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S O L V E N T E X T R A C T I O N
I N
A N A L Y T I C A L G E O C H E M I S T R Y

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"No man is an Iland, intire of it selfe"

(Donne, 1623)

ABSTRACT

A procedure combining solvent extraction enrichment techniques and spectrographic analysis was developed for the quantitative determination of many trace elements in a wide range of silicate rocks and in a series of highly saline Antarctic lake waters.

Since a great deal of the work depended on spectrographic analysis, an investigation was carried out to improve the precision and sensitivity of existing methods. An improved method for the determination of spectral line intensities was developed. This was based on the author's modification of the partial Seidel function, referred to as B-functions. A conversion table for these is given. A scale calibrated in B-functions was incorporated into a Hilger microphotometer enabling such values to be obtained directly without the use of conversion tables. B-values can be plotted directly on to the linear ordinate of semi-log paper if the self-calibration method is used for evaluating line intensities. This results in a straightening of the characteristic curve with an attendant time saving and an improvement in the accuracy of the background extrapolation. A nomographic technique was also developed for use in conjunction with this scale and resulted in a rapid evaluation of line intensities but with some loss in precision.

Cathode excitation as distinct from cathode-layer was compared with anode excitation under the same conditions. Data on 33 elements were used to study relative self-absorption effects, absolute sensitivities, volatilisation curves, times for complete combustion, and background effects. Data on 14 elements and 35 line pairs were used to study reproducibilities in the three matrices, NaCl, CaCl_2 and carbon. It was shown that cathode excitation in a carbon matrix afforded the greatest precision for a number of the more volatile elements. Anode excitation provided generally better precision if a NaCl matrix was used. CaCl_2 was a very unsatisfactory matrix. For the more volatile elements cathode excitation provided a higher sensitivity than anode excitation but with increased background and cyanogen emission.

The extraction of the elements Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb and Bi from hydrochloric acid into the three solvents cyclohexanone, cyclohexanol and cyclohexane was studied as a function of acid concentration. Cyclohexanone is a more efficient, but less selective extractant, than cyclohexanol. Cyclohexane has little extracting power for these elements.

Solvent extraction of hydrochloric acid solutions of a series of highly saline Antarctic lake waters into cyclohexanone was used to enrich the elements Zn, Pb, In, Bi, Fe, Mn, Mo prior to spectrographic analysis. For

(iii)

this, the percent extraction of Fe, Mn and Mo into cyclohexanone from 3N hydrochloric acid was obtained. This investigation has shown that one of these lakes, Lake Bonney, has most probably had a sea water origin. It is also possible that another of these lakes, Lake Fryxell, may also have contained sea water in the past. From the relative abundance of the various elements in the other lakes, it was possible to conduct a geochemical reconnaissance of the areas surrounding the lakes. This suggested that the two most likely areas for mineralisation in the McMurdo Oasis area of Antarctica are the region surrounding and feeding water to Lake Hoare and the region surrounding Lake Joyce.

A consideration of the theory of discontinuous countercurrent liquid-liquid extraction has shown that it is possible to simultaneously determine the extraction characteristics of a large number of elements for a given solvent system. If this technique is coupled with spectrographic analysis the determination is particularly rapid. The extraction of the elements Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, La, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb and Bi from hydrochloric acid into methyl isobutyl ketone was studied as a function of acid concentration. The data were obtained by studying spectrographically the distribution patterns of the elements after equilibration on a discontinuous countercurrent liquid-liquid extraction apparatus. A comparison

of some of the data so obtained with results for the same system as reported by other workers showed that the technique is valid and accurate.

Using these data it was possible to devise a scheme which could separate Fe from the majority of the trace elements extracted by cyclohexanone from a hydrochloric acid solution of a rock. By a combination of batch extraction with cyclohexanone and countercurrent distribution with methyl isobutyl ketone it was possible to obtain quantitative data for Zn and Ga and semiquantitative data for In in a wide range of silicate rocks by spectrochemical analysis. By the use of extraction into cyclohexanone coupled with atomic absorption spectrometry it was possible to determine the concentration of Pb, Cd and Bi in the same suite of rocks.

By the use of these techniques it was possible to obtain fresh abundance data for the above elements in the four standard rocks, G-1, W-1, CAAS syenite and CAAS sulphide.

The cyclohexanone/hydrochloric acid extraction system provides a satisfactory enrichment technique for the spectrographic analysis of trace elements in material with a low Fe content. For material containing a high concentration of Fe, it is necessary to combine this technique with discontinuous countercurrent liquid-liquid extraction to separate the Fe before spectrographic analysis.

However, under these conditions, certain elements can be determined by direct atomic absorption spectrometry of the cyclohexanone extract.

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INTRODUCTION

Of the wide range of analytical techniques available to the geochemist today, only a few are suitable for the determination of trace elements in rocks, minerals etc. (Vincent, 1960) defines trace elements as being those present in concentrations less than 0.01% by weight, expressed as the oxides). These methods include flame photometry, colorimetry, X-ray fluorescence, mass-spectrometry, activation analysis, polarography, atomic absorption and atomic fluorescence spectroscopy and emission spectrography. Of these, emission spectrography has the advantage of extreme sensitivity coupled with the ability to simultaneously determine a large number of elements. If, in this technique, elements are present in concentrations below their spectrographic detection limits then it is necessary to carry out some enrichment procedure. This can be either by preliminary treatment of the sample or by instrumental modifications such as the double-arc furnace electrode (Shaw, Joensuu and Ahrens, 1950; Wedepohl, 1953), for the determination of volatile elements, and the boiler electrode of Hall and Lovell (1958). The pre-treatment can be chemical or physical e.g. the fractional distillation of volatile elements from a comparatively large quantity of sample with condensation onto electrodes (Keck, MacDonald and Mellichamp, 1956; Degtyareva and Ostrovshaya, 1963 etc.). Chemical pretreatment can be divided into four main groups:-

1. Co-precipitation, as in the determination of In, Ge and Te by co-precipitation with $\text{Fe}(\text{OH})_3$ (Bronshtein, 1962).

2. absorption onto ion-exchange resins with subsequent elution, as in the determination of Sn, Cd, Bi, Tl and Sb in silicate rocks by absorption onto an anion-exchange resin (Brooks, Ahrens and Taylor, 1960; Brooks and Ahrens, 1961; Ahrens, Edge and Brooks, 1963).
3. five-assay techniques - restricted to the noble metals.
4. solvent extraction techniques, where the trace elements are concentrated by extraction from an aqueous solution with a suitable solvent or complexing agent.

One of the advantages of an enrichment procedure that is not immediately obvious is an improvement in the precision of the analytical procedure. Ahrens (1957) has shown that the precision of classical methods for the determination of an element is inversely proportional to the concentration of the element, so that if an increase in concentration can be effected then there is a corresponding improvement in the accuracy of the determination.

While there are now analytical techniques available with greater sensitivity than emission spectroscopy (especially neutron activation), it is still one of the most rapid and sensitive methods of analysis available, particularly if accompanied by an enrichment technique of some sort. Minczewski (1962), in considering methods for determining

trace element concentrations, shows that, for routine analysis, emission spectroscopy, with chemical enrichment if necessary, is the most suitable method. Of the enrichment techniques listed above, co-precipitation and ion-exchange have both been extensively used in trace element analysis in geochemistry whereas solvent extraction has received very little attention.

The following are among the few examples of applications of this latter technique:- Jeffery (1956) determined Mo and W in silicate rocks by extraction with α -benzoinoxime into chloroform. Gallium has been determined in rocks by extraction with 8-hydroxyquinoline and hydroxylamine into chloroform (Ishibushi, Shigematsu and Nishikawa, 1957; Nishikawa, 1958). Lounamaa (1957) has determined Ag, Bi, Cd, Cu, Co, Ni, Pb, Sn and Zn in granites by extracting them as the dithizonates into chloroform followed by spectrographic determination and Hahn-Weinheimer (1957) extracted noble metals from a solution of a gneiss with quinidineselenol in chloroform. Oeschlager (1960) determined Sn in soil by extraction from thiocyanate into ethyl acetate; Cu in soils has been extracted with dithizone in benzene and diethyl dithiophosphate in carbon tetrachloride (Curtis, 1961; Busen and Borzenkova, 1961; Nemodruk and Stasyuchenko, 1961). Indium in cassiterite has been determined colorimetrically by extraction with rhodamine B into benzene (Rozbianskaya, 1961). Brooks (1961) has determined In and Tl in silicate rocks by extraction of their

iodo-complexes into ethyl ether with subsequent spectrographic analysis. Edge, Dunn and Ahrens (1962) have determined Mo in silicate rocks by extraction into tributyl phosphate. Iron in limestone has been determined by extraction as the chloro-complex into methyl isobutyl ketone (4-methyl-2-pentanone) (Morimoto, 1962). Magnesium has been extracted from silicate rocks with 8-quinolinol in chloroform (Geilmann, 1961). Minczewski, Wieteska and Marizenko (1961) have determined Tl in rocks by extraction into dithizone in chloroform; Greenland (1963) used extraction with dithizone for the determination of Zn in the standard granite and diabase, G-1 and W-1 (Fairbairn and others, 1951). Dithizone in chloroform has also been used to determine Au in geochemical investigations by an extractive titration method (Pakhomora and Vysotskaya, 1963).

A completely new field of study has been opened with the development of applications of discontinuous, counter-current, liquid-liquid extraction to inorganic analysis, especially geochemistry (Brooks, 1965 a, b, c; Boswell and Brooks, 1965).

Since relatively little has been done on the use of solvent extraction for enrichment prior to spectrographic analysis it was decided to investigate the potentialities of the technique for geochemical analysis.

When a metal ion is extracted into an organic solvent it must first form a neutral species, in general an uncharged complex, before it can be extracted into such a solvent.

The uncharged complexes so formed can be divided into two general classes:-

(i) neutral chelate complexes, characterised by a reaction of the form $M^{n+} + nR^{-} \rightarrow MR_n$ where R is the anion of a suitable chelating agent such as acetylacetone or dithizone.

(ii) ion association complexes, where oppositely-charged ions form a neutral ion pair. It has been shown that, in the case of rare earth nitrates and for Bi in HI, the neutral aggregate can contain more than one pair of ions (Lavrukhina and Chzhu, 1959). In the neutral species the metal can be present in either the cation, as in $Cu(2,9\text{-dimethylphenanthroline})_2^{+} ClO_4^{-}$, or in the anion as in $H^{+}AuCl_4^{-}$.

The nomenclature used here differs from that used by the authors of one of the standard texts on solvent extraction (Morrison and Freiser, 1957) who call the so-called "neutral chelate complexes", co-ordination complexes. This implies that the "ion-association complexes" are not, in fact co-ordination complexes, whereas the majority of them are, e.g. $H^{+}FeCl_4^{-}$, $H^{+}InI_4^{-}$ and $WO^{+}SCN^{-}$. Furthermore, it is unlikely that some of the species they list in this category are in fact co-ordination complexes; in particular $GeCl_4$, when extracted into an organic solvent, will almost certainly have simple Ge-Cl bonds and not any other type of bonding. The term "neutral" in the name for the chelate complexes is necessary since many elements which are extracted as ion

association complexes are present in either the anion or the cation of the uncharged species as a chelate. In their regular reviews of the use of solvent extraction in analytical chemistry, Morrison and Freiser (1958, 1960, 1962, 1964) list many chelating agents in their discussion of ion association extraction systems thus forcing this distinction between chelate complexes and neutral chelate complexes. In their latest review (Morrison and Freiser, 1964), they recognise this problem but even in their revised system, there is still the possibility of ambiguity in the nomenclature.

When considering the application of solvent extraction to geochemical analysis, several factors must be born in mind in deciding whether to use a "neutral chelate" extraction system or an "ion-association" extraction system.

Reagents which form neutral chelate complexes with metal ions are weak acids of the form HR and since the formation of a chelate complex is essentially an acid base reaction, the more basic the acid the stronger the chelate formed. The extent of chelate formation depends not only on the value of the equilibrium constant of the reaction but also on the concentration of the reagent anion. The lower the pH of the solution the lower will be the concentration of the latter so that less chelate will be formed. It therefore follows that, to have optimum conditions for chelate formation, a high pH is desirable. This is not always satisfactory when dealing with solutions of rocks etc. which at high pH, are liable to

hydrolyse and precipitate insoluble hydroxides and oxides, with the concomitant risk of co-precipitation of any trace elements present. Most rocks are only soluble in acid solutions and, to obtain optimum conditions for extraction with chelate systems, it often would be necessary to add a base to raise the pH. Addition of more reagents to the solution thus increases the possibility of contamination with the elements under study. While correction for this can be made with a "blank" determination, it involves another source of error and is therefore undesirable. Two chelating reagents which have been developed recently and which are relatively strong acids (thereby removing some of the above objections) are thenoyltrifluoroacetone and β -isopropylone.

Many of the elements of interest to geochemists, although forming chelate complexes, are not readily extracted into organic solvents. For example although acetylacetone forms chelates with over 60 metals (Freiser, 1963), complete extraction into organic solvents is achieved for only 22 of these metals and among those not extracted, even after repeated extraction are Au, Cd, Hg, Tl, Sn, As and Sb all of which are of interest to the geochemist.

While some ion-association systems involve the use of chelating agents to form a charged chelate (e.g. the extraction of Fe into chloroform as the phenanthroline complex with I^- as the counter ion (Vydra and Pribil, 1959)) so that the difficulties mentioned above are still present, there are many

systems that do not. Many ion association extraction systems use simple ions such as Cl^- , I^- , NO_3^- etc. with oxygenated solvents such as ketones, alcohols, esters and ethers. In general, a rock is in an acid solution prior to solvent extraction so that if the acid is able to supply ligands for forming an ion association complex capable of extraction into an organic solvent, no further reagents are necessary and the problem associated with blanking is reduced. Also, in general, extraction of metal ions as ion association compounds increases with increasing concentration of ligand so that the high acid concentrations required to keep a rock in solution facilitate extraction rather than retard it (as in neutral chelate extraction), provided that the acid anion is the ligand in the metal complex. Of particular interest in this type of extracted species are the halo-metallic acids where metal ions capable of forming negatively charged halogen-complexes are extracted in association with solvated hydrogen ions. Diamond and Tuck (1960) have reviewed this system and Marcus (1963) has an extensive section on it. In these systems the anion normally has one negative charge and is associated with a proton, solvated, either with water, or with the organic solvent. This means that the organic solvent must be basic and, in general, the more basic the solvent, the more efficient the extraction. The extraction of Ga from hydrochloric acid solution into various oxygen-containing solvents showed that esters were better extractants

than alcohols which were better than ethers (Bol'shakov and Sergakov, 1961) and a similar study on the extraction of ion association complexes of Zr and Hf into 80 different solvents (Honshino, 1962) showed that the partition coefficients decrease in the sequence: ketones, esters, alcohols, ethers which, except for ethers, is the order of decreasing basicity. A new series of even more basic solvates that have received increased attention are the alkyl and aryl phosphates and phosphine oxides such as tributyl phosphate and tri-n-octyl phosphine oxide (for an excellent discussion of these see Marcus, 1963). These have proved to be very powerful extractants for inorganic ions and are receiving extensive use as such.

From the above discussion it is clear that ion-association extraction systems appear to be much more suitable for geochemical analysis than do neutral chelate extraction systems. It was therefore decided to investigate the potentialities of the former system. As has been mentioned above, the best solvents in this system will be the most basic i.e. the alkyl and aryl phosphates and phosphine oxides but these have a major disadvantage in geochemical analysis. One of the advantages of using solvent extraction, particularly ion association systems, is that once the two phases have been separated, the organic phase into which the trace elements have been extracted, can be removed simply by boiling, leaving the trace elements as solids, ready for spectrographic analysis. The

phosphorus compounds however, are solids, so that to obtain maximum enrichment and hence greatest sensitivity, it would be necessary to strip the trace elements from the organic phase. This involves the use of more reagents, with the possibility of increased levels in the blank, and therefore lower precision. Furthermore, the conditions necessary to completely remove one element from the organic phase might give incomplete removal of other elements thus requiring further manipulations of conditions with consequent loss of simplicity and ease of operation, as well as increased probability of contamination from the additional reagents. If, as mentioned above, a ketone, alcohol, or ester is used as the extracting agent, then evaporation will readily remove the solvent and extracting agent without the possibility of further contamination from other reagents. From these considerations, it is clear that when dealing with trace elements, phosphorus compounds will not be as satisfactory as pure organic compounds. It was therefore decided to investigate several organic solvents as potential extracting agents.

From a study of the absorption of metal chloro-complexes onto anion exchange resins (Kraus and Nelson, 1956), Edge, Brooks, Ahrens and Amdurer (1959) showed that, of the elements which form 99% of the earth's crust (O, Si, Fe, Al, Na, K, Ca, Mg, Mn, and Ti) only Fe forms an anionic chloro-complex. Although this is extracted as an ion association compound into organic solvents, the degree of extraction is, in the

case of diethyl ether, low at low acid concentrations. Hydrochloric acid is a convenient solvent for rocks in that the only insoluble chlorides are those of Ag, Hg, and Pb. This, together with the fact that most elements present in silicate rocks in trace amounts form chloro-complexes whereas the major elements do not, makes the chloride ion a suitable ligand for solvent extraction studies.

Other possible ligands such as the other halogens and pseudohalogens, nitrates and sulphates are all unsuitable for various reasons. Morrison and Freiser (1957) have shown that fewer elements are extracted into ethyl ether as fluorides than in the comparable chloride, bromide, thiocyanate and nitrate systems and this will almost certainly be true for other solvents. The bromide and iodide systems are also unsatisfactory in that there is the possibility of oxidation of the ligand to the halogen especially in the case of iodide. Any halogen so produced can be removed by reduction with SO_2 but this produces sulphur in the solution with the possibility of absorption of the trace elements. Also, it is preferable to have only one ligand present in the rock solution to prevent uncertainty as to what species are being extracted. If iodide or bromide systems were to be used, this would necessitate the use of pure HBr or HI as the acid for keeping the rocks in solution which would not be very satisfactory. For the same reason thiocyanate cannot be used as a ligand. Since a high acid concentration is necessary to keep the rocks in

solution, the use of cyanide as ligand is unsatisfactory because of the health hazard. Many sulphates and perchlorates are insoluble and because of this, these ions are not suitable for use as ligands in the solvent extraction of rock solutions in spite of the fact that with these ions the difficulties associated with mixed ligands can be overcome by dissolving the rocks in the respective acids. The only other ion that could prove a satisfactory ligand is the nitrate ion. It has been shown (Morrison and Freiser, 1957, 1958, 1960, 1962, 1964) that while many rare earths and some of the actinides are extracted into organic solvents from nitrate solutions, many other elements are not. From the above, it seems clear that in the extraction of trace elements from rock solutions, the use of chloride ions as ligand appears the most satisfactory.

It was decided to investigate the extraction of the elements Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb, As, Sb, and Bi from hydrochloric acid solutions into organic solvents. These elements all occur in trace concentrations in silicate rocks and with few exceptions are below spectrographic detection limits (see Table 1) so that an enrichment technique is necessary before they can be determined spectrographically. (Tl is normally present in concentrations below spectrographic detection limits but Willis, Kaye and Ahrens (1964) have developed a method for the direct spectrographic determination of this element. Kolbe (1965) has determined Sn and Tl directly by use of an oxygen jet).

Table 1

Abundance of Elements in Igneous Rocks
and Their Spectral Sensitivity.

	<u>concentration in rocks</u>	<u>detection limit</u>
	(ppm)	(ppm)
Cu	55	.5
Ag	0.08	.5
Au	0.002	10
Zn	40	100*
Cd	0.15	10
Hg	0.08	100
Ga	19	3
In	0.11	1
Tl	1.3	1
Ge	1.1	5
Sn	2	10
Pb	15	5
Ag	2	100
Sb	0.1-0.2	20
Bi	0.2	20

* for Zn 3345, if Zn 2138 is used the sensitivity is 3 ppm.
Data from Ahrens and Taylor (1960).

