being the same as in Sec. 5–4 (2nd step) and Sec. 5–5. Alkali metal distillation from chondrites is increased from 15–20 seconds to $\sim 80$ seconds. K $\begin{cases}6939\\6911\end{cases}$ are distinctly visible, although the background contribution is quite large. Reproducibility is not high because the discharge is fairly erratic and all determinations should be made at least in triplicate.

Mixtures of granite G-1 and a chondrite have been used as standards for the determination of potassium in the meteorite by means of the addition method. An accurately analysed chondrite may be used for the construction of a single-point working curve because variation of concentration is extremely slight in chondrites and hence extrapolation through the plotted point is small.

Three determinations of potassium in the Homestead and Kernouve chondrites are given in Table 5–6, the first by PINSON (1951), the second by SULLIVAN (see AHRENS, PINSON and KEARNS (1952)) who used a flame-photometric procedure and who carried out this determination in order to verify the spectrochemical value, and the third, a spectrochemical determination by HOLYK (1952) using a method described in Sec. 5–7.

The values agree closely, and as the methods are more or less independent, this may be taken to support the validity of these concentrations. Further support is given by a chemical determination (see Table 5–7) of 0·1% K in the Homestead meteorite. In many chondrites, however, chemical values are higher than this and the average abundance of

TABLE 5–6

% POTASSIUM IN TWO CHONDRITES

| | PINSON | SULLIVAN | HOLYK |
|---|---|---|---|
| Homestead ... ... ... | 0·11 | 0·12 | 0·115 |
| Kernouve ... ... ... ... | 0·11 | 0·10 | 0·115 |

potassium in chondrites as determined chemically is almost twice as high as the average of the spectrochemical determinations (AHRENS, PINSON and KEARNS). This discrepancy is serious and further disagreement between spectrochemical and chemical determinations becomes apparent when various individual determinations, Table 5–7, are compared.

Whereas the spectrochemical determinations indicate a high degree of uniformity of concentration of potassium in chondrites, the chemical determinations indicate just the reverse.*

There is evidence (AHRENS, PINSON and KEARNS, 1952) that some of the chemical determinations, particularly the older ones, may be much too high. This is probably due to the fact that blank potassium (and sodium) in the $CaCO_3 + NH_4Cl$ (see GROVES, 1951, p. 78, for example) used in the Lawrence-Smith fusion procedure is often comparable in magnitude with the amount in chondrites. Repeated leaching with water does not necessarily remove all potassium and sodium (HEY, 1952). The *chladnite* analysis is particularly instructive in this respect. This meteorite is free from feldspar which contains the alkali metals and which is always present

* W. H. PINSON and the author are of the opinion that variation of concentration may be considerably less than indicated by the spectrochemical determinations in Table 5–7 because much is undoubtedly due to analytical error. It should be recalled (p. 62) that this method is not regarded as highly reproducible.

(usually ~10%) in chondrites. The potassium content should therefore be very low. The spectrochemical determination of ~10 ppm is in conformity with this observation whereas the chemical value is × 80 as high and may well be nearly all

TABLE 5–7

A COMPARISON OF SOME CHEMICAL DETERMINATIONS OF POTASSIUM AS GIVEN BY BROWN AND PATTERSON (1947) WITH SPECTROCHEMICAL DETERMINATIONS GIVEN BY AHRENS, PINSON AND KEARNS (1952). THREE FLAME PHOTOMETRIC DETERMINATIONS BY SULLIVAN (AHRENS, PINSON AND KEARNS, 1952) ARE INCLUDED

| Description | %K Chem. | %K Spec. | %K Flame photo. |
|---|---|---|---|
| Homestead, Iowa ... | 0·13 | 0·11 | 0·12 |
| Holbrook, Ariz. ... | tr; 0·13 | 0·08 | — |
| Bjurbole, Finland ... | 0·30 | 0·10 | — |
| Forest City, Iowa ... | 0·065 | 0·05 | — |
| Hessle, Sweden ... | — | 0·08 | — |
| Kernouve, France ... | tr. | 0·09 | 0·07 |
| Mocs, Rumania ... | 0·19 | 0·11 | — |
| Tennasilm, Esthonia ... | ($Na_2O+K_2O$, 2·61%) | 0·10 | — |
| Monroe, N. C. ... | — | 0·07 | — |
| Long Island, Kan. ... | 0·024 | 0·06 | — |
| Beaver Creek, Can. ... | 0·11 | 0·08 | — |
| Estacado, Tex. ... | 0·32 | 0·07 | — |
| Haye's Centre ... | — | 0·07 | 0·096 |
| Johnstown, Col.* ... | 0·08 | 0·001 | — |

blank. These observations lead one to conclude that the discrepancies in Table 5–7 are due to errors of chemical and not spectrochemical determination.

## Sec. 5–7. Determination of potassium in ultramafic rocks (from ~10 ppm to >0·1%) and chondrites

HOLYK (1952) sought to investigate the abundance of potassium in ultramafic rocks, notably, dunite, serpentine, pyroxenite and other peridotites. These rocks often contain

* Chladnite (bronzite).

10–100 ppm K*, in which case neither K $\begin{cases}6939\\6911\end{cases}$ nor K $\begin{cases}4047\\4044\end{cases}$ are detectable and the most sensitive lines, K $\begin{cases}7665\\7699\end{cases}$ must be used. In this particular investigation it was desirable also that the method should be able to handle higher concentrations (up to ~0·1–0·3%) as well, first because some felspathic and micaceous ultramafics contain comparatively high concentrations, and second, because some further analyses of chondrites were to be made at the same time. The method that was developed is more versatile and accurate than the one described in Sec. 5–6.

The $\frac{1}{8}$″ anode is used. Each sample is mixed with two parts of carbon powder. The discharge may otherwise be

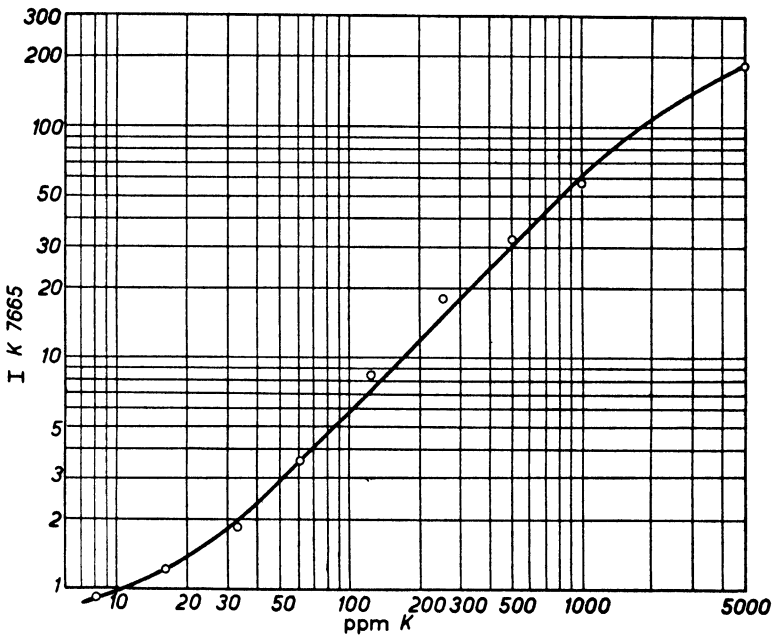



Fig. 5.6. Working curve for the determination of potassium in ultramafic rocks and chondritic meteorites.

* The Lawrence-Smith fusion method should not be attempted at such magnitudes because blank potassium (and sodium) may be many times higher than in the unknowns. This probably accounts for the fact that previous determinations of potassium in dunite and serpentine are probably too high by whole orders of magnitude (Holyk and Ahrens, 1958).

extremely erratic if the total alkali metal concentration is low ($<\sim 0{\cdot}2\%$) and complete loss of the silicate bead from the anode cavity is quite common. Expose for 25 seconds at 8 amp.

Serpentine arcs badly despite the presence of carbon powder, mainly because of a sudden rapid release of water vapour from the specimen when the arc is struck. This disturbing behaviour may be overcome by preheating the loaded electrode for ~20–30 seconds in the flame of a gas burner.

Holyk used a mixture of granite G-1 and varying proportions of a potassium-poor peridotite as standards. A typical working curve is shown in Fig. 5.6. The development of a toe is due mainly to ~7 ppm K in the peridotite whereas the development of a shoulder is due to the onset of self-absorption at $\sim 0{\cdot}1\%$.

Table 5–8 gives a few typical replicate determinations of potassium in pyroxinite from Rhodesia.

TABLE 5–8

REPLICATE DETERMINATIONS OF POTASSIUM IN RHODESIAN PYROXINITE

| No. | K (ppm) |
|---|---|
| 1 | 88 |
| 2 | 72 |
| 3 | 72 |
| 4 | 90 |
| 5 | 72 |
| 6 | 82 |
| Av. | 80 (0·008%) |

Relative deviation is ~10% and is adequate for several purposes.

Pinson (1951) has made the general observation that potassium determinations tend to be extremely erratic at a very low concentration ($<\sim 30$ ppm). This has been confirmed by Holyk (1952) who found perspiration from the fingers as the cause, a source of error far more in evidence on hot days. Perspiration contamination is also clearly

observable when determining low concentrations of sodium. Spectrograms given by HOLYK (1952) clearly show that a large amount of contamination can be introduced this way. Manipulation of the electrodes with the fingers can be avoided by loading the sample as indicated in the three steps of Fig. 5.7. Holder and pin are of stainless steel. Firm and uniform packing of the sample is ensured when the loading device is used; this usually improves the burning quality of the discharge.

Inadvertent perspiration contamination can, if necessary, be overcome by heating the tip of the loaded electrode in a gas burner flame for a few seconds: this removes sodium and potassium from the perspiration but not from the sample.

DENNEN and FRITTS (1952) and DENNEN and WILFERT (1953) have investigated the abundances of potassium, sodium and lithium in quartz from a variety of sources. Quartz powder arcs reasonably well by itself and consequently no carbon powder was added; the procedure is otherwise the same as above. As the total alkali metal concentration is always low, as in dunite, serpentine and pyroxenite, no characteristic alkali metal phase is observable when quartz is arced and hence an arbitrary exposure is used. DENNEN and co-workers chose 25 seconds. This is long enough for complete distillation of the alkali metals, and at the same time comparatively short for the purpose of holding CN red emission to a fairly low level (Sec. 5–9). Standards were prepared by mixing granite G-1 with a specimen of quartz of high purity, the impurity content of which was determined by means of an addition plot. Some typical determinations are given in Table 5–9.

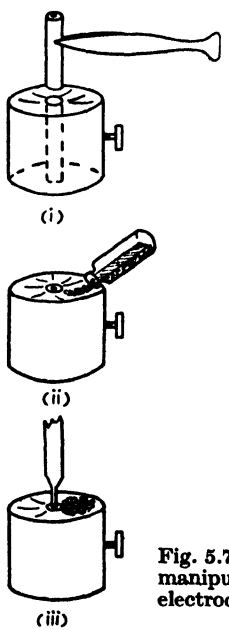



Fig. 5.7. Method of loading electrode so as to avoid finger manipulation (after HOLYK, 1952). (i) Insertion of carbon electrode into stainless steel holder; (ii) and (iii) addition and loading of powdered specimen.

The overall sensitivity in quartz, dunite, serpentine and pyroxenite has been observed to be considerably poorer than indicated elsewhere in this chapter and in Table 1–1. This applies particularly to potassium which is not detectable in several specimens of quartz (two examples appear in Table 5–9) because of the development of fairly intense CN red emission when the *total* alkali metal concentration is low ($<\sim 0{\cdot}2\%$).

TABLE 5–9

SOME EXAMPLES OF K, NA AND LI IN QUARTZ FROM A VARIETY OF SOURCES

| Source and description | K (ppm) | Na (ppm) | Li (ppm) |
|---|---|---|---|
| Geode ... ... ... ... ... ... | <25 | 70 | 0·1 |
| Massive clear vein quartz ... ... ... | <25 | 90 | 0·5 |
| Quartz-orthoclase vug ... ... ... | 1000 | 450 | 0·8 |
| Quartz-microcline pegmatite ... ... ... | 2000 | 1300 | 0·3 |
| " Blue " quartz pegmatite ... ... ... | 22 | 340 | 0·7 |
| Quartz " eyes " in metasediment ... ... | 220 | 120 | 0·3 |

## Sec. 5–8. Notes on the determination of extremely low concentrations (<10–20 ppm) of potassium and other alkali metals when the total alkali metal concentration is low

Three possible methods of improving sensitivity by quenching CN red emission will be noted.

The salt of an alkali metal which is not to be determined may be mixed with the sample. This is effective, but the method has not been adopted as a general procedure for the determination of *extremely* small concentrations because the purity of the added salt may not be adequate.

HOLYK (1952) found that a very satisfactory discharge in which CN emission is at a minimum may be obtained by using a $\frac{1}{8}''$ copper anode with a carbon cathode, arced at 8 amp. The spectra shown by HOLYK may be inspected for determining the efficacy of the above procedure. No exhaustive investigation has however been attempted.

DENNEN and WILFERT (1958) chose to excite their sample in a nitrogen-free atmosphere. The specimen was loaded in a

$\frac{3}{16}''$ anode and arced for 45 seconds at 7 amp in a helium-filled chamber of simple design, similar to one described by OWEN (1951). Three exposures were superimposed. A manometer served to ensure steady gas flow as the valves attached to helium tanks do not allow proper control of very low pressures. The detection limit in quartz and dunite is lowered by $\times$ 5–10 when the sample is excited in a helium atmosphere and is about equivalent to that in Table 1–1 ; that is, more or less the same as normally attainable in a silicate matrix in which the concentration of at least one alkali metal is more than $\sim$0·5%. The source is, however, not highly reproducible.

## Sec. 5–9. Potassium as a variable internal standard for the accurate determination of rubidium and cesium in sediments

Flame-photometric determinations of potassium in 324 North American sediments, mainly shales, have been reported by WHITEHEAD *et al.* (1952). CANNEY (1952) undertook to determine rubidium and cesium in the same specimens. As the potassium content of each specimen was accurately known this element was chosen as an internal standard, in accordance with the general recommendation of using one alkali metal as an internal standard for the accurate determination of others.

