THE APPLICATION OF ANION-EXCHANGE ENRICHMENT TECHNIQUES TO THE SPECTROCHEMICAL DETERMINATION OF TRACE ELEMENTS IN SILICATE ROCKS AND SEA WATER.

A thesis submitted for the degree
of Doctor of Philosophy,

By

R.R.BROOKS. BSc (Hons).

Dept. of Chemistry,
University of Cape Town,
March 1960.

Geochimica et Cosmochimica Acta, 1959, Vol. 15, pp. 337 to 341. Pergamon Press Ltd. Printed in Northern Ireland

Some reconnaissance observations on the combined use of ion-exchange enrichment and spectrochemical analysis for the determination of trace constituents in silicate rocks

R. A. EDGE,*‡ R. R. BROOKS,* L. H. AHRENS* and S. AMDURER†

(*Received* 2 *July* 1958)

Abstract—A reconnaissance investigation has been made of the possible combined use of ion-exchange enrichment (cation and anion) and spectrochemical analysis for the determination of several rare elements, notably Ag, Be, Bi, Cd, Cs, In, La, Mo, Nb, Sn, Pb, Tl, Y and Zn, in silicate rocks and allied materials. Observations which have been carried out on granite G-1, a specimen of Cape granite, and diabase W-1, indicate that many of these elements should be easily detected in a wide variety of rocks and soils. The scope of the combined procedure seems to be immense and it is evidently possible to determine several elements in a single operation; the combined procedure should be particularly useful for investigating the general geochemistry of Bi.

INTRODUCTION

SPECTROCHEMICAL methods of analysis are perhaps the most widely used general procedures for determining trace elements in rocks, soils, minerals and meteorites. The advantages of spectrochemical methods are many (TAYLOR and AHRENS, in press; AHRENS, 1957), but it is nevertheless not possible to employ them for the determination of a large number of trace elements because their concentrations are below spectrochemical detection limit concentrations, and other methods must be used. Though the other methods may be most effective they are invariably specific and a thorough investigation of the composition of a rock, soil, mineral or meteorite involves a large number of lengthy separate analytical operations. There is clearly a place therefore for procedures which are more sensitive than the usual spectrochemical methods of direct excitation of sample powders and which are comparatively rapid and applicable to many elements.

If the concentration of an element is very low it is often necessary to enrich it before a determination can be carried out by one of the several general procedures, spectrography, polarography, or colorimetry, for example. Many enrichment procedures are chemical and specific for one or a small number of elements; several have been used in conjunction with the spectrograph, for example by MITCHELL and co-workers (MITCHELL, 1957: several elements in plants and soils), LIEBENBERG (1956: Cs in rocks), and BERMAN (1957: La, Ce, Nd, Yb and Y in granite G-1 and diabase W-1). Apart from the fact that many enrichment procedures are restricted, chemistry may be complex and errors can arise from absorption and occlusion. A simple versatile enrichment procedure which involves a minimum number of chemical operations would offer most advantages and in this respect the use of an ion-exchange procedure seems a likely possibility.

In our present paper we wish to discuss the combined use of ion-exchange procedures (anion and cation) and spectrochemical analysis. We have prepared this brief and preliminary account because although many of the investigations

---

* Dept. of Chemistry and † Dept. of Geology, University of Cape Town
‡ Also at the Government Chemical Laboratories.

are still in their reconnaissance stage they have revealed so clearly the potential value of the combined procedure: it will be our main purpose to illustrate the general principles of the procedure and its scope in geochemistry and cosmochemistry; details of analytical methods will be given elsewhere.

Our investigations have been carried out mainly on the standard rocks G-1 and W-1 (for recent review of data, see AHRENS and FLEISCHER, in press), a sample of Cape granite kindly provided by Prof. E. S. W. SIMPSON (Department of Geology, University of Cape Town) and a specimen of Limerick chondrite.

DISCUSSION

(1) *Elements which have been investigated*

The investigations so far have been concerned mainly with several elements whose concentrations in igneous rocks and soils lie either in the neighbourhood of their spectrochemical detection limits or somewhat lower than these limits: we have not investigated extremely rare elements such as Re and noble metals such as Pt, Pd, Os, etc. Table 1 lists these elements together with their estimated crustal abundances (RANKAMA, 1954, among other sources) and their approximate detection limit concentrations in the d.c. arc (AHRENS, 1951). The remarks in the appropriate column in Table 1 have been inserted to provide an indication as to whether or not an element is likely to be detected by direct spectrochemical excitation in common rock types such as granite and basalt. Most of the elements listed in Table 1 are either only occasionally detected or never at all.

Table 1. Estimated crustal abundances and approximate spectrochemical detection limits (d.c. arc) of some rare elements

Elements	Abundance (p.p.m.)	Detection limit (p.p.m.)	Remarks
Ag	0·1	0·5	Virtually never
Be	2	10	Very uncommon
Bi	0·2	20	Never
Cd	0·15	10	Never
Cs	6	2	Sometimes in granite
In	0·11	1	Never
La	18	10	Sometimes
Mo	1	5	Fairly common
Nb	24	30	Never
Nd	24	10	Rare
Pb	15	5	Sometimes in granite
Sn	40	10	Sometimes in granite
Tl	1·3	1	Occasionally in granite
Y	28	10	Sometimes
Zn	110	100	Occasionally in ferro magnesians

Before turning to discuss the combined procedure we shall mention one specialised fairly general spectrochemical procedure, the so-called double-arc. It is highly sensitive for several of the spectrochemically volatile elements, notably Tl, In, Zn and Pb, and has been used for their determination (Shaw *et al.*, 1950; Shaw 1952a,b; Wedepohl, 1953, 1956).

2. *Principles of the combined procedure*

The principles of ion exchange have been described in several texts (Samuelson, 1953 and Kitchener, 1957, for example). For the purpose here we shall briefly recall a few relevant points. Ion exchange resins are of two types, cation resins and anion resins. Each has been investigated for the purpose at hand; we shall consider first cation exchange chromatography with HCl elution. When a solution containing several cations and anionic complexes (e.g. $SnCl_6{}^{2-}$) is adsorbed on a cation resin and eluted with HCl, most of the anionic complexes pass through the column first followed by the cations. The order in which the cations appear in the eluate is usually M^+ cations, M^{2+} cations, and finally M^{3+} cations. Within each charge group the order is usually according to size, cations with smaller radius moving through more rapidly than those with a large radius; for example, in the alkali metals the order is Li^+, Na^+, K^+, Rb^+ and Cs^+. Irregularities can occur and certain cations of given charge may appear in the same volume eluate as others of different charge. An element may be separated or obtained in a highly concentrated form (see, e.g., Pinson, 1953; Schumacher, 1956; Aldrich *et al.*, 1953), by careful control of the column conditions but for our purpose it is necessary only to concentrate the element to within the detection limit concentration of the spectrograph. In most d.c. arc spectrochemical procedures, up to about 100 mg of powder may be accommodated into the electrode; accordingly, on the basis of 1 g of original sample, an increase in sensitivity by a factor of about ten may be anticipated provided the total quantity of trace metal can be concentrated into a volume of eluate which yields up to 100 mg or so of residue. Greater sensitivity may be achieved by using a larger sample.

In our experiments, the powdered sample is treated with HF and $HClO_4$ and taken to dryness; the residue is taken up in a minimum volume of HCl and poured on to Dowex 50 resins (8×, 200–400 mesh) in the hydrogen form. Elutions with 1, 2, 2·5, 3 and 6 N HCl have been made. For monitoring purposes 20–30 ml fractions were collected on an automatic fraction collector, taken to dryness and arced to completion at 3A. The spectrograph is useful in this respect because the spectrum of each fraction provides a fairly complete and permanent record of its composition. These experiments showed that, apart from some irregularities and surprises (Edge and Ahrens, in preparation), the sequence in which elements moved through the column accorded with that anticipated from various papers in the literature. This sequence is given as the first horizontal column in Table 2.

For the purposes of analysis, rather than of monitoring, several of the comparatively small fractions may be consolidated into a large volume fraction, according to the principal constituent which happens to be present, as indicated by the second horizontal column in Table 2. Figure 1 shows spectra of the residues from some of these eluate fractions which have been obtained from a gram of granite G-1; the sharp change in composition is clear.

Many elements form chloro-complexes in concentrated or fairly concentrated

HCl and when a solution of chlorides is passed through an anion exchange column, the anionic chloro-complexes are held on the column whereas the cations appear in the eluate. Several of the 18-electron elements such as Ag, Cu, Au, Cd, Zn, Tl, Bi and Pb, together with a few others including Fe^{III}, form stable chloro-complexes. These elements may be removed from the column by destroying the complex: either by eluting with dilute HCl, dilute HNO_3 or dilute H_2SO_4, and in this way a fraction concentrated in the above elements may be obtained. Figure 2 shows the results of an experiment which has been carried out on the anion resin.

Table 2

Pt	Sn	Ti	Fe	Na	K	Rb	Cs	Ca	Sr	Ba	RE_s
Ti			Fe	Na	K				Ca		

A 10 g sample of Cape granite was decomposed with HF and dried. The residue was taken up in HCl and passed through a column packed with Amberlite IR 400 (Cl form); this was eluted with HNO_3 and Fig. 2 shows the spectrum of the residue of the 50–500 ml eluate fraction. Many lines of the heavy metals Pb, Bi, Tl, Zn, Cd (barely detectable) and Ag appear. Several of the lines are very intense indeed. Direct excitation of the Cape granite powder showed only very weak Pb 4057 and no sign of the other elements. A similar experiment on diabase W-1 revealed detectable Bi, Tl, Ag, Pb and Zn.

The concentration of an element in a fraction is determined spectrochemically with the aid of appropriate synthetic standards and on the assumption that recovery is complete, it is possible to obtain a quantitative estimate of the element in the original rock, soil or meteorite sample itself.

Some conclusions on the apparent scope of the combined procedures

It will not be possible to demonstrate fully the scope of the combined procedures in geochemistry until they have been thoroughly tested on a wide variety of rocks, minerals, soils and meteorites. Nevertheless, the reconnaissance investigations on G-1, W-1, the Cape granite and a meteorite lead to the conclusion that the scope should be wide and the application useful; they indicate clearly that provided 5–10 g of sample are taken, most of the rare elements listed in Table 1 will be determinable in a large variety of igneous, metamorphic and sedimentary rocks and many meteorites and, of considerable significance, that several of the elements may be determined in a single analytical operation. For certain of these elements the combined procedures should be invaluable for obtaining general basic geochemical data; Bi is perhaps the best example, as virtually no data on its abundance in common rocks and soils are known.

REFERENCES

AHRENS L. H. (1951) *Wavelength Tables of Sensitive Lines.* Addison–Wesley, Brookline, Mass.

AHRENS L. H. (1957) The spectrograph in geochemistry and cosmochemistry. *Soil Science* **83,** 33.

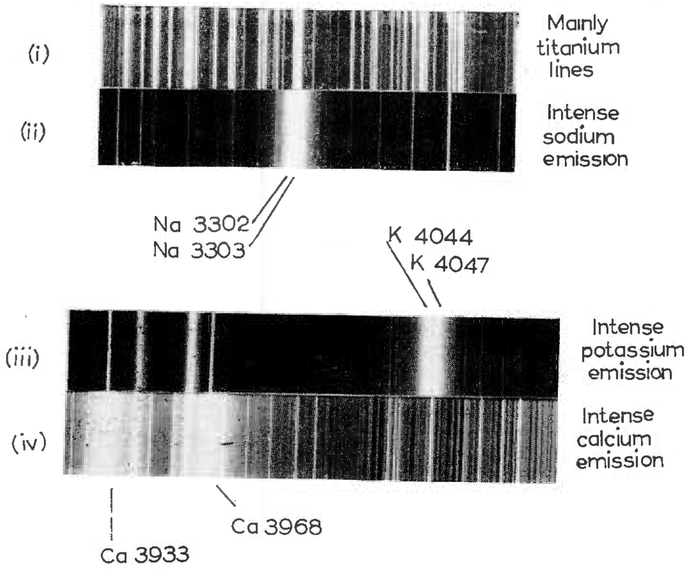


Fig. 1. Arc spectra (over two wavelength ranges) of residues from successive eluate fractions; cation column. Granite G–1.

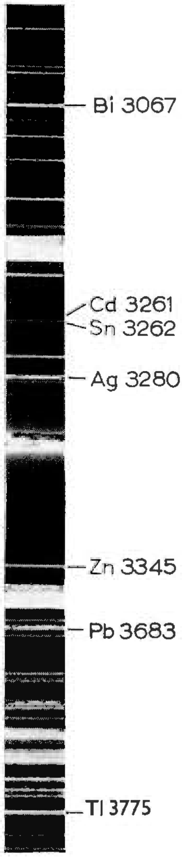


Fig. 2. Arc spectrum of residue from 50–500 ml eluate fraction (HNO_3); anion column. Residue mixed with 20 mg NaCl to clear CN emission and provide bulk. Cape Granite. Note particularly the presence of Bi 3067 and the high intensity of Tl 3775.

ACKNOWLEDGEMENTS.

The author is indebted to his supervisor, Professor L.H.Ahrens, for his valuable guidance and advice without which this work could never have been undertaken.

He is also indebted to Professor E. Simpson for the sample of Cape granite which was used so extensively in these investigations, to Dr S.R.Taylor for the many geological specimens provided by him and for his valuable assistance in the spectrographic part of the studies ; also to Dr.R.Arnold for his valuable assistance and advice.

The author is grateful to Mr.G.G.Du Plessis of the Division of Fisheries for permission to use his research laboratories for the experiments on sea water. He would also like to thank the staff of the Division for their valuable co-operation and help.

INDEX.

PART.I.

PART II.

PART III.

PART IV.

fortunate fact that none of the major constituents of the rocks and sea water is strongly absorbed under the conditions used.

Using this combined procedure, Zn, Bi, Sn, Tl and Cd have been determined quantitatively in a suite of twenty-nine rocks. Qualitative observations on other trace elements were made simultaneously.

A modification of this procedure has been employed for an investigation into the platinum metals and Au in silicate rocks.

In the studies on rocks, enrichment factors of up to 10,000 were achieved, limitations being imposed partly by reagents blanks when very large quantities of sample were employed and partly by practical handling considerations.

In investigations on sea water, much higher enrichment factors of up to 20,000,000 were achieved because it was unnecessary to employ large quantities of reagents for dissolution of the "sample". In addition, the high chloride content of sea water so aided the formation of chloro-complexes, that an appreciable economy was possible in the amount of HCl that had to be added to the water to allow the complexes to be formed.

In these latter studies, certain trace elements were absorbed from ¼ ton of sea water and quantitative data were obtained for the concentrations of Au, Bi and Cd in this medium.

The investigations demonstrate the versatility of anion exchange enrichment procedures in the determination of trace elements in a wide range of geological materials.

SECTION II

INTRODUCTION.

Many methods have been used to estimate the so-called trace elements in geological materials and include colorimetric, spectrochemical and neutron activation techniques as well as many others. Of these procedures, the spectrochemical methods are perhaps the most important since not only are they extremely sensitive for certain elements but they also permit the simultaneous estimation of a large number of different ions. (For a review of the relative accuracy of conventional analytical methods as applied to minor constituents of silicate rocks , see Ahrens, 1957).

Some trace elements are present in such low concentrations that even very sensitive analytical methods are not able to permit a direct determination to be carried out and in a case of this nature it is necessery to combine the selected analytical technique with an enrichment procedure.

Enrichment techniques may be conveniently classified into five main groups :-

(1) Chemical precipitation methods :- These usually involve precipitation of the trace elements together with a carrier; for example, co-precipitation of In with ferric hydroxide.

(2) Solvent extraction :- The general procedure is to dissolve the sample, adjust the pH to a certain value and extract the element with a suitable solvent or complexing agent; for example, the extraction of Cd with dithizone in carbon tetrachloride.

(3) Fire assay procedures :- These are usually only specific for a few elements; namely, the noble metals.

(4) Methods based essentially on spectrochemical techniques :- For example, the double arc technique of Mannkopf (1949) developed from the original work of Rose and Böse (1935).

(5) Ion exchange enrichment techniques :-.

These latter procedures have been little explored up to the present time, although Cranston and Thompson (1946) have used cation exchangers for the enrichment and isolation of traces of Cu in milk, and Nydahl (1951) has used the same type of resin for the enrichment and determination of some of the alkali metals and alkaline earths in lake water. (For a review of enrichment techniques as applied to rocks and soils, see Ahrens & Taylor: 1960).

In the work described in this thesis, anionic exchange enrichment procedures were developed which, in combination with spectrochemical techniques, appeared to have certain advantages over other enrichment methods.

In the first place, the methods are simple and involve the addition of only relatively small amounts of reagents which themselves are easily purifiable by distillation.

Secondly, the techniques are very versatile and many elements can be determined simultaneously.

Thirdly, enrichment factors higher than those possible by most other methods were achieved. For example, an enrichment factor of 20,000,000 has been obtained for sea water.

Finally, it was possible to use a constant matrix for the subsequent spectrochemical operations since the final eluate residue, which is usually very small, is collected in a much greater mass of a NaCl matrix. This is admittedly a feature of some, though not all, other enrichment procedures.

The need for enrichment techniques is further emphasised by consideration of two main limitations of the spectrograph which otherwise is well suited to the determination of trace elements.

In the first place, some elements such as Ta, have such a low spectral sensitivity that they must be present in fairly high concentrations before they can be detected. A second limitation is the fact that only about 100 mg of sample at the most can be arced at any one time and even if recourse is made to the superimposition of several arcings on the same plate, background effects tend to nullify any advantages that might otherwise accrue.

The author has confined himself to the study of those elements that can be truly classified as "trace elements" (usually less than 100 ppm and in many cases less than 0.1 ppm), and which at the same time are of particular interest geochemically, either because of extreme rarity or else because of the lack of reliable and consistent abundance data . Good examples of such elements are Bi and Cd. It has been discovered, (Edge, Brooks, Ahrens and Amdurer : 1959) that ion-exchange techniques can be employed in the enrichment of several trace constituents in silicate rocks to the threshold of spectral sensitivity ; these authors have discussed the scope of the combined procedure and both anionic and cationic exchange chromatography could evidently be used. Cationic exchange chromatography has been applied successfully to the determination of certain trace elements (Edge : 1959).

This thesis is concerned solely with anionic exchange enrichment and all the work has been [illegible] carried out on a strongly basic anion exchange resin. A wide study has been made of the application of this technique to the spectrochemical determination of trace elements in silicate rocks and sea water.

In order to absorb trace elements onto an anion exchanger, many ligands such as cyanide, thiosulphate, citrate, tartrate etc were considered but the final choice was made of the chloro-complexes since, as will be seen later, these possess certain distinct advantages over the others.

To give some idea of the basis of the anion-exchange enrichment technique, reference must be made to the work of Kraus and Moore and other workers :- Blasius and Wachtel (1954), Campbell and Nelson (1953), Jentszch and Frotscher (1955), Kraus and Moore (1953), Kraus and Nelson (unpub.), Kraus and Nelson (1954), Kraus, Nelson, Clough and Carlston (1955), Kraus, Nelson and Smith (1954), McNevin and Crummet (1953), Miller and Hunter (1954), Nachod (1945), Nelson and Kraus (1954). The above workers have made extensive investigations into the absorption of the anionic chloro-complexes of certain elements onto a strongly basic anion-exchanger. Their work is based on the fact that many elements are able to form anionic chloro-complexes at certain well defined HCl concentrations.

For example, Bi forms $(BiCl_4)^-$, $(BiCl_5)^{2-}$ and $(BiCl_6)^{3-}$ in the range from 0.1 to 10 N. HCl.

Kraus and his co-workers have measured the volume distribution coefficients of nearly all the elements of the periodic table when their solutions in varying strengths of hydrochloric acid are absorbed onto the strongly basic anion exchanger Dowex.1.

The volume distribution coefficient of an element or complex is a measure of the degree of absorption of that substance on to a particular ion exchange resin. When a solution of the element is in equilibrium with the exchanger, the volume distribution coefficient:-

$$D_v = \frac{\text{Amount of element absorbed per ml of resin bed.}}{\text{Amount of element remaining per ml of solution.}}$$

Those elements that will complex in hydrochloric acid can be divided into three groups. Firstly, those whose distribution coefficients steadily decrease with increasing acid concentration :- examples of these are Au, Tl, Hg, Ag, Bi and all the platinum metals. The coefficients of the second group steadily increase with increasing acid concentrations: as for example, Fe, Ga and W. Other elements like Sn, Zn, Cd and In, attain a maximum or minimum at certain acid concentrations and in this respect contrast sharply with the other two groups. In Table I are recorded the distribution co-efficients of those elements that complex in 2N HCl.

TABLE.1.

The volume distribution coefficients of certain elements.

(from 2N. HCl solutions).

Element.	Oxidation state.	log D_V
Au	III	6.0
Tl	III	5.0
Hg	II	4.5
Os	III	3.8
Ir	IV	3.8
Bi	III	3.5
Pt	IV	3.4
Sn	IV	3.2
Sb	III	3.2
Cd	II	3.1
Zn	II	3.0
Re	VII	2.8
Sn	II	2.7
Ru	IV	2.6
Pd	II	2.5
Ag	I	2.0
Cu	I	2.0
Pb	II	1.5
Nb	V	1.3

TABLE I (Continued)

Element	Ox. State	log D_v
Mo	VI	1.2
Fe	III	1.0
Ta	V	1.0
U	VI	1.0
In	III	1.0

If it is possible to selectively absorb certain trace elements from a hydrochloric acid solution of a comparatively large quantity of rock, (say 20 g.) subsequent elution may yield a product in which the concentrations of these elements are above their spectrochemical detection limits and they may therefore be determined quantitatively by spectrochemical procedures. This forms the basis of the method that was developed.

In considering the possibility of separating the trace constituents from the major constituents of silicate rocks, the author has noted a most significant feature of the work of Kraus and Moore; this was the fact that of the elements which are so abundant that they together form over 99% of the earth's crust (O, Si, Fe, Al, Na, K, Ca, Mg, Ti), only one, namely Fe, is able to form a chloro-complex at any hydrochloric acid concentration. Fe belongs to the second group of complex-forming elements and shows a low absorption at the lower acid concentrations in marked contrast to the first group of elements. Zn, Cd and In have absorption maxima in 2N hydrochloric acid at which concentration the iron absorption is relatively low.

Nearly all the elements listed in Table I are rare and some, such as Re and Pt, are extremely rare. All of these rare elements, with the exception of Sb, Re, Ta and U have been detected by the auther in a wide range of silicate rocks and certain of them have been estimated quantitatively. Of these four elements that have not been detected, Sb was not discovered because of the fact that most elements form their strongest chloro-complexes in their highest valency states and therefore work has been carried out in oxidised solutions rather than in reduced media thus precluding the detection of Sb^{III}. The difficulty with Ta and U has been their exceedingly low spectral sensitivity coupled with relative rarity.