Preliminary investigations indicated that, in a chloride medium, cyclic solvents appeared to be very efficient extractants for the elements of interest. It was therefore decided to investigate the extraction of the elements listed above into the three solvents, cyclohexanone, cyclohexanol and cyclohexane from hydrochloric acid solutions at different acid concentrations. These three solvents were investigated because, although it was suspected that cyclohexanone would be the best extractant, it was hoped that it might be possible to make some quantitative comparisons of the relative advantages of the three solvents. Hartkamp and Specker (1956) have shown that cyclohexanone is a particularly good extractant for Cd and heavy metals compared with aliphatic ketones and ethers. Specker and Hoverman (1963) have demonstrated that the distribution of certain metals between ketones and solutions of halogen or pseudohalogen ions depends markedly on the structure of the ketone. Ketones with the oxygen in the 3 or 4 position are not nearly as good extractants as 2-ketones due to the long and bulky alkyl groups on either side of the carbonyl group in the former. In the same paper, they discussed the extraction of $\text{Zn}(\text{CNS})_2$ into a series of substituted cyclohexanones. They showed that, for cyclohexanones substituted in the 2 position the extraction decreased with increasing size of the substituted group.

They considered this was due to steric hindrance and showed that 4-methyl cyclohexanone-1 behaves in a similar manner to cyclohexanone so that steric hindrance, not substitution, appears to be responsible for the lowered extraction. They also found that, for $\text{Zn}(\text{CNS})_2$, cyclohexanone is a more efficient extractant than similar straight- or branched-chain ketones. Brubaker and Johnson (1959) have made a similar study on the extraction of Co from HClO_4 -NaCNS; ketones were found to be superior to ethers, and chain branching in either class of solvent decreased effectiveness. They interpreted the results in terms of solvent electron-donor properties and steric factors.

With the exception of Babko et al. (1963) who, in studying the extraction of complex Bi halides, showed that Bi is 43% extracted into cyclohexanone from a 1.1 M Cl^- and 1N H_2SO_4 solution, there have been no studies reported on the extraction of any of the above metals into cyclohexanone from chloride solutions.

The preceding discussion has shown that there is a wide range of extraction systems that could conceivably be used for enrichment in geochemical analysis. In the work that follows an attempt has been made to assess the potential significance of solvent extraction in geochemistry by the development of new techniques and their application to the analysis of rocks, minerals and saline lake waters.

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PART I

THE DEVELOPMENT OF IMPROVED SPECTROCHEMICAL TECHNIQUES

In view of the importance of spectrographic analysis in the investigation, it was decided to study certain aspects of the spectrographic technique in order to increase the speed and precision of the method before quantitative studies of any solvent systems were undertaken.

The two major aspects considered were:-

- (a) improved methods for the determination of spectral line intensities.
- and (b) a comparison of cathode and anode excitation in the d.c. arc.

Other minor modifications were made during the investigation as new equipment became available and will be discussed in the relevant sections.

(a) Improved Methods for the Determination of Spectral Line Intensities.

As the measurement of spectral line intensities in spectrochemical analysis has always involved a certain amount of tedious and lengthy effort, many attempts have been made in the past to develop improved methods of measurement.

In many laboratories, spectral line intensities are measured by the self-calibration method (Ahrens and Taylor, 1960) using a step sector. This involves plotting log galvanometer deflection as a function of log relative intensity. An inherent fault of such methods lies in the difficulty of accurate extrapolation of low background readings to a pre-determined constant density, since the characteristic curve of the emulsion is not linear at the extremes. The importance of background readings has recently been emphasised by Slavin (1962b). Several methods for straightening the characteristic, or H and D, curve have been developed. The first of these involved plotting the function, $\log\left(\frac{d_0}{d}\right)$, against log relative intensity to extend the linear range of the curve. (d_0 = full-scale galvanometer deflection, d = actual galvanometer deflection). The Seidel function, $\log\left(\frac{d_0}{d} - 1\right)$, (Kaiser, 1941) and the partial-Seidel function, $\left[\log\left(\frac{d_0}{d} - 1\right) + \alpha \log \frac{d_0}{d}\right]/(1+\alpha)$ (α =constant), (Honerjaeger-Sohm and Kaiser, 1944) both provide a more linear relationship between the photographic response and log relative intensity, with a consequent improvement in

accuracy of measuring low backgrounds. Indeed, by a suitable choice of α in the partial-Seidel function, a linear relationship can be obtained over the whole working range. A commercial draughting apparatus (the Respektra calculator), based on the use of the partial-Seidel function for calculating relative intensities has been produced (Kaiser, 1951; Anderson 1956). An alternative method for straightening the extremes of the characteristic curve has been developed by Kerbyson (1963), who modified the Seidel function to $\log(\frac{d_0}{d} - a)$, where a is a constant arbitrarily chosen to give a straight line when the function is plotted against log relative exposure. In all the above methods, the transformation from the linear galvanometer scale to the appropriate function was made before plotting graphically or by plotting on graph paper with the ordinate calibrated with the appropriate transformation. This latter method has been used by Wheeler (1956), who, in a method developed in conjunction with Duffy and Reed, plotted galvanometer deflections, measured on a linear scale, onto specially prepared "Seidel" graph paper and hence obtained a linear plot without the necessity of a Seidel transformation by the use of tables. An alternative approach has been made by Hodge (1961) and Haaland (1962) who have developed slide-rule readings to intensity ratios.

While a scale for incorporation into the galvanometer of the microdensitometer graduated in opacity, $(\frac{d_0}{d})$, is available commercially, there are no references in the

literature to the use of galvanometer scales calibrated in any of the transformations known to give an extension of the linear region of the calibration curve. (Crosswhite and Dieke, 1953, have made an appropriate transformation by incorporating the variable into the electrical circuit of a modified densitometer).

It was therefore decided to investigate the possibility of constructing a densitometer galvanometer scale in units of a transformation giving a characteristic curve with a greater linear range. Of these, the partial-Seidel function of Honerjaeger-Sohm and Kaiser (1944) seemed to be the most promising. These authors showed that, in the expression $\frac{1}{2} \left[-\log\left(\frac{d_o}{d} - 1\right) + \alpha \log \frac{d_o}{d} \right] / (1+\alpha)$, α was approximately 1 for most photographic plates. Consideration was therefore given to using the transformation

$$P = \frac{1}{2} \left[-\log\left(\frac{d_o}{d} - 1\right) + \log \frac{d_o}{d} \right]$$

for the construction of the galvanometer scale. This function has however two major disadvantages if it is to be incorporated into an optical scale:-

(i) since the zero value of P corresponds to a galvanometer deflection of 30.9 on a linear scale of 50 units, some readings will be negative and others positive with an attendant risk of confusion, particularly with a moving scale.

(ii) all values on the scale, except for those

corresponding to linear deflections less than 4 (full-scale linear deflection = 50) would be decimals so that decimal points, as well as numerals would have to be incorporated onto the scale.

To overcome these disadvantages, a modified partial-Seidel function, known arbitrarily as a "B" function, has been derived (Boswell and Brooks, 1965a), where

$$B = 100P + 60$$

or

$$B = 50 \left[\log\left(\frac{d_0}{d} - 1\right) + \log\frac{d_0}{d} + 1.27 \right]$$

Values of these B-functions for deflections corresponding to a linear scale graduated from 0 to 50 are given in Table 2. The zero now occurs at a galvanometer reading of 47.2 on the former linear scale so that virtually all results are positive. Furthermore, the use of unwieldy decimals has been eliminated so that, for example, a partial-Seidel value of 0.030 becomes simply 63 B-units.

A galvanometer scale calibrated directly in B-values has been constructed and incorporated into a Hilger FR300 Galvoscale attached to a L452 non-recording microphotometer. This enables these values to be obtained directly without the use of conversion tables thus giving a substantial shortening of the time involved in evaluating photometric data. This new scale is shown in Fig. 1 and extends from $-\infty$ to $+\infty$ with an effective working range of from 0 to 200 B-units, corresponding to original galvanometer readings

Table 2
Conversion Table for B-functions.

Galvo. Reading	0.0	0.1	0.2	0.3	Impr
0	$+\infty$	329.8	297.7	284.6	
1	229.5	225.5	221.5	218.1	
2	198.9	196.8	194.7	192.7	
3	180.9	179.5	178.0	176.6	
4	167.9	166.8	165.7	164.6	
5	157.7	156.8	155.9	155.1	
6	149.3	148.6	147.8	147.0	
7	142.2	141.5	140.8	140.1	
8	135.8	135.2	134.6	134.0	Massey U
9	130.2	129.6	129.1	128.6	
10	125.0	124.5	124.0	123.5	Abstrac
11	120.5	120.0	119.5	119.0	Improved methods for the measure have been developed. Such techniques a fication of the partial Seidel function, conversion table for these is given. A has been incorporated into a Hilger values to be obtained directly without B-values can be plotted directly on to log graph paper if the self-calibration line intensities, there is an attendant in the accuracy of background extrap nique developed for use in conjunctio rapid evaluation of line intensities bu It is concluded that the technique wil some existing photometric methods.
12	116.1	115.7	115.2	114.8	
13	112.0	111.6	111.2	110.8	
14	108.2	107.9	107.5	107.1	
15	104.6	104.3	103.9	103.6	
16	101.1	100.8	100.5	100.2	
17	97.9	97.5	97.2	96.9	
18	94.7	94.4	94.1	93.8	
19	91.7	91.4	91.1	90.8	
20	88.7	88.5	88.2	87.8	
21	85.9	85.6	85.3	85.1	Introducti As the measurement of spect trochemical analysis has always i of tedious and lengthy effort, r made in the past to develop impr ment.
22	83.2	82.9	82.6	82.3	
23	80.3	80.1	79.8	79.6	
24	77.7	77.4	77.2	77.0	
25	75.1	74.9	74.6	74.3	
26	72.5	72.3	72.0	71.7	
27	70.0	69.7	69.4	69.2	
28	67.3	67.1	66.9	66.7	
29	64.8	64.6	64.4	64.1	
30	62.3	62.1	61.8	61.6	
31	59.8	59.5	59.3	59.0	In many laboratories, spectra ured by the self-calibration m sector. This involves plotting lo as a function of log relative int in such methods lies in the diff polation of low background rea constant density since the ch emulsion is not linear. The in correction has recently been er The Seidel function (3) or the p provides a more linear relation graphic response and log relativ quent improvement in the acc backgrounds. Improvement in t microphotometric data has been who, in a method developed in
32	57.2	56.9	56.6	56.4	
33	54.6	54.4	54.1	53.8	
34	52.0	51.7	51.5	51.1	
35	49.3	49.0	48.8	48.5	
36	46.6	46.3	46.0	45.7	
37	43.8	43.5	43.2	42.9	
38	40.9	40.6	40.3	40.0	
39	37.9	37.6	37.3	36.9	
40	34.7	34.4	34.1	33.7	
41	31.3	31.0	30.7	30.4	
42	27.8	27.4	27.0	26.6	
43	23.8	23.4	23.0	22.6	
44	19.5	19.1	18.6	18.1	
45	14.6	14.1	13.6	13.0	
46	8.7	8.1	7.4	6.8	
47	1.6	0.8	-0.1	-1.0	
48	-8.1	-9.3	-10.6	-12.0	
49	-24.1	-26.1	-29.1	-32.3	
50	$-\infty$				

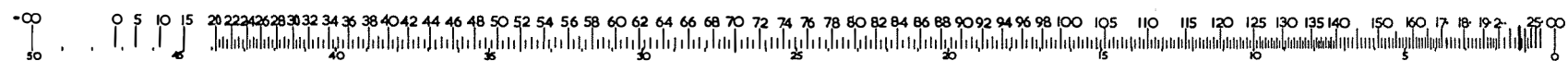


Fig. 1

Microphotometer scale calibrated in B-values.

of 47.2 and 1.9 respectively. For comparison, the original linear calibration is incorporated below the B-value scale.

Data obtained from the B-value scale may be plotted directly onto the linear ordinate of semilog graph paper followed by the standard procedure for the self-calibration method (Ahrens and Taylor, 1960). Table 3 shows a set of typical results obtained from the measurement of a stepped spectral line of As 2780 Å on an Ilford Ordinary plate, with a plot of the galvanometer readings for the analysis line and background intersecting line representing an arbitrary constant density of 100 B-value units. A 30 cm spherical lens was placed in front of the step sector to ensure vertical uniformity of illumination. The slit widths of the spectrograph and microphotometer were 0.015 mm and 0.2 mm respectively. Table 3 also shows the difference between successive step readings (ΔB). The microphotometric data are also shown graphically in Figure 2. The transmission ratio for the step sector was 2.0.

Table 3. Photometric Data for As 2780 Å

Step No.	1	2	3	4	5	6
Line Density in B-values	176.0	151.0	126.4	99.0	71.5	46.0
ΔB^*	--	25.0	24.6	27.4	27.5	25.5
Background Density in B-values	63.5	38.5	--	--	--	--
ΔB^*	--	25.0				

*The ΔB value for a particular step refers to the difference between it and the preceding step.

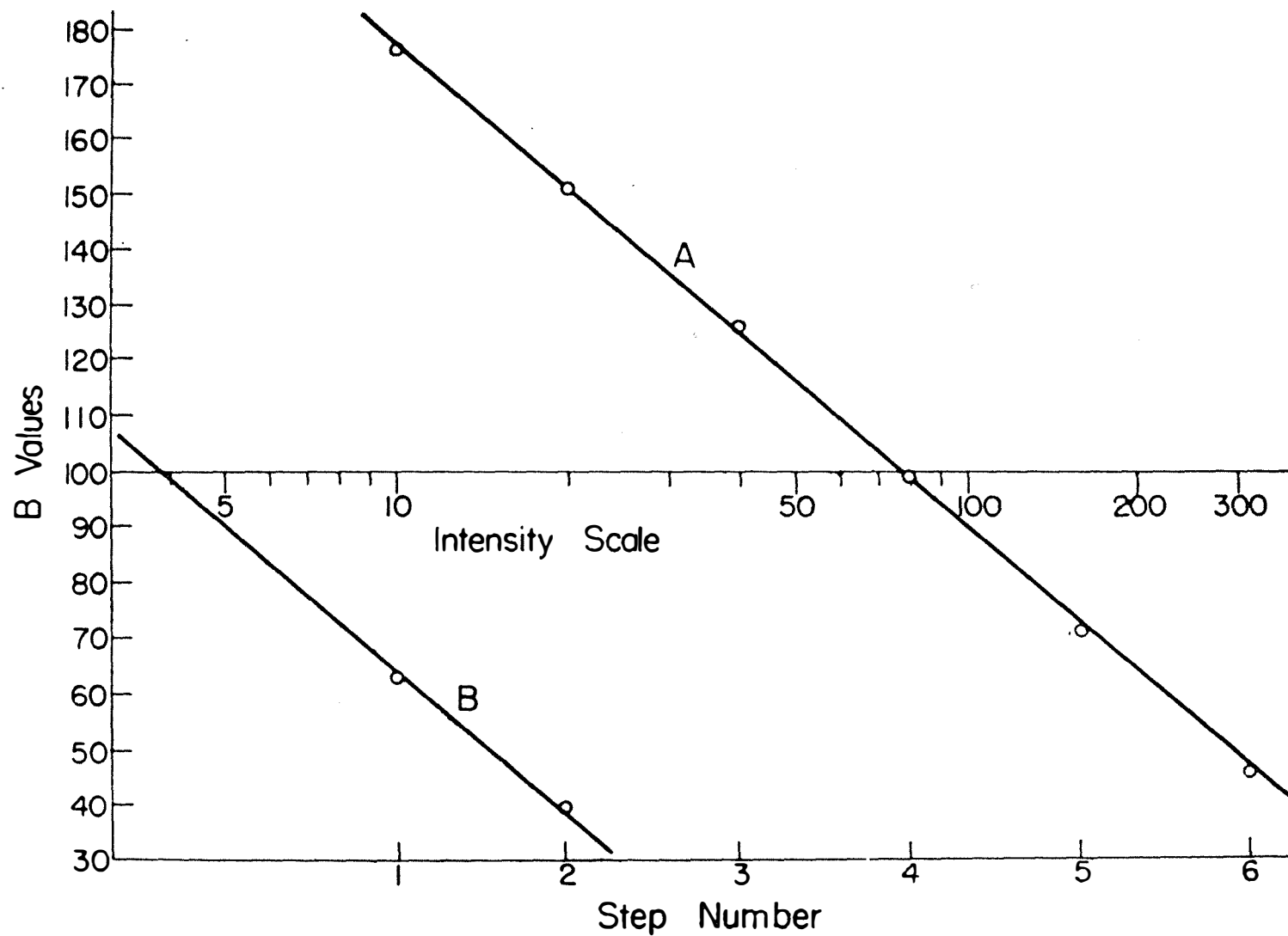


Fig. 2

Plot of microphotometric data using B-values.

If, as is generally assumed in making background corrections, the photographic response for the analysis line and the background are the same, background correction is made by drawing a line through the galvanometer reading for the background parallel to that for the analysis line. This results in increased accuracy in background correction since, by reason of the greater linear range obtained using B-values, the galvanometer reading in B-values will normally lie on the linear portion of the curve, whereas, in cases where the galvanometer reading for background is low, it would normally be on the plateau of the characteristic H and D curve when using linear deflections. There is however, considerable doubt that the photographic response for a spectral line and adjacent background are the same. Strock (1936) claims that monochromatic light has a photographic response 1.5 times greater than that for continuous radiation. Several authors including Peirce and Nachtrieb (1941) and Ahrens (1945) have found no observable differences in slope. Rieman and Gall (1962) have found background to have a different slope than spectral lines. Slavin (1962a) has found, by application of the theory developed by Arrak (1962), that the effect of the micrometer slit width in determining the slope of the spectral line and background is considerable. If the slit width is less than a certain value, the line and background will give

characteristic curves with different gradients. However, if the slit is wide enough the apparent photographic response for both line and background will be the same. He shows that for Eastman Spectrum Analysis No 1 and Ilford Line film the slit width must be greater than 100μ for this latter condition to apply.

When the slopes for the analysis line and background are not identical, background correction using the B-values scale is still simple, a separate series of curves being drawn for the analysis lines and background with the appropriate gradient.

The photographic response of a plate (γ) and the difference in B-values for adjacent steps are simply related as follows:- As shown earlier

$$B = 100P + 60$$

$$\text{where } P = \frac{1}{2} \left[\log \left(\frac{d_o}{d} \right) + \log \left(\frac{d_o}{d} - 1 \right) \right]$$

and, from the paper of Honerjaeger-Sohm and Kaiser (1944)

$$\gamma = \frac{\Delta P}{\Delta I}$$

where ΔP is the change in P corresponding to a relative intensity change of ΔI .

$$\text{But } \Delta P = \frac{\Delta B}{100}$$

where ΔB and ΔP are corresponding changes in B and P respectively.

$$\text{Whence } \gamma = \frac{\Delta B}{100 \Delta I}$$

where ΔB is the difference between B-values corresponding

to a difference in relative intensities, ΔI . It is therefore clear that the values of ΔB given in Table 3 are proportional to the photographic response of the emulsion.

A rapid nomographic method for evaluation of spectral line intensities.

Following the development of the B-function, a rapid nomographic technique for the measurement of spectral line intensities has been developed (Boswell and Brooks, 1965a). It is evident from Figure 2 that a direct relationship must exist between ΔB , the B-value for the first step of the spectral line, and the log of its intensity. Let the microphotometric reading of the first step be B and I the intercept of the calibration line with the line $B = 100$. The intensities corresponding to the first and second sector steps are ten and twenty respectively. Therefore,

$$\frac{B - 100}{\log 10 - \log I} = \frac{\Delta B}{\log 10 - \log 20}$$

where ΔB is the difference between B-values for two consecutive steps.

$$\text{Hence} \quad \log \left(\frac{I}{10} \right) = \frac{0.301 (B-100)}{\Delta B}$$

This is an expression of the form:

$$f_1(u) = \frac{f_2(v)}{f_3(w)}$$

and can therefore be represented by a nomograph of the "Z" type linking I, ΔB and B (Mackey, 1944).

A nomograph of this type enabling the transformation from B-values to intensities to be carried out rapidly and

efficiently as shown in Figure 3. A cursor is placed directly on the appropriate B-value and then laid across the correct ΔB . The intercept on the intensity axis then gives the value of the intensity of the line.

To obtain the optimum advantage from this nomograph, the following experimental procedure is recommended.