The $\frac{3}{16}''$ electrode was chosen partly because of the need for adequate sensitivity for the determination of cesium. Each specimen was arced at 6 amp for 45 seconds. In this respect the method differs somewhat from most of those discussed before; accuracy is, however, not impaired by using a fixed time cut-off procedure because at this amperage a major proportion of the alkali metals distil within 45 seconds, and in any case the distillation properties of each of these three alkali metals are very similar.

Several replicate determinations of rubidium and cesium in Woodford shale (No. 46667) are given in Table 5–10. These results are particularly instructive inasmuch that they emphasize the fact that a high reproducibility can be maintained despite a large wavelength difference between internal standard and analysis lines.

TABLE 5–10

REPLICATE DETERMINATIONS OF RUBIDIUM AND CESIUM IN WOODFORD SHALE
(AFTER CANNEY, 1952)

| Rb (ppm) | Cs (ppm) |
|---|---|
| 270 | 11 |
| 260 | 9 |
| 260 | 9 |
| 265 | 10 |
| 265 | 9 |
| 270 | 10 |
| 270 | 9 |
| 270 | 10 |
| 265 | 10 |
| 265 | 9 |
| 260 | 10 |
| 270 | 11 |
| 270 | 12 |
| 270 | 10 |
| 300 | 9 |
| 300 | 11 |
| 270 | 11 |
| Av. 270 | Av. 10 |

Relative deviations for rubidium and cesium, based on Table 5–10 and other observations, calculate at ~4% and ~8% respectively.

The efficacy of the internal standard line is demonstrated in Fig. 5.8 which shows intensity (K 6939 and Rb 7947) and

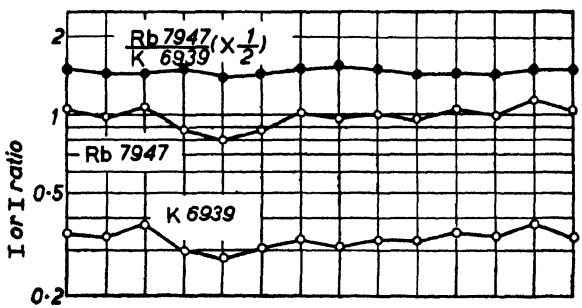



Fig. 5.8. Replicate determinations of I Rb 7947 and I K 6939; internal standardisation is excellent.

intensity ratio $\left(\frac{\text{I Rb } 7947}{\text{I K } 6939}\right)$ plots for each of the 17 replicate determinations.

Fig. 5.9 shows a typical working curve for two sets of standards ; one with 1% K, the other with 2% K. This curve

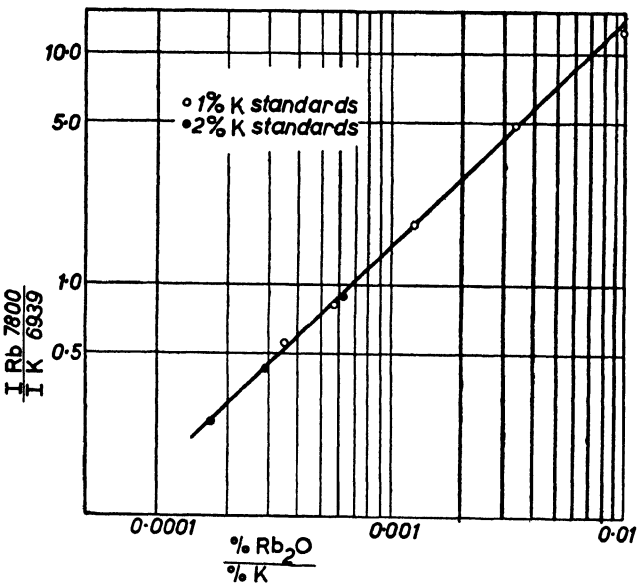



Fig. 5.9. Working curve for the determination of Rb in shale.

is particularly satisfactory and is a further demonstration of the accuracy of the method. Synthetic standards were prepared with the aid of a synthetic shale base described in Sec. 3–8.

## Sec. 5–10. Accurate determination of Li, Rb and Cs in biotite

Biotite is the principal host mineral for the three rare alkali metals, each of which is invariably enriched to a far greater extent in biotite than in any other mineral from the same rock. Moderately accurate determinations may be made by means of the method described in Sec. 5–5. The two-step internal standard method (Sec. 5–4) cannot, however, be used for greater accuracy, partly because the lithium concentration

in biotite can be significantly high compared with that in added spodumene and partly because the concentration of sodium (the variable internal standard) is often inconveniently low and in any case varies rather extensively.

WHITING (1951) investigated the distribution of Li, Rb and Cs in biotite from various igneous rocks and used the arcing procedure of Secs. 5–4 (second step) and 5–5. Each specimen was mixed with two parts of albite and Na 5688 served as the internal standard line for Li 6103, Rb $\begin{cases}7800\\7947\end{cases}$ and Cs 8521. Standards were prepared by first mixing varying proportions of $Li_2CO_3$, RbCl and $CsClO_4$ with two parts of albite; thereafter, varying proportions of this mixture were added to a mixture of two parts albite and one part of a biotite which reconnaisance had shown to be particularly low in the rare alkali metals.

## Sec. 5–11. Notes on the use of blue-violet lines

As the alkali metal lines of the blue-violet group (Table 5–2) are not capable of such wide application as those of the yellow-red group, their use does not form a main part of the analytical scheme discussed in this book. These lines may, however, be useful for several purposes and in any case the analyst may prefer to use them: either because of instrumental difficulties of working in the red or merely from the point of view of convenience. Convenience of use is due to the fact that these lines may be recorded together with the sensitive lines of the elements of the volatile group (Chap. 6): the same general arcing procedure and wavelength range are used.

For general purposes, determinations may be made without internal standardization, or the internal standard for the volatile group (Chap. 6) may be used. This internal standard (indium) is not as satisfactory as an alkali metal and precision is only sightly better than without its use. This conclusion is based on a comparison of the reproducibility of replicate determinations of I Rb 4202, I K 4047, $\frac{\text{I Rb 4202}}{\text{I In 4102}}$ and $\frac{\text{I K 4047}}{\text{I In 4102}}$ in a specimen of granite.

The comments about the need to avoid even a slight

amount of overexposure (Sec. 5–5) apply to K $\begin{cases}4047\\4044\end{cases}$ and Rb $\begin{cases}4215\\4202\end{cases}$ as both pairs of lines are within CN 4216. In addition to the possibility of CN interference there is a danger of line interference which also may be minimized by timing exposure correctly. Fe 4046 is located between K 4044 and K 4047. It is a moderately strong line usually visible in the spectra emitted by most silicates and although direct interference does not occur unless extremely small dispersions are used, halation interference can be serious. Iron is much less volatile than the alkali metals, and hence the intensity of Fe 4045 is at a minimum during the alkali metal distillation phase after which its intensity increases sharply. It is possible to determine comparatively low concentrations of potassium (from ~·04%) in a silicate which is fairly rich in iron, basalt for example. A low amperage (3 amp) is helpful in this respect because distillation differences develop fully under these conditions.

The use of Rb 4202 and 4215, Li 4603 and 3232, and Cs 4555 and 4593, in silicate rocks and minerals—sources of interference, methods for decreasing interference and sometimes for making quantitative corrections—is discussed by AHRENS (1950, Chap. 12).

CHAPTER 6

# THE VOLATILE GROUP

## Sec. 6–1. Introduction

THOSE elements which complete their distillation before or at the same time that the alkali metals complete theirs will be defined as volatile. They form a distinct group, namely, Pb, Ga, Ag, Cu, Tl, Zn, Sn, Ge, In, Bi, Hg, As and Sb. The last four elements are normally not detectable in silicate minerals, rocks, soils and meteorites. Some of the others are only rarely detectable and reference should be made to Sec. 6–5 for a discussion of special procedures for their determination at low concentrations.

Elements of this group are not equally volatile and gallium is the last to distil completely from silicates. If therefore, it can be shown that this element completes its volatilization by the time that the alkali metals complete theirs, it may be safely assumed that all other volatile elements will have distilled completely. The distillation of gallium may be conveniently examined in a wide variety of naturally-occurring silicates because of its ubiquity at concentrations well above its spectrochemical detection limit.

Fig. 6.1 shows some typical time-intensity curves for the alkali metals (as a whole), Ga, In, Al and CN in microcline, granite and diabase. These curves refer to 8 amp anode excitation of the powdered specimen from a $\frac{1}{8}''$ carbon anode, as in Secs. 5–4 (second step) and 5–5. A curve for indium is shown as this element is chosen as the internal standard (see below), whereas that of aluminium, a comparatively involatile element, is shown for the sake of comparison.

Fig. 6.1 shows clearly that distillation of gallium is complete by the time alkali metal distillation ceases. Each specimen has about the same total amount of gallium (15–20 ppm) and its distillation rate apparently depends on the total alkali metal concentration. One may conclude, therefore, that all volatile elements distil completely by the time the main

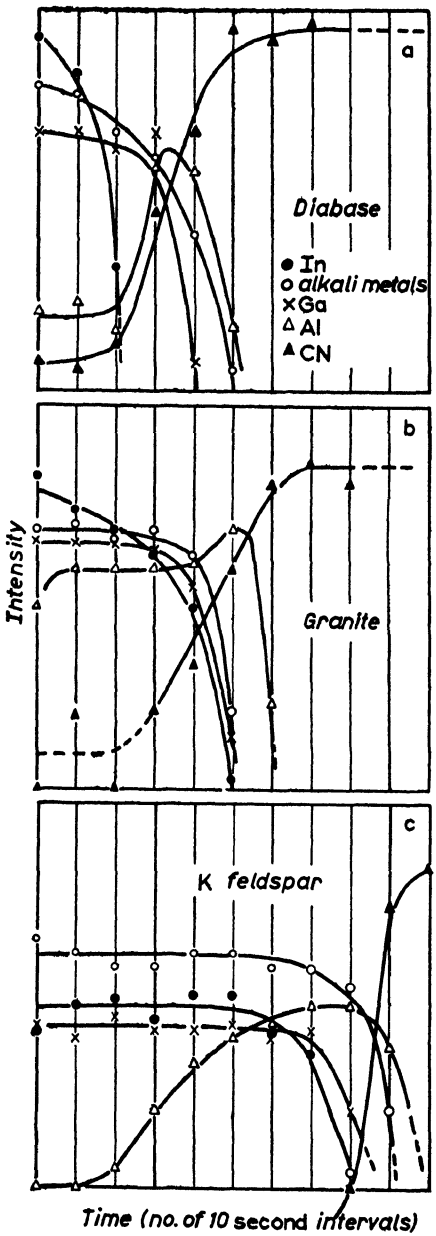



Fig. 6.1. Distillation curves for In (●), alkali-metals (o), Ga (×), Al (△) and CN (▲).

alkali metal phase of distillation ends, a conclusion which is based not only on the above observations, but also on other observed time-intensity relationships not given here, of individual volatile elements in various silicate matrices. Exposure times for the volatile elements will thus vary and arcing procedure is exactly the same as in Secs. 5–4 (second step) and 5–5. Greater overall sensitivity may be achieved by substituting a $\frac{3}{16}$" anode for one of $\frac{1}{8}$". The discharge is more erratic but accuracy is not necessarily impaired because the exposure is much longer.

## Sec. 6–2. Choice of an internal standard

The general arcing procedure may be employed with or without an internal standard. As elsewhere, the use of an internal standard improves reproducibility but decreases speed.

Indium has been chosen as an internal standard for three main reasons: first, its volatility is approximately

intermediate between the least volatile (gallium) and the most volatile elements; second, it possesses groups of lines of satisfactory excitation properties which are conveniently placed with respect to the most sensitive lines of the volatile elements; and third, the concentration of indium in most silicates is invariably well below its detection limit and hence a separate determination is rarely required: moreover, these extremely low concentrations are usually insignificantly small when compared with the amount of indium added as the internal standard. Typical concentration ranges (SHAW, 1952a) illustrate the magnitudes which can be expected in some common rock types.

TABLE 6–1

CONCENTRATION RANGES OF INDIUM
SHAW (1952A)

| | In (ppm) |
|---|---|
| Basalt ... ... ... | ·12 — ·32 |
| Gabbro ... ... ... | ·02 — ·13 |
| Granite ... ... ... | ·02 — ·2 |
| | (one specimen, 2 ppm) |
| Shale, clay, graywacke ... | ·02 — ·23 |

The possibility of detecting indium should, however, not be overlooked, particularly in the minerals amphibole, biotite, muscovite and lepidolite, where concentrations greater than a few ppm are not uncommon.

Indium is added as $In_2O_3$. A mixture of $In_2O_3$ (2%) and $K_2SO_4$ are first prepared, and 1% of the mixture is added to the specimen.

## Sec. 6–3. Analysis lines and internal standard lines

Internal standard lines and the most sensitive lines of the volatile group of elements are given in Table 6–2. It will be observed that most lines fall more or less into two wavelength groups—the first from 2800–3400A and the second from 3775–4170A. In 3256 (or In 3258) and In 4101 serve as the internal standard lines for members of each respective group.