The technique of using anion exchangers for the determination of trace elements was influenced by two main factors. Firstly, it was essential to be able to enrich the elements to above their spectrochemical detection limits and indeed, it was found subsequently that enrichment factors of over 10,000 could be achieved in silicate rocks and over 20,000,000 in sea water.

The second factor of importance was that partial separation, at least, of Fe was essential since this element has a complex spectrum likely to cause widespread interference (particularly with Bi 3067.7 A) and moreover, by its high abundance would add an undesirable bulk to eluate residues enriched in trace elements.

This thesis includes work in which eighteen different trace elements have been studied, of which five, namely Zn, Bi, Cd, Sn and Tl were given special attention and systematically determined in a suite of twenty-nine silicate rocks. Work on trace elements in sea water is also described.

By adjusting the column conditions and acidic concentrations, it is possible to make the technique specific for any one element or group of elements. In 2N HCl it appears to be possible to simultaneously determine the greatest number of trace elements ; on the other hand, by using a decinormal solution of the acid, more efficient absorptions of Tl, Bi, Au, Hg, Pt and Ag can be achieved. There is also the added advantage that Fe is virtually unabsorbed at this lower acid concentration.

In general, lower acid concentrations are preferable because of Fe interference but this is no reason why higher concentrations cannot be employed to make the method specific for other elements, particularly if a reduced solution is used where Fe^{2+} is not absorbed at all in hydrochloric acid concentrations below 8.N.

It may be borne in mind that the sensitivity of the combined procedure can be increased by taking into solution larger quantities of rock until a limit is imposed by practical considerations.

PART I

SECTION III.

THE APPARATUS.

The apparatus used for the investigations described in this thesis was basically very simple and consisted of three main units : namely, the ion-exchange column, the fraction collector and the spectrograph. Each of these will be considered in turn.

(a) The column.

The column itself (illustrated in Fig.1.), consisted of a borosilicate glass tube approximately 60 cm long, one end of which had a diameter of 20 mm extending to about half the length of the column ; the other half of the tube was much narrower and had a diameter of 12 mm hence giving a cross-sectional area of 1 sqcm.

In the initial experiments, an attempt was made to adjust flow rates by means of a glass tap attached to the bottom of the column. It was however discovered that glass taps were unsatisfactory since the flow rates

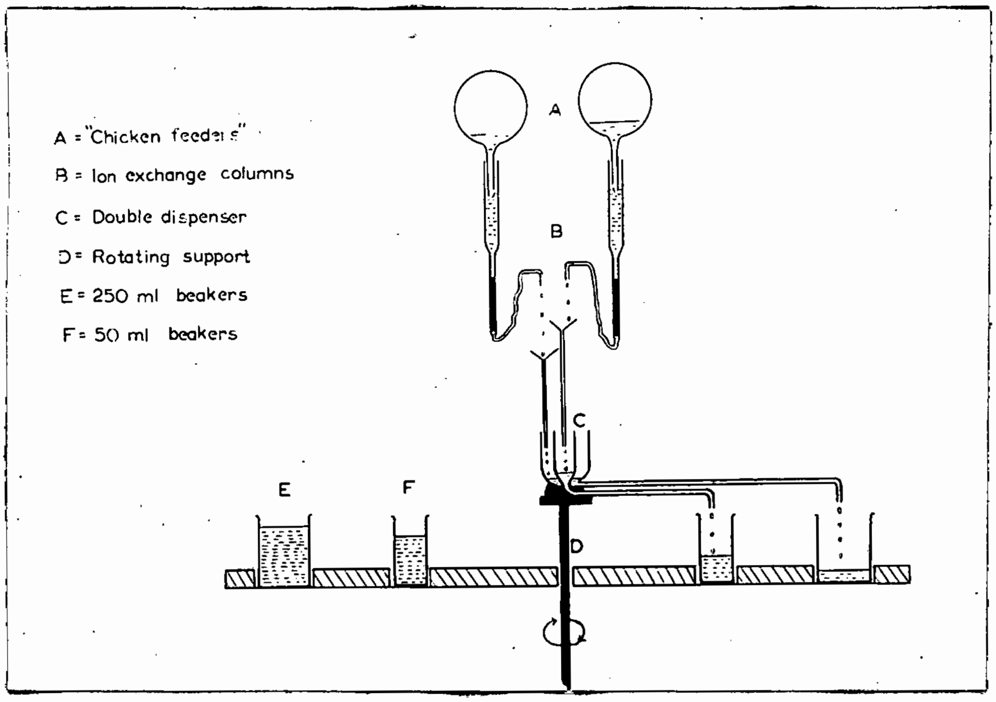
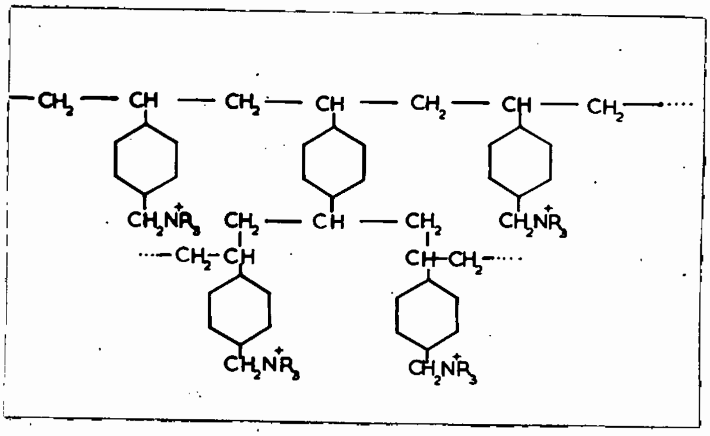


FIG.1. The column and fraction collector.

tended to slow down and finally cease altogether. On replacing the glass taps with polythene screw valves, little improvement was noted but the problem was finally solved by regulating flow rates by the adjustment of the hydrostatic pressure. In order to achieve this, a 3/16" tygon tube, approximately 50 cm. long, was attached to the bottom of the ion exchange column and a short extruded glass tip attached to the other end. The level in the column was kept constant and the flow rates adjusted merely by raising or lowering the glass tip and it was found that very constant flow rates could be achieved by this simple hydrostatic method of control. A further advantage was that there was no danger of the column "running dry" because it was a simple matter to ensure that the outlet of the tygon tube was always higher than the top level of the resin bed.

(b) The Resin.

The same type of ion exchange resin was used throughout all the investigations, and this was a special chromatographic grade of the strongly basic anion exchanger Amberlite IRA 400 (100-200 mesh) manufactured by Rohm and Haus. The basic structure of this resin is shown below and it can be seen that it consisted of polystyrene cross-linked with 8% divinyl benzene. The active group was a quarternary amine and such a structure is capable of a high degree of ionisation coupled with a marked degree of insolubility in aqueous media.



The resin is said to be fully stable over the pH range 0-12 and this has been fully confirmed in practice, the only difficulty being experienced with strong oxidising agents such as nitric acid where very slight decomposition of the resin seemed to occur.

This exchanger was similar to, but not identical with, the Dowex.1. anion exchanger used by Kraus and his co-workers. As a result of the author's own investigations into the distribution coefficients of certain elements on IR 400 resin, (See Part I section 4 and Part IV section 7) it was concluded that any differences in behaviour between the two resins were very slight and unless particularly accurate data were required, the results of Kraus et al could be applied with confidence to the Amberlite resin.

The reasons for using IR 400 in place of Dowex.1. were twofold :- Firstly, the former was more readily available and secondly, spectrographic examination of the ash of ignited resin revealed that the Amberlite resin was appreciably freer from contamination than Dowex.1. particularly in relation to Zn and Sn.

Zn contamination is not particularly serious as this element is easily removed but Sn is troublesome to elute and requires a double cycle of sulphuric and nitric acids before a reasonable degree of purity is achieved.

<u>(c) The fraction collector</u>.

The above was used in conjunction with the ion-exchange column and served to collect fractions at predetermined time intervals (5 min to 2 hrs.). Part of the apparatus is shown in Fig.1.

In order to conserve space which was at a premium and in order to reduce costs, a double fraction collector was constructed in which the beakers were arranged in two concentric circles. The outer circle comprised 24, 250 ml squat beakers and the inner circle 24, 50 ml units.

The rotating arm of the collector consisted of two concentric tubes (as illustrated) leading to two separate smaller dispensing arms, one of which supplied the outer ring of beakers and the other the inner circle.

With this apparatus it was possible to operate two columns simultaneously, with the consequent saving of time and cost. The timing device was a Sangamo electric time clock which activated a solenoid controlling the rotating arm.

d) <u>The spectrograph</u>.

A spectrograph was used almost exclusively for both qualitative and quantitative determinations except for a few of the column studies and distribution coefficient investigations where colorimetric techniques were sometimes used.

The spectrograph was far superior to the latter mainly because of its speed and the fact that an overall picture is given where very many elements can be studied simultaneously.

A large Hilger quartz glass instrument was available in which the discharge was focussed on the slit by means of a Hilger E.958 quartz lens. A rotating step sector with a transmission ratio of two served to provide a graded series of exposures.

The spectra were recorded on Kodak 103-O blue-sensitive plates over ranges varying from 2400 A to 4400 A. Further details are given later in this thesis.

SECTION IV.

PRELIMINARY COLUMN WORK.

a) Theoretical aspects.

A series of general column experiments were carried out in order to investigate the behaviour of IR 400 resin towards certain chloro-complexes. One of the purposes of these investigations was to establish the fact that the behaviour of this resin was similar to that of Dowex 1 which had been used by Kraus and his co-workers. Without this confirmation it would have been impracticable to use the data of Kraus and Moore as a basis for the author's work.

In considering the quantitative aspects of chromatographic absorptions and elutions, two important constants are used . The volume distribution coefficient D_v has already been defined and must not be confused with the distribution coefficient K_d. When a solution containing a given ion is in equilibrium with a resin and if M_r and M_l are the fractions of the ion M in the resin & liquid phases respectively then:-

$$K_d = \frac{M_r \ V}{M_l \ m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

Where V is the volume of solution and m the mass of the resin.

Similarly the volume distribution coefficient can be represented as :-

$$D_v = \frac{M_r \ . \ V}{M_l \ . \ V_b} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

Where V_b is the volume of the resin bed.

Therefore:-

$$K_d / D_v = V_b / m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (4)$$

In order to establish this relationship experimentally, a quantity of the resin was converted to the chloride form, and then dried for 24 hours over anhydrone in a vacuum at 60°C. Three g. of the resin were then weighed out, placed in about 50 mls. of 2N HCl and allowed to stand overnight. On the following morning the resin was transferred to a 10 ml. measuring cylinder and the volume of the resin bed recorded. This was found to be 7.2 mls.

Substituting in equation (4) above, we obtain the relationship :-

$$K_d = 2.4.\ D_v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5).$$

This expression holds only of course for this particular size of resin.

This relationship is important since there is little uniformity in the way in which workers in the ion-exchange field express their results, some give K_d and others D_v so that it is important to be able to readily convert one to the other. Fortunately, the work of Kraus and his co-workers was carried out with a resin of identical mesh size to that used in these investigations.

(b) <u>The selection of suitable column dimensions</u>.

The elution characteristics of an ion exchange column can be represented by the following expression :-

$$d = \frac{V}{(i + D_v)\ A} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where d is the distance travelled by an absorbed ion down an ion exchange column of cross-sectional area A, when V mls of eluent have been passed through the column and i i s the fractional interstitial space.

Experiments were carried out to establish the value of i for this particular resin. The bed was first of all pretreated with 2N HCl and a solution of $NiCl_3^-$ in the same strength of acid passed through the column. The Ni solution has the double advantage of being both coloured and non-absorbed on the resin. The volume of eluate collected up to the time that the coloured solution first appeared at the bottom of the column was measured and compared with the total volume of the resin bed which was found to be exactly 20 mls. The coloured solution first appeared when 9 mls had been passed through the column and therefore the value of i was 9/20 or 0.45.

If we therefore choose a column with a cross-sectional area of 1 sq cm (diam. 1.2 cm) and if D_v is greater than 10, then we can ignore i and the equation reduces to :-

$$d = \frac{V}{D_v} \quad \dots\dots\dots\dots\dots\dots\dots \quad (7)$$

This equation was used to a great extent in calculations of column dimensions. It was subsequently found that approximately 400 mls of 2N HCl were required to keep into solution approximately 20 gm of silicate rock and moreover, all the elements that were to be investigated had values of D_v greater than 20. Substituting these values in equation (7), it was deduced that a column 20 cm in length would be required to quantitatively retain the elements that were to be investigated.

(c) <u>Comparison of the properties of IR400 and Dowex 1.</u>

Having selected the dimensions of the column, three important problems remained to be solved before commencing studies on silicate rocks. In the first place, it was essential to ensure that the data of Kraus et al. would apply equally well to IR 400 resin.

Secondly, if we are attempting to use ion-exchange resins for the selective absorption and elution of trace elements, not only must the resin be capable of absorbing the elements rapidly and quantitatively but it must also be possible to elute these trace elements in a quantitative manner.

Finally, the eluting agent should be able to elute the elements in a not inordinate number of column volumes, otherwise bulks become unmanageable and there is increased danger of contamination from impurities in the eluent itself.

In order to solve the first of these problems, break-through curves for Zn, Cd and Bi were plotted in which the following procedure was adopted. Solutions containing approximately 300 m.eq. of Zn, Bi and Cd per litre were prepared and the acidity of each adjusted to 2N with respect to HCl. Each solution was passed separately through 20 cm columns at a constant flow rate of 34 mls/hr and successive 17 ml fractions were collected by the fraction collector. The cations in each fraction were determined by titration with EDTA using eriochromeblack-T as indicator for the Zn and Cd and Pyrocatechin Violet for the Bi. From these data, the breakthrough curves for each element were plotted and are shown in Fig. 2. and in Table 2 below.

TABLE 2.

Break-through curves for Zn, Bi, and Cd.

C_0 = original conc of solution. C = conc in eluate.
(C_0 in all cases 300 m.e.q. per litre.)

Bismuth		Cadmium		Zinc	
m.e.q. passed through column	C/C_0	m.e.q. passed through column	C/C_0	m.e.q. passed through col.	C/C_0
60	0	40	0	42	0
77	0.04	46	0103	48	0.268
89	0.30	51	0.43	54	0.81
101	0.83	56	0.93	60	0.95
113	0.99	60	1.00	66	0.99
125	1.00	65	1.00	72	1.00

These curves gave values of 50 m.e.q. for Zn and Cd and 92 m.e.q. for Bi as the break-through values.

These figures are in proportion to their

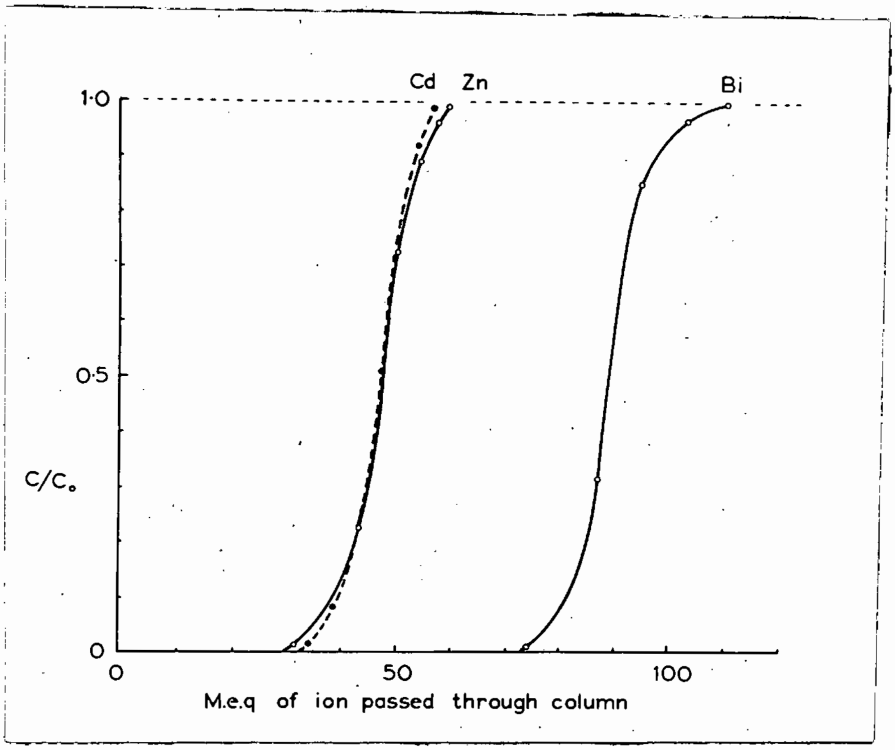


FIG.2. Exchange isoplanes (break-through curves) for Zn, Bi and Cd from 2N HCl solution.

distribution coefficients which should thereBore be in the ratio of 1 : 1 : 2 (very approx). These figures are in agreement with the findings of Kraus et al who obtained figures of 2,000, 2,500, &,5000, which are also very approximate in the ratio 1 : 1 : 2.

It would appear from these studies that IR 400 absorbs chlorocomplexes of certain metals in an analagous manner to Dowex.1 and there seems little reason to doubt that if it does so for these three elements it is most likely to do so for the other metals also. Accordingly the data of Kraus and Moore were used with perfect confidence in subsequent procedures and in no case was any difficulty encountered in using their figures. The similarity in behaviour of IR400 and Dowex 1. was further confirmed in later work on the distribution coefficients of certain elements in HCl and sea water (See Part IV, Section 7c).

(d) <u>Elution Curves</u>. The next stage of the investigations was to select a suitable eluting agent and to evaluate the optimum elution conditions. From a study of the literature and in particular the work of Kraus and Moore (1955) and Miller and Hunter (1954), two possible eluting agents were considered: namely sulphuric acid and nitric acid.

Experiments were carried out in which 500 µg amounts of Bi, Cd and Zn were absorbed on the anion exchange resin which had previously been converted to the chloride form by repeated washing with 2N HCl. After absorptio the column was eluted with 2N H_2SO_4 and a duplicate run was carried out in which elution with N/4 HNO_3 was attempted.

Successive fractions were analysed colorimetrically using an Evelyn Photoelectric Colorimeter. The Zn was determined by the dithizone method (Sandell 1950), Cd by precipitation as the colloidal sulphide and Bi by the iodide method (Sandell ibid). The elution curves were plotted and are shown in Fig.3. where it can readily be seen that :- The H_2SO_4 removed all the ions sharply and within approximately 25 column volumes although even then there was some tailing of Bi.

It was possible to derive much information from these curves. In the first place, the colorimetric determinations of the separate fractions enabled a quantitative evaluation of the percentage removal of the ions from the column to be established. The results are shown in Table 3.

TABLE.3.

Percentage removal of various absorbed ions by different eluents

Elution with 2N sulphuric acid			Elution with N/4 nitric acid.		
Cd	Bi	Zn	Cd	Bi	Zn
93%	104%	103%	100%	87%	99%

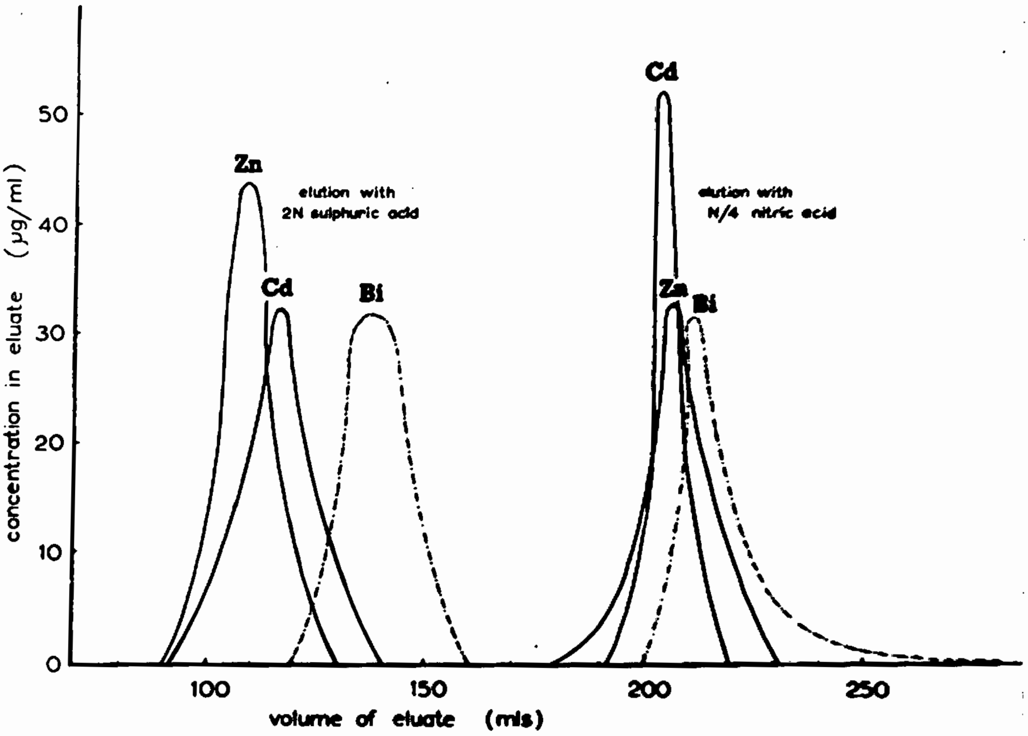


FIG.3. Elution curves for the elution of Zn, Bi and Tl with nitric acid and with sulphuric acid.

The values of over 100 % are due to experimental error but the overall picture is one of almost complete removal of all ions except Bi where only 87% was removed. It was later discovered that this element could be completel removed by using a greater volume of eluting agent.

Although the primary object of the research was enrichment of trace elements, separation was also an important factor, particularly with respect to Fe since interference from the complex spectrum of this element was to be anticipated at a later stage.

(e) <u>The Evaluation of Elution Efficiencies.</u>

In order to evaluate the efficiency of a particular eluting agent with regard to its likelihood of producing good separations, use was made of the findings of Martin and Synge (1941) and Mayer and Tomkins (1947) who have shown that an ion exchange column can be related to a fractionating column and its efficiency determined by measuring the number of theoretical plates. The theory has been further extended by Glückauf (1955) who has shown that the number of theoretical plates can be determined from an elution curve by application of the following formula:-

$$N = \frac{8\,(v + \bar{v})^2}{w^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

Where N = No of theoretical plates. v = column volume.