A total of 23 separate spectra are recorded on a single 10"x4" plate. A seven-step sector with a transmission ratio of two is used for the first spectrum and the remaining 22 are obtained with a two-step filter having a transmission ratio of four. The purpose of this latter procedure is to afford an alternative weaker step for photometric measurement in cases where the density of the original line is too great for accurate measurement. In such cases the derived intensity must be multiplied by a factor of four. From the photometric readings for the stepped spectrum, the ΔB -value at that particular wavelength is obtained by calculation or by graphical means. The technique is extremely rapid and results may be obtained in a fraction of the time required for the self-calibration method. This advantage of time-saving is to some degree offset by the fact that a method depending on a single reading must of necessity be less accurate than one where the estimated line of best fit is drawn through three or more points. Nevertheless, the nomo-

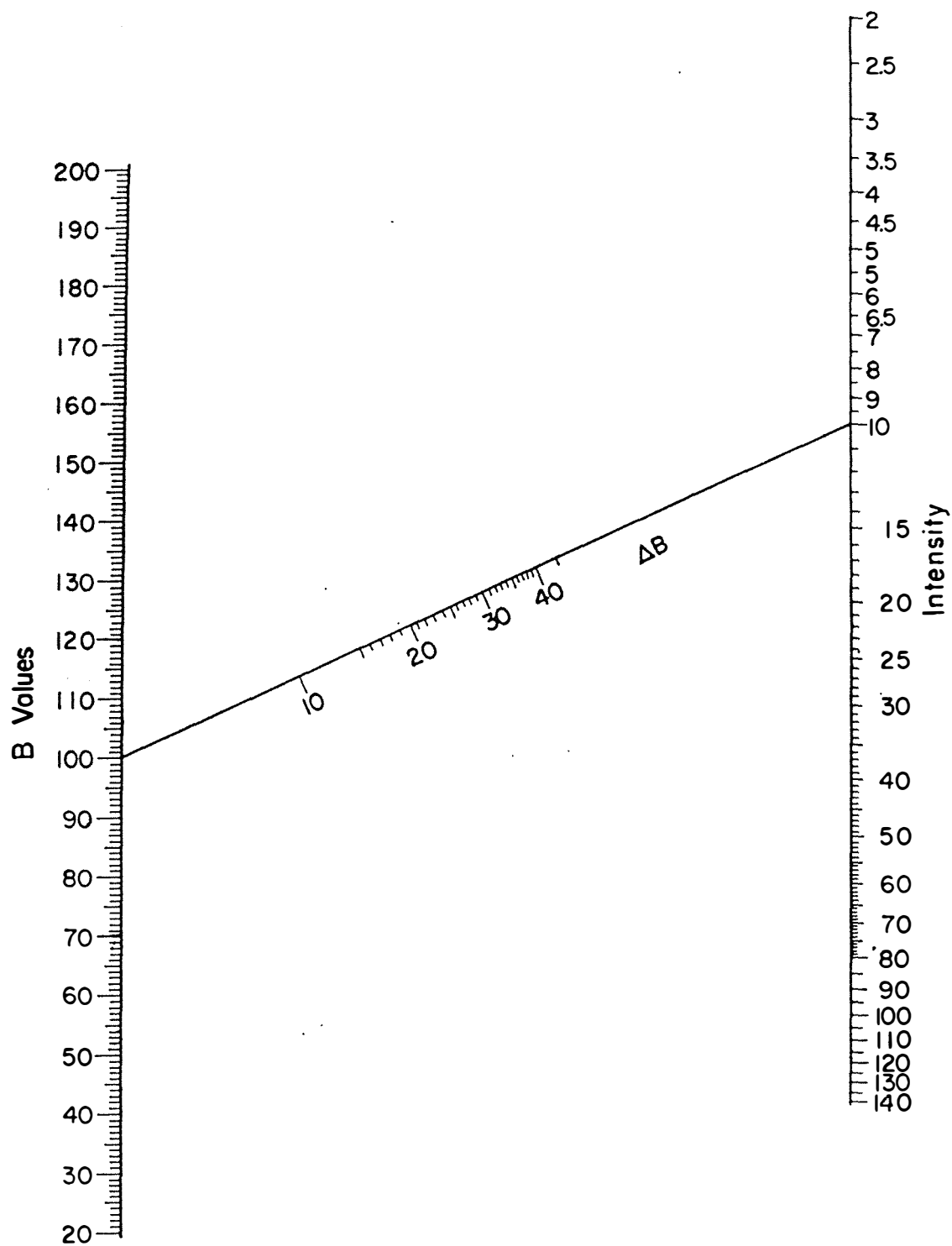


Fig. 3

Nomograph for evaluating spectral line intensities
from B-values.

graph may safely be used in semi-quantitative spectrochemical analysis, and also in quantitative work where relatively large coefficients of variation are encountered.

A comparison of spectral line intensities of replicates of Au 2676 Å obtained by the self-calibration and nomographic methods is shown below in Table 4.

Table 4. Line Intensities of Au 2676 Å Without Background Correction.

Replicate No.	1	2	3	4	5	6	7	8	9	10
Intensity by self-calib- ration method*	64.0	42.0	44.0	36.0	30.3	30.7	26.5	27.3	35.0	36.0
Intensity by nomographic method	64.8	42.0	42.5	34.6	30.0	30.2	26.4	27.6	34.0	34.8

* Determined using B-values.

The microphotometer scale calibrated in B-values has been used exclusively in this laboratory over the past three years and has proved to be completely satisfactory. It may be read as easily as a linear scale and the plotting of the results is carried out more readily than before. Its main advantage is that low background readings can be extrapolated to the constant density level with more confidence than in the classical method using linear galva-

nometer deflections for the characteristic curve. Furthermore, because of the increased linear range obtained when using the scale, the number of points used in plotting the curve can be increased to give a more accurate estimate of the straight line of best fit with a consequent improvement in the accuracy of the intercept of the line with the constant-density level.

The nomographic technique is used with advantage where only a single photometric reading is used to calculate the intensity of a spectral line. To do this it is necessary to know the gamma of the plate (expressed as ΔB). This can be obtained either from measurement of several steps of a stepped spectrum at one particular wavelength on the plate (provision is made for this in the procedure recommended above for using the nomograph, by incorporating a seven-stepped spectrum at the top of the plate) or from use of the method of Dieke and Crosswhite (1943), in which certain Fe multiplets of known intensity are measured and used to calibrate the plate. The former method is preferable since, by using it, it is possible to calibrate the plate at any point whereas the latter method suffers from the disadvantage that the emulsion is assumed to be of constant gamma over the wavelength range on the plate, a doubtful assumption (Ahrens, 1960). ^{and $\tau_{4,1}$} A further advantage of the nomograph method is that background corrections are obtained directly without the use of Gaussian subtraction

logarithms (Honerjaeger-Sohm and Kaiser, 1944; Mitchell, 1964).

(b) A Comparison of Cathode and Anode Excitation.

Before the introduction of cathode-layer excitation in the d.c. arc, (Mannkopff and Peters,^{1931,} 1943) anode excitation was the usual technique in spectrochemical analysis. Although the use of anode excitation declined somewhat following the discovery of the cathode-layer effect, it has been more widely used in recent years and both methods would appear to be of equal interest today. Little has been published on a comparison of the two methods of excitation from experiments carried out under the same conditions and cathode excitation, as distinct from cathode-layer excitation, has received an even briefer mention. Ahrens and Taylor (1960) have however, used the data of a number of independent workers to compare anode and cathode-layer excitation and have come to the conclusion that the advantages of cathode-layer excitation have been overstated in the past. They appear, on balance, to favour anode excitation but stress the difficulty of making comparisons on data obtained under different experimental conditions. The merits of either of the two methods have been discussed by several other workers. (Thiers et al, 1955; Peirce et al, 1940; Ahrens and Liebenberg, 1946; Mitchell, 1964; Strock, 1938, 1946)

Strasheim and Camerer (1955) have compared anode and cathode-layer excitation for the analysis of Cr, Co,

Ni, Zn, Ti, V, Sn, Mo and Pb and conclude that precisions obtainable by the two methods are similar. However, their conclusions are based solely on the slopes of working curves for the various line pairs and bear no relation to coefficients of variation of replicate arcings. Skornyakov (1955) has discussed relative volatilisation of some 15 elements in anode and cathode-layer excitation.

In this study the potentialities of cathode excitation (as distinct from cathode-layer excitation) in spectrochemical analysis have been investigated and compared directly with anode excitation under the same experimental conditions.

In order to obtain a meaningful comparison of the two techniques, the following properties were studied. Absolute sensitivity, times required for complete consumption of the sample, rates of volatilisation, times for complete volatilisation of each element, background intensities, self absorption and finally, the reproducibility of intensity ratios of a number of line pairs in three different matrices. Although the results will only hold for the experimental conditions used in these studies, there is little reason to suppose that they will not apply to a much wider range of experimental conditions.

A study of spectral longitudinal intensity distribution was not carried out since this is already

well known (Ahrens and Taylor, 1960; Vainshtein and Belyaev, 1958). For the same reason no study was made of arc temperatures.

The experiments were carried out on a Hilger E742 large automatic spectrograph with quartz optics. In all cases the operating conditions were as summarised in Table 5.

Table 5

Spectrographic Operating Conditions.

Slit length	12mm
Slit width	0.015mm
Wavelength range	2400 - 3400 Å
Photographic plates	Kodak IN
Current	7 amp d.c.
Exposure	To completion
Electrodes	Johnson Matthey 4B graphite. 1/16" internal diameter x 6 mm deep
Photographic processing	4 min. at 20° in Kodak D. 19b
Densitometry	Hilger microphotometer with Galvoscale calibrated in B-values.
Optical System	Convex quartz lens placed at slit to give even illumination at this point and to provide an image of the arc at the collimator.
Arc gap	4 mm.

Absolute sensitivities, background intensities and volatilisation rates.

Experiments on absolute sensitivities were carried out by arcing identical weights of a charge of two parts of carbon powder to one part of Johnson Matthey R.U. powder and measuring the spectral line intensities of 33 elements. In order to avoid errors due to variation between plates, samples were arced in triplicate on the same plate for each of the two methods of excitation. Good agreement between the triplicates of each series was obtained by careful control of the conditions. Photometric measurements of line intensities were carried out by a Hilger microphotometer with a scale calibrated in B-values (see previous section) to provide a linear response for the photographic emulsion. Table 6 shows line intensities, background values and the ratios of both these quantities for the two methods of excitation.

The table also shows the times needed for complete volatilisation of 12 elements Pb, Tl, Sn, Ga, In, Au, Sb, Ag, Bi, Zn, As and Cu, together with the ratio of these times for cathode and anode excitation. The volatilisation experiments were carried out separately on samples containing trace amounts of the elements in a carbon matrix. The arcings were in triplicate and the plate holder was racked at 5 sec. intervals to obtain volatilisation curves. The curves for Pb, which typify those for the other

Table 6

Relative Intensities and Intensity Ratios for Cathode and Anode Excitation.

Element	Line (Å)	Cathode excitation			Anode excitation			D	E	F
		A	B	C	a	b	c			
Tl	2767	27	—	4	8	—	2	—	3.4	2.0
Mn	2798	116	—	—	47	—	—	—	2.5	—
Sn	2839	7	—	24	3	—	12	—	2.3	2.0
Ga	2943	7	—	24	3	—	9	—	2.3	2.3
Fe	3020	37	—	—	18	—	—	—	2.1	—
In	3256	14	45	24	7	23	10	2.0	2.0	2.4
B	2497	321	—	—	168	—	—	—	1.9	—
Si	2514	115	—	—	60	—	—	—	1.9	—
Pb	2833	13	—	21	7	—	7	—	1.9	3.0
Mg	2942	37	—	—	21	—	—	—	1.8	—
Au	3122	18	41	24	10	15	11	2.7	1.8	2.2
P	2535	25	—	—	15	—	—	—	1.7	—
Sb	2598	20	—	22	12	—	10	—	1.7	2.2
V	3184	44	40	—	28	17	—	2.3	1.6	—
Ag	3280	57	49	24	36	23	10	2.1	1.6	2.4
Al	3082	125	26	—	81	12	—	2.2	1.5	—
Bi	3067	20	32	20	16	12	8	2.7	1.3	2.5
Na	3303	370	—	—	309	—	—	—	1.2	—
Zn	3282	777	48	15	628	23	6	2.1	1.2	2.5
As	2860	12	—	7	11	—	2	—	1.1	3.5
Be	3131	76	—	—	68	—	—	—	1.1	—
Mo	3170	16	45	—	15	20	—	2.2	1.1	—
Cr	2843	10	—	—	10	—	—	—	1.0	—
Ti	3234	100	34	—	117	19	—	—	0.9	—
Cu	3247	80	39	24	86	19	8	2.1	0.9	3.0
Eu	3930	111	—	—	119	—	—	—	0.9	—
Y	3216	14	—	—	23	—	—	—	0.6	—
Ca	3179	665	50	—	1380	17	—	2.9	0.5	—
La	3337	20	—	—	41	—	—	—	0.5	—
Zr	3273	13	—	—	39	—	—	—	0.3	—
Yb	3289	5	—	—	23	—	—	—	0.2	—

^a A, a = Line intensities, corrected for background.

B, b = Background intensities.

C, c = No. of 5-sec time intervals to completely volatilise the element.

D = Ratio B/b.

E = Ratio A/a.

F = Ratio C/c.

elements, are shown in Fig. 4.

Self absorption

Samples containing from 5 p.p.m. to 50% of a single element in a carbon matrix were arced under the conditions of Table 5. Intensity ratios of a high-intensity strongly-absorbing line and a weaker non-absorbing line of the same element were measured and the results plotted as a function of concentration. Where possible, a pair of lines of the same multiplet was used. The line pairs used were, In 3256/3274, Cu 3247/3274, Ag 3280/3383, Tl 2918/2921, Ag 2349/2456, Bi 3067/3025, Zn 3345/3346, Au 2676/3122, Pb 2833/2823 and Sn 2850/3175. In most cases, results of high precision were hard to obtain because of the inherently irreproducible nature of the onset of self-absorption. However, there was little difference in effect whichever method of excitation was used and the pattern throughout was, in most cases, of intensity ratios rising to a limiting value at low concentrations.

Reproducibility

Reproducibility measurements for the two methods of excitation were carried out by arcing up to 14 replicates of trace amounts of a number of elements. Three matrices, NaCl, CaCl₂ and carbon, were used to study the effects of different arc temperatures and matrices on reproducibilities. These three matrices were chosen for the following reasons:- NaCl and carbon are both common matrices

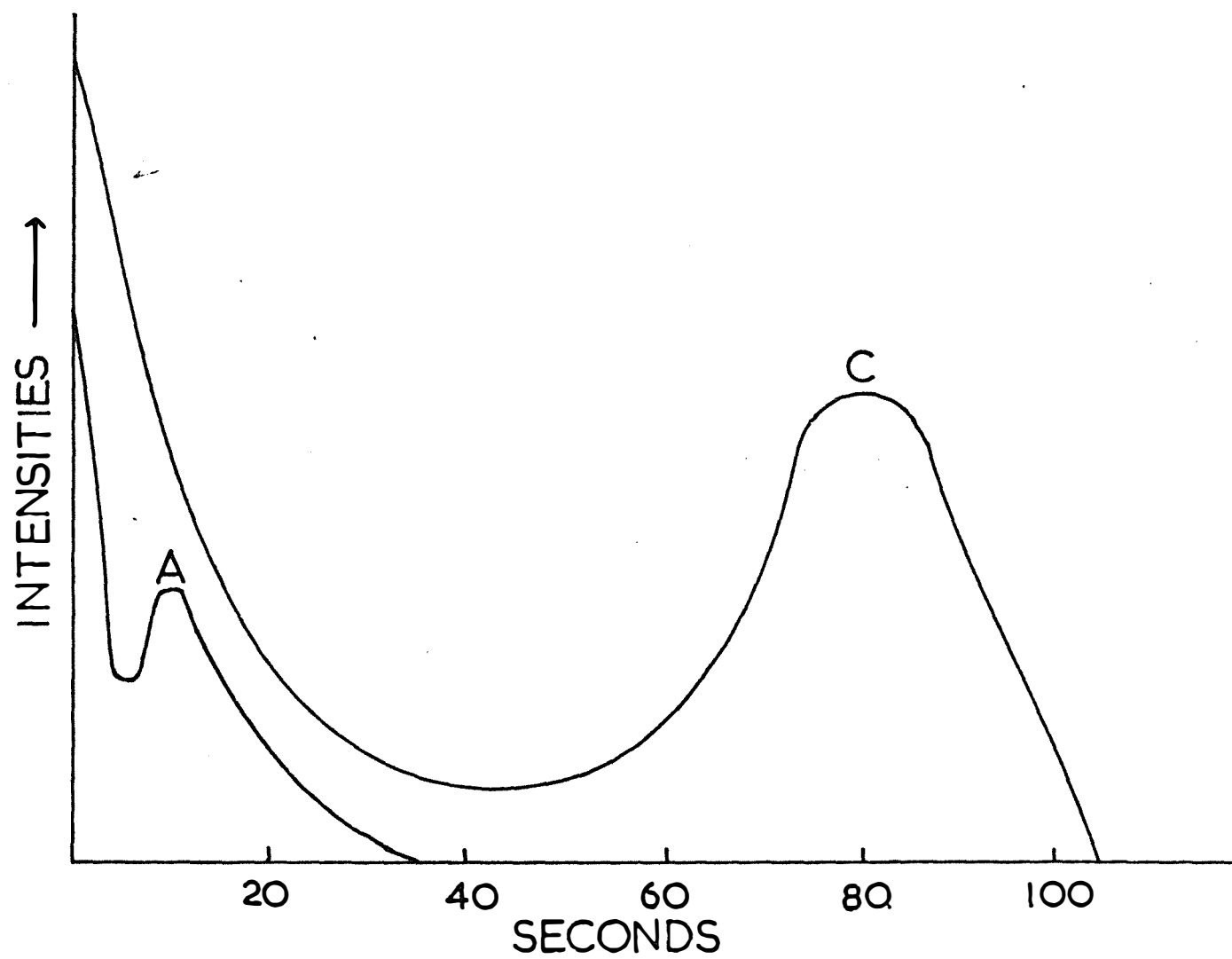


Fig. 4

Volatilisation curves for Pb

A - anode excitation

B - cathode excitation

so that a comparison of their behaviour is of intrinsic interest. Marks and Hall (1946) studied the effects of various matrices on the intensity of Sn 2840 and found that of the matrices studied CaO gave maximum intensity for Sn 2840. Scott (1945) showed that of the three matrices Na_2CO_3 , $\text{Na}_4\text{P}_2\text{O}_7$ and NaCl, the latter, in general, enhanced line intensity for a number of elements. It was therefore possible that CaCl_2 would give even more intense emission than CaO and thereby enhance sensitivity.

The relative intensities of 35 line pairs were measured and the coefficient of variation of each of these was determined. The results are shown in Table 7. During these experiments, the times for the complete combustion of the samples were recorded and are shown in Table 8.

From Table 6 it is clear that for most of the elements studied, cathode excitation afforded greater sensitivity in a carbon matrix. For the remainder of the elements, anode excitation provided greater sensitivity. Attempts to correlate these results with excitation potentials and ionization potentials were not successful. However, those elements showing greater sensitivity for anode excitation were in the main refractory, whereas the remainder included a large proportion of more volatile elements.

Table 7

Reproducibility Tests on Three Different Matrices.

Line pair	Coefficients of variation					
	NaCl matrix		CaCl ₂ matrix		Carbon matrix	
	Anode	Cathode	Anode	Cathode	Anode	Cathode
Ga/Cu	19.1	10.7	36.0	23.0	29.6	6.8
Ga/Pb	34.0	17.0	42.6	24.5	14.1	4.1
Ga/Sn	17.3	17.0	54.6	35.4	5.8	9.6
Bi/Pb(I)	18.3	9.2	58.3	11.2	19.0	10.3
Bi/Pb(II)	13.0	16.0	37.2	28.8	11.2	5.5
Hg/Ga					13.8	17.9
Hg/As					13.4	14.7
Cd/As	15.6	28.2	42.5	43.3	57.2	11.4
Cd/Cu	33.0	41.7	55.1	56.7	12.2	5.9
Cd/Bi	17.1	33.3	23.5	45.6	8.2	7.9
Sn/Ag	17.0	10.5	43.0	39.0	17.0	8.4
Sn/Sb	16.9	31.1	42.5	34.9	9.2	3.5
Sn/Ga	17.4	15.3	51.6	41.9	5.6	9.0
Pb(I)/Ga	14.2	17.0	28.4	25.8	11.5	4.1
As/Zn	8.2	15.3	50.0	14.1	10.3	13.3
As/Sb	8.5	18.0	18.6	21.6	8.3	6.2
As/Ga	23.1	32.4	34.9	30.4	6.3	14.0
Ag/Cu	5.0	7.9	24.9	4.3	8.4	3.5
Ag/Bi	21.1	27.7	58.0	48.7	7.8	5.7
Ag/Pb(I)	9.2	19.5	26.4	46.0	14.8	7.0
Zn/Pb(I)	11.6	12.0	27.4	35.7	11.6	14.7
Zn/As	7.3	15.2	42.0	16.3	9.7	10.4
Zn/Sb	16.9	16.9	44.8	25.5	4.9	17.0
Sb/Sn	10.5	24.1	32.4	35.9	8.8	2.5
Sb/Zn	10.9	15.6	52.3	21.1	11.5	18.0
Cu/Ag	5.0	8.2	26.0	8.4	7.0	4.5
Cu/Bi	21.9	19.0	50.3	56.0	7.3	7.1
Tl/In	10.4	20.0	20.0	22.6	9.0	3.6
Tl/Sb	7.6	21.0	57.7	47.3	45.5	11.3
In/As	17.4	12.6	49.8	34.3	35.0	13.2
In/Tl	8.3	22.7	35.0	32.1	9.4	10.4
Au/Cu	20.1	10.5	54.9	42.8	11.7	12.2
Au/Ag	21.8	14.0	75.5	38.3	20.6	11.8
Pb(I)/Bi	15.3	9.3	51.7	18.7	12.1	10.8
Pb(I)/Ga	18.9	19.3	46.9	50.5	9.3	7.5
Averages	15.5%	18.4%	41.6%	32.1%	14.2%	9.2%

^a Lines used were: As 2860, Ag 3280, Au 2676, Bi 3067, Cd 3261, Cu 3274, Ga 2943, Hg 2536, Pb(I) 2823, Pb(II) 2833, Sb 3267, Tl 3229, Zn 3345, In 3256.