Many analysts are inclined to favour the use of lines of short wavelength because those of longer wavelength are liable to interference from CN emission. Such emission may, however, usually be held to an insignificant minimum provided exposure is not carried past the main alkali metal phase of

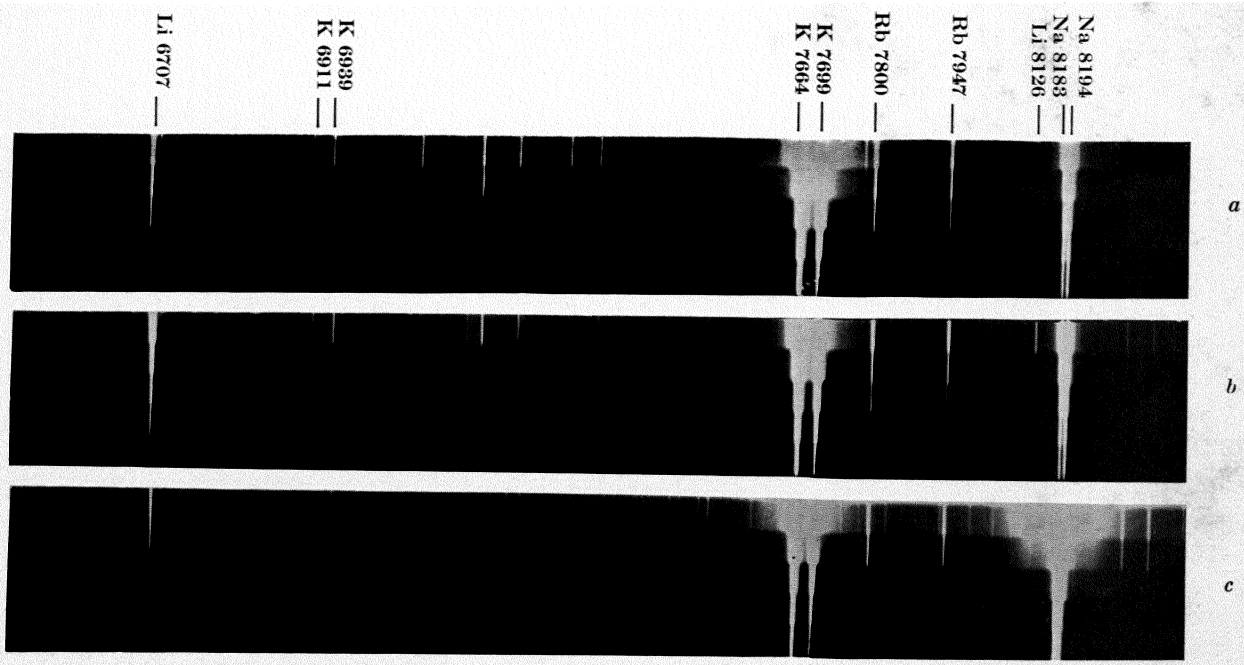



*Plate* 1. Alkali metal spectra of (*a*) granite G-1, (*b*) a Pacific Ocean sediment and a chondrite (Rancome). Procedure for (*a*) and (*b*) as in Sec. 5–4 (second step) using $\frac{1}{8}''$ anode, whereas in (*b*) $\frac{3}{16}''$ anode used (Sec. 5–6).

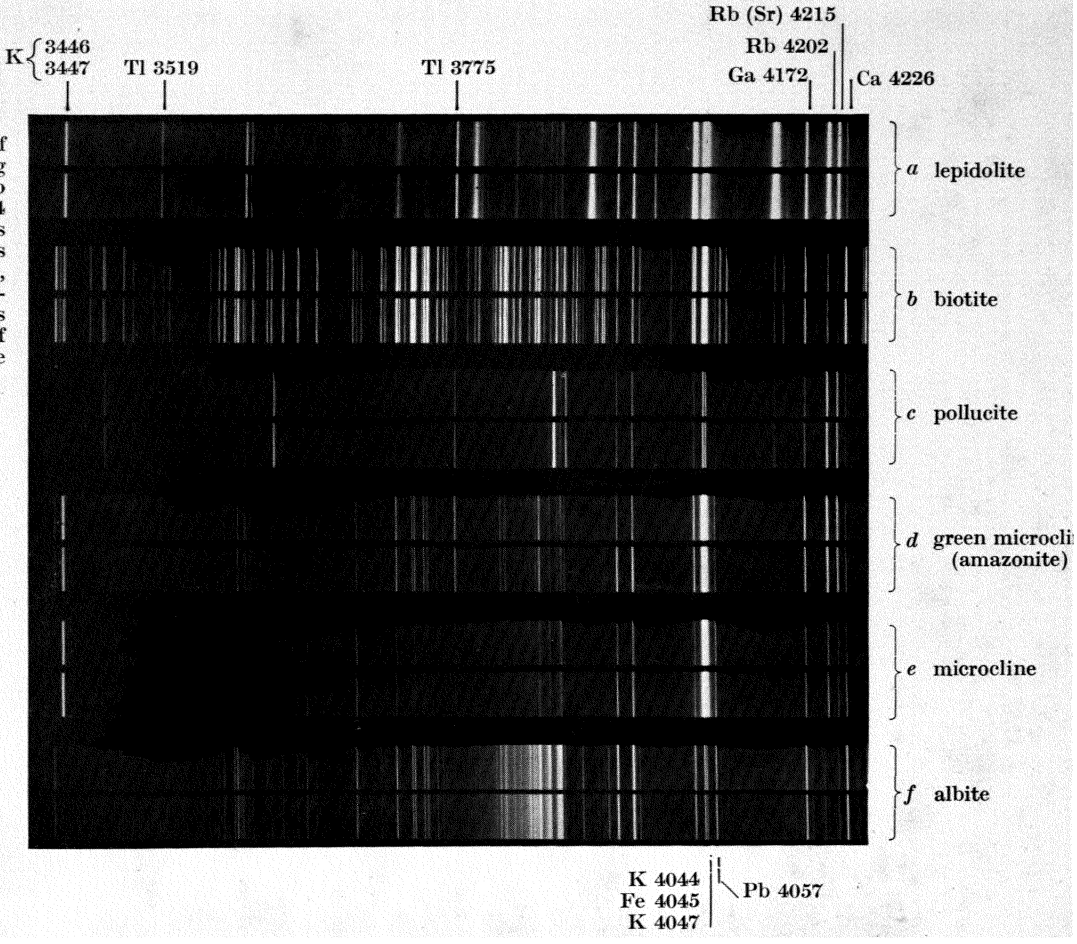



*Plate* 2. Duplicate spectra of several silicate minerals using arcing procedure similar to that described in Sec. 5–4 (second step). CN emission is at a minimum which permits satisfactory use of Rb 4202, Ga 4172, Pb 4057, and particularly Tl 3775, as well as a few other sensitive lines of the volatile elements over the 3500–4200 A range.

distillation; see CN curves in Fig. 6.1 in this respect. The duplicate spectra of Plate 2 show clear emission of Tl 3775, Pb 4057, Ga 4172 and Rb 4202 from a variety of silicate minerals, using the arcing procedure of Sec. 5–4. CN emission is virtually absent.

Exposure need not be timed so critically when lines of short wavelength are used but should not in any case be continued much past completion of alkali metal distillation

TABLE 6–2

ANALYSIS AND INTERNAL STANDARD LINES

| Element | Wave-length A | Ex. Pot. (low-high) volts | Element | Wave-length A | Ex. Pot. (low-high) volts |
|---|---|---|---|---|---|
| In | 3256·09 | —3·01 | In | 4101·77 | 0·0—3·01 |
| | 3258·56 | | | | |
| | (3039·36 | —3·9) | | | |
| Pb | 2833·07 | 0·0—4·4 | Pb | 4057·82 | 1·3—4·36 |
| Ga | 2943·64 | 0·1—4·3 | Ga | 4172·06 | 0·2—3·06 |
| Ag | 3280·68 | 0·0—3·75 | | | |
| | 3382·89 | 0·0—3·15 | | | |
| Cu | 3247·54 | 0·0—3·8 | | | |
| | 3273·96 | 0·0—3·77 | | | |
| Zn | 3345·02 | 4·1—7·75 | | | |
| Sn | 3175·02 | 0·4—4·31 | | | |
| | 3262·33 | 1·1—4·85 | | | |
| Ge | 2651·18 | 0·1—4·8 | | | |
| | 3039·06 | 0·9—4·94 | Tl | 3775·72 | 0·0—3·27 |
| | | | | 5350·46 | 1·0—3·27 |

because of background addition. A general advantage of the use of the short wavelength group is that it includes a larger number of elements. Moreover, almost all photographic emulsions have a comparatively uniform contrast up to about 3300A whereas some plates show a maximum $\gamma$ vs. $\lambda$ change from 3400 to 4400A, in which case allowance must be made for varying contrast, as described by MALPICA (1940) and NACHTRIEB (1950) for example. In the Cabot Spectrographic Laboratory it is common practice to use plates which have a comparatively uniform contrast over most of their usable range; for example, Kodak spectroscopic No. 103-O or Spectrum Analysis No. 2.

Tl 5850 falls outside the general wavelength range discussed above and is referred to again later (Sec. 6–4).

The replicate determinations of Table 6–3 provide an idea of reproducibility. Determinations of Ga, Pb and Cu are with an internal standard and Tl without.

TABLE 6–3

SOME REPLICATE DETERMINATIONS (IN PPM) OF GA, PB AND CU (GRANITE AND DIABASE) AND TL (FELDSPAR)

| Ga | | Pb | | Cu | | Tl |
|---|---|---|---|---|---|---|
| gr. | diab. | gr. | diab. | gr. | diab. | potash feldspar |
| 19 | 20 | 33 | 7·5 | 3·3 | 48 | 4·7 |
| — | 20 | 24 | 7·0 | 7·2 | 43 | 4·0 |
| 19 | 21 | 26 | 7·5 | 4·3 | 43 | 3·6 |
| 19 | 23 | 25 | 7·2 | 5·1 | 43 | 3·6 |
| — | 21 | 26 | 7·1 | 5·4 | 46 | 3·9 |
| 17·5 | 18 | 25 | 7·0 | 3·7 | 42 | 4·4 |
| 18·5 | 21 | 28 | 6·5 | 4·5 | 38 | 5·2 |
| 19 | 20 | 27 | 7·6 | 5·3 | 47 | 3·9 |
| 20 | 17 | 24 | 7·6 | 4·2 | 42 | — |
| 17·5 | 18·5 | 24 | 7·6 | 4·9 | 40 | — |
| Av. | | | | | | |
| 19 | 19 | 26 | 7·2 | 5·0 | 44 | 4·2 |
| 5% | 8% | 11% | 5%[1] | 30%[2] | 6% | ~15% |

[1] This reproducibility is better than is usual for diabase.
[2] Reproducibility poor at low concentrations.

General reproducibility is further illustrated by the duplicate determinations (Table 6–4) of gallium and copper in nine specimens of diabase from the Lake Nipigon area, Ontario.

## Sec. 6–4. Notes on thallium and some other elements

*Thallium*

Thallium is one of the rarest elements of the volatile group, but because of its high spectral sensitivity it is quite often detectable. Its association with potassium is close in all silicates and as a result thallium is usually detectable in all potassium minerals and occasionally in rocks (igneous and sedimentary) enriched in potassium. These comments apply essentially to the general procedure discussed above because

TABLE 6–4

DUPLICATE DETERMINATIONS OF GALLIUM AND COPPER IN LAKE NIPIGON DIABASE

| | Ga | | | Cu | | |
|---|---|---|---|---|---|---|
| R 1691 | 13, 11 | 12 | Av. | 88, 84 | 86 | Av. |
| „ 1692 | 12, 12 | 12 | „ | 96, 90 | 93 | „ |
| „ 1693 | 11, 13 | 12 | „ | 98, 102 | 100 | „ |
| R 1694 | 11, 12 | 11·5 | Av. | 86, 94 | 90 | Av. |
| „ 1695 | 15, 11 | 12·5 | „ | 87, 95 | 91 | „ |
| „ 1696 | 15, 13 | 14 | „ | 71, 67 | 69 | „ |
| „ 1697 | 12, 16 | 14 | „ | 74, 74 | 74 | „ |
| „ 1698 | 17, 12 | 14·5 | „ | 74, 66 | 70 | „ |
| „ 1699 | 16, 16 | 16 | „ | 85, 79 | 82 | „ |

higher sensitivity may be attained as described below and particularly in Sec. 6–5. The analyst should bear in mind that the geochemical distribution of thallium contrasts with that of uniformly distributed gallium and large variations of concentration are found. Such a variation is about 200-fold in potassium minerals, namely, from a ppm or so in some feldspar to a maximum of 100–200 ppm in lepidolite.

The analyst must exercise particular care when using Tl 3775. Not only is it located well within CN 3883, but it coincides almost exactly with a rotational component of this band. Thallium is considerably more volatile than the alkali metals, and as it usually completes its distillation within one-half to two-thirds of the time required to completely distil them exposure may be shortened accordingly, so as to ensure that CN emission is kept at an absolute minimum.

CANNEY (1952) sought to investigate the distribution of thallium in shales (cf. Sec. 5–9). As its concentration in these materials is usually a little less than that detectable by means of the general method, a modified procedure was attempted. The larger $\frac{3}{16}$″ anode was used in place of the $\frac{1}{8}$″ anode so as to accommodate a larger quantity of sample and thereby improve

sensitivity; excitation was otherwise exactly as in Sec. 5–9 and, as in the example of rubidium and cesium, potassium (K 4047) served as a variable internal standard. Tl 5350 is slightly more sensitive than Tl 3775 and was chosen and recorded on Eastman 103-J plates.

Emission of Tl 5350 is very faint from shale and only a very minimum of general background could therefore be tolerated; consequently a large grating spectrograph (2·5 A/mm linear dispersion) was chosen. Apart from general background, Tl 5350 may have interference from three sources, namely, Ca 5349·47 and occasionally Ti 5351·08 and band emission from CaF 5291. Tl 5350, Ca 5349 and Ti 5351 are cleanly resolved at a dispersion of 2·5 A/mm, but halation interference from Ca 4349 becomes serious at moderate or high concentrations of calcium. This can usually be held to an insignificant minimum provided exposure is not carried past the main phase of alkali metal distillation. Excessive CaF 5291 emission is encountered on rare occasions, usually in phosphatic shales because of their fluorine enrichment.