$\overline{v}$ = Vol required to elute the peak of an elution curve. w = width of the elution curve at $1/e$ from its base.

The results are shown below in Table 4.

TABLE 4.

Number of theoretical plates for the elution of Zn, Cd and Bi.

Eluent.	N/4 nitric acid.			2N sulphuric acid.		
Element.	Zn	Bi	Cd	Zn	Bi	Cd.
No of plates.	1800	1339	4161	1236	484	278

The figures for the elution of Bi with HNO_3 are only approximate since the formula only applies to true Gaussian curve

The HNO_3 elutions invariably showed a higher number of theoretical plates and a better separation of Fe from the trace elements was more likely to result with this eluent.

A further factor favouring the use of HNO_3 was the fact that in order to elute a given ion, less weight of this acid was required than of H_2SO_4 although the number of column volumes was greater. The use of the former was therefore likely to reduce the magnitude of reagent blanks.

Having conducted these preliminary investigations, it was decided to use N/4 HNO_3 as an eluting agent at least in the initial stages of the work that was to follow.

PART II

SECTION V.

THE DETERMINATION OF ZINC, BISMUTH, CADMIUM, THALLIUM AND TIN IN SILICATE ROCKS.

a) Development of a technique for qualitative studies on silicate rocks.

As studies on the elution characteristics of Zn, Bi and Cd had been carried out in solutions free from other ions, a series of additional experiments were carried out on solutions of a silicate rock. These experiments were carried out on samples of a granite from the Cape peninsula, S.Africa, hereinafter referred to as "Cape granite". The purpose of the studies was to obtain further data before the development of a quantitative spectrochemical procedure.

i) Dissolution of the rock sample.

A piece of granite weighing about 1,000 g.

was scrubbed with a nylon brush, heated to about 600°C in a muffle furnace and then plunged into deionised water.

This treatment rendered the rock so friable that it could easily be crushed to the texture of coarse sand merely by rubbing between finger and thumb. The rock was further ground in an agate mortar and sieved through a 100 mesh nylon sieve. In this way, the risk of contamination was reduced to a minimum. This thermal treatment worked satisfactorily with certain rocks, but others, such as meteorites, were not rendered very friable by this procedure. It is true that there was a slight danger of losing volatile elements such as mercury, but this was offset by the advantage of being able to dispense with a jaw crusher and percussion mortar in the preliminary stages of break down.

The next stage was the dissolution of the rock using a mixture of HF, HNO_3 and H_2SO_4. This operation was initially carried out in a platinum basin using 10 g. samples of rock. After digestion, the acids were evaporated and fumed away and the soluble part of the residue dissolved in 2N HCl. In the earlier experiments, the insoluble residue was separated by centrifuging and was redissolved in the acids. Later it was discovered that sedimentation followed by decantation was a more satisfactory solution to the problem. The procedure was repeated until all the rock was in solution. A total of four operations was usually necessary for a 20 g. sample of granite.

These operations usually involved the use of the following amounts of reagent :-

120 mls of HF.
80 mls of HNO_3
50 mls of H_2SO_4
80 mls of HCl.

These totals are not inconsiderable but later a much more efficient method was discovered involving the use of Teflon beakers in place of platinum (described later) and resulting not only in considerable time saving, but also in a reduction of the quantities of reagents used.

At all stages careful blanks were carried out on the reagents and at no time was any difficulty experienced from possible contamination since, except for Pb and minute traces of Zn and Sn, none of the cations subsequently investigated was discovered in the blanks.

When the rock was in solution, a small quantity of Br was added and then removed by boiling to ensure that the solution was fully oxidised. This was necessary because most elements that form chloro complexes do so only in their highest valency states. This is particularly important in the case of thallium since Tl^+ which does not form a complex, is much more stable than Tl^{3+} which forms a strong complex. (See later in this section).

(ii) Absorption and elution of the rock sample.

A solution of a 10 g. sample of rock was absorbed onto an anion exchange column which had previously been treated with HCl of the same normality. After absorption, the column was washed with 100 ml. of 2N HCl and eluted with N/4 HNO_3.

A similar experiment was carried out in which 2N H_2SO_4 was used for elution. In both cases, fractions were taken by the collector and evaporated to dryness. The amounts of residue were exceedingly small in most of the fractions and amounted to hardly more than a stain in the beaker. A solution of 20 mg. of acidified NaCl was therefore added to each fraction to serve as a carrier and also to quench CN emission during arcing so that the sensitive lines of Tl 3775 A and Mo 3903 A could be used. (See Ahrens and Liebenberg - 1946). The individual fractions were examined spectrographically in the wavelength range 2800 A to 4400 A using Kodak 103 - 0 blue-sensitive plates. Bi, Sn, Zn and Tl were detectable in the HNO_3 fractions. A very faint line that could have been Cd 3261A was also noticed but was so faint that there was some doubt about its identity. In the H_2SO_4 fractions however, no Tl was detected but the other elements including possibly Cd, were observed. In addition, traces of In, Pb and Ag were detected.

When the column that had been eluted with H_2SO_4 was further eluted with HNO_3, Tl then appeared in the eluate indicating that this element is much more readily eluted with HNO_3 than with H_2SO_4.

(iii) Experiments with larger quantities of Rock.

For the purpose of ascertaining whether the use of greater amounts of rock would enable rarer trace elements to be detected, 20 g. and 50 g. samples of the specimen were used and treated exactly as before except that elution was carried out with N/4 HNO_3 only. In both cases two fractions only were taken, namely 0 to 50 mls. of eluate and 50 to 500 mls. In this way it was possible to separate Fe from most of the other elements since the former was found almost exclusively in the first fraction, whereas the other metals except In and Pb occurred in the second fraction. Interference of intense Fe 3067.2 A with Bi 3067.7 A was thus reduced to a minimum.

In these 20 g. and 50 g. samples, no elements other than those already detected, were found but the presence of Cd was fully confirmed by the presence of fairly strong lines at 3261 A.

The spectrum of the second fraction of the 50 g. sample is shown in Fig. 4. The electrodes had a small Ag blank but this was appreciably less than the intensity

SPECTROGRAM OF THE ELUATE RESIDUE FROM 50 G. CAPE GRANITE

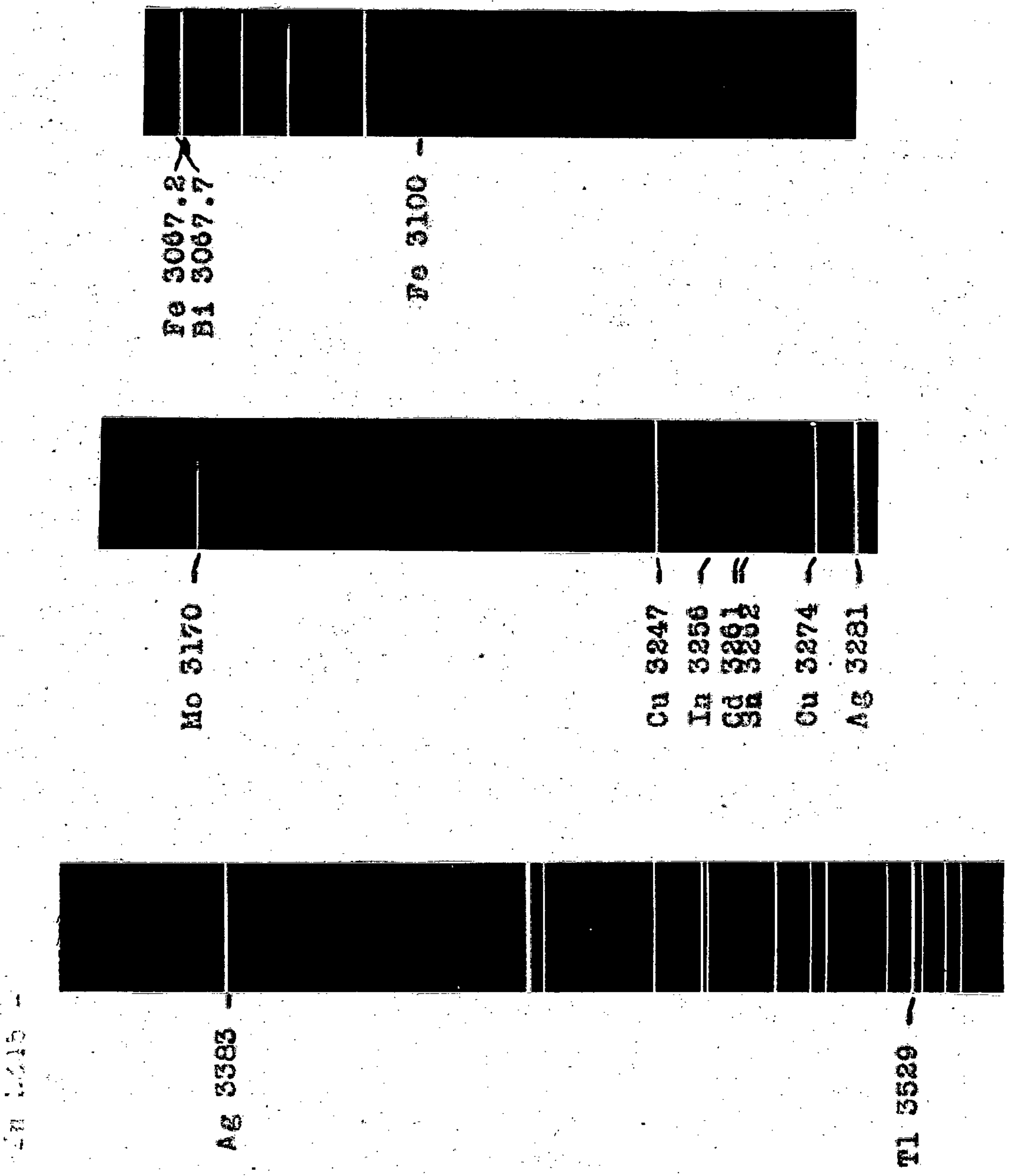


FIG.4.

of the Ag lines in the Cape granite.

In order to determine whether absorptions of these trace elements were quantitative, a solution of the rock which had beeh passed through the column once before, was reabsorbed, re-eluted and examined spectrographically. Pb and Ag which were present in the blank occurred again as might have been expected but no Tl, Cd, Zn, Sn or Bi were detected. A small quantity of In was also detected but this was due to the fact that the distribution coefficient of this element is low and a longer column would have been required for quantitative retention.

(iv) Experiment with a reduced rock solution.

The importance of oxidising the rock solution cannot be overemphasised since many elements, in particular Tl, are only absorbed in their highest valency states. Fe^{2+} does not form a chloro-complex at low HCl concentrations and this factor might conceivably allow of separation of this element from the trace metals by using a reduced rather than oxidised solution.

A further experiment was therefore carried out in which the solution of 20 g. of Cape granite was reduced with $TiCl_2$ before absorption on the column. After absorption and washing with acid, the elements were eluted with N/4 HNO_3.

The intensity of the Fe lines was indeed very much reduced by this procedure but as was to be expected, no trace of Tl was found in the eluate.

Clearly if a reduced solution were to be used it would have to be with the disadvantage that Tl and other elements would not be detected.

(v) <u>Further Elution Studies with Nitric Acid</u>.

In order to study more fully the elution of Cape granite with HNO_3, two series of investigations were carried out in which 20 g. samples of the rock were eluted with N/4 and $\frac{3}{4}$ N HNO_3 respectively, the fraction collector providing suitable volume intervals. The elution curves are featured in Figures 5 and 6. Bi, Sn and Tl tailed appreciably when eluted with this acid; this tailing is probably due to two main reasons: the formation of nitrato complexes in nitric acid (Nelson and Kraus 1954) and the difficulty of removing the last traces of chloride ion from the column thus involving slight retention of those elements with high distribution coefficients (e.g. Tl It was found that Sn, Zn and Cd were eluted faster with $\frac{3}{4}$ N HNO_3 that with N/4 acid and that Bi was eluted more slowly with $\frac{3}{4}$ N acid whereas Tl remained virtually

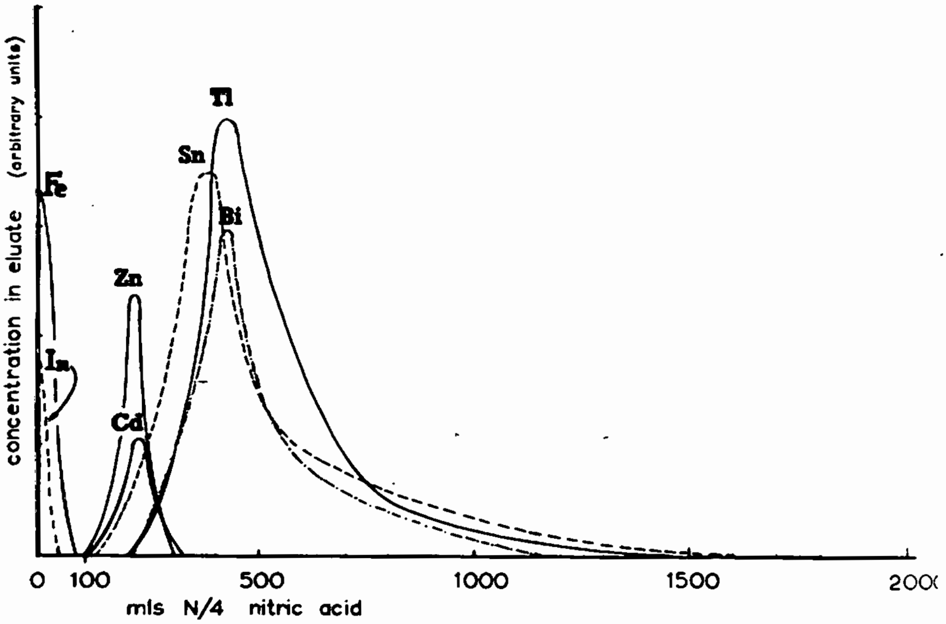


FIG.5. Elution of absorbate from Cape granite solution with N/4 nitric acid as eluent.

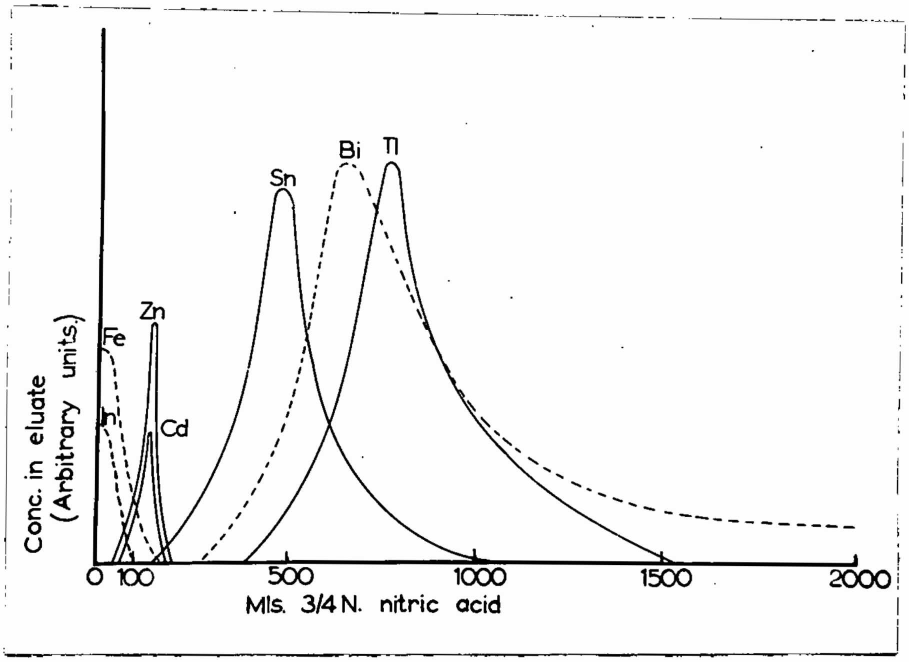


FIG.6. Elution of absorbate from Cape granite solution with $\frac{3}{4}$ N. nitric acid as eluent.

unchanged. Clearly there is no advantage in using $\frac{3}{4}$N HNO_3 in place of N/4 acid particularly as the risk of contamination would be greater if larger quantities of reagent had to be used.

At least 2,000 mls of N/4 HNO_3 were required to ensure that all the metals were eluted from the column to a concentration below their spectrochemical detection limits. This amount of eluate was a little bulky but entailed no manipulatory problems.

As a matter of interest (see Part III) Pt contamination from the Pt basins used in digesting the rocks appeared almost invariably in the fractions. It was eluted only very slowly and tailed appreciably. This element appeared later in the eluate of $\frac{3}{4}$N HNO_3 than in the N/4 acid and this fact indicates that a nitrate complex of Pt is probably formed.

(vi) Elution in the presence of hydroxylamine.

It had already been noted that with the exception of Tl, all the elements could be eluted in fewer column volumes by the use of H_2SO_4 instead of HNO_3. In order to achieve the elution of Tl also under these conditions, an experiment was carried out in which use was made of the fact that Tl does not form a chloro complex in its lower valency state. Elution was carried out with N. H_2SO_4 to which 10 gpl. of hydroxylamine sulphate had been added. The experiment was successful insofar as the Tl was readily reduced and eluted in a small number of column volumes (see Fig.7). Unfortunately however, it was not possible to obtain the reagent in a sufficiently high degree of purity free from Zn and Sn contamination.

(vii) Details of the Final Standard Procedure.

As a result of the various investigations described above, the procedure which was finally adopted as standard was as follows:-

After solution of the rock and absorption on the column, the resin was eluted with N/4 HNO_3 and two fractions taken :-

0 - 100 mls.
100-2000 mls.

The first fraction contained virtually all the Fe, In and Mo and is hereinafter referred to as the "iron fraction".

The second fraction contained all the Bi, Tl, Sn, Zn and Cd and will be referred to as the "main fraction."

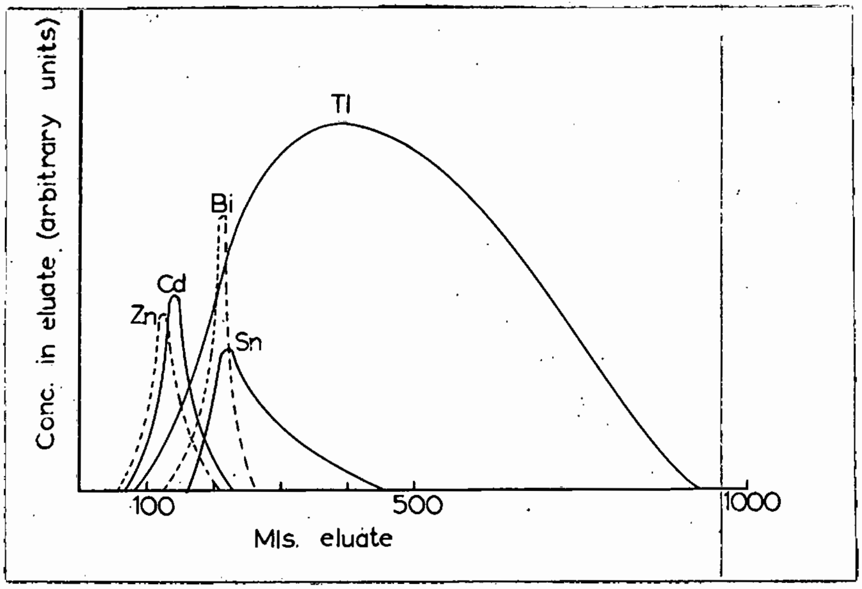


FIG.7. The elution of Tl (from absorbate of Cape granite solution) with a combined hydroxylamine sulphate - sulphuric acid eluent.

In order to ensure that the column was entirely free of contamination for the next cycle of operation, it was always further eluted with 1000 mls of 2N H_2SO_4.

The resin was discarded after every three or four successive absorptions and elutions since there appeared to be slight decomposition in the presence of HNO_3. This procedure was not particularly wasteful because only about 7 g. of resin was involved each time.

(b) Semi-quantitative observations on certain silicate rocks and other materials.

Having developed a standard procedure for the detection of trace elements in silicate rocks, a semi-quantitative examination of six materials was carried out.

These specimens included four silicates and in addition a carbonatite (as representative of non-silicate rocks) and a sample of hydrangea leaf as (as representative of biological material). The two latter specimens were included to test the versatility of the method.

A more detailed description of these materials is as follows:-

Granite G-1. This is the well-known "standard" American granite which has been examined quite extensively (see

Ahrens and Fleischer 1959) (Fairbairn et al 1951) and a considerable amount of trace element data are now available.

Diabase W-1. This is the "standard diabase which has also been extensively analysed. (See reference for G-1 above). This specimen was also useful as being representative of other basic rocks such as basalt and gabbro.

Chondrite: from Lafayette county, Texas: chondrites the commonest of the meteorites, serve as the principal source for estimating the so-called cosmic abundances of metals.

Shale: from the lower shale bed, Table Mt. series. Shale was selected as a representative of the most abundant of the sedimentary rocks which together with basalt and granite, is important for estimating the crystal abundances of elements.

Carbonatite. This rock was obtained from Otjiwarongo in S.W.A. and was completely non-silicate in nature.

Hydrangea Leaf Ash. A sample of about 15 g. of ash obtained from the Dept. of Botany, U.C.T., was used for the experiments.

All these samples were treated in the standard manner and examined spectrochemically. The results, together with those obtained on Cape granite for comparison are shown below in Table 5. In order to compare the relative intensities of the spectral lines, a scale of values from 0 to 4 have been ascribed.

0 = Absent. 1 = Just Visible. 2 = Weak.
3 = Fairly Strong. 4 = Very Strong.

Although a microphotometer was available for measuring the intensities of the lines, only visual comparisons were made as these served satisfactorily at this stage of the investigations. The evaluations were made by comparing all intensities with the intensities of a reference line of such intensity that the step sector graduations showed the seventh step as just visible. The results were then initially recorded as step values where step 7 was taken as "just visible", steps 5 and 6 as "weak", steps 3 and 4 as "fairly strong" and steps 1 and 2 as "very strong".

TABLE 5.

Spectrochemical examination of residues from nitric acid eluates.

Description.	Line and relative intensity.								
	Zn 3345	Bi 3067	Cd 3261	Sn 3262	In 3256	Mo 3139	Ag 3281	Pb 3683	Tl 3775
Cape granite	3	3	1	3	2	0	4	4	4
Granite G-1	3	2	0	3	2	3	4	4	4
Diabase W-1	4	2	1	3	1	1	3	3	2
Shale	4	2	0	4	1	0	3	4	4
Chondrite	2	0	0	2	0	0	1	3	0
Carbonatite	3	2	0	3	0	3	2	3	2
Hydrange Ash	4	0	2	3	0	2	4	4	2

One of the most interesting results of the experiments was the detection of Bi in five of the six rocks: it was not detected in the chondrite. The Bi content of Cape granite was much greater than that of the G-1.