Table 8

Time Required for Complete Combustion of the Sample

<u>Excitation</u>	<u>NaCl matrix</u>	<u>CaCl₂ matrix</u>	<u>Carbon matrix</u>
<u>Anode</u>	68 $\pm$ 3 sec	50 $\pm$ 10 sec	35 $\pm$ 2 sec
<u>Cathode</u>	100 $\pm$ 5 sec	95 $\pm$ 8 sec	80 $\pm$ 6 sec

A disadvantage of cathode excitation is the high background which in these experiments was greater by a factor of 2 or 3 than that for anode excitation. However, it is sometimes desirable to have backgrounds of sufficient intensity for them to be measured with reasonable accuracy, provided that they do not represent too large a fraction of the intensity of the analysis line.

Reproducibility experiments have produced interesting and significant data for a number of volatile elements. Of the 33 line pairs measured for the NaCl matrix, 22 showed lower coefficients of variation with anode excitation. The reverse was the case for the carbon matrix where 23 out of 35 arcings showed lower coefficients with cathode excitation. The line pairs were selected by choosing the best for each method of excitation and for each matrix and then measuring the same line pairs under all the other conditions employed. The highest precision for cathode excitation with a carbon matrix was 2.5% for the Sb/Sn

line pair and 4.9% for the Zn/Sb pair for anode excitation. That overall precision is also better for cathode excitation is shown by a study of the average coefficients of variation of 35 line pairs which give values of 14.2% and 9.2% for anode and cathode excitation respectively for the carbon matrix. The NaCl matrix gives lowest values of 9.2% for Bi/Pb with cathode excitation, 5.0% for Cu/Ag with anode excitation and average values for all line pairs of 15.5% and 18.4% respectively.

It is concluded therefore, that, at least for these 13 elements, cathode excitation with a carbon matrix would afford higher precision than anode excitation. When a NaCl matrix is used, there is less difference between the two techniques, though in this case, anode excitation would appear to offer the better results. This may be explained by the higher temperature of anode excitation enabling the depressant effect of NaCl on line intensities of various elements (Ahrens and Taylor, 1960) to be overcome to some extent, with a consequent improvement in reproducibility. The higher precision for cathode excitation in a carbon matrix may be due in part, to incomplete combustion in the anode due to the higher rate of material consumption and the physical ejection of some of the material. The slower burning cathode would tend to reduce this effect. The same conclusion would seem to

apply to the CaCl_2 matrix, but due to the poor reproducibility and irregular burns with this material, the only definite conclusion that can be made is that, for reproducibility, it is far inferior to carbon or NaCl as a matrix.

In order to summarise the findings and conclusions of the work described here, a table (Table 9) has been prepared in which the characteristics of both methods of excitation have been compared.

Table 9

A Comparison of Anode and Cathode Excitation Under Identical
Conditions

<u>Property</u>	<u>Conclusions</u>
Absolute sensitivity.	Higher with cathode excitation for a number of volatile elements. Higher with anode excitation for some refractory elements.
Time required for complete consumption of sample.	Consumption occurs approximately twice as fast with anode excitation for each of the three matrices used in these experiments.
Time for complete volatilisation of an element.	Considerably higher for cathode excitation, a two to threefold factor being involved.
Volatilisation curves.	Curves are similar in shape for both methods of excitation but with considerable compression of the time axis for anode excitation.
Self absorption.	Appears to be approximately the same for both excitation methods.
CN emission.	Greater for cathode excitation.
Background emission.	A two to threefold increase for cathode excitation.
Reproducibilities.	Overall, slightly better for anode excitation with a NaCl matrix but appreciably better for cathode excitation with a carbon matrix.
General conclusions.	Cathode excitation appears to offer advantages in sensitivity for a number of non-refractory elements and gives greater overall precision in a carbon matrix for a number of volatile elements.

PART II

A STUDY OF THE EXTRACTION OF A
NUMBER OF ELEMENTS INTO CERTAIN
CYCLIC SOLVENTS.

(a) Introduction and Preliminary Investigation:

Three solutions of the elements Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Ge, Sn, Pb, As, Sb, and Bi were prepared in approximately 11N, 6N and 3N hydrochloric acid with the elements present in the same concentration in each. Aliquots of these three solutions were then oxidised with Cl_2 and equilibrated with the solvents cyclohexanol, carbon tetrachloride, isopropyl ether, amyl acetate and methyl isobutyl ketone. The organic phases were then separated from the aqueous phases, mixed with NaCl, taken to dryness and arced. Visual inspection showed that cyclohexanol extracted more elements than any of the other solvents, and the amount extracted into the organic phase was higher for cyclohexanol than for any of the other solvents.

Although Ge was included in the solution which was equilibrated with the organic solvents, this element was not found in the residues of either the organic or aqueous phases. This was most probably due to the fact that GeCl_4 is very volatile (Hodgman, 1955) and will be lost on evaporating a solution containing Ge in the presence of chloride ions. This was confirmed by evaporating in the presence of NaCl, a solution containing an amount of Ge well in excess of the spectrographic detection limit. On arcing, the residue showed no trace of this element.

As mentioned previously, Honoshino (1962) has

shown that the partition co-efficients for Zr and Hf decrease in the sequence, ketones, esters, alcohols, ethers, so that cyclohexanone should be a more efficient extractant than cyclohexanol. It was therefore decided to investigate the extraction of the above elements from hydrochloric acid solutions into the three solvents, cyclohexanone, cyclohexanol and cyclohexane, in order to obtain a comparison of the extraction properties of the three solvents. Since it was proposed to carry out the study by spectrographic analysis of the residue from the organic and aqueous phases after equilibration and evaporation, a preliminary investigation was made as to the feasibility of the technique. This showed that, as well as Ge, the extraction of Cu and Ag could not be determined spectrographically because of the presence of these two elements in the reagents in such concentrations that a blank correction would have been inordinately high. While Pb was also present as an impurity in the reagents, its concentration was such that an accurate correction was possible.

The extraction of the elements measured as percent extraction (%E) given by:-

$$\%E = \frac{100 D}{D + r} \quad (2.1)$$

where D is the distribution co-efficient for the element and r is the ratio of the volumes of the aqueous and the organic phases at equilibrium (Morrison and Freiser, 1957).

The distribution co-efficient is obtained as follows:-

The fundamental assumption in quantitative spectrochemical analysis is that the intensity of light emitted by an element is proportioned to the number of atoms present. Provided effects such as self absorption are absent, the intensity of light emitted by the source can be replaced by the intensity of the line as actually measured (I) and the number of atoms of the element replaced by the concentration (C) of the element in the sample, i.e.,

$$I = KC \quad (2.2)$$

That these assumptions are valid is supported by the fact that curves of log intensity plotted against log concentration (known as "working curves") in general have unit slope, as expected from the relationship:

$$\log I = \log K + \log C. \quad (2.3)$$

If an internal standard is to be used for quantitative analysis then, if its concentration is kept constant we have:

$$\log \frac{I_x}{I_s} = \log K' + \log C_x \quad (2.4)$$

where I_x and I_s are the measured intensities of the analysis and internal standard lines respectively and C_x is the concentration of the element to be analysed [Ahrens and Taylor (1960) have a comprehensive discussion on internal standards etc.,]. The concentration of an element in a sample therefore is directly proportional to the ratio of the

intensity of a spectral line of the element to that of an internal standard.

The distribution co-efficient, D , for an element distributed between two solvents is the ratio of the concentration of the element in the organic phase to that in the aqueous phase, i.e.,

$$D = \frac{C_o}{C_a} \quad (2.5)$$

where the subscripts o and a refer to the organic and aqueous phases respectively. Since, as discussed above, the concentration of an element is proportional to the ratio of the intensities of the spectral lines of the element and internal standard, (2.5) becomes:

$$D = \frac{(I_x/I_i)_o}{(I_x/I_i)_a} \quad (2.6)$$

which can then be substituted into (2.1). It is therefore clear that the percent extraction of an element can be obtained spectrographically without the necessity of constructing working curves for each element.

(b) An Investigation of cyclohexanone, cyclohexanol and cyclohexane as extracting solvents for the chloro-complexes of Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi.

It was proposed that a solution containing all the above elements in the appropriate strength of hydrochloric acid be equilibrated with the appropriate solvent, taken to dryness and arced using another element as a common internal standard. This however was impractical as all the elements being considered constituted the so-called volatile group for spectrographic analysis (Ahrens and Taylor, 1960). Since a good internal standard must have approximately the same volatility as the element to be analysed, the internal standard must also come from this group. The only other elements included in the volatile group are the alkali metals. These were investigated as possible internal standards but found unsatisfactory.

Since it was not possible to use a single, common internal standard, a different approach was made. From an inspection of Table 7 (Part I) it was clear that, for the elements under consideration and the systems studied, cathode excitation of a carbon matrix afforded the highest precision in spectrographic analysis. From the data presented in Table 7, the element giving the lowest coefficient of variation for each element to be analysed, was selected and used as the internal standard. In this

way it was possible to prepare two solutions such that all the elements in the one solution had their corresponding internal standards in the other solution. The composition of the two solutions and the internal standards for each element are given in Table 10 together with the coefficients of variation of the intensity ratios of the various line pairs. The concentrations of the elements were adjusted to give intensities in the range 10-200 intensity units (see Part I). The approximate concentrations of the elements in the aqueous phase before extraction are given in Table 10.

Solutions of the elements in the appropriate strength of hydrochloric acid were shaken for approximately 30 minutes with an equal volume of the organic solvent which had been pre-equilibrated with the corresponding strength of acid. (The solutions of the elements in the hydrochloric acid were so prepared that, in all cases, the concentration of a particular metal was the same). The solutions were allowed to settle, were separated into two phases, centrifuged and filtered through dry filter paper to ensure complete separation of the phases. Equal volumes of the two phases were mixed with 1 ml. of the appropriate internal standard solution and 40 mg. of Johnson Matthey "Specpure" carbon powder, taken to dryness and arced on a Hilger E742 large automatic spectrograph with quartz

Table 10

Solution Composition, Internal Standards and Co-efficients of Variation of Intensity Ratios.

Element	Concentration (g./l.)	Internal Standard	Co-efficient of Variation
<u>Solution A.</u>			
Au	0.06	Cu	12.2
Cd	0.2	Cu	5.9
Ga	0.03	Pb	4.1
Bi	0.03	Pb	5.5
Tl	1	In	3.6
Sb	1	Sn	2.5
Zn	1.6	As	10.4
Hg	4	As	14.7
<u>Solution B.</u>			
Pb	0.1	Ga	4.3
In	0.03	Tl	7.4
Sn	0.1	Sb	3.5
As	1	Sb	6.2

Lines used were: As 2860, Au 2676, Bi 3067, Cd 3261, Cu 3274, Ga 2943, Hg 2536, In 3256, Pb 2833, Sb 3267, Tl 3229, Zn 3345.

optics. The spectrographic operating conditions are given in Table 11. All extractions were carried out at 25°C. All determinations were done at least in duplicate and in some cases up to six determinations were made. The distribution co-efficient for each element was calculated from equation (2.6) and this, together with the appropriate value for r substituted into equation (2.1) to obtain the percent extraction.

Although the organic phases were pre-equilibrated with the appropriate strength of hydrochloric acid before extraction, it was not practical to do this for the acid solution. Accordingly, in the case of cyclohexanone, there was a volume change during extraction due to the solubility of the ketone in the acid. The volume ratios at equilibrium (r) after mixtures of equal volumes of acid and pre-equilibrated solvent at 25°C were determined and are given in Table 12.

Table 11

Spectrographic Operating Conditions.

Slit length	12 mm
Slit width	0.15 mm
Wavelength range	2500-3400 Å
Photographic plates	Ilford N-30
Current	7 amps d.c.
Excitation	Cathode
Exposure	To completion
Electrodes	Johnson Matthey 4B graphite, 1/16" internal diameter by 4 mm deep.
Photographic processing	4 min at 20° in Kodak D19b developer
Densitometry	Hilger microphotometer with Galvoscale calibrated in B-values
Optical system	Convex quartz lens placed at slit to give even illumination at this point and to provide an image of the arc at the collimator.
Arc gap	4 mm

Table 12

The Ratio of the Volumes of Pre-equilibrated Cyclohexanone
and Hydrochloric Acid at Equilibrium.

Acid concentration (N)	$r = \frac{\text{Vol. org. phase.}}{\text{Vol. aq. phase.}}$
0.5	1.28
1	1.33
2	1.38
3	1.52

(c) Results and Discussion.

The percent extraction of the elements as a function of hydrochloric acid concentration for the solvents cyclohexanone, cyclohexanol and cyclohexane are given in Table 13. The data for the two former solvents are shown graphically in Fig. 5.

Table 13

Extraction of Certain Elements from Hydrochloric Acid Solutions into the Solvents Cyclohexanone, Cyclohexanol and Cyclohexane.

Metal	Acid Conc. (N)	% Extraction.		
		cyclohexanone	cyclohexanol	cyclohexane
Au	0.5	100	100	0
	1	100	100	2.6
	2	100	100	1.3
	3	100	100	0
	4		100	0
	5		100	0
Zn	0.5	9.9	0	0
	1	66.7	23.8	0
	2	89.6	59.8	0
	3	88.6	65.1	0
	4		61.0	0
	5		54.2	0
Cd	0.5	0	0	0
	1	39.6	14.7	0
	2	74.5	41.0	0
	3	80.6	54.8	0
	4		71.6	0
	5		63.9	0

(contin.)

Hg	0.5	52.5	29.3	0
	1	81.8	20.6	0
	2	94.0	54.0	0
	3	94.1	34.2	0
	4		52.7	0
	5		39.8	0
Ga	0.5	7.0	0	6.9
	1	30.4	0	5.2
	2	94.9	2.2	1.7
	3	100	29.2	7.0
	4		69.7	5.3
	5		88.6	0
In	0.5	15.1	0	0
	1	38.7	0	0
	2	76.3	10.8	0
	3	100	9.9	0
	4		7.9	0
	5		12.5	0
Tl	0.5	100	100	0
	1	100	100	0
	2	100	100	0
	3	100	100	0
	4		100	0
	5		100	0
Sn	0.5	43.1	79.6	0
	1	93.6	97.3	0
	2	100	99.4	0
	3	100	99.5	0
	4		99.5	0
	5		99.6	0
Pb	0.5	17.8	8.3	0
	1	22.4	18.7	0
	2	41.8	18.4	0
	3	46.1	19.7	0
	4		18.9	0
	5		19.2	0
As	0.5	12.7	0	0
	1	11.1	39.4	0
	2	7.8	59.6	0
	3	0	71.5	0
	4		75.0	0
	5		78.0	0

(contin.)

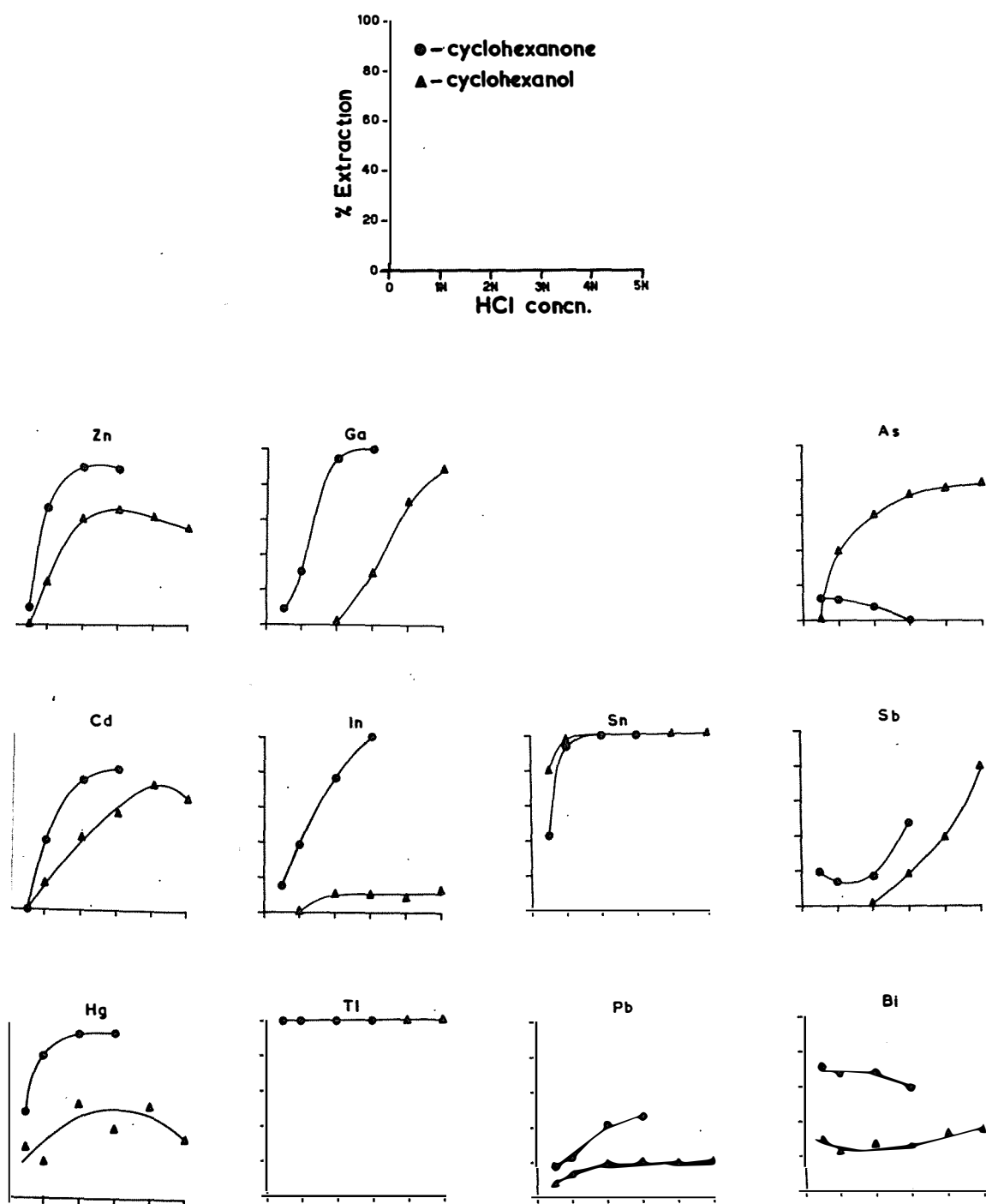


Fig. 5

The extraction of elements into cyclohexanone and cyclohexanol as a function of hydrochloric acid concentration.

Sb	0.5	18.8	0	0
	1	13.6	0	0
	2	16.6	1.3	0
	3	47.4	18.2	0
	4		38.9	0
	5		78.9	0
Bi	0.5	71.7	29.5	17.8
	1	67.4	22.1	7.7
	2	67.8	26.2	27.1
	3	59.1	26.3	13.5
	4		32.1	0
	5		34.9	0

When cyclohexanone is mixed with a solution approximately 4N in hydrochloric acid, a single homogeneous phase is formed. For this reason extraction data for cyclohexanone at acid concentrations greater than 3N were not obtained. For the same reason no results were available for cyclohexanol above 5N hydrochloric acid.