*Other elements*

Gallium is easily detectable in almost all silicates, except those that are aluminium poor, such as dunite. Lead is usually detectable in feldspar, some mica and most granite; its concentration variation is quite extreme (AHRENS, 1954). In basalt, diabase and gabbro, its concentration usually borders on its detection limit. Copper is easily detected in mafic and ultramafic rocks, but its concentration may sometimes approach its detection limit in feldspar and granite: under these conditions, possible interference from electrode copper may become serious and should not be overlooked. The same comment sometimes applies to silver. Its concentration is usually undetectably low in rocks, except in mafics where it is sometimes definitely evident; the level is so low, however, that electrode impurity can be serious. Tin is sometimes detectable in granite and invariably in mica. Its abundance and distribution in this mineral has been investigated by AHRENS and LIEBENBERG (1950) who used a method similar to the general arcing procedure discussed in this chapter. Synthetic standards were avoided by using mixtures of cassiterite and a muscovite free from detectable tin.

Mica is a principal host mineral to several other elements of the volatile group, in addition to tin, some of which are not usually detectable in any other silicate minerals ; namely, In, Tl, Zn and Ag.

## Sec. 6–5. Highly sensitive procedures for the volatile elements

Fractional distillation of the volatile elements from a comparatively large quantity of sample may be used to lower their detection limits. The detection limit of any element can of course be lowered by direct arcing of a large amount of sample, but practical difficulties soon impose a limit on the quantity which can be arced successfully.

The first application of fractional distillation of volatile elements from a comparatively large quantity of sample is found in the investigations of ROSE and BÖSE (1935) and BÖSE (1936) on the analysis of condensed sublimates. See also VESELOVSKII (1941). PREUSS (1940) has developed a more direct procedure in which the sample (1–3 gm) is heated in an auxiliary furnace, from which, with the help of a stream of $CO_2$, A or $N_2$, vapours of the volatile elements pass into a hollow electrode and are excited as they flow into the discharge. The detection limits of several volatile elements is usually lowered to about $\times$ 1/100 of that normally detectable.

The general idea of the use of a furnace has been used for two similar procedures, which because of their simplicity and ease of operation, may be co-ordinated into the analytical scheme of the book as a whole. Each employs the principle of the double-arc—one discharge to heat the furnace electrode and the other to excite the escaping vapour. The idea of the double-arc originated at a discussion between R. W. MANNKOPFF, the late J. B. HALE and the author at Harpenden (England) in 1948, from whence it was passed on to O. I. JOENSUU and D. M. SHAW, working at Chicago, and K. WEDEPOHL working at Göttingen, who developed the two methods (SHAW, JOENSUU, AHRENS, 1950 ; and WEDEPOHL, 1958) described below. According to WEDEPOHL (1958) MANNKOPFF had already in 1947 referred to the double-arc. In any event, the development of the two versions of the double-arc principle has greatly facilitated geochemical

investigations of the distribution of some of the volatile elements.

The method described by SHAW, JOENSUU and AHRENS (1950) has been applied to the determination of Tl (SHAW, 1952b), In (SHAW, 1952a) and Pb (data as yet unpublished) in a large variety of geological materials, most of them silicates. Plate 3 shows the electrode and furnace assembly and Fig. 6.2 details of the dimensions of the graphite furnace. Because of the fact that a comparatively large area of the anode tip is heated to incandescence in an arc discharge, the base of the furnace is made the anode and its top (the cap—see Fig. 6.2) the cathode; the lower electrode ($\frac{3}{16}$" graphite) is therefore negative and the upper ($\frac{1}{8}$" graphite), positive. The lower arc has a comparatively short length of 2 mm; the length of the upper arc is 9 mm. Both discharges are run at 7 amp and the first 90 seconds of excitation are exposed.

At the commencement of an analysis CN emission is likely to be intense. Radiation emitted during this phase, usually of a few seconds duration, may be screened; alternatively, CN emission may be reduced by impregnating the furnace cap with the salt of an alkali metal, lithium carbonate for example. The cap is saturated with a concentrated salt solution and dried rapidly on a hot plate.

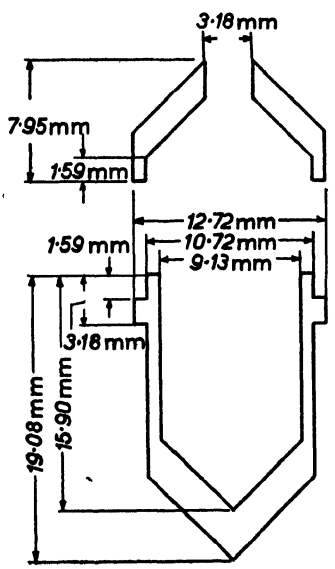



Fig. 6.2. Double-arc furnace electrode (after SHAW, JOENSUU and AHRENS, 1950).

The total charge in the furnace is usually 560 mg and is composed of three parts sample and one part of a flux of one part $NH_4Cl$ and three parts $Li_2CO_3$. Tin is used as the internal standard and is incorporated into the flux as $SnO_2$ (1/50). The presence of the flux improves sensitivity and decreases CN emission. SHAW (1952a and 1952b) reports detection limits of 0·05 ppm Tl and 0·02 ppm In, when using Tl 5350 and In 4511, respectively. Such detection limits are adequate for the determination of thallium and indium in a large proportion of

naturally-occurring silicates. The discharge is, however, fairly erratic and despite the use of internal standards (analysis pairs, $\frac{\text{Tl } 5350}{\text{Sn } 4525}$ and $\frac{\text{In } 4511}{\text{Sn } 4525}$), the relative deviation is given as 30%*.

The procedure described by WEDEPOHL (1953) has been used to determine zinc in many naturally occurring silicates, as well as a few other geological materials. Normally zinc has a rather poor detection limit of a 100 ppm or so, which is unsatisfactory except for a few silicate minerals such as biotite. The detection limit may, however, be lowered by about $\times$ 1/100 to $\sim$1 ppm by using the double-arc method described by WEDEPOHL.

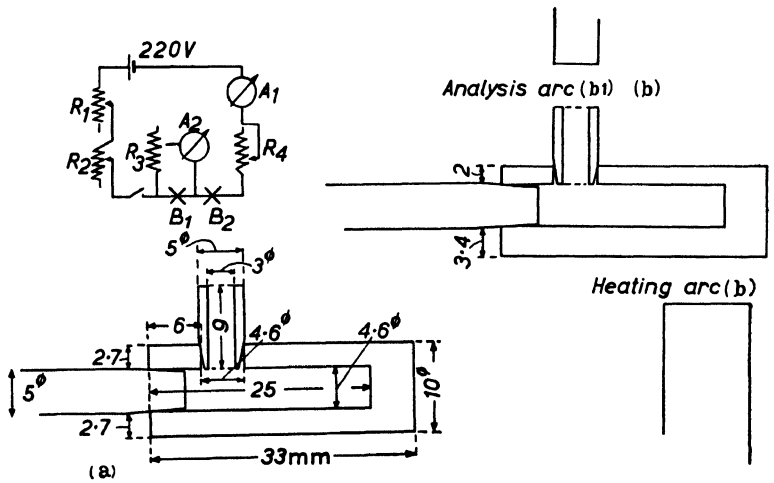



Fig. 6.3. Double-arc furnace electrode and circuit (after WEDEPOHL, 1953).

Plate 4 shows the furnace and electrode assembly, and Fig. 6.3 gives details of their dimensions. Unlike the previous method, a horizontal furnace is used. The lower arc is displaced with respect to the upper one and this arrangement is claimed to decrease CN emission. The lower discharge is run at 10·5 amp, the upper at 6–7 amp, and, under these conditions, about five minutes are required to distil zinc

* As this means a fairly large dispersion, the statement of precision is not quantitatively satisfactory; see Chap. 4.

completely from the charge (usually 300 mg). Polarity is the same as in the previous example. Independent regulation of each arc is achieved by means of a circuit shown diagrammatically in Fig. 6.8.

WEDEPOHL chose cadmium, added as CdS (0·13%) as the internal standard and either $\frac{\text{Zn } 3345}{\text{Cd } 3261}$ or $\frac{\text{Zn } 3345}{\text{Cd } 3252}$ as the analysis pair. Precision appears to be about the same as in the previous procedure.

The double-arc procedures can undoubtedly be applied to the determination of other volatile elements. There is room evidently for further research on improving the design and operating conditions of this general procedure so as to develop a method which will combine utmost sensitivity with a higher standard of precision.

CHAPTER 7

# THE INVOLATILE ELEMENTS

## Sec. 7–1. Introduction

No very sharp dividing line can be drawn between those elements which have been classed as volatile and those which will be classed as involatile. The latter group may be taken to include all elements which emit their maximum line intensity after the main phase of alkali metal distillation has subsided. These elements are V, Ni, Co, Zr, Cr, Y, Sc, La, Nd, Sr, Ba, Mo, B, Be, Ti, Ca, Fe, Mg, Si and Mn. The last five are discussed separately in Chap. 9 ; titanium is discussed both in this chapter and Chap. 9.

Elements placed in the involatile group differ considerably in their distillation rates. Iron, cobalt, manganese and nickel are among the most volatile of the group and could be classed as medium-volatile, whereas scandium, the rare earths and zirconium in particular, are characteristically involatile. As a result, highest accuracy is probably attained by using two or perhaps three internal standards. Thus, for example, SCOTT (1945 and 1946) has demonstrated the excellence of iron as an internal standard for cobalt and for optimum accuracy, therefore, iron could be used as a variable internal standard for the determination of cobalt, and possibly a few other elements, as has been done by PIERUCCINI (1946 a and b). Our experience has shown that although some accuracy is lost by using one internal standard for all elements of the group it is nevertheless satisfactory for most purposes.

## Sec. 7–2. Choice of an internal standard

BRAY (1942) has described the use of palladium as an internal standard for silicate rock and mineral analysis. He chose cathode layer excitation and used this internal standard for a wide variety of elements. In the procedure discussed here anode excitation replaces cathode layer excitation ; palladium

is retained as the internal standard but its use is restricted to elements of the involatile group.

An examination of distillation behaviour, when using conditions of excitation discussed in Sec. 7–3 shows that although the distillation *trend* of palladium is highly satisfactory for many elements, intensity variations of palladium lines within the trend is rarely sympathetic with those of the analysis lines. Apparently $PdCl_2$ does not participate properly in the general electrode reaction and distils more or less as a vapour phase of its own. The behaviour of palladium as an internal standard is in this respect not wholly satisfactory and its efficacy does not compare with that of the inter-alkali metal internal standardization, for example. Nevertheless, despite comparatively poor internal standardization satisfactory accuracy may be achieved (Table 7–1) because the arc burn is smooth. As a result, the use of other internal standards has not been attempted although the possibility of improving accuracy in this way is not overlooked.

Palladium is an element of extreme rarity ($\sim$0·01 ppm in surface igneous rocks) and although very little is known about its geochemical distribution, it is highly unlikely that much greater concentrations are ever present in the naturally-occurring silicates. Such a magnitude is insignificantly low when compared with the amount of added palladium which corresponds to 0·02% in the mixture that is arced.

## Sec. 7–3. Working details, lines and precision

If the internal standard is to be used, it is added (one part) to one thousand parts of powdered carbon; two parts of this mixture are added to one part sample. (Without the internal standard the mixture is simply two parts carbon and one of sample.) Either a $\frac{3}{16}$″ or a $\frac{1}{8}$″ anode may be used. The larger size is preferable if a high sensitivity is sought on a comparatively slow spectrograph, but may produce excessive background on a fast spectrograph in which case the $\frac{1}{8}$″ anode is preferable. A 7 amp current is used for both. Distillation from the $\frac{1}{8}$″ anode is usually complete in about 1 minute whereas 4–5 minutes are required for the $\frac{3}{16}$″ anode. Complete distillation is easily determined by a sudden change in the appearance of the discharge. Most silicates arc smoothly

when using these conditions and as a result reproducibility is invariably good. As many elements are usually determined line intensity is likely to vary widely and a large range in transmission must be used.

Carbon is added for three principal reasons : first, selective distillation of members of the involatile group of elements is decreased and thereby the need for several internal standards is reduced ; second, the presence of carbon in excess usually improves the burning quality of the discharge, and third, very

TABLE 7–1

INTERNAL STANDARD AND ANALYSIS LINES

| Element | Wavelength | Excitation potential (volts) low | | high |
|---|---|---|---|---|
| Pd | 3481·152 | 1·25 | — | 4·78 |
| | 3242·703 | 0·81 | — | 4·62 |
| Ba | 4934·086 (II) | 0·0 | — | 2·50 |
| | 4554·042 „ | 0·0 | — | 2·73 |
| Co | 3453·51 | 0·4 | — | 4·00 |
| | 3405·12 | 0·4 | — | 4·05 |
| Cr | 4289·721 | 0·0 | — | 2·88 |
| | 4274·803 | 0·0 | — | 2·89 |
| | 4254·346 | 0·0 | — | 2·90 |
| La | 4333·734 (II) | 0·2 | — | 3·02 |
| | (3988·518) „ | 0·4 | — | 3·50 |
| | (3949·106) „ | 0·4 | — | 3·53 |
| | 3337·488 „ | 0·4 | — | 4·10 |
| Mo | 3170·347 | 0·0 | — | 3·89 |
| Nd | 4303·573 (II) | 0·0 | — | 2·87 |
| | (4247·367) „ | 0·0 | — | 2·91 |
| | (4061·085) „ | 0·5 | — | 3·50 |
| | (4012·250) „ | 0·6 | — | 3·70 |
| Ni | 3414·765 | 0·03 | — | 3·64 |
| Sc | 4246·829 (II) | 0·3 | — | 3·22 |
| | (4023·688) | 0·0 | — | 3·09 |
| | (3911·810) | 0·0 | — | 3·18 |
| Sr | 4607·331 | 0·0 | — | 2·68 |
| V | 4384·722 | 0·29 | — | 3·10 |
| | 4379·238 | 0·3 | — | 3·12 |
| | 3185·896 | 0·1 | — | 3·94 |
| Y | 4374·935 (II) | 0·2 | — | 3·51 |
| | 3710·290 „ | 0·3 | — | 3·23 |
| | 3242·280 „ | 0·2 | — | 3·99 |
| Zr | 3438·23 (II) | 0·1 | — | 3·68 |
| | 3391·975 „ | 0·2 | — | 3·80 |

nearly complete distillation of all elements, particularly those which are refractory, zirconium for example, is assured. Analysts are well aware of the fact that a residual spectrum of zirconium is frequently observable when a supposedly exhausted electrode is arced. The intensity of this residual zirconium spectrum may amount to from 5–10% of the total intensity. It is doubtful, however, whether continued arcing past apparently complete distillation should be recommended because of the addition of background.