As far as is known, this was only the second time that Bi had been determined (albeit semi-quantitatively) in a silicate rock. (See Brooks, Ahrens and Taylor: 1960).

The first values for Bi were obtained by Preuss (1941) using a double arc spectrographic enrichment procedure.

The results for Tl were also of especial interest since data on the abundance of this element in silicate rocks (particularly basic types such as dolerite and basalt) are very few in number and it is believed that the only other spectrographic data are those of Shaw (1952) and Preuss (1941) both of whom used [illegible] modifications of the double arc technique.

The possibilities of determining some of these trace elements quantitatively in a suite of several rocks were now considered.

Ag and Pb were not given serious study because of a high Pb blank in the reagents and an Ag blank in the electrodes. Of the remaining elements, only Zn, Bi, Tl, Cd and Sn were absorbed quantitatively under the conditions used in the "standard procedure". The other elements In and Mo form only weak chloro-complexes and their quantitative determination would have involved a much larger column with the added disadvantage that separation from Fe would have been a major problem.

In view of these preliminary investigations, it was decided to quantitatively estimate Zn, Bi, Cd, Tl and Sn in a suite of nineteen rocks, since not only were these elements all of interest geochemically but they were all virtually absent in reagent blanks and could both be absorbed on and eluted from the column in a quantitative manner.

(c) Development of a quantitative spectrochemical procedure.

The first prerequisite of a quantitative procedure was the selection of a suitable internal standard (see Ahrens and Taylor 1960)

A good internal standard should fulfill the following conditions :-

a. It should volatilise in a similar manner to the elements under investigation

b. It should have a relatively simple spectrum with lines as near as possible in wavelength to the lines that are to be measured.

c. It should be entirely absent in the material that is to be analysed.

d. It should be available in a high degree of purity.

e. The line selected as the standard should be free from self-absorption.

Of these criteria the first is very important and it is indeed fortunate that the five elements that were to be investigated were all relatively volatile since it seemed likely that a single internal standard of similar volatility might serve for the simultaneous quantitative estimation of all five metals.

After consideration of the above factors, the following elements were investigated as possible internal standards:-

In, Sb, Ga, K, Ge and Na.

The latter was to serve also as a matrix as has already been mentioned.

The respective volatilisation rates of the standards and elements under investigation were studied by arcing a mixture of compounds of these metals in a NaCl matrix at 7 amps and racking the spectrograph plate-holder at 5 second intervals. Typical volatilisation curves are shown in Fig.8. It can be seen that with the exception of Ge, all the elements complete their volatilisation in approximately the same time. By terminating the burn at the point where nearly all the NaCl had vaporised, it was possible to avoid an appreciable amount of Fe interference since this element is significantly less volatile than the others studied. This desirable "end point" was achieved by terminating the burn at the point where the sodium D colour started to wane to an extent where the blue Fe colour became visible through it.

Ga was subsequently rejected as a possible standa because it was found that traces of this element occurred in the silicate rock eluate residues. In view of this and also the lower volatility of Ge, it was decided to only investigate Sb, In and Na as possible internal standards. Before doing so, a suitable arcing amperage had to be selected.

This point is of considerable importance since it had already been noted that Zn and Cd were particularly sensitive to arcing amperages and line intensities for a given amount of either of these elements appeared to diminish with decreasing amperages. A series of mixtures containing compounds of all those metals used for the

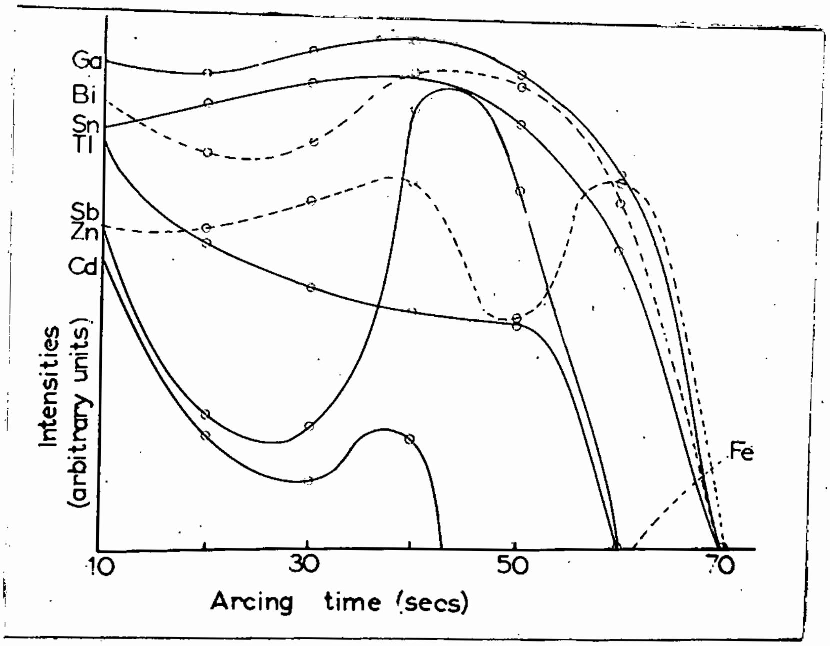


FIG.8. Volatilisation curves for certain elements in a NaCl matrix.

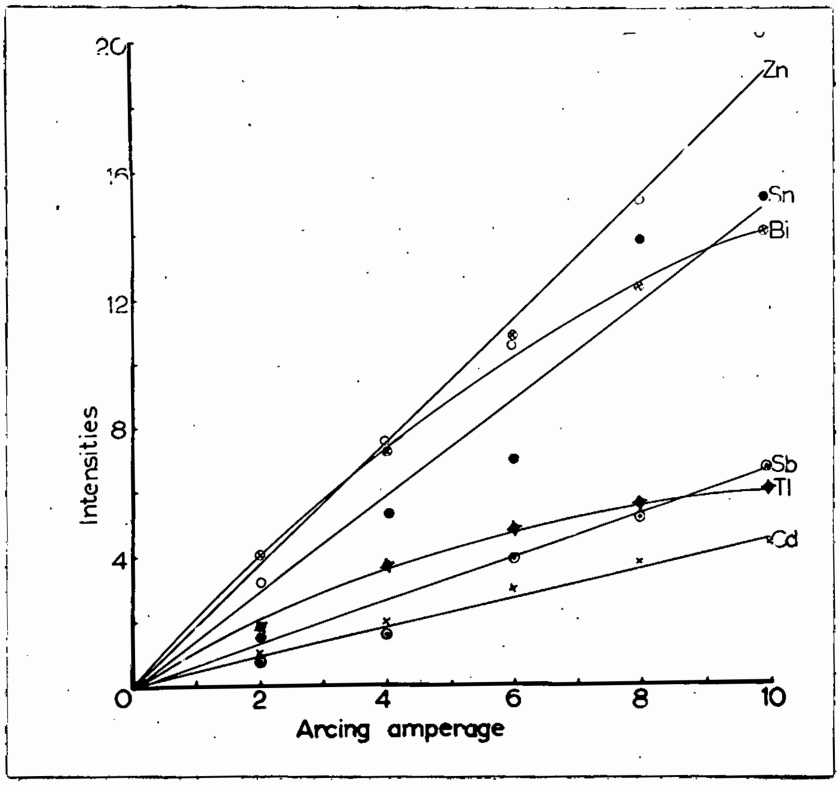


FIG.9. The effect of arcing amperage on the intensities of certain elements.

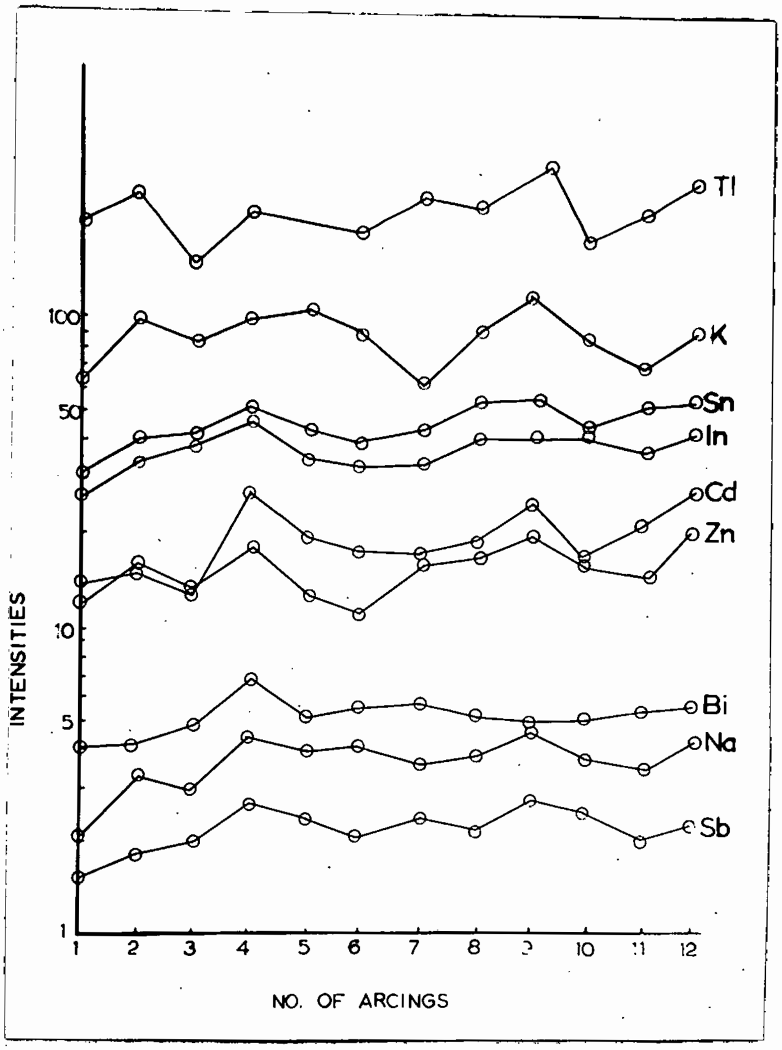


FIG.10. Reproducibility tests on replicate arcings for the evaluation of a suitable internal standard for the spectrochemical analysis of Zn, Bi, Sn, Tl and Cd.

Cd because later results did not confirm this. It was also discovered that traces of K contamination were often present in the samples analysed and this precluded the use of this element as an internal standard. In any case it was desirabl if possible to have one internal standard serving for all five metals. It was noted that although Sb was the best internal standard for Sn and Zn it was also reasonably satisfactory for the other three metals and this fact is demonstrated in Table.7. which shows the intensity ratios of the five line pairs.

TABLE.7.

Sb as internal standard for Zn, Bi, Cd, Sn and Tl.

Line Pair	No. of arcings and intensity ratios.											
-	1	2	3	4	5	6	7	8	9	10	11	12
Cd/Sb	0.90	0.83	0.63	1.00	0.83	0.85	0.71	0.86	0.95	0.64	1.10	1.21
Sn/Sb	2.06	2.22	2.10	1.93	1.83	1.95	1.83	2.40	2.15	1.80	2.20	2.34
Bi/Sb	2.64	2.33	2.45	2.55	2.17	2.68	2.38	2.32	1.82	2.04	2.19	2.56
Zn/Sb	0.77	0.89	0.65	0.69	0.53	0.54	0.71	0.79	0.73	0.54	0.72	0.90
Tl/Sb	1.03	1.33	0.73	0.78	0.98	0.88	0.95	1.00	1.12	0.80	1.05	1.10

On the basis of these determinations, the relative deviations were calculated from the formula :-

$$s = \sqrt{\frac{\sum d^2}{n-1}}$$

Values of 20.4%, 9.6%, 9.6%, 17.7% and 17.5 % were obtained for the line pairs Cd/Sb, Sn/Sb, Bi/Sb, Zn/Sb, and Tl/Sb respectively.

Although some of the intensity ratios were not highly reproducible, it was considered that the precision would nevertheless be satisfactory for the purpose of the investigation.

The feature of a single NaCl matrix for all samples coupled with a single internal standard was of great importance since this very much simplified the technique and eliminated one of the disadvantages of spectrochemical procedures where synthetic standards often have to be prepared to ensure a reasonable quantitative relationship between the standards and unknowns.

Reference has already been made to the so-called "standard procedure" which so far had been concerned only with column procedures and dissolution of the rock specimens. Details of the spectrochemical part of the "standard procedure" are as follows :-

The standards and unknowns were prepared in a matrix of 20 mg of NaCl and arced at 6 amps in graphite electrodes 3/16" (external diameter) X 3.2 mm (internal diameter) X 5mm (depth). Exposure was continued until the intense Na D colour had almost disappeared which was usually after about 1½ min. The small amount of Fe in the sample did not usually cause undue interference under these conditions.

The "standard procedure" was now applied to the preparation of working curves for the quantitative determination of Zn, Cd, Bi, Tl and Sn. A series of six standards each in triplicate was now prepared in which the concentration of each element ranged from x to 100 x where x represented a certain weight in mg. of the metal concerned. Each standard contained in addition 20 mg of NaCl and 0.8 mg of Sb. The weights of the various elements in these standards are shown below in Table.8.

TABLE.8.

Weights in mg of standards used for working curves.

Element	x	2x	5x	10x	30x	100x
Bi	0.001	0.002	0.005	0.010	0.030	0.100
Tl	0.0004	0.0008	0.0020	0.0040	0.0120	0.0400
Sn	0.005	0.010	0.0250	0.050	0.150	0.500
Zn	0.04	0.08	0.20	0.40	1.20	4.00
Cd	0.002	0.004	0.010	0.020	0.060	0.200

These standards were then arced at 6 amps with the step sector providing a graded series of exposures.

The line intensities were measured and the results plotted on logarithmic graph paper. These working curves are shown in Fig.11 and as can be seen, relatively good straight lines were obtained although with some self absorption in the higher concentrations of Tl, Cd and Bi.

d) The determination of zinc, cadmium, bismuth, thallium and tin in selected silicate rocks.

A quantitative determination of the above elements in a suite of nineteen rocks was now carried out using the standard procedure. The eluate residues were arced concurrently with the working curve standards in order to minimise errors due to changes in the optical system of the spectrograph which might have otherwise occurred over a long period.

The rocks selected, comprised a comprehensive range of many different silicates (and in addition one carbonatite) with a wide geographic scatter extending from Spitzbergen in the north to Antarctica in the south.

As usual, the fractions were divided into two, namely, 0 - 100 mls the "iron" fraction and 100 - 2000 ml the "main" fraction.

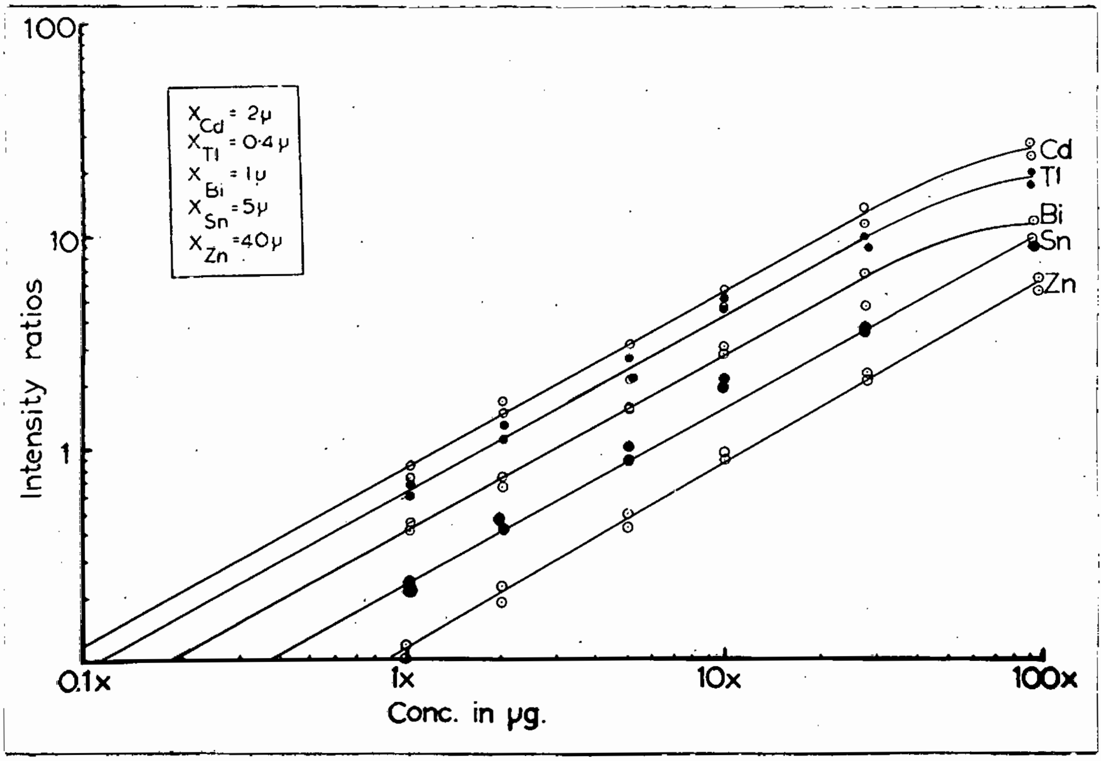


FIG.11 Working curves for spectrochemical analysis of Zn, Bi, Cd, Tl and Sn using Sb as internal standard.

In most cases, a 15 g. sample of rock was taken in duplicate and the two main fractions arced separately as duplicates; the iron fractions were however combined together and arced on a separate plate for subsequent semi-quantitative observations. These latter fractions of course represented 30 g of rock. The main fractions were arced using the step sector to afford graduation ; a slit setting of 0.005 mm being employed.

The line intensities were then measured and from the working curve, values for the abundance of all five elements in nearly all the rocks were obtained. These results are shown in Table 9 and a fuller description of the rocks is given in Table 10. In addition, a blank determination was carried out on all the reagents used in the standard procedure. Tl, Bi and Cd could not be detected in the blank but there were traces of Zn and Sn. The Sn represented a figure of 0.3 ppm on a 15 g. rock sample whereas the Zn represented 8 ppm on the same weight of sample. These figures would certainly have been serious if the concentrations of Zn and Sn in the rocks had been very low but it was found subsequently that the samples usually contained at least ten times as much Zn or Sn as the blank ; therefore little or no difficulty was experienced.

The same batch No. of each acid was used throughout the determinations to ensure that the reagent blank was not variable.

On measurement of line intensities, it seemed as if the internal standard Sb had a lower intensity in the rock samples than in the standards used for the preparation of the working curve. To determine whether in fact this was so, further samples were prepared in which the same amount of Sb was mixed with a wide variety of matrices and arced under the same conditions as the working curve standards and nineteen rock samples. These intensities together with those for the rock samples and standards are shown in Fig.12 in which they are designated as "synthetic standards","eluate residues" and "pure standards" respectively. It can be seen that there is a slight apparent diminution of intensities in those arcings other than the standards ; on the other hand, it was easy to explain this anomaly because whereas it was not difficult to transfer all the amount of standards from the porcelain basins to the electrodes, the eluate residues being somewhat glutinous (due to traces of Fe and alumina) tended to stick to the basins and were not completely transferred. Greater amounts could have been transferred by scraping the porcelain but this might have introduced impurities.

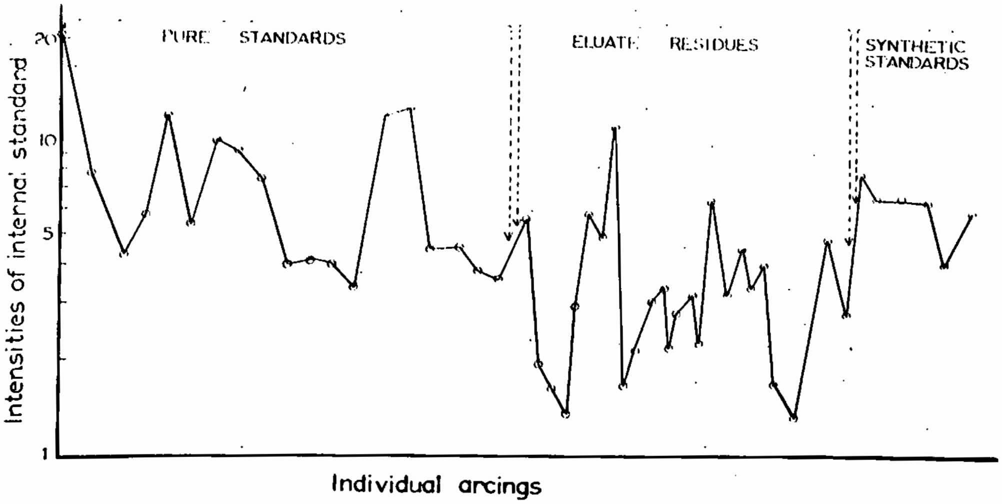


FIG.12. The variation in intensities of the Sb internal standard under different conditions.

TABLE. 9.

The Concentrations of certain metals in 19 rock samples.

(Expressed in ppm).

No	Type of rock.	Sn	Zn	Cd	Tl	Bi
1.	Cape granite.	19	72	0.10	0.70	0.6
		25	96	0.12	2.16	1.1
	Av.	22	84	0.11	1.40	0.9
2.	Granite G-1.	8.0	100	*c.0.05	1.4	0.09
		9.6	89		1.1	0.09
	Av	8.8	95		1.3	0.09
3.	Grey Gneiss.	22	260	0.16	2.4	0.03
		21	190	0.12	2.0	0.06
	Av	21	225	0.14	2.2	0.04
4.	Rhyolite.	12	72	-	-	-
		18	100	-	-	-
	Av	15	86			
5.	Trachyte.	1.5	150	-	-	0.08
		2.1	150	-	-	0.09
	Av	1.8	150			0.09
6.	Ijolite.	11	210	0.13	-	-
		12	220	0.16	-	-
	Av	12	215	0.15		
7.	Basalt.	8.0	160	-	*0.01-0.05	-
		7.7	120	-		-
	Av	7.8	140			
8.	Dolerite. (Diabase)	18	280	0.30	0.41	0.15
		24	390	0.30	0.67	0.15
	Av	21	335	0.30	0.54	0.15
9.	Olivine Basalt.	3.0	70	0.05	c.0.05	-
		4.7	75	0.04		-
	Av	3.8	73	0.05		
10.	Diabase W-1	8.7	67	0.07	0.05	-
		8.7	69	0.09	0.04	-
	Av	8.7	68	0.08	0.04	

TABLE.9. (Cont'd)

No Type of rock	Sn	Zn	Cd	Tl	Bi
11.Norite	1.1	150	-	-	0.05
	1.4	170	-	-	-
Av	1.3	160			
12.Eclogite.	0.7	64	-	-	0.07
13.Peridotite.	1.0	37	-	-	1.20
	0.8	21	-	-	1.20
Av	0.9	29			1.20
14.Lherzolite.	0.3	220	-	0.12	0.03
15.Hortonolite dunite.	1.7	180	-	-	-
	0.9	270	-	-	-
Av	1.3	225			
16.Olivine bomb.	-	77	-	-	-
17.Shale.	17	240	-	0.30	2.0
	21	270	-	0.70	2.2
Av	19	260		0.50	2.1
18.Ocean Mud.	4.3	110	0.12	0.06	0.03
	3.3	100	-	0.21	0.10
Av	3.8	105		0.13	0.06
19.Carbonatite.	12	24	0.90	-	0.06

* Precise values unobtainable because of high backgrounds.