In almost every case there was increased extraction with higher acid concentration and, with the exception of As and Sn, all elements had a higher percent extraction in cyclohexanone than in cyclohexanol. Cyclohexane is clearly a very inefficient solvent, as would be expected since there is no possibility of the cyclohexane molecule being incorporated into the co-ordination sphere of the metal complex or solvating the protons in the ion association complex to facilitate extraction. The extraction of Au, Bi and Ga by cyclohexane, although minor, was unexpected in view of the inert nature of the solvent.

The possibility of entrainment could be ignored since none of the other elements present in the same solution prior to extraction were observed in the organic phase after extraction, showing that separation of the phases was complete. The possibility of interference from other spectral lines was investigated but found unlikely.

The results given here confirm the work of Honshino (1962) who found that, in general, ketones are better extractants than alcohols (exceptions here are in the cases of Sn and As).

It is clear that when these solvents are to be used for the selective extraction of a particular element, cyclohexanol is more satisfactory than cyclohexanone. For example, indium and thallium in a 0.5 N solution of hydrochloric acid can be quantitatively separated with cyclohexanol but not with cyclohexanone. Similarly, tin and lead can be separated more efficiently at low acid concentrations by cyclohexanol than by cyclohexanone.

When an efficient but not selective extracting medium is required, then cyclohexanone with an aqueous phase containing a high concentration of hydrochloric acid is preferable. Halmekoski and Sundholm (1963) have found that ethyl methyl ketone/ hydrochloric acid is a better solvent for paper chromatography of cations than cyclohexanone/hydrochloric acid, presumably because the

former (a weaker extractant than cyclohexanone) enables the cations to be better separated.

(d) Preliminary investigations into the geochemical applications of the cyclohexanone/hydrochloric acid extraction system.

Since cyclohexanone is an efficient extracting medium capable of extracting a large number of trace elements from hydrochloric acid solutions it was decided to investigate the possibility of using it in conjunction with spectrographic analysis for trace element determinations in material of geochemical interest.

It is clear from Fig. 5 that, with the exception of Bi, all elements are better extracted by cyclohexanone from 3N hydrochloric acid than any lower acid concentration. Therefore, a solution of a granite-gneiss from the Charleston area, New Zealand and a sample of water from Lake Bonney, Victoria Land, Antarctica, were made 3N in hydrochloric acid and extracted with cyclohexanone. The organic phase was taken to dryness and the residue arced. The elements for which extraction data have been obtained and which have been identified spectrographically in these residues are listed in Table 14.

Table 14

Elements Detected in Cyclohexanone Extracts of a Solution of a Granite-Gneiss and Lake Bonney Water.

Material	Elements present							
	Zn	Cd	Ga	Tl	Sn	Pb	Sb	Bi
Granite-gneiss	+		+	+	+	+		
Lake Bonney water	+	+		+	+	+	+	+

While studying the extraction of the granite-gneiss solution it became clear that in 3N hydrochloric acid Fe was appreciably extracted by cyclohexanone. While this is of no consequence in material containing little or no Fe, and indeed is an advantage, enabling trace amounts of Fe to be determined, this is not the case for material in which Fe is present in moderate or high concentrations. Since most silicate rocks contain between 1% and 10% Fe, the extraction of Fe gives rise to two problems. Firstly Fe has a very complex spectrum likely to cause excessive interference particularly with Bi 3067.7, and secondly, because of its high abundance, the extracted residue containing the trace elements will have undesirable bulk with consequent loss in sensitivity.

For the highest sensitivity therefore it will be necessary either to prevent the Fe extracting into the organic phase or to separate the Fe from the other extracted elements either before or after extraction. The two principle techniques for preventing an otherwise extractable species from extracting into an organic solvent are the use of masking agents or the alteration of the valence state of the element. Both these possibilities were investigated as follows and found unsatisfactory.

(i) Use of masking agents: Identical solutions containing all the elements under consideration, together with Fe, were mixed with the following possible masking

agents: citric acid, tartaric acid, trichloroacetic acid, ethylenediamine tetraacetic acid, dipyridyl and orthophenanthroline. After extraction from 3N hydrochloric acid into cyclohexanone the aqueous and organic phases were separated and arced. The spectra were examined to find the phase containing the Fe. In all cases the Fe occurred in high concentration in the organic phase. Two reagents which have been extensively used as masking agents for Fe in solvent extraction are the F^- and CN^- ions. These however could not be used with the high acid concentrations necessary for good extraction under the above conditions, the former because of the ability of HF to etch glass and the latter because of the health hazard.

(ii) Alteration of Valence State: Morrison and Freiser (1957) state that Fe(III) is better extracted by oxygenated solvents from a chloride media than is Fe(II). If the Fe in solution is reduced to the lower valence state then it might not be extracted. A similar solution to that used in (i) above was therefore reduced by the addition of lithium borohydride, extracted from 3N hydrochloric acid into cyclohexanone, the phases separated, arced and the spectra examined. Large quantities of Fe were found in the organic phase indicating that either Fe(II) is extracted by cyclohexanone or that Fe (II) was oxidised to Fe (III) during the extraction. In any case reduction would have proved unsatisfactory since it would have considerably

reduced the extraction of Tl, Au and Sb.

The possibility of removing the iron prior to extraction was investigated but found impractical. The two possible methods of doing this are precipitation or extraction with another solvent. Precipitation is not satisfactory because of the ever present risk of co-precipitation of trace elements. Prior extraction with another solvent is also unsatisfactory because of the possible co-extraction of trace elements, no simple system specific for Fe and applicable to the high acid concentrations necessary to keep rocks in solution being known to the author.

The remaining possibility, that of separating the Fe from the remainder of the extracted elements after extraction, was therefore investigated. In a recent study (Brooks, 1965a) the potentialities of discontinuous, counter current, liquid-liquid extraction for inorganic separations have been highlighted. It was therefore decided to investigate this technique with a view to applying it to the separation of Fe from the trace elements extracted with it from a rock solution by cyclohexanone. This is discussed in Parts IV and V.

PART III

THE USE OF CYCLOHEXANONE FOR THE DETERMINATION OF
Zn, Pb, In, Bi, Fe, Mn and Mo
IN THE LAKES OF McMurdo Oasis, Antarctica.

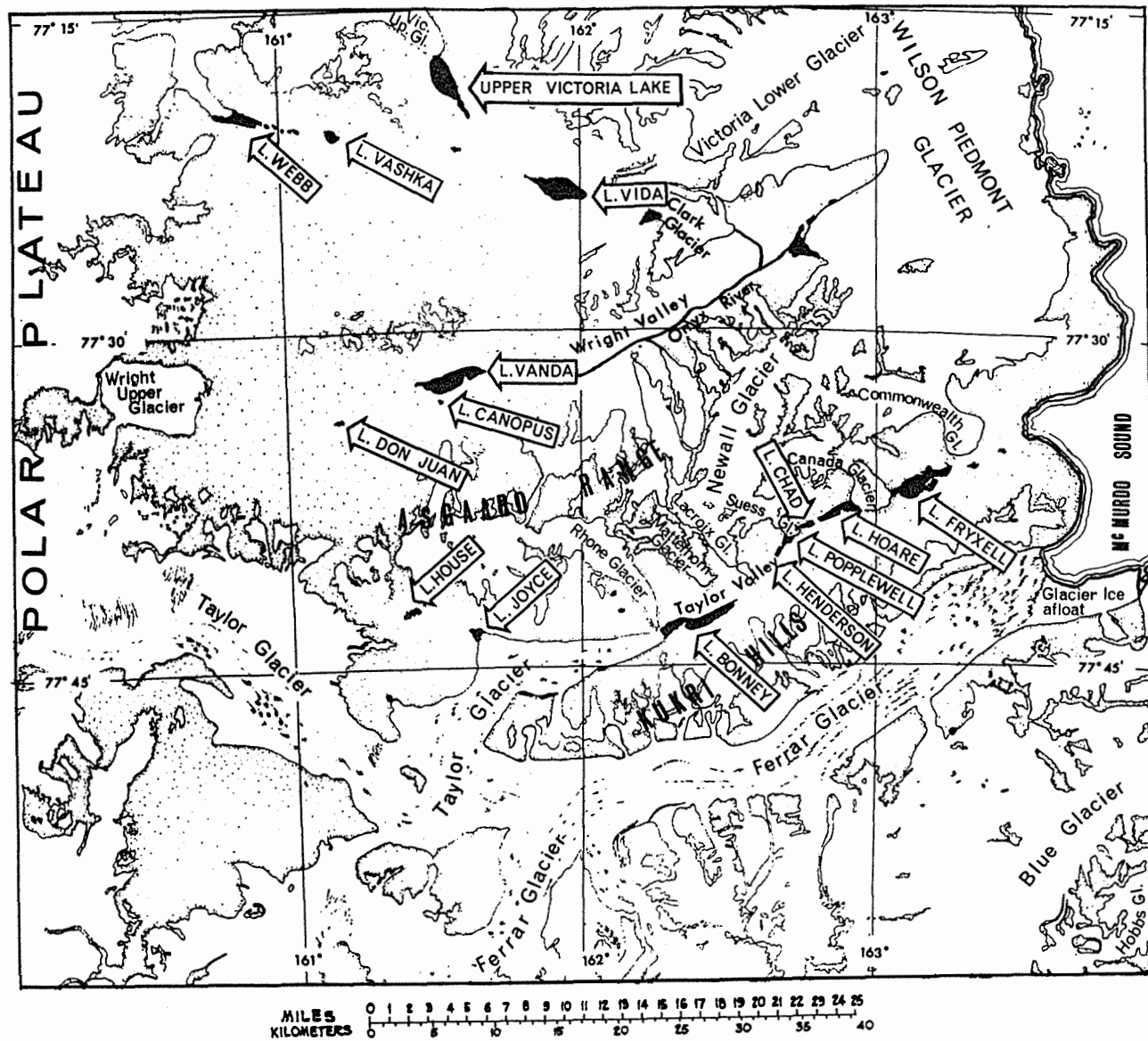
(a) Introduction

Although the preliminary investigation into the application of the hydrochloric acid/cyclohexanone extraction system to geochemical trace analysis showed that Fe was well extracted, this causes no problems in systems in which there is little or no Fe. In material which has only trace amounts of this element, its extraction by the solvent can indeed be used to determine the amount of Fe present in the original material, provided the percent extraction of Fe is known.

The Taylor and Wright Valleys, McMurdo Sound, Antarctica, contain a series of lakes of particular interest to the geochemist. These are Lakes Bonney, Joyce, Fryxell and Hoare in the Taylor Valley and Lake Vanda in the Wright Valley (see map, Fig. 6). Although ice covered, the deeper regions of the lakes are not frozen, Lake Bonney having a maximum temperature of 7°C approximately 15m. from the surface (Angino, Armitage and Tash, 1964; Hoare et al, 1964). The maximum temperature for Lake Vanda occurs in the bottom 6m. and is 25°C (Armitage and House, 1962; Wilson and Wellman, 1962; Angino and Armitage, 1963). Lake Fryxell has a maximum temperature of approximately 2.25°C at a depth of approximately 9m. (Angino, Armitage and Tash, 1962; Hoare et al, 1965).

These lakes, especially Bonney and Vanda, are

Fig. 6
Map of McMurdo Oasis, Victoria Land, Antarctica.



saline and strongly density stratified (see references for Bonney and Vanda above), with the waters at the bottom of the lakes containing large amounts of dissolved solids (see Table 15).

Table 15

Total Dissolved Matter and Macro Element Composition of Bottom Water of Certain Antarctic Lakes.*

Lake	Solid Matter (%)	Composition (%)					
		Na	K	Mg	Ca	HCO ₃	Cl
Vanda	17.65	6.4	0.2	20.0	0.9	0.2	72.4
Bonney	39.09	24.1	1.0	11.0	0.3	0.1	63.4
Fryxell	0.97	23.1	1.5	4.0	0.9	33.3	38.3
Joyce	0.50	24.9	1.9	4.3	0.7	23.7	43.1
Hoare (West Lobe)	0.11	18.8	3.3	4.3	1.7	61.7	10.1
Hoare (East Lobe)	0.10	18.8	3.2	4.3	1.7	61.7	10.1

* From data supplied by Professor A.T. Wilson, Chemistry Department, Victoria University of Wellington.

Wilson (1964) and Roberts and Wilson (1965) have shown that by approximately 1,000 years ago Lake Vanda had lost most of its water by evaporation (the lake has no outflow) and all that remained was a few feet of saturated salt solution, principally CaCl₂. At this time the climate changed, fresh water began flowing in on top of the strong salt solution and since then the salts have been diffusing upwards. A similar mechanism is proposed for the formation of density gradients in the other lakes (Wilson, person-

al communication). The ions present in the water at the bottom of these lakes are therefore much more concentrated than they were in the original water present in the lakes.

The ions in the water originally present in the lakes can be regarded as coming from a combination of any or all of the following sources:-

(i) Atmospheric precipitation.

It is well known that rain water at considerable distances from the sea contains appreciable quantities of several inorganic ions (Junge, 1963; Erickson, 1959, 1960; Komabayasi, 1962; Oddie, 1960) and it is possible that the salts in the lakes are in part, obtained from melted snow. Wilson (1965) has shown the presence of inorganic salts at the South Pole. Angino, Armitage and Tash (1962) have postulated salts from sea spray blown from McMurdo Sound as contributing to the salts in Lake Fryxell.

(ii) Relic sea water.

This has also been suggested as an origin for the salts in Lake Fryxell by the latter authors and also for Lake Bonney (Angino et al. 1964).

(iii) Thermal Springs.

By a consideration of the temperature profile of Lake Vanda and the ratio of concentration of certain elements in the water of this lake, Angino, Armitage and Tash (1965) claimed evidence for thermal springs entering the lake, several elements being provided in this way.

For the same reasons they considered that Lakes Bonney and Fryxell were also fed by thermal waters (Angino et al. 1964). Wilson et al have shown that for these three lakes, solar heat alone is sufficient to maintain the temperature profiles in the lakes, (Hoare et al. 1964, 1965; Wilson and Wellman 1962) and consider that the possibility of thermal waters entering the lakes is very remote.

(iv) The surrounding rocks.

Tedrow et al. (1963) claimed evidence for widespread alteration of rocks and minerals under the Antarctic environment which converts normally stable minerals into readily soluble forms. Elements which are thereby released can be collected into lakes and pools if periodic flushing of the soil occurs, as in the annual thaw. Keller and Reesman (1963) have shown that the melt waters of glaciers contain small amounts of dissolved rocks. Since all these lakes are fed by the melt waters of glaciers, it is reasonable to expect that elements extracted from the rocks near the glaciers and contained in the melt waters would contribute to the salts in the lakes.

In their consideration of Lake Fryxell, Angino et al. (1965) dismissed the relic sea water hypothesis but claimed some evidence for the presence of sea water in Lake Bonney (Angino et al. 1964). Since Lakes Vanda, Bonney and Fryxell have been shown to derive their heat directly from the sun, the possibility of thermal springs

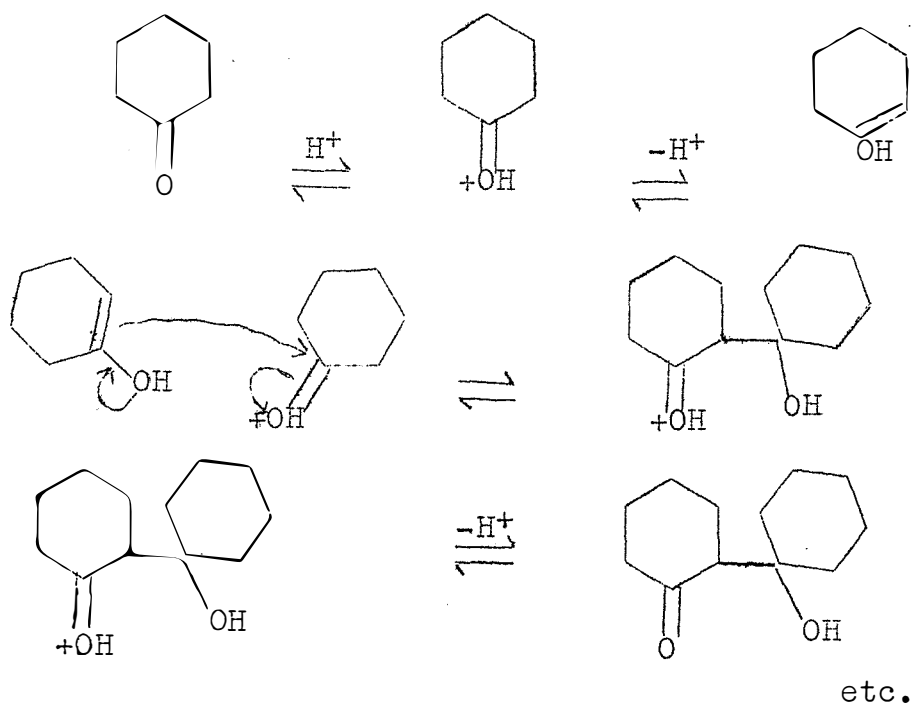
in these lakes can be neglected. (This does not mean that thermal springs have not been there in the past.) It is therefore probable that the salts present in the lakes are from atmospheric precipitation and/or the surrounding rocks. The lakes therefore represent, in part, a large amount of concentrated melt water so that analysis of these waters for heavy metals should constitute an integrated geochemical survey for minerals in the area supplying the lake. Since the bottom waters of these lakes are the most concentrated, they will be the most valuable in such a survey. However, because of the high concentration of dissolved solids in these waters, direct spectrographic determination of trace constituents is not feasible and an enrichment procedure is necessary. Preliminary investigation had shown that the extraction into cyclohexanone from 3N hydrochloric acid solutions enabled a number of trace elements to be determined in a sample of water from the bottom of Lake Bonney. A quantitative procedure was therefore developed and applied to the determination of Zn, Pb, In, Bi, Fe, Mn and Mo in Lakes Vanda, Bonney, Joyce, Fryxell and the East and West Lobes of Hoare.

The object of the investigation was to determine, if possible, the origin of the salts in the lakes, and also to determine whether anomalous concentrations of certain trace elements were any indication of mineralization in the drainage areas of the lakes.

(b) Development and Application of a Quantitative Procedure

In the preliminary work on the extraction of the trace elements from the solution of the granite-gneiss and the water from the bottom of Lake Bonney (see Part IIId), it was found that on evaporating the cyclohexanone extract, after the majority of the solvent had been removed, a red-black extremely viscous tar was left in the container. Prolonged heating at approximately 250°C caused this to harden but when the crushed residue was arced it tended to extrude from the electrode in the early stages of arcing. Because very little of the material was therefore entering the arc, the sensitivity was consequently reduced and various attempts were made to overcome this problem.

The formation of this tar is most probably due to polymerisation of the cyclohexanone in the presence of the high concentration of hydrochloric acid. On standing in the presence of 3N hydrochloric acid for a considerable time, cyclohexanone gradually becomes an increasingly darker yellow indicating that some reaction has taken place. On addition of concentrated hydrochloric acid to cyclohexanone this same change takes place very rapidly. Heating the mixture also increases the rate of the reaction. A possible reaction scheme for the formation of the polymer is given below (following House, 1965 p.217)



The reaction must be catalysed by the acid since no tar is formed on evaporating pure cyclohexanone.

Since direct evaporation of the cyclohexanone extract of solutions 3N in acid resulted in the formation of the tar, the possibility of stripping the organic phase of the extracted elements was investigated. It has been shown (Part II) that, with the exception of Bi, the extraction of the elements considered here decreased with decreasing acid concentration. Accordingly, if the organic phase, after extraction of the acid solution, is separated and shaken with a neutral or basic aqueous phase it is probable that many elements would redistribute themselves between the two phases, concentrating mainly in the aqueous phase.

By suitable adjustment of conditions it may be possible to remove completely all elements from the organic phase.

If, as is the case here, extraction decreases with decreasing acid concentration an alkaline aqueous phase would prove the most efficient stripping agent. The use of such a phase however, involves the addition of reagents with the consequent risk of contamination and also increases the bulk of the extracted residue after evaporation, thus lowering sensitivity. Both problems could be overcome by use of an aqueous phase such as dilute ammonium hydroxide which had been prepared by distillation of ammonia gas into distilled or de-ionized water. A solution containing all the elements considered in Part II dissolved in 3N hydrochloric acid was oxidized with chlorine and extracted with cyclohexanone. The organic phase was separated, equilibrated with a dilute ammonia solution, and the aqueous phase taken to dryness. The residue consisted of large quantities of ammonium chloride from the reaction of excess hydrochloric acid in the organic phase with the ammonia. Since this contributed to the bulk of material and thus reduced sensitivity, it was decided to investigate the possibility of stripping the cyclohexanone phase with water.