Table 7–1 lists recommended lines. It should be emphasized that lines other than those listed may be used. These lines have been used at a large dispersion (2·5 A/mm) and some may not be usable at smaller dispersion—for example Nd 4303 and La 4333—in which case others should be attempted. Most elements of the involatile group have, in any case, a fairly large number of lines of about equal sensitivity. The sensitive lines of boron (B 2497·733 and B 2496·778) fall outside the general wavelength range covered by lines of the other elements and its determination usually involves a separate operation.

TABLE 7–2

SOME TYPICAL REPLICATE DETERMINATIONS (PPM) IN GRANITE AND DIABASE

| | Zr | | Co | Sc |
|---|---|---|---|---|
| | gr. | diab. | diab. | gr. |
| | 310 | 105 | 26 | 4·4 |
| | 305 | 105 | 29 | 3·5 |
| | 300 | 95 | 27·5 | 4·0 |
| | 300 | 105 | 26 | 3·9 |
| | 270 | 90 | 22 | 3·7 |
| | 280 | 105 | 27 | 3·6 |
| | 290 | 105 | 25 | 4·4 |
| | 290 | 95 | 27 | 3·4 |
| | 300 | 95 | 21 | 3·9 |
| | 280 | 90 | 27·5 | 4·2 |
| Av. | 290 | 100 | 26 | 3·9 |
| C | 4% | 8% | 11% | 8% |

As noted elsewhere (Chap. 2) no serious decrease in accuracy is caused by using fairly widely separated internal standard and analysis lines. As a result Pd 3242 or Pd 3481 may be used with all lines listed in Table 7–1.

Reproducibility is illustrated by typical replicate determinations given in Table 7–2. Relative deviations range from ~4–~11%.

The reproducibility of the zirconium and scandium determinations are good despite the fact that Zr 3392 and Sc 4247 are ion lines. This should not be taken to mean that the use of an atom-ion line pair is recommended as general practice. Reproducibility happens to be high here only because the discharge is smooth; under certain conditions, however (AHRENS, 1950, p. 87), extreme inaccuracy can sometimes be caused by using atom-ion line pairs.

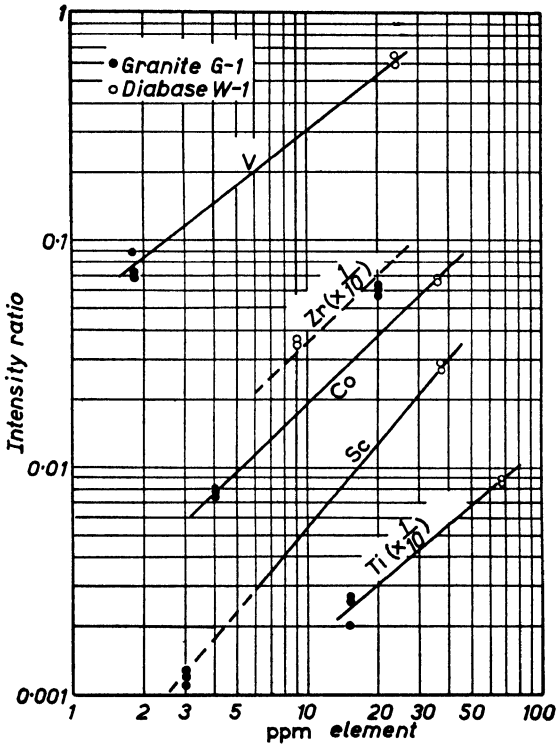



Fig. 7.1. Two-point working curves using G-1 and W-1 as standards.

YOUNG (1953) has applied the involatile procedure to an investigation of the geochemistry of several elements in ocean bottom cores. As the composition of these materials is similar in a general way to that of the standard rocks G-1 and W-1, they were chosen as standards for the construction of working curves. Some examples of two-point working curves (Co, Sc, V, Ti—see below—and Zr) are shown in Fig. 7.1. All are satisfactory with the exception of that of zirconium where the slope of a line drawn through the plotted pairs of points is exceptionally small. The curves for V, Co, Sc and Ti support the validity of the recommended values of Table 3–3, whereas that for zirconium indicates a need for some revision of either or both G-1 and W-1 values.

## Sec. 7–4. Note on titanium

Titanium is neither a typical major constituent element nor a really rare one. It is quite often determined in a routine chemical analysis but as titanium can in any case be determined together with the involatile elements, with an accuracy comparable to that of chemical methods at moderate concentrations and surpassing them at low concentrations, it may be more satisfactory to determine titanium spectrochemically.

TABLE 7–3

SOME TYPICAL DETERMINATIONS (EACH IN DUPLICATE) OF TI AND V IN SWISS ROCKS (AFTER H. P. EUGSTER)

| No. | Description | % Ti | % V |
|---|---|---|---|
| 544 | Quartzite ... ... ... ... | 0·060 | 0·058 |
| | (with 5% graphite) ... ... | 0·054 | 0·060 |
| 552 | Quartzite ... ... ... ... | 0·095 | 0·016 |
| | (with 5% graphite) ... ... | 0·095 | 0·016 |
| 714 | Phyllite ... ... ... ... | 0·29 | 0·0055 |
| | (with 40% sericite) ... ... | 0·33 | 0·0051 |
| 989 | Phyllite ... ... ... ... | 0·56 | 0·014 |
| | (with 40% sericite) ... ... | 0·59 | 0·014 |
| 1084 | Phyllite ... ... ... ... | 0·24 | 0·17 |
| | (with graphite and sericite) ... | 0·27 | 0·15 |

It emits many sensitive lines in the ultraviolet and the analyst has therefore considerable freedom of choice.

EUGSTER (1954) chose the pair $\frac{\text{Ti } 3241{\cdot}986}{\text{Pd } 3242{\cdot}703}$ to determine titanium in a suite of Swiss metamorphic rocks. G-1, W-1 and a mixture of these two rocks served as standards. Trial replicate determinations in each showed satisfactory reproducibility and this is borne out by the duplicate determinations given in Table 7–3. Vanadium determinations which were made at the same time are included. Their reproducibility is also satisfactory over the whole range of investigated concentrations.

## Sec. 7–5. The determination of boron

The presence of boron impurity in electrode carbon (or graphite) has in the past led to the general use of copper electrodes. The data of Table 2–1 show, however, that high-grade graphite of the National Carbon Co., and of the United Carbon Products Co., is free from detectable boron and H. P. EUGSTER, working in the Cabot Spectrographic Laboratory, has found this to apply also to high-grade carbon from the National Carbon Co. As a result, carbon electrodes were chosen for an investigation on the distribution of boron in Swiss metamorphic rocks. The general arcing procedure which was used is the same as described in Sec. 7–2 ; some details follow.

Beryllium, added as beryl, serves as the internal standard ; one part is added to 99 parts carbon and two parts of this mixture are mixed with one part of sample. Both B 2497 and B 2498 may serve as analysis lines, although B 2498 is in general more satisfactory ; Be 2348 is the internal standard line.

Although no interference from electrode boron was ever observed, SiO band emission is sometimes troublesome in silicates as one component of a sequence which straddles λ 2500 coincides exactly with B 2497. Provided SiO emission is not excessive and B 2497 not extremely faint, a reasonably satisfactory correction may be made as follows,

$$\text{I B } 2497{\cdot}73 = \text{I B } 2497{\cdot}73 + \text{SiO } 2497{\cdot}73 - \text{I SiO } 2497{\cdot}56$$

SiO 2497·56 is a component neighbouring SiO 2497·78 and of equal intensity.

A detection limit of 2·5 ppm may be reached; this was satisfactory for the particular investigation as concentrations were usually higher and reached as much as 180 ppm. Reproducibility appears to be highly satisfactory. Standards may be prepared by mixing borax with a synthetic base (Sec. 3–8).

## Sec. 7–6. Notes on sundry involatile elements

*Chromium*

Shows very extreme variations of concentration in specific rock types (see AHRENS, 1954). Consequently a wide range of transmission is usually necessary and several lines may have to be used.

*Strontium and barium*

The most sensitive lines are intensely emitted from a large proportion of silicates and are not measurable unless strongly sectored.

*Yttrium, lanthanum and neodymium*

For discussion of possible line and CN interference, see AHRENS (1950, Chap. 16). SMITH and WIGGINS (1949) should be consulted for a discussion of the most sensitive lines of these and other rare earths.

*Some other elements*

Zirconium is usually easily detectable in all silicate rocks with the exception of some ultramafics. Scandium is also detectable in nearly all silicates, although its concentration may be below its detection limit in some acid rocks. This comment applies equally well to nickel and cobalt. Molybdenum is often at the threshold of its detection limit.

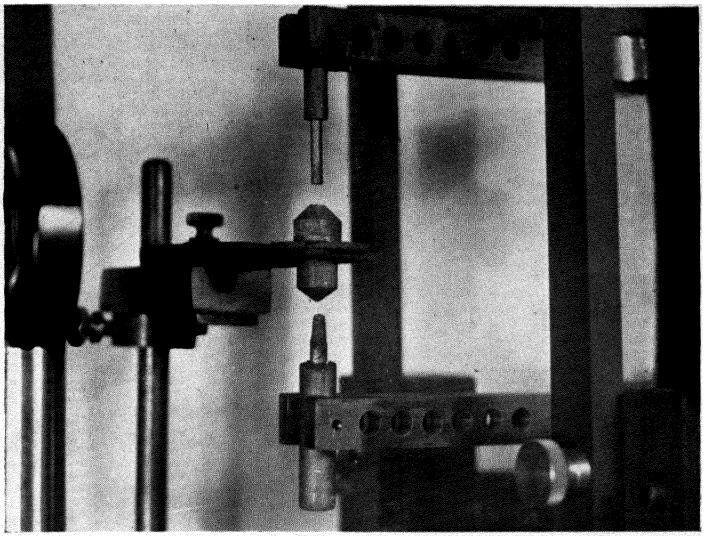
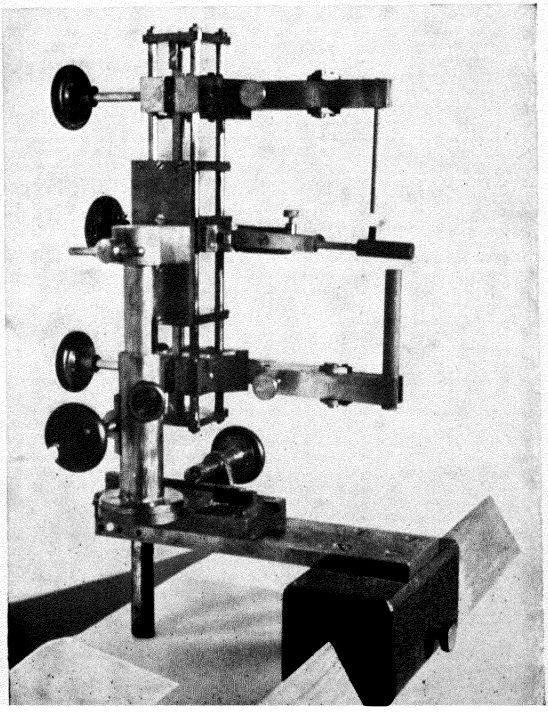


*Plate* 3. Double-arc assembly, as described by SHAW, JOENSUU and AHRENS (1950) for the determination of very low concentrations of some volatile elements. (See Sec. 6–5.)

*Plate* 4. Double-arc assembly, as described by WEDEPOHL (1953) for the determination of low concentrations of volatile elements. (See Sec. 6–5.)



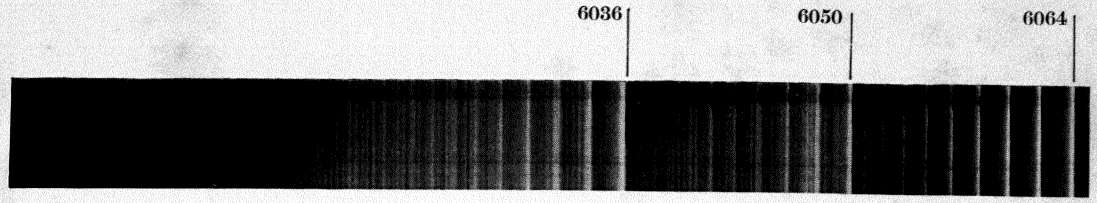



*Plate* 6. Structure of the orange sequence of CaF as recorded on a grating spectrograph. Masking interference from CaO emission (see text) is absent as sample of pure $CaF_2$ was arced.

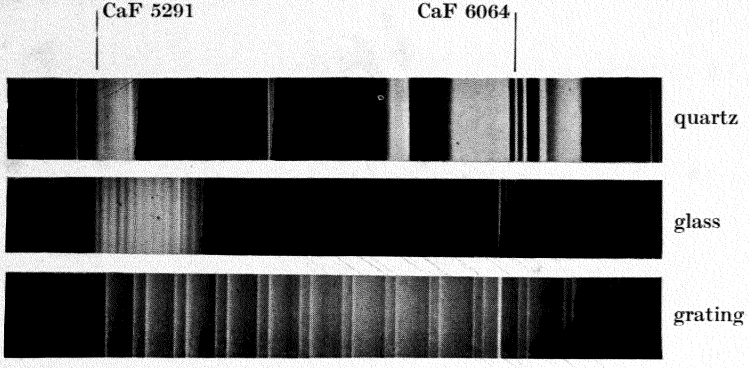



*Plate* 5. Spectra of CaF 5291 as recorded with quartz, glass and grating optics. The structure of CaF 6064 (quartz optics) may be contrasted with *Plate* 6.