TABLE.10.

Locality Details of selected rocks used for the investigatio

No.	Name of rock.	Locality.
1.	Cape granite.	Cape peninsula area.
2.	Granite G-1.	Westerley. Rhode.I. USA. (Fairbairn et al 1951)
3.	Grey Gneiss.	W.Ongul I. Lützow-Holm Bay, Antarctica.
4.	Rhyolite.	Mensons peninsula, Lyttelton. N.Z.
5.	Trachyte.	Devils Gap, Akaroa, Banks Penin. N.Z.
6.	Ijolite.	South of Melteig, Fen area, Norway.
7.	Basalt.	Mt Herbert flow, Old ballast quarry, Diamond harbour, Lyttelton. N.Z.
8.	Dolerite.	Kloof Nek, Camps Bay Rd, Cape Town.
9.	Olivine Basalt.	Devils Gap, 2400 ft, Akaroa, N.Z.
10.	Diabase. W-1.	Centerville, Va. USA. (Fairbairn et al 1951)
11.	Norite.	Merensky reef, Lydenburg, Tvl, S.A.
12.	Eclogite	Almeklovsaeter, Almeklovdalen, Sunnmore, Norway.
13.	Peridotite.	Råna, Tysfjord, Norway.
14.	Lherzolite.	S. end Lac Lherz, Pyrenees, France.
15.	Hortonolite dunite.	Lydenburg, Tvl, South Africa.
16.	Olivine bomb in lava.	The volcano "Sverresfjell", Bock Bay, Spitzbergen.
17.	Shale.	Lower shale bed, Table Mt series, Rhodes Monument, Cape Town, S.A.
18.	Ocean Mud.	Lutzholm Bay, Near Cook penin. 68°S, 32°E. Mud at 500 m.
19.	Carbonatite.	Ondurakorume carbonatite complex, Otjiwarongo Dist, S.W.A.

e) The determination of Bi, Tl and Cd in a suite of basic rocks

In addition to the work carried out on the above suite of nineteen rocks, a further investigation was carried out into the abundances of Bi, Cd and Tl in a suite of ten dolerites. These rocks were all taken from the upper dolerite sill, main shaft, Jagersfontein diamond mine, Jagersfontein, Orange Free State, South Africa. The total thickness of the sill was 425 feet, the upper contact being 150 ft below the surface. (For further details of rocks see Truswell, 1955 and for further details of method see Brooks and Ahrens 1960b).

Since the elements that were to be investigated all had very high distribution coefficients, it was possible to devise a simpler method of anion-exchange enrichment.

The procedure that was adopted was as follows :- A substantially smaller column was used (dimensions 3 cm X 0.5 sqcm cross-section) and the rock solution was absorbed onto the resin in the normal manner. The washing with 2N HCl resulted in an almost complete removal of the Fe since the column was so much smaller than hitherto and it was not necessary to take two fractions as before. The single fraction comprised 1000 mls of N/4 HNO_3 eluate instead of the 2,000 mls of the "main" fraction as previously.

The spectrographic operations were exactly as before and Bi, Tl and Cd were determined quantitatively in all ten samples. The results are shown in Table 10a below.

TABLE 10a

The determination of Bi, Tl and Cd in dolerites from upper dolerite sill, Jagersfontein Diamond Mine.

Sample No	Location	Conc. in p.p.m.		
		Tl	Bi	Cd
1	260 ft below surface	0.08	0.15	0.10
2	280 " " "	0.10	0.80	-
3.	300 " " "	0.06	0.96	0.26
4.	360 " " "	0.15	0.28	0.25
5.	420 " " "	0.10	0.47	0.07
6.	460 " " "	0.07	0.17	-
7.	480 " " "	-	0.16	*c.0.01
8.	500 " " "	0.03	0.76	0.26
9.	520 " " "	0.03	0.13	0.08
10.	Chilled upper margin of sill.	1.10	0.23	0.24

f) Notes on other elements.

i) General During the determination of the five elements in the first suite of nineteen rocks it was also possible to make semi-quantitative observations on Ag, In, Mo and Nb. In Table 11, rough estimates have been given for these elements but no observations could be made on the suite of dolerites referred to in Table 10a above.

ii) The determination of niobium and molybdenum.

In the initial treatment of the first 14 samples

TABLE.11.

Semi-quantitative observations on In, Mo, Nb & Ag in rocks

Rock No	In	Mo	Nb	Ag
1.	3	2	-	3
2.	2	2	-	2
3.	3	-	-	2
4.	-	-	3	1
5.	-	-	3	3
6.	1	1	-	1
7.	-	2	3	1
8.	2	2	-	2
9.	1	2	-	1
10.	2	2	-	1
11.	1	-	-	2
12.	-	-	-	1
13.	1	1	3	3
14.	-	-	-	2
15.	-	-	-	1
16	-	1	1	1
17	3	2	-	1
18.	2	3	-	3
19.	2	3	-	3

\- Signifies not detected.
1. " faint lines detected.
2. " medium strength lines detected.
3. " strong lines detected.

Pt basins had been used but soon showed signs of breakdown.

This difficulty was solved by the use of Teflon beakers which are completely inert to all chemicals except molten alkali metals and which can be used at temperatures up to 300°C without any sign of breakdown or softening.

When Teflon beakers were used for dissolution of the samples, a slightly different procedure was adopted and this consisted of using a mixture of aqua regia and HF instead of H_2SO_4 as before. The samples were taken to dryness on a water bath and redissolved in 2N HCl. After absorption and elution, it was noticed that the eluate residues were far bulkier than usual due no doubt to the formation of anionic fluoro-complexes from residual fluoride ions which had hitherto been destroyed by fuming with H_2SO_4. This greater bulk increased background emission and precluded the estimation of rarer elements such as Cd.

The most interesting observation was the appearance of strong lines of Nb in some of the rock samples (Nos 4, 5,7,13 and 16 of the nineteen-rock suite) due no doubt to the formation of fluoro-complexes of this element. Mo was also detected and this was not surprising as other workers have studied the fluoro-complexes of Nb and Mo. (See :- Freund and Miner, 1953 ; Hague, Brown and Wright, 1954 ; Huffman, Lilly and Iddings, 1951 ; Kraus and Moore, 1949 and 1951).

Since the quantitative determination of Nb and Mo was of some interest, studies were made on the possibilities of determining these elements.

The procedure adopted was as follows :- After digestion in HF and aqua regia, the rock sample was redissolved in a mixture of N.HCl and N. HF and the solution absorbed on a column of dimensions 20 cm X 1 sqcm cross-section. The resin was contained in a polythene container instead of glass. After washing the column, the metals were eluted with 0.25 N. HNO_3.

Initial experiments had been carried out in which the degree of absorption of Mo and Nb was studied by absorbing these elements on the column and eluting with the same HCl/HF solution. These elution curves are shown in Fig.13 and show appreciable absorption of these elements from the mixed medium. This degree of absorption was not however great enough to allow a greater volume of rock solution than 150 mls without using a larger column.

Attempts to determine Nb and Mo in three silicate rocks using Pt as internal standard were not very reproducible and the studies were not continued further.

g) Discussion.

Bismuth. Very few abundance data are available for this element although a number of estimates based apparently on indirect evidence have been made. Clarke and Washington (1924) have given values of 0.01 to 0.1 ppm , Berg (1925) has estimated 0.034 ppm and the Noddacks (1934) have given a figure of 0.07 ppm also apparently based on indirect evidence.

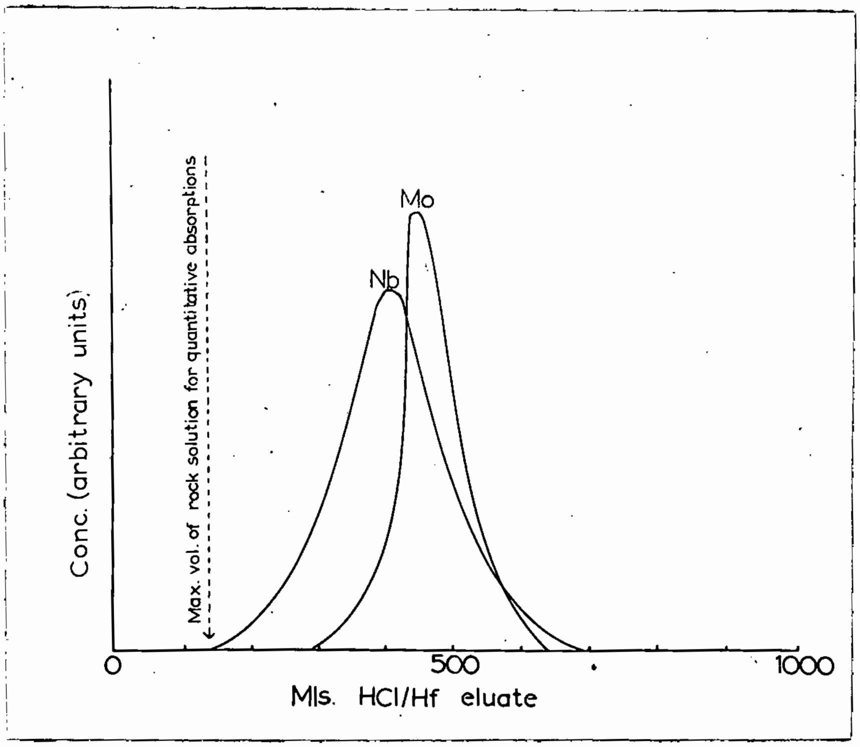


FIG.13. Elution curves for Mo and Nb using a mixed HCl/HF eluent.

Goldschmidt (1938) has estimated the abundance as at least 0.2 ppm, based on the proportion of As : Sb : Bi in ferruginous bauxites and sedimentary iron ores.

As far as can be ascertained, there are at present only two sets of data on the direct determination of Bi in silicates.

Preuss (1941) employed a novel spectrographic distillation technique for the determination of certain volatil elements in silicate rocks. This method, developed by Rose and Böse (1936) involved the heating of the rock sample to a very high temperature (over 2,000°C) in a carbon arc furnace. The vaporised volatile elements were then introduced into a spectrographic arc by means of a stream of inert gas such as argon. Although the method suffered from the disadvantage of low reproducibility (± 30 %) and limitations to the amount of sample that could be employed, it was nevertheless possible to obtain many abundance data for the first time by direct means. Preuss has published Bi figures averaging 2 ppm for granites and 1 ppm for sedimentary rocks.

Ehmann and Huizinga (1959) have just published figures for Bi in stone meteorites. The results were obtained by neutron activation. They have reported an average of 0.0022 ppm for six meteorites.

On the basis of twenty-one determinations on various silicate rocks including granite, basalt, dolerites and norite, the author has obtained values of 0.3 ppm for igneous rocks and a figure of 2.1 ppm for a shale. These values are in good agreement with Goldschmidt but lower than those of Preuss. It must be emphasised however that this estimate of 0.3 ppm is only a very rough approximation because Bi can apparently vary very appreciably even in identical rock types. (Cf Cape granite and G-1 where figures of 0.9 and 0.1 ppm respectively were obtained). Both the author's and Preuss' values have been obtained from a relatively small number of silicates and are not therefore necessarily in conflict if we consider the wide apparent variation referred to above. The lowest values obtained by the author were 0.03 ppm in Lherzolite and the highest, 2.1 ppm in shale.

The number of analyses available are really too few to obtain a comprehensive picture of the distribution of Bi but it is nevertheless possible to make certain general observations. Bi shows both lithophilic and chalcophilic properties with the latter predominating to a marked degree. The similarity of the ionic radii of Bi and Ca (0.96 A and 1.01A respectively) could conceivably lead to substitution in Ca minerals (See goldschmidt 1954) in which case enrichment in basalt, diabase and norite relative to granite might be expected. This is not apparent in the available data and in addition it has been noted that appreciably high Bi figures are obtained in rocks in which we might expect a lower Ca content relative to granite (e.g. Peridotite and shale).

The apparent enrichment in shale relative to granite can be explained if we consider the marked chalcophilic nature of Bi since the sulphur content of shale is about 5 times that of most other igneous rocks (Rankema and Sahama 1950) and on this basis enrichment might occur.

Although it would seem that enrichment based on chalcophilic considerations is likely to predominate over substitution in Ca minerals, the presence of Bi in the carbonatite may well be due to such substitution.

The author's figures for Bi in G-1 are the first available for this rock.

Cadmium.

As with Bi, abundance data for Cd in silicate rocks are somewhat few in number : this is probably due in part to the low concentration of this element in silicates and also to the difficulty in finding suitable specific methods for its determination.

One of the earliest estimates of the abundance of this element was given by Clarke and Washington (1924) who published a value of 0.1 to 1 ppm on the basis of indirect evidence. Goldschmidt (1937) has given a figure of 0.5 ppm but this was also an estimate. The earliest reliable direct determinations were those of Preuss (1941) using the distillation technique and Sandell and Goldich (1943 using colorimetric methods.

Preuss has reported an average of 0.2 ppm for granites and 0.3 ppm for sedimentary rocks, whereas Sandell has reported 0.19 ppm for basic silicates and 0.12 ppm for granites on the basis of determinations on eight samples, three of them being composites.

As a result of determinations on sixteen silicates, the author has reported an average of 0.10 ppm for granites and 0.14 ppm for basic rocks which is very close indeed to the figures reported by Sandell and Goldich. These figures are also a little lower than those of Preuss.

In some of the samples, difficulty was experienced in measuring the intensities of the spectral lines of Cd due to a combination of high backgrounds and low line intensities. In such cases, the data for this element are subject to a somewhat higher degree of uncertainty than the previously determined standard deviation would appear to indicate. Such samples have been marked with an asterisk in Tables 9 and 10a. There is nevertheless a fairly uniform pattern of enrichment of Cd in the more basic rocks as for example in dolerite (Klbof Nek) where a figure of 0.30 ppm has been reported.

Values of 0.05 ppm and 0.08 ppm have been reported for G-1 and W-1 respectively and are far lower than the 5 ppm obtained polarographically by Smythe and Gatehouse (1953). There seems little doubt that these latter figures are far too high even if the author's figures were ignored since Rankama has suggested that the Zn/Cd ratio in silicate rocks should be of the order of 900/1 and this figure can be compared with an estimate of 500/1 by Sandell. The polarographic estimations give a ratio of 12/1 which seems far from likely. The author's figures average about 800/1 (i.e. intermediate between Rankama and Sandell). A second factor that would seem to cast doubt on the results of Smythe and Gatehouse is the recent work of Vincent (1959) who has employed a neutron activation method for the determination of Cd in G-1 and W-1. His results agree well with the author's figures for G-1 but are somewhat higher for W-1 although at the same time much lower than the polarographic values. The lower value reported by the author for W-1 may be due to the error involved in reading Cd line intensities only slightly higher than the background value which is quite high for this rock.

In the carbonatite there is a distinct enrichment of Cd relative to Zn (27/1)and this may be due to the greater ease with which Cd is accepted by carbonatite since the ionic radius of Cd^{2+} (0.97 A) is close to that of Ca^{2+} (1.01 A). Zn^{2+} is much smaller (0.69 A) and could hardly be expected to substitute.

Tin.

The geochemistry of Sn is better known than that of the two preceeding elements and abundance data of many workers are available. These data show two main trends in the distribution of the element. In the first place, it has been shown that the abundances of Sn are subject to wide regional and geographic variations (Goldschmidt 1954) and secondly, there is a marked enrichment in the more acidic rocks.

It is difficult to explain this enrichment because Sn^{4+} (radius 0.71 A) might presumably substitute for Fe^{3+} (radiuss 0.61 A) and Sn^{2+} (0.93 A) for Ca^{2+} (1.02 A). We might therefore expect enrichment in basic rocks (high Fe and high Ca). Although the ionic radius of Fe^{2+} (0.74 A) is closer to that of Sn^{4+} than Fe^{3+}, substitution of the Sn for the ferrous iron is less likely because of the difference in charge. According to Rankama, the explanation of the anomaly of enrichment in basic rocks is that Sn is closely associated with the P content of the rock and this may well be the explanation for enrichment in the less basic rocks.

Goldschmidt and Peters (1933) have reported the following figures for Sn in silicates :-

Dunite	none
Basalt	4 ppm
Av of 11 German gabbros	8 ppm
Av of 14 " granites	80 ppm
Av of 36 European shales	40 ppm

Otteman (1941) has reported 56 ppm for granites. It would appear from these figures that Sn averages about 4 - 10 ppm in basic rocks and 40 - 80 ppm in acidic rocks.

Recent work by Onishi and Sandell (1957) does not confirm these figures and their average of 3 ppm, 1.5 ppm and 0.5 ppm for granites, mafic rocks and ultramafics respectively are far lower than those of earlier workers.

The author has found that it was possible to estimate Sn in all the nineteen samples studied and the values were in general, somewhat higher than those of Onishi and Sandell but lower than those of Goldschmidt and Peters. This is borne out by direct comparison of G-1 and W-1 (all determin's in duplicate).

Rock	Onishi and Sandell.	Brooks.
G-1 granite.	2, 2.5	8.0, 9.6
W-1 diabase.	2.5, 3.0	8.7, 8.7.

The differences involve factors of 3-4 and the cause is not known. The relative agreement is good and G-1 and W-1 evidently contain about the same amount of Sn.

The two characteristic trends of the geochemistry of Sn (see above) are fully apparent in the author's results. Not only are there wide regional variations in similar rock types (e.g. 8.8 and 22 ppm for G-1 and Cape granite), but there is also a distinct enrichment in the more acidic rocks.

This is very evident if we compare Hortonolite dunite (1.3 ppm) with Cape granite (22 ppm).

The fact that the author's values tend to lie between those of Goldschmidt and Peters on the one hand and Onishi and Sandell on the other, may not be significant if we consider the wide regional differences in tin which are said to exist.

Thallium.

The geochemistry of Tl is quite well known (see Shaw 1957) and a not unsignificant amount of abundance data are available for acidic rocks though somewhat few for basic types. Some of the earliest estimates of the abundance of this element were made by Clarke and Washington (1924) but their figure of 8.5×10^{-4} ppm is far too low. The Noddacks (1930) published a figure of 1 ppm which they subsequently amended to 0.1 ppm (1934). Ahrens (1947) has estimated an abundance of 3 ppm based on the apparent constancy of the Tl/Rb ratio in silicate rocks Goldschmidt reviewed the Noddack figures on the basis of a few new analyses and published a figure of 0.3 ppm. Rankama (1949) has suggested that a figure of 0.6 ppm is closer to reality and his conclusions were based mainly on the work of Preuss (1941) who obtained figures of 0.3 ppm in German gabbros and an average of 3 ppm in granites. The work of Otteman (1941) who found 1.5 ppm in German granites was also taken into consideration in making this estimate. Both Preuss and Otteman used the distillation technique to estimate the Tl. Goldschmidt and Hörmann have also published an estimate of 0.5 - 1 ppm for Tl in granites. The neutron activation technique of Ehmann and Huizinga (1959) has yielded abundance data for Tl in stone meteorites and these workers have reported 0.0004 ppm as the average of 6 samples.

A comprehensive review of the geochemistry of Tl has been made by Shaw (1952) and he has suggested that Rankama's estimate of 0.6 ppm is too low and that the correct figure is nearer 1.3 ppm for the average distribution of this element in silicate rocks. The above data all refer to igneous rocks and the data on sedimentary types are fewer in number. Preuss has reported 2 ppm in shales and sandstones.

A most striking feature of the geochemistry of Tl is its enrichment in acidic rocks relative to basic types and this is said to be due to the similarity of the ionic radii of Tl^+ and K^+ (1.47 A and 1.33 A respectively) and consequent replacement of K by Tl. Tl^{3+} seldom exists in nature in igneous rocks (though perhaps in sediments) because the oxidation potential needed for its formation is so high.

The author's results are in general in very good agreement with those of other workers and fully show the trend of increasing enrichment of Tl in the more acidic rocks. The relatively high number of determinations on basic rocks (fifteen) is of particular interest since abundance data on these types are very sparse. The average figure reported here for basic rocks is about 0.18 ppm and approximately 1.5 ppm for granites ; the range was from 0.04 ppm in diabase to 2.2 ppm in grey gneiss.

The author's estimate of the crustal abundance of the element on the basis of 20 determinations is of the order of 0.9 ppm for a 1 : 1 basic/acidic rock ratio and this is very close to Rankama's estimate of 0.6 ppm. A 2 : 1 ratio would give 1.1 ppm and 1 : 2 would result in a figure of 0.7 ppm.

For the first time, values have been obtained for G-1 and W-1. The abundances given are 1.3 ppm and 0.05 ppm respectively. Recent work at the Brunel College of Technology (See Morris.1960) based on neutron activation has indicated 1.0 - 1.5 ppm for G-1 and 0.13-0.20 ppm for W-1 and these figures are reasonably close to those of the author.

Zinc.

The geochemistry of zinc has been extensively investigated by many workers and Goldschmidt has given an estimate of 100 ppm as the abundance of this element in igneous rocks. This is somewhat higher than the value of 80 ppm obtained by Sandell and Goldich (1943) but appreciably higher than the earlier figure of Clarke and Washington (1924) who have estimated the abundance as 40 ppm. Rankama has given a figure of 132 ppm but this value seems rather high and has been contradicte by recent work of Wedepohl (1953) who, using a novel double-arc technique, obtained the values of 118 ppm and 45 ppm respectively for basic and acidic rocks. This double-arc technique similar to that of Shaw, Joensuu and Ahrens (1950), was developed from the method of Mannkopf (1947) which in turn had been based on Preuss' technique.

This enrichment in basic rocks is, according to the data of Sandell and Goldich, due to the fact that the zinc content of silicate rocks is proportional to the combined Mg and Fe^{2+} concentrations. Such enrichment can take place because of the similarity in the ionic radii of Zn^{2+}, Mg^{2+} and Fe^{2+}.(0.69 A, 0.64 A and 0.74 A respectively).