The elements under study were dissolved in 3N hydrochloric acid, the solution chlorinated and extracted with cyclohexanone. The organic phase was separated,

equilibrated with an equal volume of distilled water and taken to dryness with 40 mg of NaCl. The procedure was repeated three times except that the organic phase was subjected to three, five and six equilibrations respectively with equal volumes of distilled water. Even after 6 strippings with distilled water, spectrographically-detectable amounts of Au, Bi, Sb, Sn, and Tl remained in the organic phase. The possibility of using this technique was therefore rejected.

Although the plasma jet was developed in 1954 (Weiss, 1954), its potentialities as a spectrochemical source were not appreciated until much later (Margoshes and Scribner, 1959; Korolev and Vainshtein, 1959). Although used extensively for the examination of petroleum products (Rozsa et al., 1962, 1963; Vigler and Failoni, 1965) and oilfield waters (Collins and Pearson, 1964), relatively little use has been made of the technique in spectrochemical analysis. Serin and Ashton (1964) and Mitteldort and Langdon (1963) have reviewed the published literature on the subject. The use of the plasma jet provides a satisfactory means of introducing a solution into the d.c. arc permitting the direct determination of elements in solution. The possibility of using this jet for the analysis of the lake waters was therefore investigated.

A sample of water from the bottom of Lake Bonney was made 3N in hydrochloric acid, oxidized with chlorine

and extracted with an equal volume of cyclohexanone. The organic phase was separated and taken to one tenth of its original volume. Attempts were made to aspirate this into the plasma jet but it proved too viscous. The solution was then diluted 1:1 with acetone and introduced into the plasma jet. This procedure was repeated for each lake water. The only elements found in the resultant spectra were Mn and traces of Sn and Pb. Since Cd, Tl, Sn, Pb, Sb, Bi together with Fe, Mo and Mn had been found by direct spectrographic examination of the residue from the organic phase after extraction with cyclohexanone, the sensitivity obtained with the plasma jet was not sufficient and investigations with it were not continued.

It was decided to ash the residues left after evaporation of the cyclohexanone extracts in order to remove the tar. Willis, Kaye and Ahrens (1964) have shown that Tl volatilises quite readily from manganese nodules if temperatures greater than 450°C are used. It was therefore necessary to investigate the possible loss of elements on ashing the residue from the cyclohexanone extract. If ashing is to be carried out at a temperature able to remove carbonaceous material in the residue then clearly carbon cannot be used as a matrix. A mixture of the elements under study in NaCl was prepared and placed in seven beakers. These were then placed in a muffle furnace, the temperature

was increased and at intervals of 100°C a beaker was removed. The material in the beakers was loaded into electrodes and arced. The intensity of sensitive lines of the elements were measured and plotted against temperature. The results are shown in Fig. 7. From this figure it is clear that, with the exception of Tl, trace elements in a NaCl matrix do not appear to be lost from the solid below 500°C. Some elements however volatilize rapidly above this temperature.

Thallium appears to start volatilising from the material between 300 and 400°C. This temperature is lower than the corresponding value found by Willis, Kaye and Ahrens (1964) but this could be due to the use of a different matrix.

Because of the low temperature of volatilisation of Tl, attempts were made to ash the cyclohexanone tar below 300°C but were unsuccessful. Since ashing at a higher temperature would mean that this element could not be determined, an attempt was made to remove the cyclohexanone tar by boiling it with concentrated nitric acid. This also was unsuccessful. Furthermore, the residue obtained by this treatment needed just as high a temperature for ashing as did the original tar.

Since the samples were to be ashed before arcing, a carbon matrix, as used for obtaining the extraction data, could not be used and a NaCl matrix was preferable.

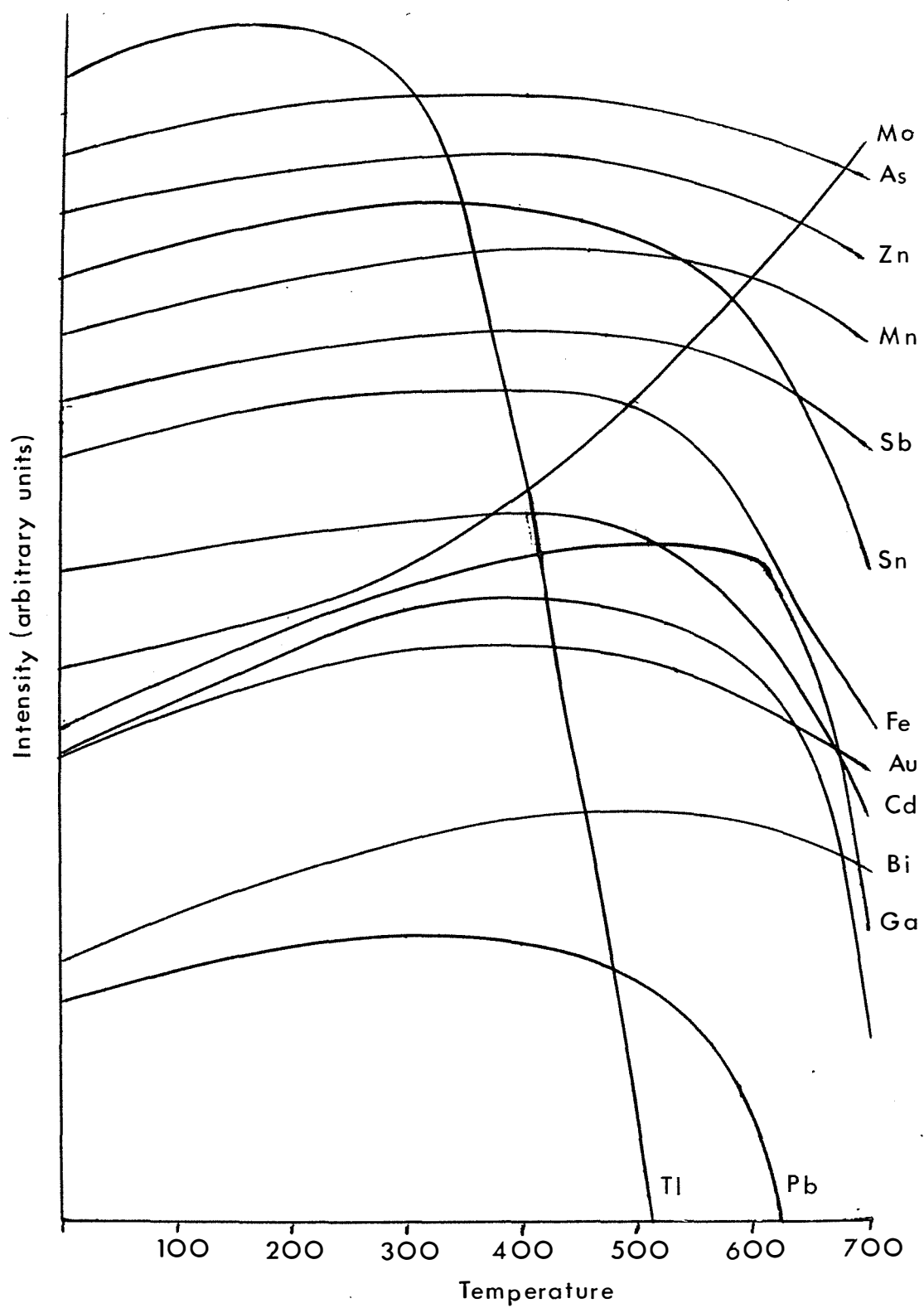


Fig. 7

Spectral intensity of certain elements as a function of temperature.

In Part I (b) it was shown that although cathode excitation gave higher reproducibility for a carbon matrix, anode excitation was better for a NaCl matrix. It was therefore decided to use anode excitation in obtaining the spectra of the lake water extracts. The arc was focussed directly onto the slit instead of on to the collimator as in part I(b) and was found to give a sixfold increase in sensitivity. Ilford Zenith photographic plates were used to obtain maximum sensitivity.

Preliminary study showed the presence of the following elements in cyclohexanone extracts of the lake water:- Cu, Zn, Cd, In, Tl, Sn, Pb, Sb, Bi, Mo, Mn and Fe. Accordingly none of these could be used as internal standards in the quantitative spectrographic analysis of the lake waters. A consideration of the remaining elements in the "volatile" group for the spectrographic analysis (Ahrens and Taylor, 1960) using the data obtained in Part I(b), showed that Ga seemed to be the most promising as an internal standard. Since the optical system to be used in the determination of the trace elements was not the same as that used in Part I(b), it was necessary to find the reproducibility of the modified technique.

It was decided to investigate quantitatively the elements Zn, Pb, In, Bi, Fe, Mo and Mn. Eleven replicate arcings were therefore undertaken of identical samples containing the above elements and Ga. The

spectrographic operating conditions are given in Table 16.

Table 16

Spectrographic Operating Conditions.

Slit length	12 mm
Slit width	0.15 mm
Wavelength range	2500-3400 Å
Photographic plates	Ilford Zenith
Current	7 amps d.c.
Excitation	anode
Exposure	to completion
Electrodes	Johnson Matthey 4B graphite, 1/16" internal diameter by 4 mm deep.
Photographic processing	4 min at 20°C in Kodak D19b developer.
Densitometry	Hilger microphotometer with Galvo-scale calibrated in B-values.
Optical system	Convex quartz lens placed to give an image of the arc at the slit.
Arc gap	4 mm

The arc was sheathed by a stream of CO₂ by use of a modified Stallwood jet (Margoshes and Scribner, 1964).

The intensities of the various lines are given in Fig. 8 and the ratio of the intensities of the lines of the elements to that of Ga are given in Table 17.

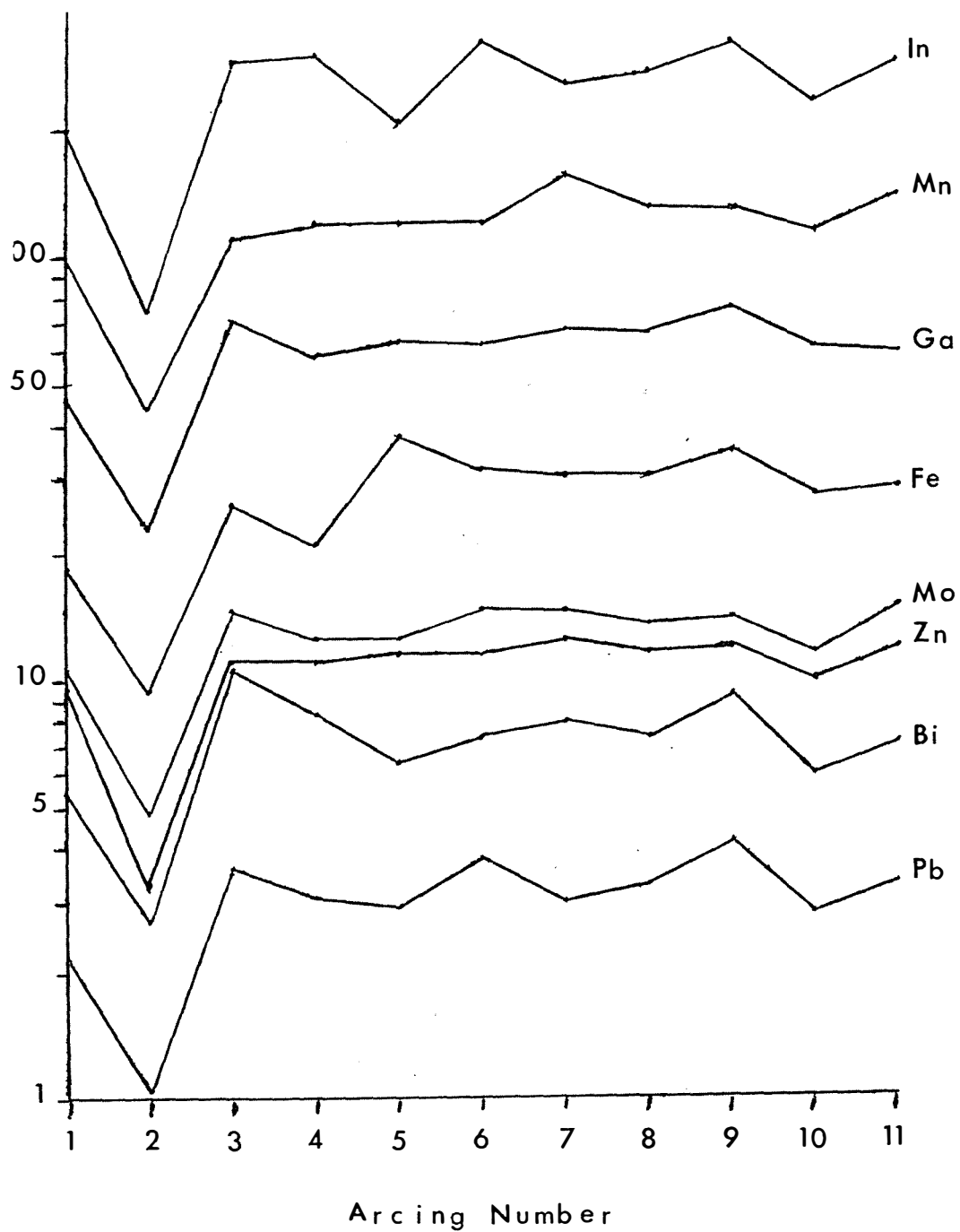


fig. 8

Line intensities for determining the reproducibility of Ga as an internal standard for the spectrochemical determination of In, Mo, Fe, Mn, Zn, Bi and Pb.

Table 17

Ga as Internal Standard for Zn, Pb, In, Fe, Mo and Mn.

Line Pair	Intensity ratio										
	Arcing number.										
	1	2	3	4	5	6	7	8	9	10	11
Zn/Ga	0.14	0.08	0.11	0.12	0.12	0.12	0.13	0.11	0.10	0.11	0.14
Pb/Ga	0.46	0.44	0.51	0.51	0.46	0.61	0.44	0.49	0.54	0.45	0.56
In/Ga	0.84	0.63	0.81	1.03	0.67	1.05	0.76	0.81	0.84	0.75	0.98
Bi/Ga	1.13	1.16	1.53	1.42	0.94	1.11	1.13	1.6	1.67	0.92	1.11
Fe/Ga	0.79	0.84	0.75	0.72	1.23	1.02	0.90	0.91	0.92	0.89	0.95
Mo/Ga	2.3	2.2	2.1	2.1	2.0	2.4	2.2	2.0	1.9	1.9	2.6
Mn/Ga	2.1	2.0	1.6	2.1	2.0	2.0	2.4	2.0	1.9	1.9	2.4

Values of 14.4%, 11.2%, 16.4%, 18.3%, 15.9%, 7.0% and 9.8% were obtained for the coefficient of variation of the line pairs Zn/Ga, Pb/Ga, In/Ga, Bi/Ga, Fe/Ga, Mo/Ga and Mn/Ga respectively. Lines used were Zn 3345, Pb 2833, In 3256, Bi 3067, Fe 3020, Mo 3170, Mn 2576 and Ga 2943.

The apparatus used for sheathing the arc with CO₂ was similar to that described by Margoshes and Scribner (1964). While the principle use of this type of device is to prevent the formation of cyanogen bands by exclusion of N₂ from the arc, it has also been shown to give improved steadiness of the arc (Kalinin et al., 1957), reduce background (Shaw et al., 1958; Hammaker et al., 1958) and increase the sensitivity of volatile elements (Shaw et al., 1958; Hammaker et al., 1958; Masuda and Onishi, 1962).

Although the intensity ratios were not highly reproducible, it was considered that the precision would never-

theless be satisfactory for the purpose of the investigation.

The procedure used for the quantitative determination of the above elements was as follows:-

The lake waters were made 3N in hydrochloric acid by addition of the appropriate quantity of Analar-grade acid, oxidized with Cl_2 gas and shaken with pre-equilibrated cyclohexanone. The volume of cyclohexanone was adjusted such that, at equilibrium, equal volumes of both phases were present. The organic phase was evaporated in the presence of 40 mg of NaCl and 1 mg of a Ga solution, and the resultant tar ashed at 450°C . The residue was then arced under the conditions given in Table 16.

A series of working curves was prepared by duplicate arcings of known amounts of the elements in NaCl, together with 1 ml of the Ga solution. The spectrographic operating conditions were as in Table 16.

Line intensities were measured and plotted on logarithmic graph paper. These working curves are shown in Fig. 9 and, as can be seen, relatively good straight lines were obtained, although some self absorption occurred at higher concentrations of In, Pb and Fe. The extract 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 line intensities of the elements found in

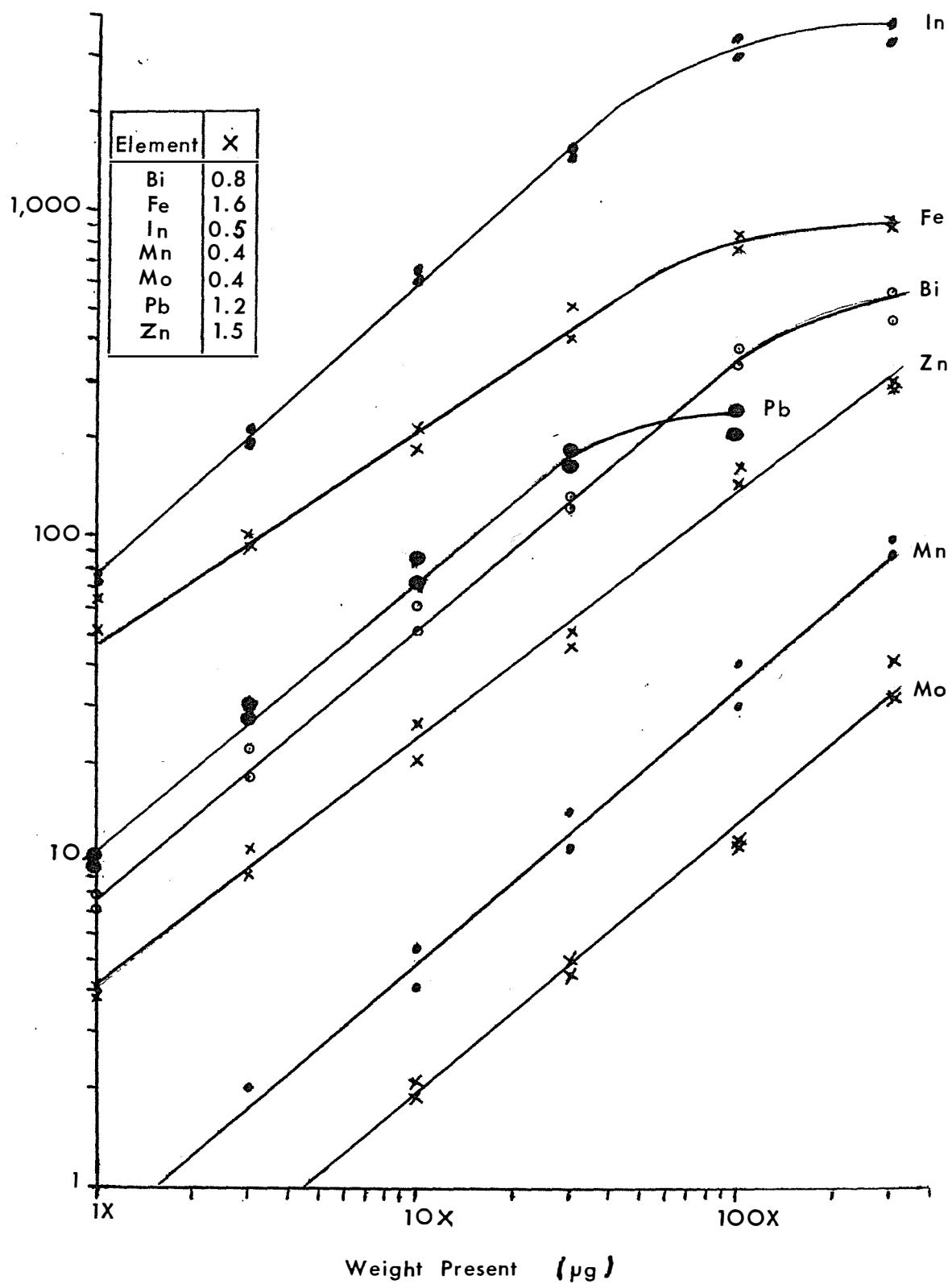


Fig. 9

Working curves for the spectrochemical analysis of In, Fe, Bi, Zn, Pb and Mn using Ga as an internal standard.

the lake water extracts were measured and from the working curves the amount of each element present in the extracted residue obtained. Using the extraction data of Part II, the amount present in the original lake water was calculated and the concentration of each element in the water obtained. In addition, a blank determination was carried out on all the reagents used in the procedure. Traces of Pb, Zn, Fe, Mo and Mn were found in the blank and corrections were made for these. Since the extraction of Fe, Mo and Mn from HCl into cyclohexanone had not been studied previously the percent extraction of these elements in this system at 3N acid concentration was obtained in the same way as described in Part II. The spectrographic conditions used were those described in Table 16 and Ga was used as an internal standard. The percent extraction for these elements was found to be 99.4%, 81.8% and 15.8% for the Fe, Mo and Mn respectively. The determination was done in triplicate and the values reported are the average of three observations. The coefficients of variations for the line pairs used are those given above viz., 15.9%, 7.0% and 9.8% for Fe, Mo and Mn respectively.