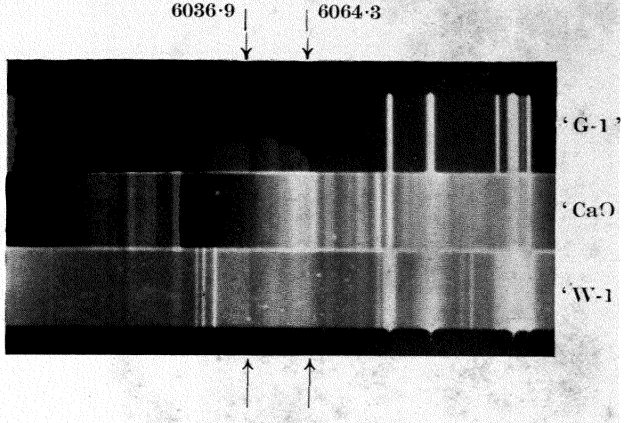



*Plate* 7. Comparative spectra of diabase W-I (·018% F) granite G-I (·076% F) and CaO. All heads (λ 6036, 6050 and 6064) of CaF 6036 clear in G-I, whereas only the head λ 6036 is distinct in W-I. The others are excessively masked by CaO emission—ru middle spectrum. Recorded on Large glass (Hilger) spectrograph, using He atmosphere for W-I and G-I. From SERAPHIM, Ph.D. thesis (1951).

CHAPTER 8

# FLUORINE

## Sec. 8–1. Introduction

FLUORINE is not normally determined in a routine chemical analysis of silicates unless requested, in which case some modification of the WILLARD and WINTER (1931) procedure is usually used. The method has recently been applied quite extensively by KORITNIG (1950), for example, who reports a detection limit of about 10 ppm. This is lower than that attainable by DC arc methods*, by means of which 100–200 ppm (Sec. 8–5) or ~50 ppm (Sec. 8–6) may be reached. The fluorine content of many silicates is, however, higher than these detection limit concentrations and spectrochemical methods are consequently of value because of their speed. Moreover, calculations by SERAPHIM (1951) indicate that the precision ($C = \sim 15$–$20\%$) attainable by the spectrochemical methods is similar to that achieved chemically by KORITNIG.

## Sec. 8–2. Structures of CaF bands

Spectrochemical methods of detecting and determining fluorine have been used to some extent at least ever since RYDE and YATES (1926) discussed the intense and sensitive emission of CaF 5291 from a DC arc. See AHRENS (1950, Chap. 14) for bibliography and also for a brief discussion on the possible use of SrF emission.

Plate 5 shows the appearance of CaF 5291 as recorded on a large grating spectrograph (2·5 A/mm), a large glass spectrograph and a quartz spectrograph. Components of the sequence are fully resolved at 2·5 A/mm dispersion and band structure is clear. Band components are barely resolved in the glass spectrogram and not at all in the quartz spectrogram. Maximum intensity of emission develops somewhat inward from the band head.

* An extremely low detection limit may be reached by using a hollow cathode discharge, as described by MCNALLY, HARRISON and ROWE, *J. Opt. Soc. Amer.*, 37, 93 (1947).

The structure of CaF 6086, as recorded on a grating spectrograph, is shown in Plate 6. Unlike CaF 5291, it is degraded toward the blue; distinct heads appear at λλ 6086·92, 6050·78 and 6064·4A. The 6086 and 6050 heads are about 5–6 times more intense than the most intense components of CaF 5291 (SERAPHIM, 1951) and are therefore the most sensitive bands emitted by CaF. CaF 5291 has usually been regarded as the most sensitive band and earlier recognition of the greater sensitivity of CaF 6086 and CaF 6050 is undoubtedly due to interference from ubiquitous CaO orange bands. CaO interference is at a minimum in Plate 6 and may be compared with the varying degrees of interference shown in Plate 7. The use of CaF 6086 in the presence of CaO interference is discussed in Sec. 8–6.

Table 8–1 gives the wavelengths of individual components and heads of the CaF 5291 (green) and 6086 (orange) sequences.

TABLE 8–1

WAVELENGTHS OF SOME BAND COMPONENTS

| (Green system) | (Orange system) (principal heads only) |
|---|---|
| 5291·00 A | 6086·91 A |
| 5292·86 ,, | 6064·40 ,, |
| 5296·85 ,, | 6050·78 ,, |
| 5298·62 ,, | 6086·92 ,, |
| 5302·73 ,, | |
| 5304·44 ,, | |
| 5308·68 ,, | |
| 5310·32 ,, | |
| 5314·69 ,, | |
| 5316·24 ,, | |
| 5320·72 ,, | |
| 5326·86 ,, | |

## Sec. 8–3. Some properties of CaF bands and a few general considerations on their use

A comparatively cool arc is most conducive to the development of maximum emission from CaF bands because they excite easily (excitation potential = 2–3 volts) and dissociate easily (heat of dissociation = ~3·3 volts—JOHNSON, 1928). As a result, CaF emission is probably at a maximum in the flamy fringe of the arc and at a minimum in the core of the

discharge : this is similar to emission from AlO, but not from CN, which shows the exact reverse.

The alkali metals (K, Rb and Cs in particular) produce an ideal discharge in this respect when present at concentrations greater than about 1–5%, but because they suppress the distillation of calcium and not of fluorine, their presence can completely spoil a determination. This effect of the alkali metals may be usually, though by no means always, overcome by mixing the sample with carbon powder.

Calcium should, of course, be present in abundant supply and if necessary may be added to the sample in the form of any one of its compounds. It is quite common practice to add both carbon powder and a calcium compound to the specimen to ensure an excess of calcium atoms (Sec. 8–5).

## Sec. 8–4. Choice of standards and photographic plate

As the intensity of CaF band emission is fairly sensitive to matrix changes, standards should be chosen with considerable care.

Two sets of standards were used by SERAPHIM (1951) for an investigation on the geochemistry of fluorine. The first was prepared by mixing U.S. Bureau of Standards (No. 120) phosphate rock (3·8% F) with varying proportions of standard diabase W-1 ; the second set was prepared in the same way except that amphibole with 2·1% fluorine replaced phosphate rock. Working curves, prepared by relating the intensity of a band component to the fluorine concentration, showed no displacement, and consequently either set of standards seems satisfactory. W-1 contains about 150–200 ppm F, which is approximately the detection limit of the method described in Sec. 8–5.

Mixtures of granite G-1 (0·074% F) and diabase W-1 are useful standards for the determination of fluorine in a fairly wide variety of igneous rocks.

The choice of an appropriate photographic plate is more critical than is usual for line spectra, because sensitivity is not particularly good and because the band components are fairly diffuse and tend to merge into background. A combination of maximum sensitivity and high contrast is desirable. Eastman 111-J plates have been used for CaF 5291 and Eastman 1-L for CaF 6036.

## Sec. 8–5. Analytical procedures

A mixture of one part sample and two parts of a 1 : 1 mixture of $CaCO_3$ and carbon powder is satisfactory; an equally satisfactory mixture of one part sample and one part of a 2 : 1 mixture of $CaCO_3$ and carbon powder was used by SERAPHIM (1951). The sample is excited in a $\frac{3}{16}$" carbon anode for 30 seconds at 7 amp. CaF emission is usually exhausted completely by this time, and in any case exposure should not be continued because of the need to keep background at a minimum. The presence of added $CaCO_3$ sometimes causes an extrusion of material from the electrode cavity in which case the analysis should be repeated.

The above arcing procedure refers to the use of any CaF band. The specific use of CaF 5291 will be discussed in the rest of this section, whereas a separate procedure, using CaF 6086 in a helium atmosphere, is discussed in Sec. 8–6.

As the reproducibility of a determination is not high (*C* calculates at approximately 15–20%) SERAPHIM (1951) attempted to use an internal standard. Indium compounds gave disappointing results, but some improvement was achieved by using CaO 5488, a component of the CaO orange band as an internal standard for CaF 5291. (See Fig. 8.1.) The assumption must of course be made that the calcium concentration varies insignificantly from specimen to specimen. The calcium content of most silicate rocks varies from somewhat less than 1% to about 5% and as added calcium

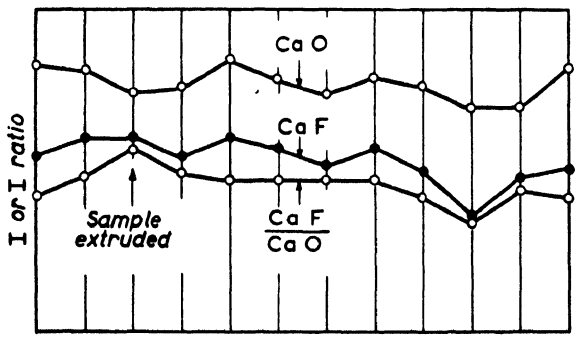



Fig. 8.1. Replicate determinations of CaF 5921 and CaO 5488. CaO 5488 provides some internal standardization and consequently $\frac{\text{CaF } 5291}{\text{CaO } 5488}$ is a little more reproducible than CaF 5291.

is equivalent to 12% of the total charge, variation is from ~18–15% : this is not large and may be ignored for many purposes.

The triplicate determinations of Table 8–2 (after SERAPHIM, 1951) illustrate the scope and reproducibility of the method.

TABLE 8–2

SOME TYPICAL REPLICATE DETERMINATIONS OF F IN VARIOUS MATERIALS (RANGE FROM 0·035 TO 0·55% F)

| | 1 | 2 | 3 | Av. |
|---|---|---|---|---|
| *Hornblende from nepheline syenite, Magnet Cove, Arkansas ... ... | 0·13 | 0·12 | 0·10 | 0·11 |
| Biotite from granite, Idaho Batholith... | 0·45 | 0·60 | 0·60 | 0·55 |
| Basalt from Columbia river ... ... | 0·065 | 0·04 | 0·065 | 0·060 |
| Granite from Westwood Quarry, Westwood, Mass. ... ... ... ... | 0·04 | 0·03 | 0·035 | 0·035 |
| Granite from New Milford Quarry, Milford, New Hampshire ... ... | 0·15 | 0·20 | 0·13 | 0·15 |
| Chatanooga shale, East Kentucky ... | 0·05 | 0·05 | 0·07 | 0·06 |
| Deep-sea core (A 160–8)... ... ... | 0·11 | 0·12 | 0·10 | 0·11 |

A detection limit of about 100–200 ppm may be reached under favourable conditions.

## Sec. 8–6. Use of CaF 6036 in a helium atmosphere

CaO band interference with sensitive CaF 6036 has been noted (Sec. 8–2). Such interference is insignificant in fluorine-rich materials but becomes excessive at low fluorine concentrations. SERAPHIM (1951) investigated the use of a nitrogen atmosphere but found CN emission excessive. Excitation in a helium atmosphere provided considerable improvement over air, because despite the fact that overall emission is feebler in helium, that of CaO is decreased to a far greater extent than CaF. A satisfactory photographic response can be obtained by superimposing three exposures of 60 seconds. Any of the usual chambers can presumably be used, but for simplicity and convenience, the types referred to in Sec. 5–8 are most satisfactory.

* The concentration range in hornblende is large, namely, 0·05–2·5% (see, for example, SERAPHIM, 1951).

Adequate dispersion must be used otherwise interference will remain excessive. Dispersion in a large quartz spectrograph is not sufficient whereas that in a large glass spectrograph and most grating spectrographs is satisfactory.

Plate 7 shows helium atmosphere spectra recorded on a large glass spectrograph. CaF emission from the granite G-1 is clean and free from CaO emission whereas that from diabase W-1 ($\sim$·018% F) shows fairly intense CaO emission and heads $\lambda\lambda$ 6064 and 6050 are obscured. The head, CaF 6036, is, however, quite distinct (some detail is lost in reproduction) and may be used to determine fluorine under these conditions. (CaF 6086 is completely swamped by CaO emission in an air atmosphere.) The determination is a delicate one and the analyst may require some experience before he feels able to report a determination with confidence.

A detection limit of about 40–50 ppm may be reached. Although this 3–4 fold improvement in sensitivity is not large it is significant because the fluorine content of many rocks (basalt and diabase, for example) is only just below the detection limit of the Sec. 8–5 procedure and consequently can usually be determined by excitation in a helium atmosphere.

CHAPTER 9

# THE COMMON ELEMENTS
*other than Na and K*

## Sec. 9–1. Introduction

THE fact that spectrochemical methods of analysis are rapid* and inexpensive is well known and need not be emphasized. It is not surprising, therefore, that the possibility of supplanting some chemical determinations of common elements by spectrochemical determinations has been the cause for much speculation and investigation.

The extent to which quantitative spectrochemical methods might be used for major constituent determinations will hinge largely, though by no means solely, on the comparative precision and accuracy of chemical, spectrochemical and other possible methods. Although accuracy is often a prime consideration, there are many problems and investigations where emphasis is not on accuracy but rather on speed and cost, in which case a spectrochemical method is an obvious choice. Some examples follow.

A spectrochemical method has been used by DENNEN (1951) to investigate the concentration variation of several common elements across igneous rock contacts. Such an investigation usually requires many determinations and as the concentration changes are fairly large, moderate accuracy suffices to bring out the general pattern of behaviour. Although the absolute concentration might not be determined with utmost accuracy, the quality of some ratio determinations (Na/K and K/Rb, for example) is excellent. The fact that the behaviour of several of the rarer constituents may be observed on the same spectrogram† is an added advantage. DENNEN

* Chemical methods of rapid silicate analysis have recently been developed by chemists of the U.S. Geological Survey (see Sec. 9–7).

† The investigator should never overlook the power of a spectrogram as a permanent, quantitative and fairly complete record of the composition of a sample as a whole. For example, PINSON, AHRENS and FRANCK (1953) spectrochemically determined Sc, Sr, Ba and Zr in a suite of 21 chondritic

(data as yet unpublished) has also investigated the concentration variation of several elements, common and rare, in borehole samples from sediments.

A petrologist may find a preliminary reconnaissance of a suite of igneous rocks by spectrochemical methods helpful for selecting a smaller number of samples for careful analysis. Spectrochemical methods are admirably suited for investigating major element–minor element associations (K–Rb–Tl; Ca–Sr–Ba; Al–Ga; Si–Ge, for example) in various environments. A spectrochemical method is also useful for investigating compositional changes in rocks and minerals which have been weathered to different degrees or which have been subject to different grades of metamorphism.