The author's results show this latter trend quite clearly and are in fair agreement with other workers although tending on average, to be somewhat higher.

It was possible to estimate Zn in all nineteen of the suite of rocks listed in Table 9 including G-1 and W-1. The value for W-1 (68 ppm) is in good agreement with other workers but the figure for G-1 is somewhat higher. The figure of 234 ppm for shale is in conformity with the work of Palmqvist (1935) and Lundegårdh (1948).

PART III

SECTION.VI.

QUALITATIVE STUDIES ON THE DETERMINATION OF THE PLATINUM METALS AND GOLD IN SILICATE ROCKS.

a) Introduction.

It has been shown in previous pages that it was possible to enrich at least nine trace elements to the threshold of spectral detection limits by the use of the "standard procedure" and involving relatively small amounts of rock sample. Using a 20 g. sample, it was possible to attain an enrichment factor of about 2,000 which compares very favourably with other methods of concentration such as the double arc methods of Mannkopf (1949), Wedepohl (1953) and Shaw, Joensuu and Ahrens (1950) where factors of up to 200 were obtained.

High enrichment factors can be achieved through the use of fire assay procedures but such methods have the double disadvantage of limited applicability and a serious risk of contamination from reagents that are not easily purifiable.

Neutron activation methods have a special place in the analysis of trace elements and have the decided advantages of very high senstivity and a relative freedom from contamination risks. They do not however have the same simplicity and speed of the procedures described in this thesis and require special equipment.

A special mention must be made of the work of P.Hahn-Weinheimer (1956 and 1958) who has been able to enrich the noble metals (except Au) from a solution of a silicate rock by means of the complex with 2-quinolineselenol which can be extracted with $CHCl_3$. This author has reported 0.01-0.05 ppm for the platinum metals in eclogites. The elements were finally determined spectrochemically and the detection limits reported were 2.0 ppm for Os, 0.05 ppm for Ir, Ru and Rh, and 0.01 ppm for Pt and Pd.

Of the twenty-one elements that form chloro-complexes in 2N oxidised HCl solutions (See Table 1.) all except iron are usually only present in small amounts in silicate rocks and some are so very rare that they often cannot usually be determined even with a moderate degree of prior enrichment. Examples of such elements are Au, Re and all the platinum metals.

In order to fully study the application of anion exchange enrichment techniques, an investigation was carried out on this third group of trace elements. It was clear at this stage that much higher enrichment factors than those already reached would have to be attained and this would involve not only employing larger quantities of rock but possibly even selecting rocks known to be richer in some of these elements.

The scope of the combined procedure as applied to rocks is not infinite and there are in practice three limiting factors to the amount of enrichment that can be achieved :-

In the first place, if the rock sample is very large, appreciable quantities of reagents have to be used in order to dissolve the specimen and there is a consequent danger of contamination from the reagents.

Secondly, the distribution coefficient of the element with respect to the resin must be fairly high, otherwise a large amount of exchanger would be required to quantitatively retain the absorbate, this would in turn also involve, inter alia, elution difficulties.

The final factor to be considered is the practical one of handling large quantities of rock.

In 2N. HCl solution, Re, Au and all the platinum metals have relatively high distribution coefficients (all greater than 400 - See Table I) and in fact Au has the highest of all the elements at this acid concentration. (10^6)

(For further details see :- Blasius and Wachtel (1954), Kraus and Nelson (1954), Kraus, Nelson, Clough and Carlston (1955), Kraus, Nelson and Smith (1954), McNevin and Crummet (1953), Meloche and Preuss (1954), Nachod (1945), and Sussman, Nachod and Wood (1945)).

This factor, coupled with the general rarity and interest of these elements, rendered a study well worthwhile and investigations were undertaken with a view to at least detecting some or all of these elements in silicate rocks.

Despite the low abundance of these elements, an appreciable amount of data is available on some of them, in particular on Au, Pt and Pd. Many workers have, however, concentrated on two aspects ; namely, separations by ion-exchange and the use of these resins to recover the metals from waste products (See Sussman, Nachod and Wood (1945)): the use of ion-exchange resins for the enrichment and subsequent analysis of the elements has been largely ignored.

Most methods of determination of the noble metals involve fire assay procedures but the purpose of the investigation described here was to determine whether the "standard procedure" or a modification of it, might be employed for the estimation and detection of these elements.

b) Preliminary analytical work.

A preliminary study of the column behaviour of the elements was made by absorbing a mixture of Au, Re, Pt, Pd, Os, Ir, Rh and Ru onto a column of length 20 cm and cross-sectional area 1 sqcm. The mixture was dissolved in 2N HCl and the absorbed band was washed with an equal volume of acid of the same normality.

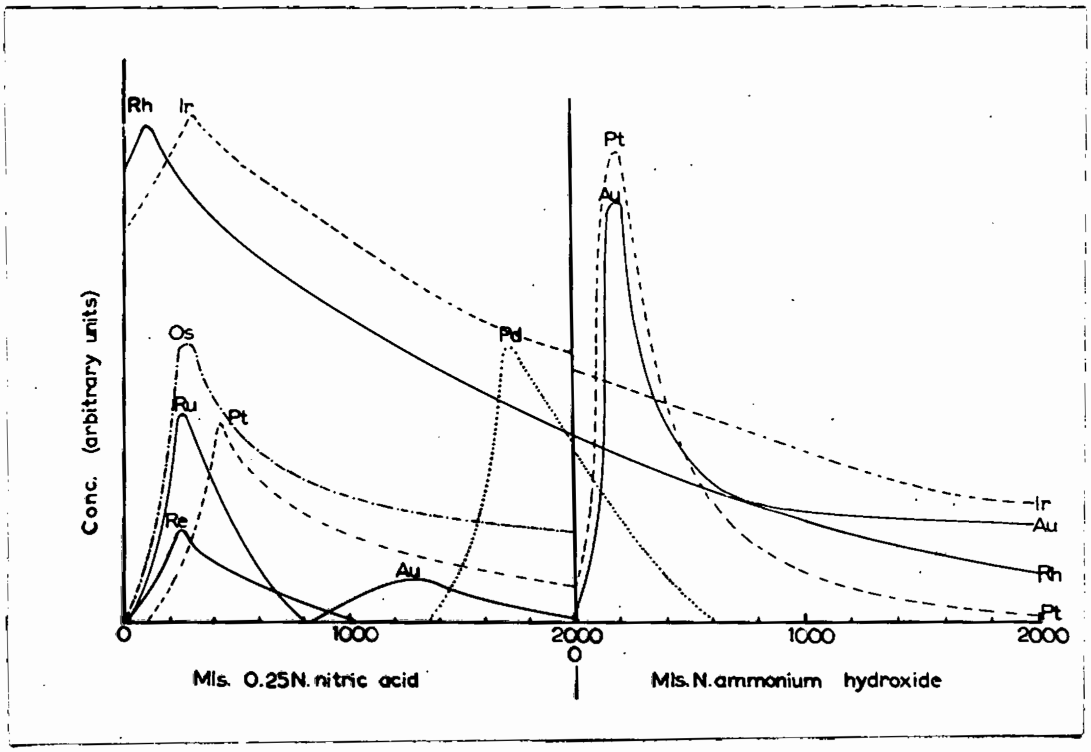
McNevin and Crummet (1953) have made a study of the chloro-complexes of the Pt metals and have discovered that it is possible to elute some of them with ammonium hydroxide. This is made possible by the formation of positively-charged ammine complexes such as :-

$$Pd\ (NH_3)_4^{2+}$$

these workers found that Pt and Pd could easily be eluted, Rh and Ir less readily and Os and Ru not at all. No data are available about the elution of Au and Re with ammonium hydroxide.

In view of these findings and in view of the author's own observations that is was possible to elute Pt with HNO_3, the absorbed mixture of metals was eluted firstly with N/4 HNO_3 and subsequently with N. ammonium hydroxide. Suitable volume intervals of eluate were taken by means of the fraction collector and the individual fractions were taken to dryness, collected in the NaCl matrix and examined spectrographically. The resin itself was ignited and the ash treated as a separate fraction which was also examined.

These data enabled approximate elution curves to be plotted and these are shown in Fig.14.



<u>FIG.14</u>. Elution curves for the Pt metals, Re and Au using N/4 nitric acid followed by N. ammonium hydroxide.

The observations can be summarised under the respective elements :-

Platinum. This element was eluted slowly with HNO_3 and with considerable tailing. On further eluting with NH_4OH , a much faster rate of release from the column was achieved and this was virtually complete after about 2,000 mls of ammonia had been employed.

Gold The behaviour of this element was particularly interesting, there appeared to be two elution peaks ; a small one with HNO_3 elution and a sharper one with NH_4OH. This latter peak is probably due to the formation of an auramine complex.

Elution of the Au from the column was not complete even with this double treatment and this is believed to be due to two main factors :- In the first place, the distribution coefficient of Au is so high in 2N HCl (10^6) that elution difficulties can be associated with the retention of small amounts of chloride ion by the column. The second factor is that the resin appears to have a slight reducing action (See Kraus and Nelson 1954) and hence easily reduced metals such as Au and Pt can be retained in the metallic state on the column.

Palladium.

This element was eluted equally readily with both eluents.

<u>Rhenium.</u> This metal was very readily eluted with the acid and it was not possible to ascertain whether ammonia would also serve for this purpose because the column was completely clear of the element before elution with the ammonia was initiated.

<u>Ruthenium.</u> As with Re, this element was completely eluted with the acid and its behaviour with ammonia was not studied.

<u>Osmium.</u> Os was eluted only very slowly with the acid and not at all with the ammonia. Even after the passage of 2,000 mls of HNO_3 through the column, a considerable amount of Os still remained. This is also probably due in part to reduction of the complex by the resin.

<u>Rhodium and Iridium.</u> The behaviour of these two elements on the column was very similar. The elution with HNO_3 was slow and involved tailing. No improvement in the elution rate was noticed on treatment with ammonia and at the end of the operation, a substantial amount of Ir remained on the column although most of the Rh had been removed.

The conclusions that could be drawn from these preliminary investigations were as follows :-

Ru and Re may be quantitatively eluted with N/4 HNO_3 only.

Pd, Pt and Rh may be almost completely eluted with a combination of both eluents.

Os, Au and Ir are incompletely eluted even when both eluting agents are employed.

The above column data were used in deciding what modifications of the "standard procedure" would have to be used in detecting or determining these rare elements in silicate rocks.

c) The detection of the Pt metals and gold in silicate rocks.

i) Experiments with a platinum-bearing rock.

A sample of Hortonolite dunite platinum-bearing rock from Swartklip mine, Rustenburg, Transvaal, was selected for the initial experiments. On the basis of the known average composition of the reef (See Wagner (1929)), the rock was estimated to contain about 3 ppm of noble metals of which :-

Pt	formed	approx.	2.2 ppm.
Pd	"	"	0.4 "
Rh	"	"	0.06 "
Ir	"	"	0.03 "
Os/Ir	"	"	0.02 "
Au	"	"	0.8 "

In order to afford a reasonable opportunity of detecting all these elements in the specimen, 150 g. of rock were employed and the noble metals concentrated to about 10 mg by a modification of the "standard procedure" which is now to be described. In this manner an enrichment factor of approximately 15,000 was achieved.

The rock was digested in a mixture of aqua regia and HF contained in a 150 ml Teflon beaker. The mixture was taken to dryness very slowly on a water bath, transferre to a porcelain basin and fumed with H_2SO_4. The purpose of this latter operation was to remove all traces of fluoride ion. This was of particular importance because in a preliminary reconnaissance experiment carried out on 100 g. of Cape granite, this precaution was not taken and the resultant eluate residue was so large as to be virtually unmanageable. It has also been discovered that an excess of sulphate ions is not desirable and accordingly after fuming with H_2SO_4, the rock sample was ignited at about 800°C. The residue was then redissolved in N HCl. This latter procedure was rendered very difficult and tedious because of the formation of insoluble ferric oxide due to the high ignition temperature employed. In a later experiment, the fault was rectified by igniting at a lower temperature and no difficulty was then encountered.

The rock specimen was particularly high in Fe and this factor, coupled with the large amount of rock employed rendered the effective separation of Fe from the trace elements somewhat problematical. In order to solve this difficulty, a double absorption and elution technique (analagous to double precipitation in gravimetric analysis) was used , in which the solution of the rock in 2N HCl was absorbed on the resin, the absorbate washed with 100 ml of 2N HCl and eluted in the normal manner with N/4 HNO_3. In this case however, only one fraction was taken instead of two.

After elution with acid, the column was further eluted with 2,000 mls of N. NH_4OH . This ammonia fraction was taken to dryness, collected in the usual NaCl matrix and held for subsequent spectrographic examination. The HNO_3 fraction however, was taken to dryness, redissolved in a small volume of 2N HCl, reabsorbed on the column and washed with acid of the same strength. The column was then eluted again with N/4 HNO_3 and in this case the usual "iron" and "main" fractions were taken.

The resin itself was ignited, the ash collected in the NaCl matrix and treated as a separate fraction. The latter, a blank on the reagents, the ammonia fraction and the two acid fractions were then examined on the spectrograph in the range 2600 A to 3300 A using Kodak 103-O blue-sensitive plates. By using this range it was possible to oberve the sensitive Au line at 2676 A.

Not only is this line very sensitive but it is also remarkably free from interference.

Au and all the platinum metals except Os were detectable in one or more of the fractions. No trace of Re was observed.

The spectrogram of the HNO_3 "main" fraction is shown in Fig 15a.

A summary of all the noble metals detected in the rock specimen is shown in Table 12 below :-

TABLE.12.

The qualitative spectrographic determination of the noble metals in a platinum bearing rock ex Merensky reef.

(This table shows under the relevent metal the lines used).

Fraction	Au	Pt	Pd	Ir	Rh	Ru
Iron	0	0	0	0	3323 3397	0
Nitric acid.	2676	2659 3064 et al.	3404 3421 3634	3220	3323 3397	3498
Ammonia	2676	2659 3064 et al.	3404 3421 3634	3220	3323 3397	3498

Besides the above elements, the following were

THE PLATINUM METALS AND GOLD IN SILICATE ROCKS.

SPECTROGRAMS OF ELUATE RESIDUES.

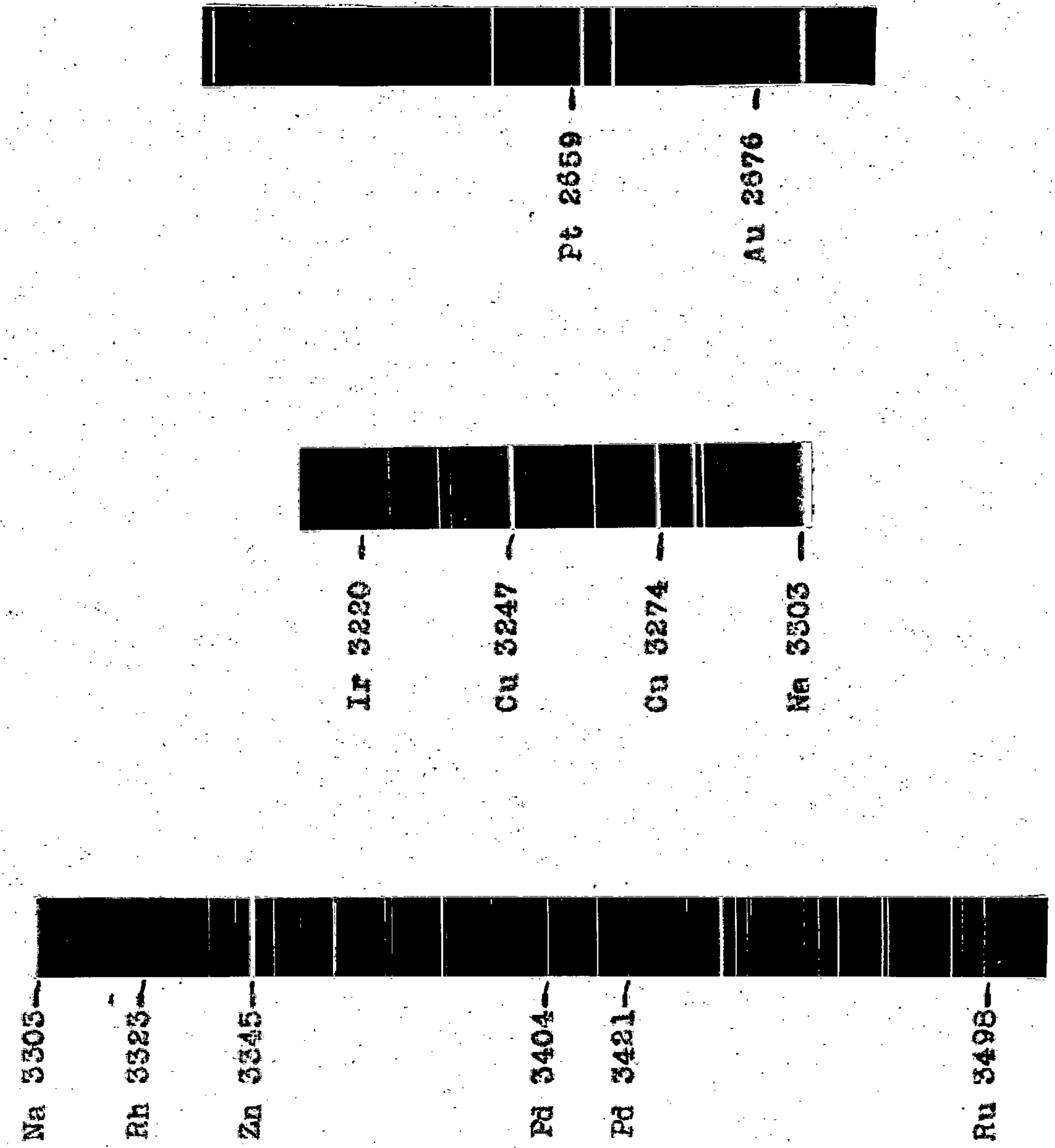


Fig. 15a (150 g. Pt-bearing rock ex Merensky Reef).

also detected :- Mo, Zn, Cd, Bi, Sn, Pb and Ag. There was no trace of Tl or Nb.

ii) <u>Investigations on Cape granite</u>.

The previous investigations had been carried out on 150 g. of rock and judging from the intensities of the Pt lines, a smaller quantity of material (say 15 g.) would have shown this element quite easily on the spectrograph. This does not of course apply to the rarer elements such as Ru where the full quantity of specimen was required to ensure detection. That particular rock had been selected because its platinum-bearing nature rendered detection of at least some of the noble metals likely but the question as to whether a common silicate such as granite was also likely to show any of these elements was of more than academic interest.

An investigation was therefore subsequently carried out on a large sample of Cape granite in order to establish which, if any, of these very rare elements could be detected.

A 200 g. sample of the rock was used for the study and this is probably the upper limit of sample size that can be taken without special purification of the reagents although no trace of any of the noble metals was detected in the blank.

The technique used for the treatment of the previous rock sample was furthermodified to eliminate difficulties that had been encountered and a final enrichment factor of about 20,000 was achieved. The revised procedure was as follows:-

The 200 g. sample was digested with the usual mixture of HF and aqua regia in Teflon beakers and fumed as before but in this case ignition was carried out at a much lower temperature (c.500°C). The result of this procedure was that no difficulty was experienced in the redissolution in 2N HCl. This solution was now absorbed on the standard size column (20 cm. length and 1 sq. cm. cross-sectional area) and washed with HCl of the same normality.

Instead of eluting as before, the entire resin was ignited, the ash redissolved in a small volume of HCl and this solution absorbed on a much smaller column of only a quarter of the capacity of the former. This smaller column was then washed and eluted first with HNO_3 and then with ammonia. The resin itself was also ignited and treated as a separate fraction as before.

The fractions were taken to dryness, collected in the usual NaCl matrix and arced in the range 2600 A to 3300 A.

The spectrogram of the HNO_3 fraction is shown in Fig. 15b.

Pt 2659 and Au 2676 and 3145 were clearly visible, but no lines of the other platinoids were detectable. By this new procedure very effective separation of the Fe had been achieved.

d) Discussion.

The experiments have clearly demonstrated that even the very rarest of elements can be detected by the combined procedure provided that sufficiently high enrichment factors can be achieved.

It is clear that it should be possible to determine many of these elements quantitatively the main limitation being the difficulty of removing certain metals such as Au from the column. This problem may, however, probably be surmounted merely by washing the second column after reabsorption, then igniting without elution and determining the elements in the resin ash. This procedure has indeed been employed in determination of trace elements in sea water. If it is also desired to determine volatile elements such as Zn, Cd, Bi, Sn and Tl at the same time, these must be eluted selectively from the column in a separate operation.

THE PLATINUM METALS AND GOLD IN SILICATE ROCKS

SPECTROGRAM OF ELUATE RESIDUE.

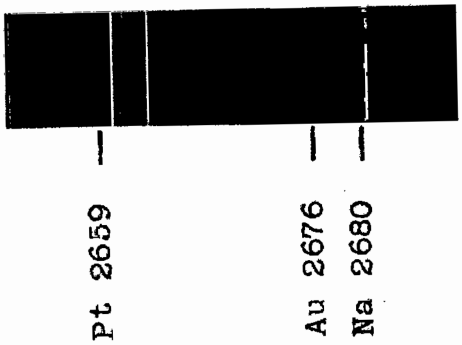


FIG.15b - 200 g. of Cape granite.

PART IV

SECTION VII.

THE DETERMINATION OF TRACE ELEMENTS IN SEA WATER.

a) Introduction.

The scope of the anion exchange enrichment technique as applied to silicate rocks has already been fully discussed. It has been shown that enrichment factors of up to 20,000 can be achieved but beyond this somewhat arbitrary limit it is likely that specially purified reagents would have to be employed for the determination of some elements.

Of the reagents that are used in the "standard procedure", by far the greater amounts are used in the dissolution of the rock sample itself. If a material can be found which is already in solution, clearly, higher enrichment factors could be achieved and moreover if the properties of this solution were such that lower HCl concentrations could be used then even higher enrichment factors should be attainable.

These latter considerations have led to this investigation into the possibilities of detecting and estimating trace elements in sea water since here is a case where no dissolution of sample is needed. In addition, as will be shown later, the high chloride concentration of sea water considerably affects the distribution coefficients of the chloro-complexes of certain elements. The extent of this change is such that a low HCl concentration in sea water will produce the same degree of absorption of a given element onto the exchanger as a much higher acid concentration in a pure aqueous medium.