(c) Results and Discussion.

Waters from the bottom of Lakes Vanda, Bonney, Joyce and Fryxell and the eastern and western lobes of Lake Hoare were treated in the manner described in the previous section. The concentration of the elements found are given in Table 18 together with the corresponding data for sea and river waters.

Table 18

Concentration of Certain Elements in the Bottom Waters of Lakes of McMurdo Oasis, Antarctica (data for sea and river water included for comparison).

Lake	Concentration ($\mu\text{g/l}$)						
	Zn	Pb	In	Bi	Fe	Mn	Mo
Vanda	5400	<30	<0.10	6.1	490	44	2.1
Bonney	150	<30	0.56	7.1	640	23	8.7
Fryxell	28	42	0.79	<2	14	2.9	0.23
Joyce	38	340	0.29	3.8	500	27	7.0
Hoare (East Lobe)	31	83	<0.10	<2	130	11	1.0
Hoare (West Lobe)	20	91	1.71	<2	500	18	31
Sea water*	10	0.03	<20	0.2	10	2	10
River water**	-	4	-	-	300	20	0.35

*Data from Goldberg (1965)

** Data from Durum and Haffty (1963)

To the author's knowledge, this is the first reported study of the determination of the trace element composition of highly-saline surface waters. Since no similar work has been reported, the data given here cannot be compared with those for any other comparable systems.

The only saline water for which trace element compositions are known is sea water and the accepted concentrations for the appropriate elements are included for comparison in Table 18 (Data from Goldberg, 1965). Also included for comparison are median values for trace elements in river waters (after Durum and Haffty, 1963). By comparing the data for these lakes with those for sea water and natural water, it should be possible to draw some conclusions as to the origin of the water in the various lakes (i.e. whether it is trapped sea water, glacial melt water, etc.).

Provided there has been no precipitation of any dissolved material during the period in which the lakes are assumed to have evaporated to low bulk, the ratio of trace element concentration to that of total dissolved solids in the lakes now will be the same as in the water originally present in the lakes. If the water in the lakes was provided by glacial melt waters only, any anomalously high relative concentrations of trace elements in the lakes should provide a guide to mineralization in the area. If the lakes had a sea water origin then the concentration ratios for the elements would be very similar to that of sea water unless there had been subsequent filling by mineral-carrying glacial melt waters. Under these conditions the ratios would have a value depending on the relative concentration of the elements in the different media and the relative amounts of each supplied

to the lake.

The provision that no precipitation has taken place does not hold completely, since the bottom of Lake Vanda has been shown to contain precipitated CaCO_3 , together with traces of NaCl and Na_2SO_4 (Angino, Armitage and Tash, 1965). Moreover, CaSO_4 , CaCO_3 and Na_2SO_4 have been found on the floor of Lake Bonney (Angino, Armitage and Tash, 1964). Despite this, the ratio of the concentration of the trace elements to that of the dissolved solids should give some measure of the relative abundance of the various elements present in the feed waters (see Table 19).

Table 19

Ratio of the Concentration of Certain Elements to the Concentration of Total Dissolved Solids in the Bottom Waters of Lakes of McMurdo Oasis, Antarctica (Sea water included for comparison.).

Lake	Ratio ($\times 10^6$)						
	Zn	Pb	In	Bi	Fe	Mn	Mo
Vanda	31	<0.18	0.0006	0.035	2.8	0.25	0.011
Bonney	0.38	<0.077	0.0014	0.018	1.6	0.059	0.022
Fryxell	2.9	4.3	0.081	<0.21	1.4	0.30	0.024
Joyce	7.6	68	0.058	0.76	100	5.4	1.4
Hoare (East Lobe)	31	83	<0.10	<2	130	11	1.0
Hoare (West Lobe)	18	83	1.5	<2	450	17	26
Sea water	0.29	0.00035	<0.57	0.0057	0.29	0.057	0.29

From Table 19 it can be seen that the ratios of Zn and Mn to total dissolved solids for Bonney agree very

closely with the same ratios for sea water. In Table 20 the ratios of the concentrations of Zn and Mn to Na and K and also the ratio of the concentration of Zn to Mn are given for the lakes and for sea water. Consideration of this table shows that of all the lakes, only Bonney has

Table 20

Concentration Ratios for Certain Elements in the Bottom Water: of Lakes of McMurdo Oasis, Antarctica (sea water included for comparison).

Lake	Concentration Ratio				
	Zn/Na*	Zn/K*	Mn/Na*	Mn/K*	Zn/Mn
Vanda	480	15300	3.9	125	123
Bonney	1.58	38.5	0.22	5.9	6.5
Fryxell	12.5	200	1.3	21	9.6
Joyce	31	422	21.6	300	1.4
Hoare (East Lobe)	163	1033	5.8	367	2.8
Hoare (West Lobe)	100	667	9.0	600	1.1
Sea water	0.95	26.3	0.19	5.25	5

* ($\times 10^6$)

values of Zn/Na, Zn/K, Mn/Na and Mn/K that are close to those of sea water while the Zn/Mn ratio for Bonney and to a lesser extent Fryxell, resembles the corresponding value for sea water. This, together with the data given by Angino, Armitage and Nash (1964), tends to support a sea water origin for Bonney and also the possible presence of some sea water in Fryxell. This latter conclusion is based on the Zn/Mn ratio only and is therefore not as definite as that for Bonney. There is however, justification for assuming the presence of at least some sea water in

Fryxell. Lifshits (1961) determined the concentration of Zn and Mn in river waters and found values of 4.4 - 7.8 and 1.7 - 7.1 $\mu\text{g/l}$ respectively. Using these data the ratio of concentrations of Zn to Mn for river water will lie between 0.62 and 4.6 and will most probably be of the order of 2. The value of this ratio for sea water is 5, just outside the above range, and for Fryxell is 9.6 which is considerably higher. This would therefore imply either that the Mn has been supplied to Fryxell by glacial melt water and subsequently removed from solution, or that some sea water was originally present in the lake.

The concentration of dissolved material in Bonney is so high that, assuming a seawater origin, addition of dissolved inorganic ions from glacial melt waters etc., are unlikely to appreciably alter the ratios considered here.

From Table 15 it is clear that the relative concentrations of the macro-elements in Lakes Vanda, and Joyce and the two lobes of Hoare differ considerably from those of sea water, indicating either a non-seawater origin or extensive chemical alteration of sea water if originally present. The trace element data in Tables 18, 19 and 20 confirm this.

Since Lake Bonney is the only one of these lakes to have a probably sea water origin (with the possibility of some sea water in Fryxell) the trace element data obtained

for the other lakes can be used in an attempt to conduct a comprehensive geochemical survey of the area on the assumption that these trace elements are being supplied by local surface water. If this is to be done it is preferable to discuss each element individually.

Zinc.

Although Zn is commonly found in hot springs and mineral waters (Shinkarenko, 1948; Lagrange and Urbain, 1953; Ikeda, 1955; Zyka, 1957; Nagy and Polynik, 1957; Bradis et al., 1961), it is not listed among the commonly detected elements in river water (Durum and Haffty, 1960; De Villiers, 1962). It has however, been detected in river waters coming from highly-mineralized areas (Dolukhanova and Grigoryan, 1961) and in underground waters near ore deposits (Popov, 1962). Zinc has also been determined spectrographically in lake waters of northern Maine (Kleinkopf, 1960) and Lifshits (1961) claims a Zn concentration of 4.4 - 7.8 $\mu\text{g/l}$ in river waters. This latter observation should be treated with caution, especially as Durum and Haffty (1963) showed Zn to be not detectable spectrographically in more than half the North American river waters they studied.

The most significantly high relative concentrations of Zn are in Lakes Vanda and Hoare with lesser amounts in Fryxell and Joyce. Lake Hoare is fed by the Canada Glacier on the Asgaard Range while Lake Vanda is fed by

melt waters of the Wilson-Piedmont Glaciers, the Clark Glacier and subsidiary glaciers flowing into the Wright Valley from the Asgaard Range. Accordingly it is probable that the region of the Asgaard Range near the Canada Glacier may contain significant Zn deposits. This is also supported by the occurrence of Zn in Lake Fryxell which is also fed by the Canada Glacier and the Commonwealth Glacier both of which are on the Asgaard Range.

Lead:

The lakes containing the highest relative concentration of Pb are Joyce and Hoare. Lake Joyce is principally fed by waters from a local glacier with some melt water from the Taylor Glacier. Lead was not detected in Lake Bonney, which is fed solely by the Taylor Glacier, so that the presence of this element in the material in the Taylor Glacier is unlikely. It is therefore probable that Pb occurs in the area of the local glaciers supplying Joyce and also in the area surrounding Hoare. The relative concentration of Pb in Lake Fryxell is considerably less than in Hoare, paralleling the trend for Zn. This would seem to imply that the area containing relatively high amounts of Zn and Pb in the region of the Canada Glacier does not extend to the Commonwealth Glacier.

Although Durum and Haffty (1960) show that Pb is among the most commonly found minor elements in river

waters so that it would therefore be expected to be found in waters as concentrated as those considered here, the fact that it is below detection limits in the two most concentrated lakes (Vanda and Bonney) makes the relatively high concentrations in the others significant.

Indium:

No In was found in Lake Vanda but it was found in all the lakes in the Taylor Valley (with the exception of the eastern lobe of Hoare). This would imply a generally higher concentration of In in the Taylor Valley than in the Wright Valley or in the region of the Wilson-Piedmont Glacier. There seems to be no apparent reason for the relatively high concentration of this element in the western lobe of Hoare and its absence in the eastern lobe as the two lobes are joined by a shallow, narrow neck and the concentration of macro-elements in the bottom waters of the two lobes are similar. This discrepancy between the two lobes is also apparent for Fe and Mo.

Indium is principally chalcophilic and has been shown to occur with galena (Goldschmidt, 1954) which suggests that the relatively high concentration of this element in Hoare may be associated with the increased concentration of lead in that lake.

Bismuth:

De Villiers (1962) reported concentrations of Bi in the water of the Orange River ranging between 1 and

4 $\mu\text{g}/\text{l}$. Water flowing from the Tandzut pyritic deposits in the Armenian S.S.S.R. was reported to contain spectrographically detectable quantities of Bi (Dolukhanova and Grigoryan, 1961) but with the exception of reports of this element occurring in thermal waters (Lagrange and Urbain, 1953; Ikeda, 1955), these appear to be the only determinations of Bi in natural waters. The concentrations of Bi relative to total dissolved material in Bonney is only three times that in sea water (Table 19) and, in view of the possible sea water origin of Bonney, need not necessarily be significant. The high relative concentration in Joyce would imply a probable deposit of Bi in this area, especially when the common occurrence of this element in galena is considered (Goldschmidt, 1954). Joyce contains a high concentration of Pb and also some In, so that the presence of Bi in this lake is probably associated with that of the other two elements. The Bi in Lake Vanda is most probably derived from the granitic rocks in the Wright Valley (McKelvey and Webb, 1961) since this element is also lithophilic and found in granite pegmatites (Goldschmidt, 1954). Tedrow et al. (1963) found Bi, Pb and In in concentrations less than 1 ppm in a saline lake in the southern fork at the western end of the Wright Valley.

Iron:

Iron constitutes a major fraction of most igneous rocks and would therefore be expected to be present in reasonable concentrations in all the lake waters.

Its concentration in sea water is approximately 10 $\mu\text{g/l}$ (Goldberg, 1965) but it is present in far higher concentrations in river water. Durum and Haffty (1963) found that the concentration of Fe in American rivers ranged from 31 to 1,670 $\mu\text{g/l}$ with a median value of 300 $\mu\text{g/l}$, approximately 30 times that in sea water. This large difference in concentration is assumed to be due to Fe having the low residence time of approximately 140 years in sea water (Goldberg and Arrhenius, 1958).

The lakes considered here are, with the exception of Bonney, anoxic and the latter could have been so in the past. Richards (reported by Goldberg, 1965) found that anoxic water in the Cariaco Trench had concentrations of soluble Fe a thousand times greater than in normal ocean waters because of the strong reducing conditions. If this is so, then the residence time for Fe in these lakes could conceivably be higher than in ocean waters, with consequently higher concentrations of the element. Another factor that could give rise to higher Fe concentrations in these lakes compared with sea water is the pH. The bottoms of these lakes have pH values in the range of 6-7 compared with a pH of 8 for sea water. This lower pH in the lakes could increase the solubility of the Fe.

Although the relative concentration of Fe varies appreciably between the lakes, the absolute value, with the exception of Fryxell, remains relatively constant.

The concentration therefore appears to be independent of the age or composition of the lake suggesting a chemical factor influencing the solubility of the Fe.

Manganese:

This is also relatively common in igneous rocks and is readily leached from soils and rocks when in the divalent state (Goldschmidt, 1954). It is present in river waters in concentrations ranging from 0 to 185 $\mu\text{g/l}$ with a median value of 20 $\mu\text{g/l}$ (Durum and Haffty, 1963). As with Fe, the variation in absolute concentration is not large, except in the case of Fryxell, and the concentrations of Fe and Mn in the lake waters are within the range found in river waters for these elements.

Molybdenum:

Molybdenum is present in igneous rocks in trace amounts and tends to concentrate in granites, which have been shown to be present in this region (McKelvey and Webb, 1961, 1962). It is also commonly found in river waters (Durum and Haffty, 1960) in concentrations ranging from 0 - 6.9 $\mu\text{g/l}$. With the exception of the western lobe of Lake Hoare, the concentration of Mo in the lakes lies very close to this range and the variation is therefore most probably not significant.

Conclusion:

From a consideration of the relative concentrations of Zn and Mn in the various lakes it is possible to

assign a sea water origin to Lake Bonney. Lake Fryxell also could have originally had sea water present but it appears unlikely that any of the other lakes had a similar origin. Since these other lakes did not have a sea water origin it is possible to use the relative trace element abundance in them to conduct a comprehensive geochemical survey of the areas supplying these lakes with water.

This geochemical reconnaissance suggests that the two most likely areas for mineralization in the McMurdo Oasis area of Antarctica are the regions surrounding and feeding water to Lake Hoare and the region surrounding Lake Joyce.

Zinc deposits may also be present in the area between the Lower Wright Valley and Lake Hoare.

PART IV

THE DEVELOPMENT OF DISCONTINUOUS COUNTER- CURRENT EXTRACTION FOR INORGANIC SYSTEMS

(a) Introduction

It was decided to investigate the potentialities of discontinuous countercurrent extraction as a means of separating Fe from the other elements extracted by cyclohexanone from 3N hydrochloric acid (see Part II d). This technique has been applied with great success to the fractionation of organic compounds, particularly where the distribution coefficients are of the same order of magnitude (Morrison and Freiser, 1957). It has not, however, been used to any extent to separate metals for analytical determination, despite the relatively long time a suitable apparatus has been available [the first unit was reported by Craig and Post, (1949)7]. The earliest use of the technique for inorganic systems was in the separation and purification of the rare earths (Peppard, Faris, Gray and Mason, 1953; Weaver, Kappleman and Topp, 1953). The method has also been used to fractionate Th, Sc and Zr from both nitric and hydrochloric acid solutions with tributyl phosphate as solvent (Peppard, Mason and Maier, 1956) and to separate metals using acetylacetone (Krishen, 1957). More recently Ishimori and Sammour (1961 a) have investigated the use of the technique to separate Zr from Nb as well as the separation of these two elements from Ru and other fission products using tri-n-butyl phosphate and hydrochloric acid. The same authors have also separated isotopes of U and Pa from irradiated Th by discontinuous counter-

current techniques using tri-n-butyl phosphine oxide and hydrochloric acid (Ishimori and Sammour, 1961 b); while Sammour (1962) has studied the behaviour of different valence states of Np in the tri-n-butyl phosphate/hydrochloric acid system by the same technique. A paper chromatographic method has been developed for the determination of suitable solvent systems for countercurrent distributions (Waksmundzki and Soczewinski, 1961; Soczewinski et al., 1962). The only geochemical applications of this technique have been developed by the geochemical group at this university and have been reported, in part by Brooks (1965 a,b,c).

Brooks (1965 a) has pointed out the possibility of separating elements by varying the concentration of the ligand in the aqueous phase of the extraction train. It was therefore decided to apply this technique to investigate the possibility of separating Fe from the other elements extracted by cyclohexanone from a 3N hydrochloric acid solution of a rock. Several attempts were made to separate Fe by reducing a cyclohexanone extract of a rock solution to 40 ml and making it the front of the organic phase as it progressed down a discontinuous, countercurrent extraction apparatus. The organic phase was cyclohexanone and the aqueous phase contained varying concentrations of hydrochloric acid. It was found, however, that the extraction behaviour of Fe was too similar to that

of several of the trace elements for it to be possible to separate the former from the latter.

Because of increased steric effects (Morrison and Freiser, 1957), methyl isobutyl ketone (MIBK) will be a less efficient extractant than cyclohexanone. It was therefore decided to investigate the possibility of using MIBK/hydrochloric acid in discontinuous countercurrent extraction in an attempt to separate Fe by lessening its extraction and increasing the possibility of its separation from the other ions. Hydrochloric acid was chosen as the aqueous phase. Because this had been used in the preliminary extraction into cyclohexanone, no additional reagents would be required and the system would therefore be kept as simple as possible.

In order to be able to design a system suitable for the separation of Fe using MIBK/hydrochloric acid, it is necessary to know the extraction behaviour of all elements likely to be involved in the system. This was done as follows:

Craig and Craig (1956) gave a relationship between the tube number in an extraction train in which a solute is present at maximum concentration and the distribution coefficient of the solute in that particular system, viz.

$$r = \frac{n D}{D + 1} \quad (4.1)$$

where n is the total number of transfers, r is the number

of the tube with maximum concentration and D is the distribution coefficient, provided that the volumes of the two phases are equal. If therefore, after a given number of inversions, the tube, in which the maximum concentration of a certain material occurs, is found, then its distribution coefficient in that particular solvent system can be calculated.

When a solute is distributed between two immiscible solvents, the relationship between the percent extraction ($\%E$) and the distribution coefficient is given by equation (4.2), (Morrison and Freiser, 1957)

$$\%E = \frac{100D}{D + 1} \quad (4.2)$$

provided the two phases are of equal volume. Substitution of (4.2) into (4.1) gives:

$$\%E = \frac{100r}{n} \quad (4.3)$$

so that a simple relationship exists between the percent extraction, the total number of inversions, and the number of the tube containing the maximum concentration of a solute.

The expression derived by Craig and Craig (1956) relating the number of the tube containing the maximum concentration of a substance and its distribution coefficient was obtained by considering the rate at which the substance moves along the extraction train and is only valid when all the substance has left the first tube. Boswell and Brooks (1965b) have developed the following alternative

method, valid under all conditions, relating the number of the tube containing the maximum concentration of a particular species to its percent extraction.

The fraction ($T_{n,r}$) of a substance present in the r th tube for n transfers is given by:

$$T_{n,r} = \frac{n!}{r!(n-r)!} \left(\frac{1}{D+1} \right)^n D^r$$

If the r th tube contains the maximum concentration of the substance

$$T_{n,r-1} < T_{n,r} > T_{n,r+1}$$

Whence by substitution and elimination

$$\frac{r}{n-r+1} \cdot \frac{1}{D} < 1 > \frac{n-r}{r+1} \cdot D$$

therefore

$$\frac{r}{n-r+1} < D < \frac{r+1}{n-r}$$

and

$$\frac{r}{n+1} < \frac{D}{D+1} < \frac{r+1}{n+1}$$

That is

$$\frac{100r}{n+1} < \%E < \frac{100(r+1)}{n+1} \quad (4.4)$$

If $r = 1$, then in a similar manner, it can be shown that:

$$\%E < \frac{200}{n+1}$$

and if $r = n$ then

$$\%E > \frac{100n}{n+1}$$

It can easily be shown that the value for the percent extraction derived from the expression relating the number of the tube containing the maximum concentration of a substance and its distribution coefficient as calculated by Craig and Craig satisfies (4.4) provided r does not equal 1 or n .