Rock-forming minerals are not always available in sufficient quantity for complete chemical analysis, in which case a spectrochemical method of complete analysis may be found sufficiently accurate for several purposes.

The reader should not infer from the above discussion that accuracy and precision of spectrochemical methods for determining common elements are inferior to chemical methods: a chemical method is decidedly superior for the determination of silicon in all silicate minerals or rocks, but for other constituents no categorical statement can be made.

## Sec. 9–2. A comparison of the precision of classical, chemical and spectrochemical methods of silicate analysis

FAIRBAIRN *et al.* (1951) sought to compare the precision of replicate spectrochemical determinations with various chemical determinations (34 analysts and 25 laboratories) of several elements in granite G-1 and diabase W-1. Some of their conclusions are summarized in Table 9–1. Although sodium and potassium are included in Table 9–1 and also in Fig. 9.1, they are not discussed further in this chapter

meteorites. The spectra of many other elements (common and rare) were recorded at the same time. A glance at the spectra of the meteorites immediately revealed an extraordinary uniformity of composition, a rather vital fact that was hitherto unknown (except for Si and Mg to a lesser extent) despite some 800 or so earlier chemical analyses of chondrites! In fairness, it must at once be pointed out that many analyses were very early indeed and exceptionally poor—so poor in fact that they led to some wholly false conclusions (PINSON, AHRENS and FRANCK, 1953).

because the author is of the opinion that all alkali metals should be determined in a separate procedure (Chap. 5).

TABLE 9–1

CHEMICAL AND SPECTROCHEMICAL PRECISION IN GRANITE G-1 AND DIABASE W-1

| | Concentration (%) High — Low | Chemical precision (C)* | Spectrochemical precision (C) | Remarks |
|---|---|---|---|---|
| $SiO_2$ ... | 70 — 50 | 0·8—0·6 | 3·5 | Chemical method far superior |
| $Al_2O_3$ ... | 15 — 14 | 3—1 | 5·5 | Chemical method superior |
| Fe (total)... | 8 — 1 | 4—9 | 5 | C about the same, but chemical method probably somewhat superior |
| CaO ... | 6·5 — 0·8 | 1—11 | 5 | Chemical method superior in W-1, and spectrochemical method superior in G-1 |
| MgO ... | 7 — 0·4 | 6—10 | 6·5 | As above |
| MnO ... | 0·2 — 0·03 | 15—30 | ~10 | Spectrochemical method superior, particularly in G-1 |
| $TiO_2$ ... | 1·10 — 0·25 | 14—17 | ~5—8 | As above |
| $Na_2O$ ... | 2 — 4 | 6 | 2·5 | Spectrochemical method superior |
| $K_2O$ ... | 0·7 — 5 | 4—7 | 3—5 | Precision comparable |

The chemical data of Table 9–1 are presented graphically (log-log co-ordinates) in Fig. 9.1 which emphasizes the general fact that the accuracy of the routine chemical methods deteriorates with concentration. When it is taken into consideration that several of the elements have been determined gravimetrically, a few colorimetrically and Na + K by the Lawrence-Smith fusion procedure, it is a little short of

* See comments in Sec. 8–1 about the use of C as approximate measure of precision.

amazing to find such a well developed regularity*. This is an example of the power of the geometric scale to bring out the nature of regularities which are otherwise obscured or hidden completely.

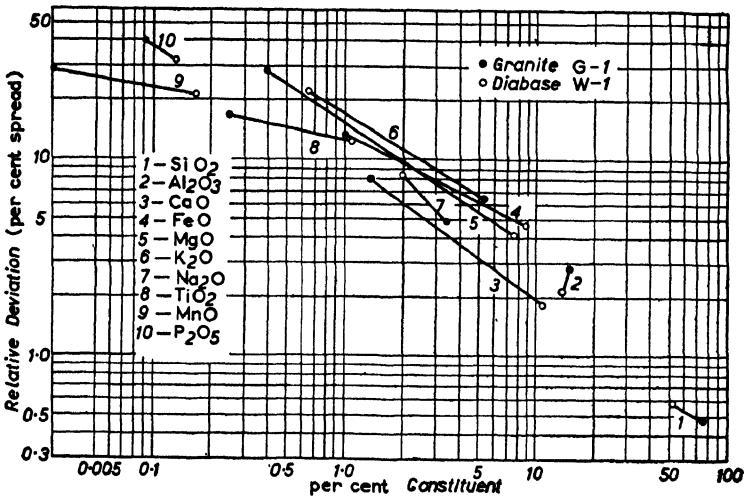



Fig. 9.1. The inverse relationship between the reproducibility of classical methods of chemical analysis and the concentration of a constituent is brought out by using geometric co-ordinate.

Before proceeding further, it should be emphasized that the comparisons of Table 9–1 are not rigorous as they are based on chemical determinations by many analysts in many laboratories and spectrochemical determinations in only one laboratory. Nevertheless, the comparisons serve as a guide. Because of their nature, however, a fairly generous margin in favour of chemical precision should be allowed and if $C$ happens to be about the same, as in the example of iron, this will be understood to mean that chemical precision is superior. It should, however, also be pointed out that the spectrochemical precision refers mainly to a particular procedure (Sec. 9–4) which is not necessarily the most accurate one that

* The reader is cautioned against the possible temptation to extrapolate the regularity of Fig. 9.1 as a means of even approximately assessing the accuracy of chemical determinations of elements at very low determinations; for example, Mo (at ~1 ppm) and Ga (~15 ppm) in igneous rocks. Accurate and specific methods are used for their determination and the use of Fig. 9.1 should be restricted.

is available; in fact, a comparison of $C$ in Table 9–1 with some published values of $C$ for some other methods indicates that some of them are likely to be superior.

Some generalizations concerning choice of method purely on merits of accuracy can be made from Table 9–1 and particularly the regularity in Fig. 9.1. Chemical methods should be used for silica determinations in all silicates; for alumina in basalt, etc.*, granite and all alumino-silicates; for lime in basalt, etc., and lime-rich rocks in general; and for magnesia in basalt, etc., ultramafics and chondrites. If ferrous and ferric iron are required, chemical methods must of course be used and should in any case be used if total iron is high as in ultramafics, basalt, etc., and chondrites. The principal constituents of individual silicate minerals should also be determined chemically, as well as $P_2O_5$ in all rocks and minerals. Spectrochemical methods appear to be superior for the determination of magnesia in granite; alumina in ultramafics and chondrites; lime in granite, ultramafics and chondrites and titanium and manganese in most rocks and some minerals.

## OUTLINES OF METHODS FOR DETERMINING THE COMMON ELEMENTS

### Sec. 9–3. Introduction

The discussions elsewhere in this book are restricted for the most part to methods which have been developed by the author and co-workers. A rather different approach is used in this chapter: certain procedures developed by others and modified in the Cabot Spectrographic Laboratory are described in some detail, but in addition, brief résumés will be given of most known quantitative methods. The main cause for this change is the fact that highest accuracy is often demanded for a common element determination and as the relative merits of each of the many described procedures is not known, reference should be made to them all.

The development of a quantitative method for determining common elements is usually approached in a way different

* Diabase and gabbro.

from that of a method for determining elements at low concentrations. A generally satisfactory method for determining low concentrations must be highly sensitive, and in achieving this, accuracy might have to be sacrificed, at least to some extent. The problem of sensitivity does not arise when developing a method for determining high concentrations and all attention can be given to the principal goal of achieving a highly reproducible discharge. Apart from electrode design and the best operating conditions, a high dilution of the specimen with an appropriate compound may be made to improve the burning quality of the discharge. Moreover, high dilution lowers the possibility, or at least the degree, of error which can arise from a change of matrix composition. Some diluents act as buffers.

## Sec. 9–4. Observations in the Cabot Spectrographic Laboratory

Most observations in the Cabot Spectrographic Laboratory which have been made on the quantitative determination of the common elements (sodium and potassium excepted) have so far been restricted to modifications of methods described by KVALHEIM (1947).

*Silicon*

In the original method (KVALHEIM, 1947) beryllium, either as BeO or $BeCO_3$ (1 part), serves as the internal standard and is added to 1 part sample and 2 of NaCl; this mixture is mixed with 2 parts powdered *C* and arced in a $\frac{1}{8}$″ *cathode* at 7 amp. Be 2494 and members of the Si multiplet group at 2530A serve as analysis pairs. Replicate determinations which have been made in the Cabot Spectrographic Laboratory indicate a relative deviation of 5–8%.

Beryllium is retained as the internal standard in the modified procedure: no NaCl is, however, added and the sample is highly diluted with carbon powder (14 parts). Under these conditions, the distillation rate of beryllium almost parallels that of silicon (AHRENS, 1950; p. 73). The relative deviation is lowered to about 3·5% over a concentration range of 100% $SiO_2$ to below 15% $SiO_2$. Some improvement could probably be achieved by using a broad spectrograph slit. In any case not much time is required to carry out

a determination in quadruplicate, in which case the relative deviation should reduce to 2% or less. This corresponds to deviations of 1½, 1 and ½% respectively, at 75, 50 and 25% $SiO_2$.

*Al, Fe (total), Mg, Ca and Mn*

Only minor changes have been made (DENNEN, 1949) to the procedure described by KVALHEIM (1947). One part sample is mixed with one part of $SrCO_3$ and four of powdered carbon; this is loaded into a ⅛″ × 1 mm (internal diameter) × 4 mm (depth) anode and arced to completion (usually ~60 seconds) at 7 amp. The following analysis lines have been used: values in parentheses indicate lower limits.

| | | | | | |
|---|---|---|---|---|---|
| Al | 2652 | (1%) | Mg | 2780 | (0·1%) |
| Ca | 3007 | (1%) | | 2783 | (4%) |
| | 3159 | (0·05%) | Fe | 2929 | (0·5%) |
| | 3179 | | Mn | 2801 | (20 ppm) |

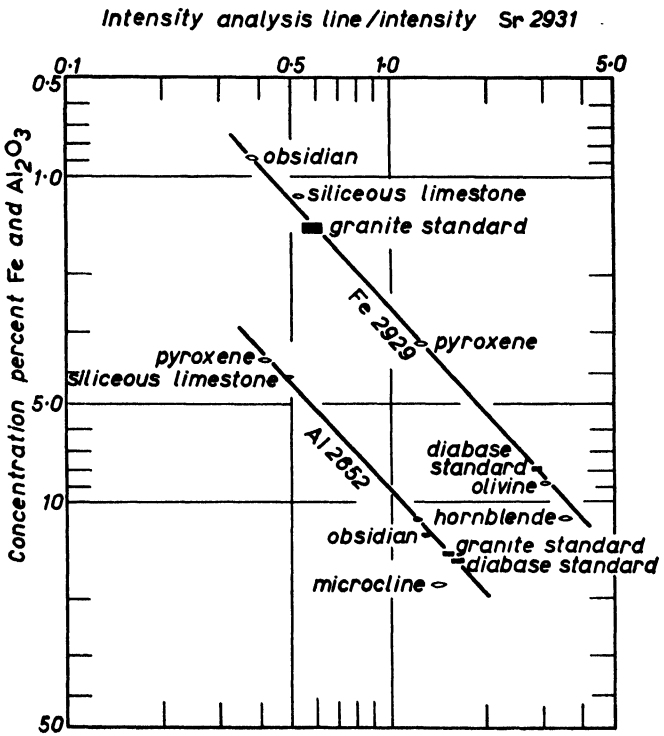



Fig. 9.2(*a*). Working curves for Fe and $AL_2O_3$.

Sr 2931 was chosen as the internal standard line in preference to Sr 3301.

All lines are atom lines with the exception of Ca 3158 and 3179 and each, with the exception of these two, shows a

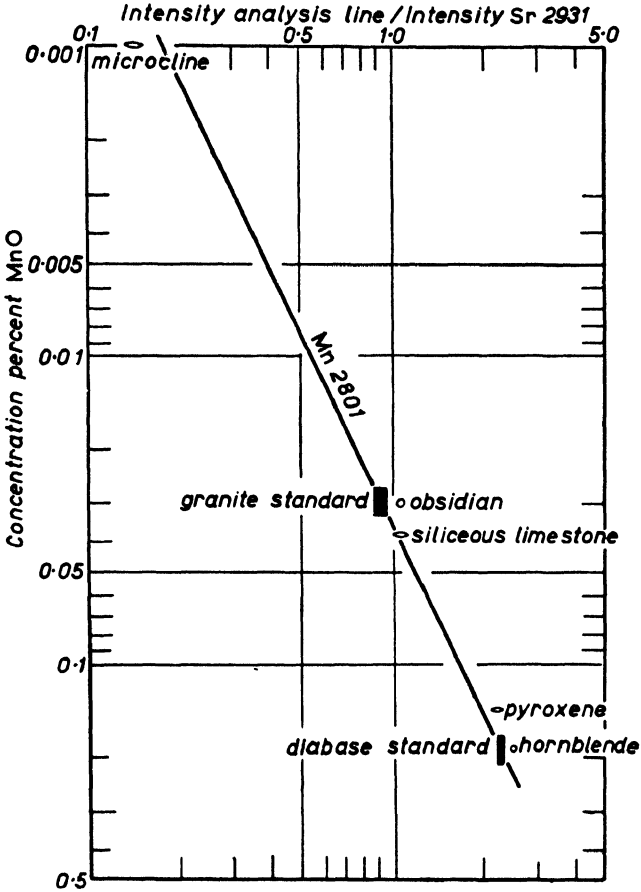



Fig. 9.2(*b*). Working curve for MnO.

similar longtiudinal intensity distribution in the arc. Serious error due to the use of an atom-ion line pair has not been apparent; this is probably due to the fact that the arc burn is smooth. The analyst should, however, not overlook the possibility that use of such an analysis pair is a potential source of serious error (cf. Sec. 7–3); in particular, change of

composition is likely to alter arc temperature and hence degree of ionization. Thus DENNEN (1949) finds that the ratio

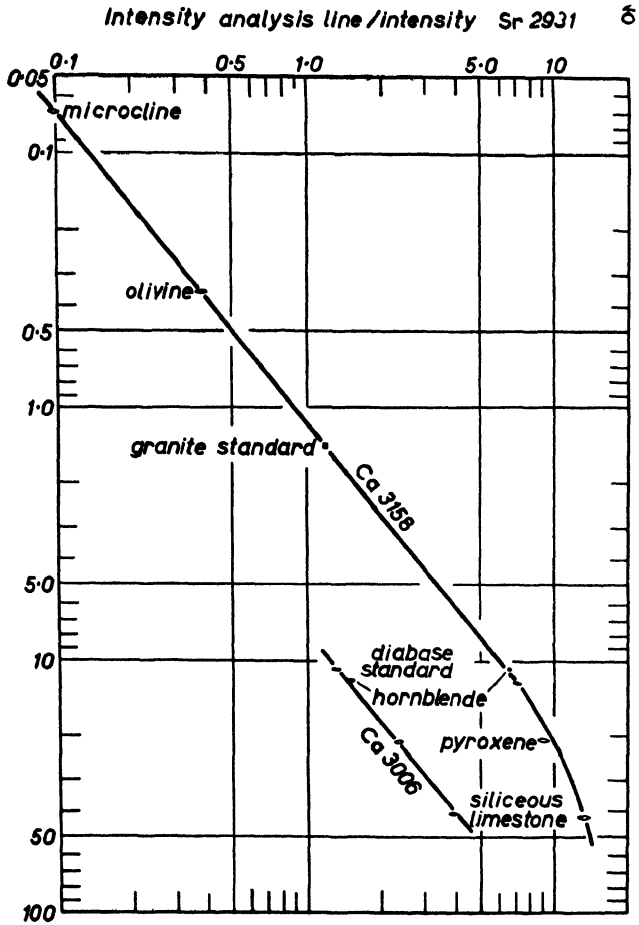



Fig. 9.2(*c*). Working curves for Cao.