Since appreciably smaller quantities of reagents are needed for the treatment of sea water, it should be possible to attain much higher enrichment factors without undue risk of contamination from the reagents. It will be shown that in fact, enrichment factors of up to 20,000,000 have been reached at which level most of those trace elements in sea water which form strong chloro-complexes should be detectable. This of course, only applies in this case to those elements that form strong complexes at relatively low HCl concentrations.

The suitability of sea water for these enrichment techniques is really quite remarkable and indeed, no better medium could theoretically be contemplated since not only does it possess the advantages mentioned above but is also significantly free of Fe (Conc c.20 ppm), the element which has caused much interference in past investigations.

Not one of the major constituents of sea water is likely to cause interference. Considering the suitability of natural waters for ion-exchange enrichment techniques, it is surprising that so little work has been done in this field. Such investigations that have been carried out have been confined mainly to Scandinavia and Russia. (See Moscow Geochemical Symposium - 1957).

Lure and Stefanovitch (1947) used a cation exchanger of sulphonic acid type to concentrate Ca and Mg from natural waters and eluted these metals with hydrochloric acid. This work was further developed by Nydahl (1951) who extended the method to include Na, K, Ca, Mg, Fe, Mn, Cl, SO_4, and PO_4, the last three ions being retained by a weakly basic anion exchanger.

The investigations which are described in this Thesis are confined mainly to the following elements:- Bi, Cd, Au and Zn. Sn was not investigated because of a relatively high reagent blank even after purification. With the exception of Zn and Au, abundance data on all these elements are exceedingly sparse.

Spectrographic procedures have been used by many workers for the detection of many trace elements in sea water after initial concentration usually by chemical methods, but, as far as can be ascertained, this is the first time that purely ion exchange enrichment techniques have been used for such studies.

In the present work, only a single reagent is used for the enrichment method (apart from a very small quantity of HNO_3 as eluent) and this is a distinct advantage over many other methods of enrichment particularly as the reagent in question is easily purifiable by distillation.

In view of the fact that quantities of up to ¼ ton of sea water were used in the work, the investigations were carried out at premises actually on the sea front in order to facilitate sampling and handling of the material.

All samples (except small amounts of water taken from out at sea for reconnaisance experiments) were taken from a stretch of beach free of any effluent discharge pipes and were taken only on still days when the sea was calm and clear. It would indeed have been preferable to have taken samples from far out at sea but this was impossible owing to the large quantities of sea water involved.

b) The apparatus.

The apparatus used for this investigation was basically similar to that used in previous studies except that modifications had to be made to suit the very much larger quantities of material handled. In addition, a smaller column than hitherto was employed. The smaller column could be used because although much larger quantities of absorbate were to be used, most of the elements under investigation had such high distribution coefficients under the conditions employed, that this size of column was long enough to ensure quantitative retention of them. (See equation 6, Part I).

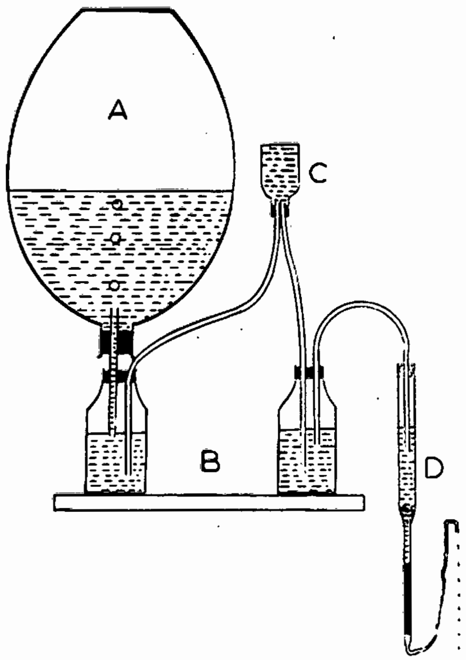
In some cases such as Cd and Zn, the column was too small to ensure quantitative retentions but this problem was to be solved by forming an estimate of the abundance of these elements by the so-called "frontal analysis" method. The principle of this technique is, that, provided the volume distribution coefficient of the element is known, accurately, it is possible to calculate the distance that an absorbed band would travel down the column. This distance is divided by the actual length of the column and a factor hence obtained. The amount of element actually on the column is determined after absorption is completed and this figure is multiplied by the factor to give the total concentration in the sea water. This frontal analysis method is not as accurate as one involving quantitative retention of the element concerned, but has the distinct advantage that prior purification of the column is not necessary since any significant impurities are eluted from the column long before the absorption step is completed. In this work however, it was necessary to purify the resin because certain elements such as Bi, were not determined by frontal analysis.

The dimensions of the column were as follows :- Internal diameter :- 8 mm. Therefore, cross-sectional area 0.5 sq. cm. Height of resin bed :- 13·2 cm. The column therefore contained about 5 mls of bed and represented 2.0 g. of resin.

The absorption of trace elements from 250 litres or more of sea water presented a problem of some magnitude not only in terms of handling large volumes, but also in the necessity of filtering any suspended solids in the material. Both problems were solved by the construction of an extremely large "chicken feeder" using a 10 gallon carboy. Removal of any suspended matter was effected mainly by sedimentation and partly by filtration via a cotton wool plug in the ion exchange column itself.

The apparatus is illustrated in Fig. 16. It will be seen that the carboy was suspended over the first of two sedimentation bottles. The latter was connected to the second bottle via a polythene siphon tube. A second syphon connected the second bottle to the ion exchange column itself. In order to obviate gas bubbles "breaking" the siphon, the siphon tubes passed through small inverted bottles filled to the neck with the sea water.

This combination of sedimentation and filtration was so successful that throughout a 100-day absorption period, no detectable slowing-down of the flow rate was noticed. This rate was fixed at 100 mls/hour, and was regulated by the usual hydrostatic pressure method. The residual "filtrate" was allowed to run to waste.



A = 10 GALL. CARBOY
B = SEDIMENTATION BOTTLES
C = SIPHON BOTTLE
D = ION-EXCHANGE COLUMN

FIG.16. Apparatus used for sea water experiments.

Since the values for D_V for these three elements were extremely high in 0.1 N. HCl, the assumption was made that they would still be very high in the acidified sea water and certainly high enough to ensure quantitative retention of the ions.

As Zn and Cd were expected to be only relatively strongl absorbed on the column, the distribution coefficients were determined colorimetrically. (i.e. colorimetric methods are not sufficiently sensitive to determine extremely high coefficients).

i) The determination of the distribution coefficients of Zn & C

Similar techniques were used for the determination of the above and the procedure was as follows :-

The "fines" from a quantity of IR 400 anion-exchange resin were removed by decantation after agitation with water. The resin was purified by elution, converted to the chloride form and vacuum-dried over anhydrone at 60^{o}C. (This was the same as the procedure used by Kraus et al, for Dowex.1.)

One g. samples of resin were then transferred to 100 ml. Erlenmeyer flasks. 50 ml. of N/1000 HCl were then added to one pair of duplicates together with about 500 µg. of Cd or Zn. The other pair of duplicates was treated in exactly the same manner except that the 50 ml. of N/1000 acid was prepared in sea water instead of distilled water. The flasks were agitated in a mechanical shaker for 24 hours and aliquots taken at the end of this period.

The aliquots were analysed colorimetrically with dithizone (Sandell 1950). The acidities of the flasks were then increased to N/100 by the addition of HCl and sufficient distilled water or sea water to restore the volume of solution to 50 mls.

The procedure was repeated several times with gradually increasing HCl normalities of N/10, N, 2N and 3N and in this way it was possible to plot curves of distribution coefficients as a function of HCl normalities.

The curves for Zn and Cd are shown in Fig 17 and the data are recorded below in Table.13.

TABLE 13.

The distribution coefficients of Zn and Cd in pure HCl solutions and in acidified sea water.

Sample	HCl normality	K_d	D_v
Zn in pure HCl	0.1	20	8
" " " "	1.0	910	364
" " " "	2.0	2400	960
Zn in sea water	0.001	102	41
" " " "	0.01	172	68
" " " "	0.1	441	176
" " " "	1.0	1375	550
" " " "	2.0	1721	688
Cd in pure HCl	0.001	10	4
" " " "	0.01	71	28
" " " "	0.1	2120	848
" " " "	1.0	3900	1560
Cd in sea water	0.001	312	124
" " " "	0.01	812	324
" " " "	0.1	3640	1456
" " " "	1.0	4916	1966
" " " "	2.0	2482	993

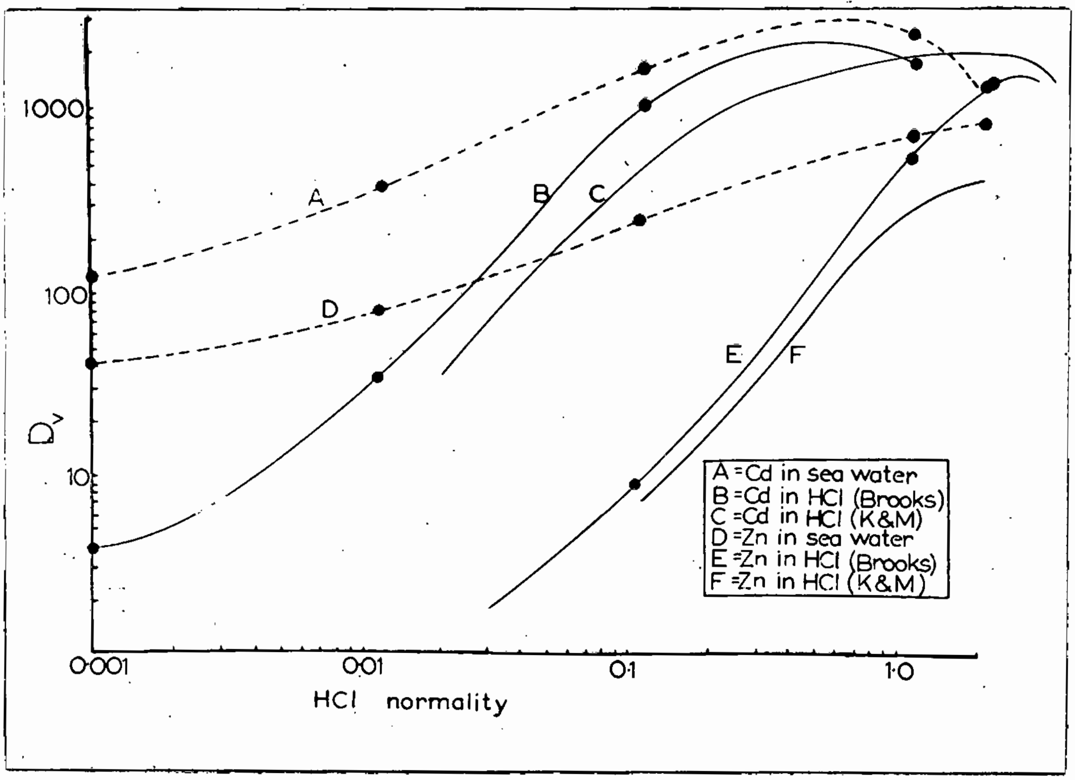


FIG.17. The volume distribution coefficients of Zn and Cd in pure HCl and in acidified sea water. (data of Kraus and Moore are included).

In order to afford a direct comparison with the work of Kraus and Moore, the values of K_d obtained from the above experiments were converted to D_v by dividing by 2.4 (See also page.22). The Kraus and Moore curves have also been included in Fig.17 and it will be noticed that there is a marked difference in the shape of the curves for pure HCl solutions and for acidified sea water.

It will also be noted that there is good correlation between the author's data for pure HCl and those of Kraus and Moore who used a different resin.

This difference in behaviour of the sea water and pure HCl solutions is particularly well demonstrated in the virtual non-absorption of Zn in N/100 HCl whereas in sea water acidified with the same quantity of acid, a distribution coefficient of 68 resulted.

The same pattern of behaviour was apparent for Cd where a value of 28 for D_v in pure N/100 HCl contrasted with a figure of 324 in sea water containing the same acidic concentration.

The conclusions that could be drawn from these results were that the high chloride concentration of sea water results in higher distribution coefficients at low HCl concentrations than would otherwise be obtained.

It is indeed possible that Zn and Cd might be absorbed from unacidified sea water but since the pH of this material is usually slightly over 7, it is advisable to ensure that the sea water contains at least some HCl to avoid the possibility of hydrolysis.

The significance of this "reinforcement" of chloro-complexes by the high chloride concentration of sea water is great because distribution coefficients of a certain desired magnitude can now be achieved by using a significantly smaller quantity of HCl than would otherwise be required. The limitations imposed by reagent blanks were hence enormously reduced and it was possible to obtain enrichment factors of very high magnitudes. (c. 10^7).

ii) Reconnaisance experiments.

Reconnaisence experiments were carried out on 45 litre quantities of sea water acidified with HCl. The samples were taken from a point about 2 miles from shore in Table Bay, Cape Town and were contained in 45 litre carboys adapted to feed the solution directly into an anion exchange column by means of a "chicken feeder" arrangement.

The solution was passed through the column at a flow rate of approximately 100 ml/hr and after about three weeks when the sorption stage had been completed, the column was eluted with N/4 HNO_3 and examination of the eluate residue was carried out on the spectrograph. Traces of Zn and Sn were found in the residue but no Au, Tl, Bi, or Cd.

It was apparent that this quantity of sea water was insufficient to provide detectable amounts of these very rare elements and further studies were based on much larger quantities of sea water.

d) Development of a quantitative spectrochemical procedure.

The quantitative spectrochemical procedure that was adopted was similar to that used for the determination of Zn, Bi, Sn, Cd and Tl in silicate rocks. Since the NaCl matrix was identical in both cases, the reproducibility of Sb as internal standard was assumed to be the same but as Au had not been determined before, reproducibility tests were carried out on the suitability of Sb as an internal standard for this element.

A series of 12 arcings were made in which the individual electrodes were loaded with 0.0025 mg. Au, 0.8 mg. Sb and 15 mg. of NaCl matrix. The arcings were carried out at 7 amps in the range 2500A to 3800A and the spectra were recorded on Kodak 103-0 plates. The electrodes were similar to those used in the quantitative studies described in Part II.

The results of the reproducibility tests are shown in Table 14. and are also recorded in Fig.18.

TABLE.14

Antimony as internal standard for gold.

Line pair Au 2676/ Sb 3267	
Arcing No.	Intensity ratio.
1.	0.64
2.	0.54
3.	0.64
4.	0.53
5.	0.59
6.	0.56
7.	0.57
8.	0.50
9.	0.50
10.	0.59
11.	0.54
12.	0.67

The standard deviation for the variation of intensity of the line pairs was found to be 0.056 on an average intensity ratio of 0.57 and the coefficient of variation (standard deviation expressed as a percentage) was therefore 10%.

Sb was clearly a good internal standard for Au under the conditions employed.

The spectrochemical procedure that was

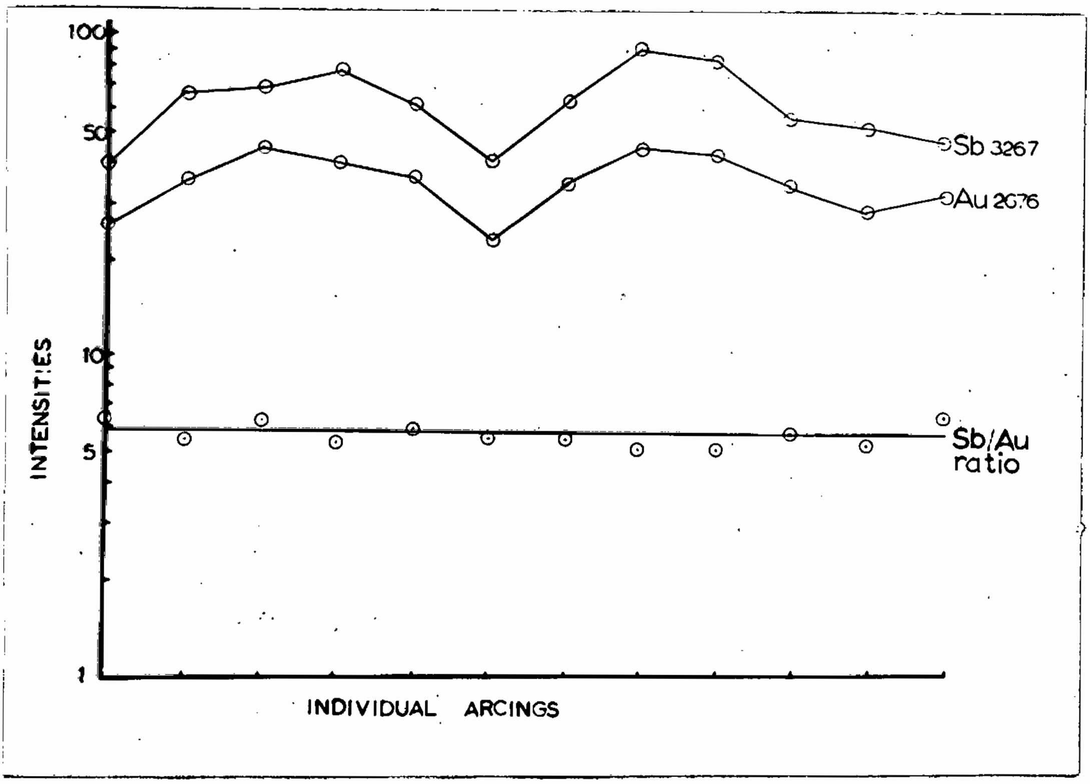


FIG.18. Reproducibility tests of replicate arcings for the evaluation of the suitability of Sb as an internal standard for Au.

finally adopted was as follows :-

After absorption of the trace elements from the sea water, the column was washed with 2N HCl and eluted with 1000 mls of N/4 HNO_3. The resin itself was ignited after elution and the ash mixed with NaCl matrix and treated as a separate fraction. The fractions were arced at 7 amps in the range 2600 A to 3800 A and the spectra recorded on Kodak 103-0 plates using the same electrodes as for the reproducibility tests.

e) The determination of cadmium, bismuth and gold in sea water

Of those elements that were to be investigated, it was probable that Au had the lowest concentration in sea water and if the data of Haber (1927) were taken as an indication, approximately 250 litres of sea water would probably have been required to afford a sufficient amount of detectable Au. The investigation was therefore based on the use of a minimum quantity of approximately 250 litres (¼ ton) of sea water.

The dimensions of the column were such that if HCl were added to the sea water to the extent of forming a decinormal solution, the distribution coefficients of Tl, Au and Bi were likely to be sufficiently high to ensure quantitative retention of these metals on the column. Cd and Zn were not likely to be retained quantitatively but since the distribution coefficients of these elements in sea water had already been determined, the abundance of each could be determined by the frontal analysis method.

Approximately 2½ litres of concentrated HCl were required for the acidification of the sea water and this acid was purified by distillation of a winchester of the AnalaR grade material in an all-glass apparatus. A reagent blank showed the entire absence of Au, Cd and Tl but small traces of Bi and Zn remained. The amount of Bi present was later found to amount to only 10% of the quantity found in the sea water.

After acidification of the sea water, sufficient bromine water was added to bring the concentration of this element up to 10 ppm in the sea water. The purpose of this procedure was to ensure that any thallium was in the oxidised state, to prevent reduction of any of the metals by the column, and to attempt to lessen the danger of absorption of gold on the walls of the containing vessel.

The sea water was now passed through the column via the apparatus described in Part IV Section b. The flow rate was adjusted to 120 /mls/hr and about 100 days were required for the sorption stage.

After absorption, the column was washed and eluted with 500 mls of N/4 HNO_3. The resin was then ignited and the ash treated as a separate fraction. This fraction together with the eluate residue was collected in the usual NaCl matrix and analysed spectrographically using Sb as the internal standard.

Distinct lines of Au 2676 , Cd 3261, Bi 3067 and Zn 3345 were detected and the spectra are shown in Fig.19. Unfortunately no trace of Tl was detected due possibly to a rather high cyanogen background in the region of the most sensitive Tl line at 3775 A.

The Zn line at 3345 A was somewhat diffuse and this precluded its accurate measurement.

In order to determine the abundances of Au, Bi and Cd in sea water, working curves were now prepared for these elements using Sb 3267 as internal standard. These curves are shown in Fig.20. Varying concentrations of x, 2x, 4x, 6x and 10x were used where x represented :-

0.0001 mg Au

0.002 mg Cd

0.001 mg Bi

To each standard were added 15 mg of NaCl and 0.8 mg of Sb. From these curves, abundance data for Au and Bi were obtained directly. From equation 6 (Part I section 4b) it was calculated that the Cd band would have travelled a distance of 32.6 cm during absorption from 250 litres of acidified sea water but

SPECTROGRAMS OF BISMUTH, CADMIUM AND GOLD IN SEA WATER.

(The first two step sector steps are shown)

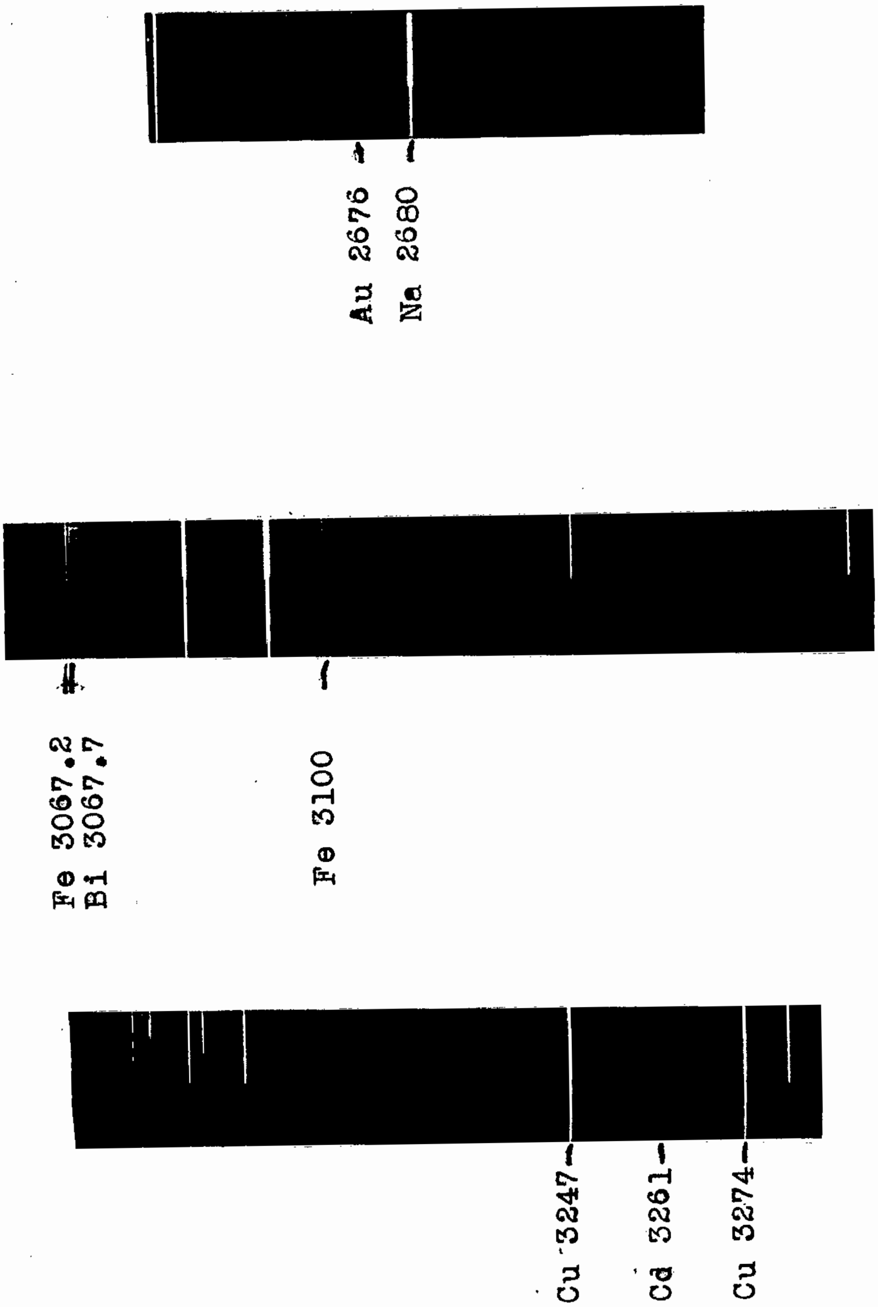


Fig.19.