Figs. 9.2 (*a*), (*b*), and (*c*), are taken from FAIRBAIRN *et al.* (1951). The shapes and dimensions of each of the plotted points may be used as a very rough guide for comparing spectrochemical and chemical precision (for details, see FAIRBAIRN *et al.*).

$\frac{\text{I Ca II 3159}}{\text{I Ca I 3006}}$ increases from 8·5 during the alkali metal phase of distillation to 9·0 after complete volatilization of these elements.

Working curves are shown in Fig. 9.2 (*a*, *b* and *c*). These have been prepared from a large variety of analysed standards; namely, G-1 and W-1; microcline, soda-feldspar, siliceous limestone, boro-silicate glass, burned bauxite refractory, plastic clay (all U.S. Bureau of Standards samples) and augite, hornblende, olivine and obsidian analysed by L. C. PECK (U.S. Geological Survey, Denver Federal Center).

Typical replicate determinations of intensity ratios emitted from a specimen of granite are given in Table 9–2. Approximate relative deviations are given for this particular suite of observations together with relative deviations (in parentheses) based on many such groups of observations.

TABLE 9–2

REPRODUCIBILITY OF INTENSITY RATIOS IN A SPECIMEN OF GRANITE

| Analysis No. | Al 2652 / Sr 2932 | Fe 2929 / Sr 2932 | Mg 2780 / Sr 2932 | Mn 2801 / Sr 2932 | Ca 3159 / Sr 2932 |
|---|---|---|---|---|---|
| 1 | 1·81 | 0·565 | 0·59 | 0·93 | 1·83 |
| 2 | 1·73 | 0·630 | 0·66 | 0·80 | 1·73 |
| 3 | 1·82 | 0·570 | 0·61 | 0·85 | 1·83 |
| 4 | 1·62 | 0·555 | 0·59 | 0·76 | 1·64 |
| 5 | 1·68 | 0·560 | 0·52 | 1·15 | 1·65 |
| 6 | 1·64 | 0·590 | 0·56 | 0·99 | 1·63 |
| 7 | 1·62 | 0·610 | 0·58 | 0·81 | 1·67 |
| 8 | 1·60 | 0·560 | 0·59 | 0·85 | 1·62 |
| 9 | 1·69 | 0·615 | 0·56 | 0·84 | 1·62 |
| Approximate relative deviation | 4·7% (4·5%) | 4·7% (4·5%) | 6·5% (6·5%) | 12·4% (5·0%) | 4·6% (5·5%) |

Variation of the intensity ratio $\frac{\text{Mn 2801}}{\text{Sr 2931}}$ is unusually large because Mn 2801 is faint in this sample of granite.

KURAOKA and TAKAHASHI (1951; a, b and c) have used modified versions of the methods described by KVALHEIM for the determination of the common elements. The sample is excited in a centre post anode. Fe, Mn and Ti are determined in one operation and Na, K, Mg and Ca, and Al + Si in two other operations.

## Sec. 9–5. Notes on other spectrochemical procedures

A high proportion of the methods which are discussed briefly have been developed specifically for ceramic materials; most of these procedures could undoubtedly be applied to the naturally-occurring silicates.

A fairly general procedure applicable both to common and some minor constituent elements in ceramic materials, minerals, rocks and soils is described by JAYCOX (1947). One part sample is mixed with 19 parts CuO and 40 parts carbon powder (1 : 9 : 20 and 1 : 39 : 80 proportions are sometimes used). The sample is loaded into a $\frac{1}{8}''$ deep cavity cut by a No. 15 drill in a $\frac{1}{4}''$ graphite anode and is excited at 10 amp for 60 seconds.

High dilution with C + CuO serves several purposes: a high proportion of *C* reduces differences in the distillation rates of several involatile elements; as a result, copper is usable as an internal standard for a variety of elements and as it is present at a high concentration it serves as a buffer*; finally, high dilution decreases the concentration of some of the common elements to levels at which their analysis lines are free from self-absorption.

A satisfactory relative deviation of about 4% is apparently usually attainable.

A high dilution with NiO in place of CuO was used by OSHRY, BALLARD and SCHRENK (1942) who describe a method for determining Si, Fe and Al in mineral powders by means of a high voltage (2,200 volts) source. Their determinations of $SiO_2$, $Fe_2O_3$ and $Al_2O_3$ in six National Bureau of Standards samples (agricultural limestone, bauxite, feldspar, burnt refractory (2) and flint clay) agree favourably with recommended values and in general a relative deviation of about 5% seems attainable.

ROZSA (1947) has used a variable (mutual) internal standard (silicon) for a comparatively complete analysis (Ca, Al, Fe, Ti, Mn and Mg) of slag. One part of sample is mixed with one part each of $NH_4Cl$ and powdered graphite and arced for 45 seconds at 8 amp in a pedestal (Scribner) type anode of $\frac{3}{16}''$ diameter. The accuracy of the method is claimed to compare with chemical accuracy.

* Although carbon is dominant its buffer action is ineffectual because its first ionization potential is excessively high.

CARLSSON and YÜ (1950) used a low-tension arc-like triggered spark, and with silicon as a variable (mutual) internal standard, an accuracy equal to that of chemical methods is claimed. Their slag procedure has been modified and applied (CARLSSON, 1951) to other ceramic materials. Because these materials vary in composition, a flux ($Na_2B_4O_7$) is first used to break down mineral structure ; the fused cake is then pulverized and 400 mg are mixed with 300 mg graphite powder, pressed into a briquet and excited.

PRICE (1952) has used borax as a flux for the analysis of slag. CoO, the internal standard, is first mixed with the slag and this is fused with an excess of borax. The product is ground, mixed with graphite powder and excited with a controlled DC arc. A very satisfactory precision of 3% is claimed.

The accuracy of the DC arc, Feussner spark and the " multisource " unit have been compared by GILLIS and EECKHOUT (1951) for the purpose of slag analysis. They conclude that the Feussner spark is superior and moreover, that determinations by means of this source are more reliable than those obtained by routine chemical methods. As the accuracy of spectrochemical methods can apparently be made to match the accuracy of routine chemical methods, one concludes that they are in general superior for several purposes of slag control because of their speed. For further reference to slag analysis see KORZH (1945), STEINBERG and BELIC (1948), IRISH (1948), MUSHA (1950) and CASTRO and LOUDE (1951).

HASLER, HARVEY and BARLEY (1948) describe a method for the determination of Al, Mg, Fe, Mn and Ti in Portland Cement. 8 mg of mixture (1 part sample, 2 of graphite) are arced to completion (~90 seconds) at 10 amp on a platform-type anode. Calcium serves as the internal standard and relative deviations of 2–7% are claimed. Sodium and potassium are determined in a separate operation. In the same paper HASLER *et al.* describe a procedure which appears to be highly reproducible. A briquet ($\frac{1}{2}''$ diameter) is first prepared from the sample and is excited by means of an interrupted DC arc. Relative deviations of 2–3% are claimed.

The use of germanium for the combined purpose of buffer-diluent and internal standard for the determination of

common elements in silicates is discussed by STROCK (1953; this paper gives references to earlier publications). Several properties of germanium—its rate of distillation, the magnitude of its first ionization potential and its liquid range of temperature are considered to be favourable. The powdered specimen is mixed with 9 parts Ge metal; one part of this mixture is mixed with an equal quantity of carbon powder and arced to completion at 6 amp in a $\frac{3}{16}$" (external diameter) × $\frac{7}{64}$" (internal diameter) × 4 mm (depth) anode.

A reproducibility of 10–15% given by GILLIS and EECKHOUT (1951) is somewhat poorer than that reported elsewhere in this section. They sought to determine Al, Fe, Ti, Ca, and Mg in clays using silicon as an internal standard. The specimens were mixed with an equal quantity of graphite and arced for 45 seconds at 10 amp. Sodium and potassium were determined in a separate operation, using lithium (added as the carbonate) as the internal standard.

## Sec. 9–6. Note on the investigations of Hegemann and co-workers

HEGEMANN and co-workers at Münich have carried out considerable research on the development of quantitative spectrochemical methods for complete silicate analysis; see HEGEMANN and ZOELLNER (1952) for example. Much emphasis is placed on determining the common elements with utmost accuracy. An intermittent (Pfeilsticker type) AC arc which excites the sample on a slowly rotating inclined disc has been chosen for this purpose. A highly satisfactory precision of 2–3% (alkali metals excepted) is claimed on the basis of some 3,500 observations. (See HEGEMANN and ZOELLNER (1952) for details of the rotating disc method of loading the sample and of methods which are used for the determination of the alkali metals and minor elements.)

## Sec. 9–7. A rapid method of chemical analysis

The complaint about the slowness of classical methods of silicate analysis has been noted (Sec. 9–1). A chemical method of analysis which is comparatively rapid but which at the same time enables the analyst to carry out determinations with an accuracy comparable with the classical methods should be valuable for many purposes.

A procedure developed by SHAPIRO and BRANNOCK (1952) at the U.S. Geological Survey appears to go much of the way toward fulfilling these requirements. Only 0·1 gm of sample is required. This is fused with NaOH in a nickel crucible. Si, Al, Fe, Ti, Mn and P are determined colorimetrically—Si and Al in one solution, and Fe, Ti, Mn and P in another solution—whereas Mg and Ca are determined titrimetrically. Table 9–3 provides an outline of the analytical scheme.

TABLE 9–3

BRIEF OUTLINE OF RAPID CHEMICAL PROCEDURE FOR COMMON CONSTITUENTS IN SILICATES (AFTER SHAPIRO AND BRANNOCK, 1952)

| Constituent | Method | | Concentration range (%) |
|---|---|---|---|
| $SiO_2$ | Colorimetric ; | Mo blue | 24—80 |
| $Al_2O_3$ | ,, | ferron | 9—86 |
| Fe (total) as $Fe_2O_3$ | ,, | $FeCl_3$ | 0·8 —16 |
| $TiO_2$ | ,, | peroxide | 0·01—1·5 |
| MnO | ,, | periodate | —0·27 |
| $P_2O_5$ | ,, | molybdivanado-phosphoric acid | 0·04—2·4 |
| CaO | titrimetric ; | versene | 0·10—15 |
| MgO | ,, | versene | 0·04—8·1 |

Each constituent has been determined in G-1 and W-1 and in twelve samples which were prepared by mixing varying proportions of several National Bureau of Standards samples. In general, the determinations agree satisfactorily with recommended values and accuracy seems to compare well with classical methods. A perusal of the results leads the writer to make these conclusions. $SiO_2$ and $Al_2O_3$ appear satisfactory ; in fact, the determinations of these two constituents in G-1 and particularly W-1 come closer to the recommended value (Table 3–1) than do a large proportion of the individual chemical determinations listed by FAIRBAIRN *et al.* (1951): the reciprocal Si-Al error (Sec. 3–2) is apparently avoided. Calcium is satisfactory at comparatively high concentrations, but may be poor below ~0·5% CaO. Similar general comments hold for magnesium and again ~0·5% appears to be a level below which accuracy deteriorates sharply; for example, the recommended values for G-1 and a standard

labelled D are 0·15 and 0·49 MgO respectively, whereas rapid determinations come out at 0·39% and 0·33%, 0·27% (two determinations). At these levels spectrochemical accuracy is probably much superior. $TiO_2$ determinations appear satisfactory down to ~0·05–0·10%, below which some serious discrepancies appear and spectrochemical accuracy is probably superior. Data on manganese are inadequate for definite conclusions but the comments about Ti, Ca and Mg may apply. All $P_2O_5$ determinations agree well with recommended values down to the lowest concentration of 0·05% $P_2O_5$ which was determined.

The reader will be aware of some limitations imposed by the usable concentration range of these rapid procedures ; for example, the lower limits for $SiO_2$ and $Al_2O_3$ are given as 24% and 9% respectively. It is understood, however, that further research on the rapid chemical procedures is continuing and we may expect improvements both in accuracy and sensitivity.

From what we now know about rapid chemical and quantitative spectrochemical methods, we may expect that a combination of such procedures should prove to be particularly fruitful for the rapid and complete quantitative analysis of the naturally occurring silicates.

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