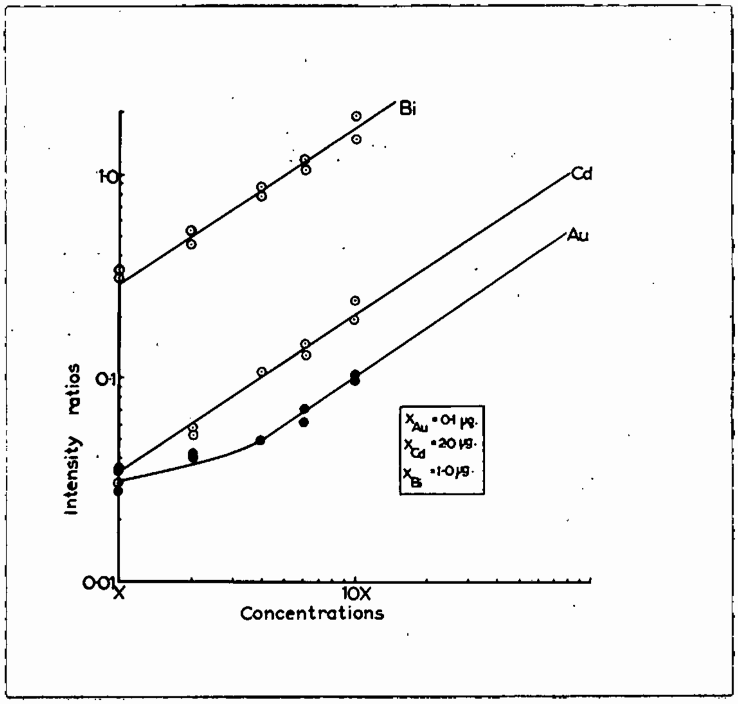


FIG.20. Working curves for the spectrochemical analysis of Au, Bi and Cd in sea water using Sb as internal standard.

the column length was only 13.2 cm. The apparent Cd concentration therefore had to be multiplied by a factor of 32.6/13.2 = 2.5.

The author's figures for Au, Bi and Cd together with those of other workers for comparison, are shown in Table 15 below.

TABLE . 15.

The abundance of cadmium, bismuth and gold in sea water.

(expressed in mg/ton)

Element.	Brooks	Other workers.
Gold	0.009	0.008 (Noddacks 1940) 0.004 (Haber 1927)
Bismuth	0.017	0.2 (Noddacks 1940)
Cadmium	0.066	0.032-0.057 (Mullin 1954)

f) Discussion.

1) Gold.

The abundance of Au in sea water is quite well known due mainly to the fundamental work of Haber (1927, 1928) and Wattenberg (1938, 1943.)

The procedure used by Haber was to co-precipitate the Au with Pb as $PbSO_4$ followed by reduction of the sulphate to the metal and subsequent determination of the Au in the Pb by fire assay. Haber has reported fairly wide regional variations in the gold content of sea water varying from about 0.001 to 0.01 mg/ton.

The Noddacks have reported a figure of 0.004 mg/ton which is in close agreement with Haber.

Other workers have reported higher figures of which the highest are those of Stark (1943) who has published a value of 2 mg/ton for the Atlantic coast of Spain and 0.2 mg/ton for samples taken from the Adriatic sea. He has also reported 0.4 mg/ton for the Mediterranean sea.

Putnam (1953) has given a semi-quantitative estimate of 0 - 46 mg/ton for the Pacific coast of USA.

Caldwell (1938) has published a figure of 0.1-0.2 mg/ton also for the Pacific coast of USA.

Except for Putnam who detected the gold on an amalgamated Ag/Zn couple, fire assay procedures were invariably used by other workers at some stage of the investigations. The author's method is therefore different from that of other workers insofar as a purely ion-exchange enrichment technique has been used.

The value of 0.009 mg/ton reported here is very similar to those of Haber and the Noddacks and lends weight to a possible average Au concentration of about 0.01 mg/ton in sea water. It is not clear whether the much higher results of other workers such as Stark are due to regional variations or to experimental error but the figure of

2 mg/ton obtained off the Spanish coast seems inordinately high.

An unknown factor in the author's work is the magnitude of absorption of Au onto the walls of the containing vessels. Haber took the precaution of applying a protective lead mirror to the walls of the vessels and removing this with the rest of the lead during the precipitation as sulphate. The author has attempted to minimise any absorption of Au by using a very large container for the sea water with a high volume/surface area ratio and also by working in an oxidising medium. By this latter procedure the likelihood of Au existing in the easily absorbed colloidal state is reduced.

ii) Cadmium.

Only one other figure is available for the concentration of Cd in sea water. Mullin and Riley (1956) have reported 0.032-0.057 mg/ton from the surface of the Irish sea. They extracted the Cd with dithizone in CCl_4 followed by spectrophotometric techniques. The results were checked spectrographically.

The author's results are in good agreement with these workers and the figure of 0.066 mg/ton reported here is only fractionally higher than the highest figures reported by the above workers.

The data available are far too few to form any definite picture of the pattern of the distribution of Cd in sea water but at least a basis has been laid for further investigations.

iii) Bismuth.

As with Cd, only one other figure is available for the concentration of Bi in sea water. The Noddacks (1940) have reported 0.2 mg/ton for this element in sea water taken from Gullmarfjord in Norway. Their method involved chemical separations followed by optical and X-ray spectrography. The investigations of these workers appear to have been mainly concerned with the distribution of Bi in marine organisms and it is possible, though not certain, that their Bi figure is an estimate based on indirect evidence. If this is so, the fact that the author's values are a factor of ten less than those of the Noddacks may not be significant.

As with Cd, too few data are at present available to allow a definite conclusion to be formed as to the abundance of Bi in sea water but on the available evidence, a figure of 0.01 to 0.20 mg/ton would seem to be the most acceptable.

SECTION VIII.

REFERENCES.

Ahrens.L.H. The quantitative spectrochemical examination
of the minor constituents in pollucite.
Amer. Min. - 30 - 616 - 1945.

Ahrens.L.H. and Liebenberg.W.R. The qualitative spectrochemical
analysis of minerals and rocks.
Trans. Geol. Soc. of S.Africa. Vol XLIX - 1946.

Ahrens.L.H. The abundance of Tl in the earth's crust.
Science - 106 - 268 - 1947.

Ahrens.L.H. Progress in the physics and chemistry of the
earth. - Vol II - Pergamon Press - 1947.

Ahrens.L.H. and Taylor.S.R. Spectrochemical analysis.
Addison Wesley Pub. Corp. Inc. , 1960.

Ahrens.L.H. and Fleischer.M. Report on trace constituents in
standard granite G-1 and standard diabase W-1.
In press - 1959.

Berg.G. A new attempt to determine the relative dissemination of the rare elements. Z. Prak. Geol. - 5 - 73 - 1925.

Black.W.A. and Mitchell.R.L. - Trace elements in the common brown algae and in sea water.
J.Mar. Biol. Ass. UK. - 30 - 574 - 1952.

Blasius.E. and Wachtel.U. Separation of the Pt metals with a strongly basic anion exchanger.
Z. Angew. Chem. - 143 - 257 - 1954.

Brooks.R.R. The use of ion-exchange enrichment procedures in the determination of trace elements in sea water.
- in press - 1960.

Brooks.R.R. and Ahrens.L.H. The application of anion-exchange techniques to the spectrochemical detection of the noble metals in silicate rocks.
- in press - 1960.

Brooks.R.R. and Ahrens.L.H. The spectrochemical determination of Bi, Cd and Tl in silicate rocks using an anionic exchange enrichment technique - in preparation-1960b.

Brooks.R.R.Ahrens.L.H. and Taylor.S.R. - The determination of trace elements in silicate rocks by a combined spectrochemical-anion exchange technique.
Geochim. et Cosmochim. Acta - 18 - 3/4 - 1960

Caldwell.W.E. The gold content of sea water.
J. Chem. Ed. - 15 - 507 - 1938.

Campbell.W.C. and Nelson.F. - Chemical separations of Pb 207 from Bi 207. Phys. Rev. - 91 - 499a - 1953.

Clarke.F.W. and Washington.H.S. The composition of the earths crust. US Geol. Survey - No.127 - 1924.

Cranston.H.A. and Thompson.J.B. Use of an ion-exchange resin in the determination of copper in milk. Ind. Eng. Chem. Anal. Ed. - 18 - 323 - 1946.

Edge.R.A. Unpublished work. 1959.

Edge.R.A., Brooks.R.R., Ahrens.L.H. and Amdurer.S. Some reconnaisance observations on the combined use of ion exchange enrichment and spectrochemical analysis for the determination of trace constituencies in silicate rocks. Geochim. et Cosmochim. Acta. V.15 -4 - 337-1959.

Ehmann.W.D. and Huizinga.J.R. The determination of Bi, Tl and Hg in stone meteorites by neutron activation analysis. Geochim. et Cosmochim. Acta - 17 - 1/2 - Aug 1959.

Fairbairn.H.W. and others. A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analyses of silicate rocks. US Geol. Survey. Bull 980-1951.

Fairbairn.H.W. The precision and accuracy of chemical analyses of silicate rocks. Geochim. et Cosmochim. Acta. - 7 - 154 - 1953.

Freund.H. and Meyer.F.J. The determination of Al in Zr. Anal. Chem. - 25 - 564 - 1953.

Glückauf.E. The theory of chromatography IX, the plate concept in column separations. Trans.Far.Soc. - 51 -34 - 1955

Goldschmidt.V.M. and Peters.C. The geochemistry of Cr, Ni and Sn in troilite nodules of meteorites.
Nach. Ges. Wiss. Gött - Kl 165 - 1933.

Goldschmidt.V.M. The principle and distribution of the chemical elements in minerals and rocks. J.Chem. Soc -655 - 1937

Goldschmidt.V.M. The geochemical distribution of the elements.
Skr. Norsk. Videns. Akad. Oslo - Kl 4 - 1938.

Goldschmidt.V.M. Geochemistry - Oxford University Press - 1954.

Haber.F. Das Gold im Meerwasser. Z. Angew.Chem.-40- 303 - 1927.

Hague.J.L., Brown.E.D., and Bright.H.A. The separation of Ti,W Mo and Nb by anion exchange.
J.Research Nat. Bur. Standards - 53 - 261 - 1954.

Hahn-Weinheimer.P. The determination of the noble metals and carbon in eclogite and alkalic metamorphites in Münchberger gneiss. Naturwiss - 43 - 324 - 1956.

Hahn-Weinheimer.P. The determination of the noble metals in rocks . Z. Anal. Chem. - 162 - 162 - 1958.

Huffman.E.H., Lilly.R.C. and Iddings.G.M.
The anion exchange of Zr, Hf, Nb and Ta in HCl solution.
J.A.C.S. - 73 - 4474 - 1951.

Jentzsch.D. and Frotscher.I.
Ion exchange in analytical chemistry. The adsorption behaviour of elements in an anion exchanger in HCl solutions.
Z.Anal.Chem. - 144 - 17 - 1955.

Kraus.K.A. and Moore.G.E. The separation of columbium and tantalum with anion exchange resins. J.A.C.S. - 71 - 3855 - 1949.

Kraus.K.A. and Moore.G.E. The separation of Zr and Nb in HCl/HF mixtures. J.A.C.S. - 73 - 9 - 1951.

Kraus.K.A. and Moore.G.E. Anion exchange studies V, the absorption of the transition elements Mn to Zn in HCl . J.A.C.S. - 75 - 1460 - 1953.

Kraus.K.A. and Nelson.F. Anion exchnage studies X. Au in HCl solutions. J.A.C.S. - 76 - 984 - 1954.

Kraus.K.A., Nelson.F., and Smith G.W. - Anion exchange studies IX. The adsorbability of a number of metals in HCl solutions. J.Phys. Chen. - 58 - 11 - 1954.

Kraus.K.A., Nelson.F., Clough.F.B. and Carlston.R.C. - Anion exchange studies XVI. Adsorption from LiCl solution. J.A.C.S. - 77 - 1391 - 1955.

Kraus.K.A. and Nelson.F. - Unpublished work.

Lundegårdh.P.H. Rock composition and development in central Roslagen - Sweden. Ann. Roy. Ag. Coll. Sweden - 15 - 1947.

Lure.Y.Y. and Stefanovitch.S.N. The use of organolites in the analysis of water. Zavodskaya lab. - 13 - 660 - 1947.

McNevin.W.M. and Crummet.W.B. The behaviour of the Pt metals towards ion-exchange resins.
Anal. Chem. - 25 - 1628 - 1953.

Mannkopff.R. The spectrochemical analysis of volatile substances. Phys. Blätter - 5 - 427 - 1949.

Martin.A.J.P. and Synge.R.L.M. Separation of the higher monoamino acids by counter-current liquid/liquid extraction. Biochem.J. - 35 - 91 - 1941.

Mayer.S.W. and Tomkins.E.R. Ion-exchange as a separation method. Theoretical analysis of the column separation process. J.A.C.S. - 69 - 2866 - 1947.

Meloche.A. and Preuss.E. Analytical separation of Re and Mo by ion-exchange. Anal. Chem. - 26 - 1911 - 1954.

Miller.C.C. and Hunter.J.A. The separation of Zn from other elements by ion-exchange.
The Analyst - 79 - 483 - 1954.

Morris.D.M. Unpublished work at Brunel Inst. Tech. - 1959.

Moscow symposium on the Geochemistry of rare elements in connection with the problems of petrogenesis.
Held under auspices of Soviet Academy of Sciences
Moscow. 1957.

Mullin.J.B. and Riley.J.P. Cadmium in sea water.
Nature - 174 - 42 - 1954.

Nachod.F. Recovering precious metals. US.Pat. 2371119 - 1945.

Nelson.F. and Kraus.K.A. Anion-exchange studies VIII.
J.A.C.S. - 76 - 5916 - 1954.

Noddack.I and Noddack.W. The distribution of chemical elements. Naturwiss. - 18 - 757 - 1930.

Noddack.I and Noddack.W. The geochemical distribution coefficient of the elements.
Svensk. Kim. Tidsk - 46 - 173 - 1934.

Noddack.I and Noddack.W. Die Häufigkeit der Schwermetallen in Meerestieren. Arkiv.Zoo.-32 - No.1 - 1940.

Nydahl.F. The determination of trace elements in lake waters. Proc. Int. Assoc. Theor. App. Limnology - 11 - 276 - 1951.

Onishi.H. and Sandell.E.B. Meteoritic and terrestrial abundance of tin. Geochim. et Cosmochim. Acta. 12 - 262 - 1957.

Otteman.J. Investigations into the distribution of trace elements, in particular Sn, in deepseated rocks. Z. Angew. Min. - 3 - 142 - 1941.

Palmqvist.S. Geochemical studies in Fe bearing Liassic series in S. Sweden.
Medd. Lunds. Geol. Min. Inst. No. 60 - 1935.

Preuss.E. The determination of volatile elements by fractional distillation. Z.Angew. Min. 3-8-1941.

Putnam.C.L. The gold content of sea water.
J.Chem. Ed. - 30 - 576 - 1953.

Rankama.K.A. A note on the geochemistry of thallium. J.Geol - 57 - 608 - 613 - 1949.

Rankama.K.A. and Sahama.T.G. Geochemistry. University of Chicago Press - 1950.

Rose.H. and Böse.R. Enrichment methods for the detection of small amounts of chemical constituents in minerals. Naturwiss. - 22 - 354 - 1935.

Sandell.E.B. and Goldich.S.S. The rare metallic constituents of some American igneous rocks. J.Geol. - 51 - 99 - 1943.

Sandell.E.B. The colorimetric determination of traces of metals. Intersci. Pub. Inc. 1950.

Shaw.D.M. The geochemistry of thallium. Geochim.et Cosmochim. Acta - 118-154-Vol.2-1952.

Shaw.D.M., Joensuu.O.I. and Ahrens.L.H. - The spectrochemical analysis of geological materials. Spectrochimica Acta - 4 - 233 - 1950.

Smythe.L.E.and Gatehouse.B.M. - The polarographic determination of traces of Cu, Ni, Co, Zn and Cd in rocks using rubeanic acid and 1 - nitroso-2-naphthol. (University of Tasmania). Anal. Chem. - 27 - 901 - 1955.

Stark.W. Uber die Goldführung der Meere. Helv. Chim. Acta - 1943.

Sussman.S., Nachod.F.C.and Wood.W. Metal recovery by anion exchange. Ind.Eng.Chem - 37 - 618 - 1945.

Truswell.J.F. A petrological study of dolerite sills in the Jagersfontein diamond mine, Orange Free State. Trans. Royal. Soc. S.Africa - 34 - 409 - 1955.

Vincent.D. Unpublished work - Dept Geol. and Min. Oxford university - 1959.

Wagner.P.A. The platinum deposits and mines of S.Africa. p.110 - Oliver and Boyd - 1929.

Wattenberg.H. Zur Chemie des Meerwassers. Z.Anorg. Chem. - 236 - 339 - 1938.

Wattenberg.H. Zur chemie des Meerwassers - über die Spuren vorkommenden Elemente. Z.Anorg. Chem. - 251 - 86 - 1943.

Webb.D.A. Studies on the ultimate composition of biological material and spectrochemical analysis of marine invertebrates with reference to the chemical composition of their environment. Sci. Proc. Roy. Soc. Dublin - 21 - 505 - 1937.

Wedepohl.K.H. Investigations into the geochemistry of zinc. Geochim. et Cosmochim. Acta - 3 - 2 - 1953.

Summary of Author's publications (actual and projected)

1. Edge.R.A., Brooks.R.R., Ahrens.L.H. and Amdurer.S. Some reconnaisance observations on the combined use of ion-exchange enrichment and spectrochemical analysis for the determination of trace constituencies in silicate rocks. Geochim. et Cosmochim. Acta. - 17 - 1/2 - Aug 1959.
2. Brooks.R.R. The use of ion-exchange enrichment procedures in the determination of trace elements in sea water. - in press - 1960.
3. Brooks.R.R.and Ahrens.L.H. The application of anion exchange techniques to the spectrochemical detection of the noble metals in silicate rocks. - in press - 1960.
4. Brooks.R.R. and Ahrens.L.H. The spectrochemical determination of Bi, Cd and Tl in silicate rocks using an anionic-exchange enrichment technique. - in preparation - 1960.
5. Brooks.R.R., Ahrens.L.H. and Taylor.S.R. - The determination of trace elements in silicate rocks by a combined spectrochemical- anion exchange technique. Geochim. et Cosmochim. Acta- 18 - 3/4 - 1960.
6. Brooks.R.R. A note on the dissolution of silicate rocks. in press - 1960. (Nature)

AHRENS L. H. and FLEISCHER M. Report on trace constituents in standard granite G-1 and standard diabase W-1. *U.S. Geol. Surv. Bull.* In press.

ALDRICH L. T., DOAK J. R. and DAVIS G. L. (1953) The use of ion exchange column in mineral analysis for age determination. *Amer. J. Sci.* **251,** 377.

BERMAN S. (1957) Determination of Y, La, Ce, Nd and Yb in test samples granite G-1 and diabase W-1 by a combined chemical spectrographical technique. *Geochim. et Cosmochim. Acta* **12,** 271.

EDGE R. A. and AHRENS L. H. In preparation.

KITCHENER J. A. (1957) *Ion-exchange Resins.* Methuen, London.

LIEBENBERG C. J. (1956) The spectrochemical determination of Cs in igneous rocks using a chemical concentration procedure. *Geochim. et Cosmochim. Acta* **10,** 196.

MITCHELL R. L. (1957) Spectrochemical methods in soil investigations. *Soil Sci.* **83,** 1.

PINSON W. H. (1953) *Ann. Prog. Report,* Dept. of Geology and Geophysics, Mass. Inst. Technology.

RANKAMA K. (1954) *Isotope Geology.* Pergamon Press, London.

SAMUELSON, —. (1953) *Ion Exchangers in Analytical Chemistry.* Wiley, New York.

SCHUMACHER E. (1956) Isolierung von K, Rb, Sr, Ba und Seltenen Erden aus Steinmeteoriten. *Helv. Chim. Acta* **39,** 531.

SHAW D. M. (1952a) The geochemistry of indium. *Geochim. et Cosmochim. Acta* **2,** 185.

SHAW D. M. (1952b) The geochemistry of thallium. *Geochim. et Cosmochim. Acta* **2,** 118.

SHAW D. M., JOENSUU O. I. and AHRENS L. H. (1950) A soluble-arc method for spectrochemical analysis of geological materials. *Spectrochim. Acta* **4,** 233.

TAYLOR S. R. and AHRENS L. H. Spectrochemical Analysis. *Physical and Chemical Methods in Geochemistry.* (Edited by SMALES and WAGER). Interscience, New York. In preparation.

WEDEPOHL K. H. (1953) Untersuchung zur Geochemie des Zincums. *Geochim. et Cosmochim. Acta* **3,** 93.

WEDEPOHL K. H. (1956) Untersuchung zur Geochemie des Bleis. *Geochim. et Cosmochim. Acta* **10,** 69.