This means that if suitable analytical methods are available, the extraction characteristics of many substances in a given solvent system can be studied simultaneously by partition on a discontinuous, countercurrent solvent extraction apparatus. Substitution of the number of the tube containing maximum concentration of each substance into (4.4) gives the range within which the %E must lie. Furthermore, substitution into (4.3) gives a reasonably accurate estimate of the actual %E provided r does not equal 1 or n .

Lieberman (1948) differentiated the expression, derived by Craig and Post (1949), relating the amount of a substance in a tube on the extraction train with its distribution coefficient and obtained a method for calculating the distribution coefficient from the number of the tube in which maximum concentration of the substance occurs. It is, however, a complicated relationship and necessitates the use of a table. The table they give is only valid for a countercurrent apparatus having 8, 24 or 48 tubes so that the method is not as versatile as that given above.

Levi (1958) has developed a method for calculating the distribution coefficient from the concentration of material in the tubes by using least squares analysis. While giving a more accurate estimate of the distribution coefficients, the concentration of the material in each tube must be known. This makes the technique of very little value since it would be simpler, and probably more accurate to determine the distribution coefficient by batch extraction, obtaining the concentration in only two phases rather than in a large number of tubes on a distribution apparatus.

An emission spectrograph used as an analytical tool in conjunction with a discontinuous, countercurrent, liquid-liquid extraction apparatus should provide a very rapid method for studying the distribution of a series of metal ions between two immiscible solvents. After a given number of equilibrations, the contents from each tube of the apparatus could be taken to dryness and arced. Examination of the spectra should enable the tube containing the maximum concentration of a given element to be located and the percent extraction calculated. This should be particularly useful when attempting to evaluate an inorganic extraction system as other methods of obtaining extraction data for a number of elements over a wide range of conditions can often be very laborious.

(b) The Use of Discontinuous Countercurrent Liquid-Liquid Extraction for Determining the Extraction of the Elements Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi, Ru, Pd, Ir and Pt from 3N Hydrochloric Acid into Cyclohexanone.

In order to show that the theory developed above does provide a means for determining percent extraction from the number of the tube in a counter current extraction apparatus containing maximum concentration of a substance, it was decided to investigate a system for which extraction data are known. Since the cyclohexanone/hydrochloric acid system had already been studied by batch extraction techniques (no countercurrent extraction apparatus being available at the time), it was decided to examine the distribution of the elements Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi, Ru, Pd, Ir and Pt from 3N hydrochloric acid solution into cyclohexanone. The extraction data for all these elements under these conditions, with the exception of Cu, Ag, Ru, Pd, Ir and Pt had been determined previously (Part II). Cu and Ag were included because it had proved impractical to determine the percent extractions of these elements by simple batch extraction and the four platinum metals were included for interest. A solution containing all the above elements in 3N hydrochloric acid was prepared. Twenty ml. of this solution were then placed in each of the first two tubes of the

extraction apparatus after having been oxidized with Cl_2 and 20 ml. of 3N hydrochloric acid were placed in the next 48 tubes. Although all theoretical expressions have been derived on the assumption that the sample is placed in the first tube only, it has been shown (Craig and Craig, 1956) that no error is caused by using more than one tube, provided that the number of tubes containing sample represent less than 5% of the total number of tubes. The acid used had been pre-equilibrated with cyclohexanone. The solvent, which had been pre-equilibrated with 3N acid, was fed into the system from the reservoir and countercurrent extraction carried out for 50 transfers. The contents of pairs of tubes were taken to dryness, NaCl was added as a carrier, and the residues, after ashing at 400°C , were examined spectrographically using anode excitation with the arc focussed directly onto the slit. The spectra were recorded on one photographic plate and the tube containing the greatest concentration of any element found by visual observation of a sensitive spectral line of that element.

The solvent extraction operations were carried out on a 120-tube, fully automatic, discontinuous, countercurrent extraction apparatus. The individual extraction tubes were mounted on a shaking rack, the axis of which was attached to a control unit which automatically effected the operations of shaking, settling and decantation.

Individual tubes had a capacity of twenty ml. for the stationary lower phase and the moving upper phase was fed into the system at the end of each cycle by means of a twenty ml. dispenser attached to a ten litre reservoir. After each shaking operation, the rack was tilted through 90° and the upper phase decanted into the next tube.

The error in the estimation of the fraction containing the maximum concentration of a particular element under the conditions used in this work is, at the most, one arcing i.e. ± 2 tubes, which, for a 50-transfer operation, corresponds to an error in the percent extraction of approximately 4%. The error involved in using equation (4.3) instead of (4.4) for calculating the percent extraction is of the order of 1%. This is less than the experimental error under the conditions in the work reported here, so that equation (4.3) can be used to calculate the percent extraction without any appreciable loss in accuracy. If, however, a method capable of giving the percent extraction with better than 1% accuracy is used, expression (4.4) would have to be applied. The precision of the method depends only on the number of tubes employed and the analytical methods available. If, for example, an extraction train of more than 100 tubes is used in conjunction with an analytical technique capable of accurately locating the tube containing the maximum concentration of a substance, it is possible to obtain an error of less than 1%.

(c) A Study of the Extraction of Certain Elements in the Methyl Isobutyl Ketone/Hydrochloric Acid System Using Discontinuous Countercurrent Liquid-Liquid Extraction.

The extraction characteristics of the elements listed below in the system MIBK/hydrochloric acid were obtained as follows:-

A solution containing the elements Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, La, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb and Bi in concentrated HCl was prepared. To equal volumes of this solution, varying quantities of water and HCl were added to make solutions 0.5, 1, 2, 3, 4, 5 and 6N in HCl so that the concentration of elements remained the same in each. At the three lowest acid concentrations there was a certain amount of precipitation of many elements due to hydrolysis but, except in the case of W, Os, Ir, Sb and As, there was still sufficient of each element present for the percent extraction to be determined as described below.

The MIBK was prepared by redistilling the commercial material. Hydrochloric acid was purified by distilling AnalaR grade HCl and diluting to the appropriate concentration with distilled water.

Twenty ml of the solution of the elements were placed in each of the first two tubes of the extraction

apparatus and 20 ml of hydrochloric acid of the same concentration were placed in the next 48 tubes. Although all theoretical expressions have been derived on the assumption that the sample is placed in the first tube only, as discussed above, no error is caused by using more than one tube under the conditions used here. All acid used was pre-equilibrated with MIBK. The solvent, which had been pre-equilibrated with the appropriate strength acid, was fed into the system from the reservoir and countercurrent extraction carried out for 50 transfers. The contents of pairs of tubes were taken to dryness, NaCl was added as carrier, and the residues were examined spectrographically in a d.c. arc using anode excitation. This process was repeated for each acid concentration. All spectra for each run were recorded on one photographic plate and the tube containing the greatest concentration of any element found by visual observation of a sensitive spectral line of that element.

(d) Results and Discussion.

(i) Cyclohexanone/3N hydrochloric acid.

Distribution curves for 50 equilibrations of the cyclohexanone/3N hydrochloric acid system are shown in Fig. 10. The percent extraction of each element from 3N hydrochloric acid into cyclohexanone was derived from equation (4.3) and is as follows (figures in parentheses are the corresponding values obtained by batch extraction, a hyphen indicates that a value had not been obtained previously):- Cu, 91 (-); Ag, 83 (-); Au, 95 (100); Zn, 83 (89); Cd, 83 (81); Hg, 83 (94); Ga, 95 (100); In, 95 (100); Tl, 95 (100); Sn, 99 (100); Pb, 39 (46); As, 19 (0); Sb, 83 (47); Bi, 71 (59); Ru, 19,75 (-); Pd, 31 (-); Ir, 79 (-) and Pt, <8, 83 (-).

Consideration of the above data shows that when the experimental errors of the respective techniques are taken into consideration, there is satisfactory agreement between the results obtained by the two methods. The data obtained for As and Sb by the two techniques however, differ by considerably more than the experimental error. This is most probably due to reduction of As (V) and Sb (V) to As (III) and Sb (III) respectively, during the operation of the extraction apparatus. Morrison and Freiser (1957) have shown that reduction enhances the extraction of these two elements. Since the counter-

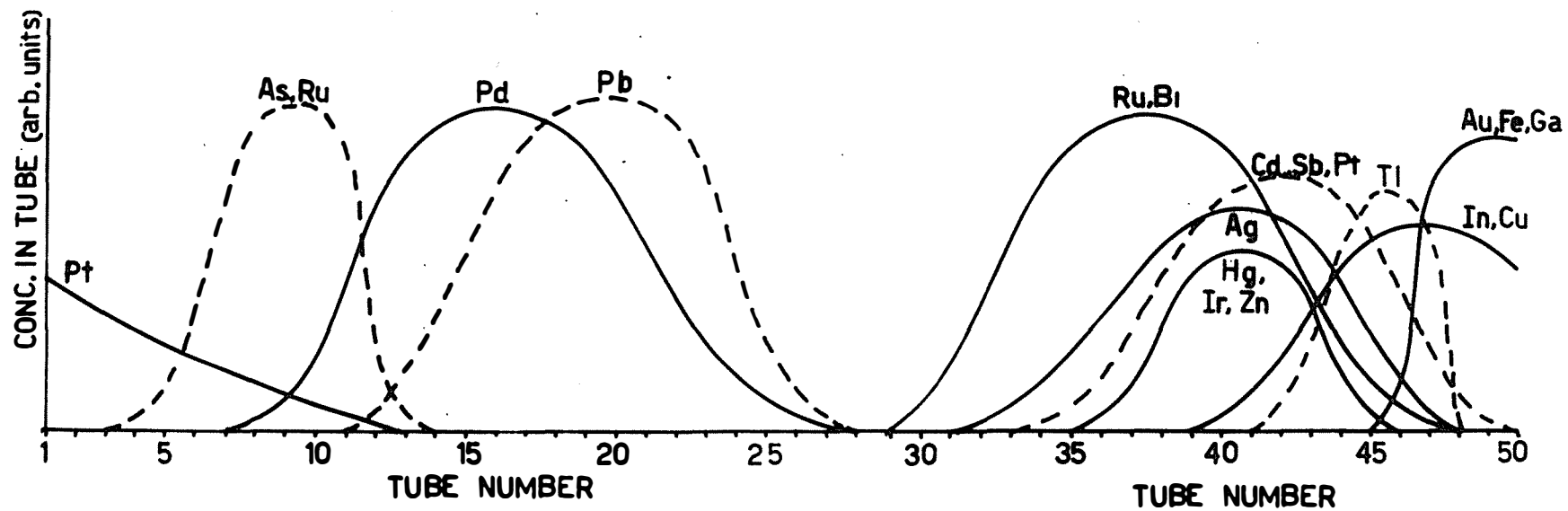


Fig. 10

Distribution curves for a number of elements after countercurrent extraction with cyclohexanone from 3N hydrochloric acid.

current extraction apparatus requires approximately seven hours to effect 50 equilibrations as compared with the half hour required for batch extraction, if the former technique is to be used there is a longer interval of time over which the reduction of the pentavalent As and Sb can take place. As the elements are reduced to the trivalent state during countercurrent extraction, there will be an enhancement in extractability with the consequent discrepancy between values for the percent extraction obtained by the two techniques.

Two values are reported for the percent extraction of both Ru and Pt. This type of behaviour has been reported before (Sammour, 1962; Brooks, 1965a) and is due to the presence of either different valence states or different complexes with low lability. Sammour (1962) has used the difference in extractability of the valence states of Np to separate three oxidation states of that element.

(ii) Methyl isobutyl ketone/hydrochloric acid.

The percent extraction of the elements as a function of hydrochloric acid concentration are given in Fig. 11. The numerical data are presented in Table 21. To check the reproducibility of the technique two solutions of selected elements were prepared, adjusted to hydrochloric acid concentrations of 2N and 3N respectively and treated as above. The data obtained from this are also included in Table 21.

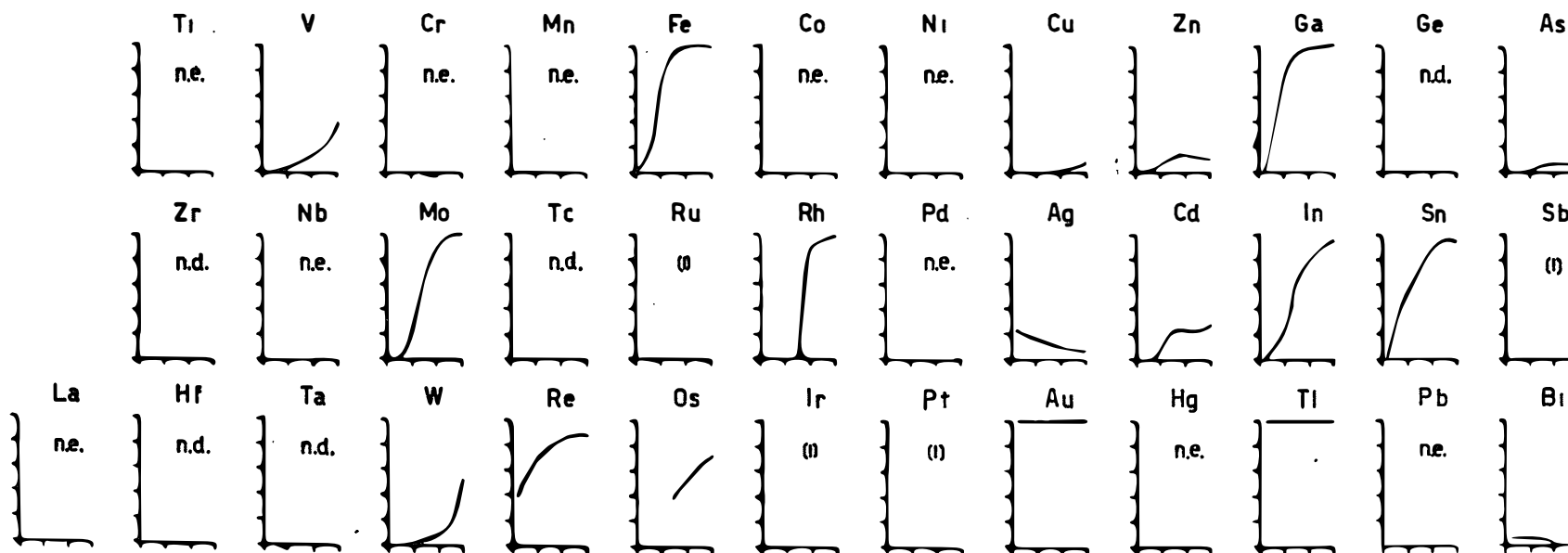
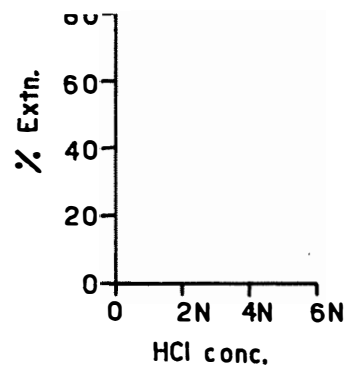


Fig. 11

The extraction of elements into methyl isobutyl ketone as a function of hydrochloric acid concentration.

n.e. negligible extraction
n.d. not determined
(1) see text

Table 21

The Extraction of Elements into Methyl Isobutyl Ketone
from Hydrochloric Acid Solutions.

Element	Extraction (%)								
	Acid Concentration (N)								
	0.5	1	2	2*	3	3*	4	5	6
Ti	0	0	0	-	0	-	0	0	0
V	0	0	5	4	5	-	11	15	39
Cr	0	0	0	-	0	-	0	0	0
Mn	0	0	0	-	0	-	0	0	0
Fe	7	15	79	70	95	95	99	99	99
Co	0	0	0	-	0	-	0	0	0
Ni	0	0	0	-	0	-	0	0	0
Cu	0	0	0	-	0	-	0	7	7
Zn	0	0	5	6	19	-	-	11	11
Ga	0	19	75	-	95	95	97	99	99
As	0	0	0	-	7	-	7	7	7
Nb	0	0	0	-	0	-	0	0	0
Mo	0	0	19	24	67	64	87	99	95
Ru	0	0	7	-	51	-	15	15, 71	13, 87
Rh	0	0	0	4	0	-	87	95	97
Pd	0	0	0	0	0	-	0	0	0
Ag	23	10	11	-	19	-	7	9	7
Cd	0	0	0	8	22	-	15	23	27
In	0	9	20	21	55	50	79	87	95
Sn	7	27	63	-	75	78	87	95	95
Sb	-	-	-	-	19, 99	-	59, 99	27, 99	11, 99
La	0	0	0	-	0	-	0	0	0
W	-	-	0	-	7	-	0	19	55
Re	39	67	67	68	75	-	83	79	83
Os	-	-	-	-	39	-	51	65	71
Ir	-	0	0	-	0	-	0	91	99
Pt	0	11	22	22	27	-	27	39, 83	3, 35
Au	99	99	99	94	99	99	99	99	99
Hg	0	0	0	-	7	-	0	0	0
Tl	99	99	99	94	99	99	95	95	99
Pb	0	0	0	-	7	-	0	7	0
Bi	7	7	7	-	11	-	0	0	7

* Results obtained from duplicate determination.

Although Ru, Sb and Pt were studied, no extraction curves are given for them in Fig. 11 since more than one peak was observed. Ru and Pt exhibited this behaviour in the cyclohexanone/3N hydrochloric acid system and probable reasons for this are discussed above. Goto and Kakita (1959) have shown that when Sb is extracted into MIBK from hydrochloric acid, the two valence states of the element have different extraction properties and in fact the graphs of percent extraction plotted against acid concentration intersect at approximately 4.5N. If two or more peaks for any element occur in an extraction train and the valence or complex corresponding to each peak is not known, extraction curves cannot be drawn with any certainty.

The extraction curve for Ir is not included in Fig. 11 because of the very rapid change in extractability between 4N and 5N hydrochloric acid.

The extraction of various elements into MIBK from hydrochloric acid has been studied by several authors. Goto and Kakita (1959) report extraction data for Fe (III), Sb (III,V), As (III,V), Sn (IV), Se (IV), Te (IV), Ge (IV), Cr (VI), V (V), Mo (VII) from hydrochloric acid into MIBK. The values they give for Mo and Sn agree closely with those reported here but their values for the extraction of Fe in 1,2 and 3N acid are lower than those obtained in this study. Their values for V in 5N and 6N acid are

higher than reported here. Goto and Kakita (1959) and Tajima and Kurobe (1960) have shown that Fe (II) is not extracted from hydrochloric acid into MIBK and the discrepancy between the formers' results for Fe (III) and those reported here could be due to partial reduction in their extraction system. The discrepancies in the case of V could be due to reduction in the extraction train. Since the potential for $V(V)/V(IV)$ increases rapidly with increasing acid concentration, V (V) will be reduced by high concentrations of hydrochloric acid. If the aqueous phase in an extraction train has a high concentration of hydrochloric acid, any V (V) ions will be reduced as they proceed along the train. The reduced species will almost certainly have different extraction properties. This is confirmed by a study of the distribution pattern of V on the extraction apparatus. Instead of a symmetrical pattern, V was present in varying concentrations in the first 30 tubes, indicating a change in distribution properties with repeated extractions.

Several workers (Specker and Arend, 1961; Pogodaeva and Stolyarov, 1960; Blundy, 1958; Dean and Beverly, 1958; Katz et al., 1962) have shown that Cr (VI) can be 100% extracted from hydrochloric acid into MIBK at medium acid concentrations. In the present study Cr was present in one of the lower valence states [most probably Cr (III)] and was not extracted. Nedilov and Diamond (1955) state

that Mo is 96% extracted with MIBK from HCl. This value agrees very closely with that obtained by the present authors.

Klimov (1961), in his study of the extraction of Fe (III) into MIBK from 6N hydrochloric acid shows that, among others, Ti, Ni, Co, Ag, Cu, Bi, Pb and Mn are not extracted under these conditions while Sn, Mo and V are. This is confirmed by the present work. Similarly, Specker and Doll (1956), Specker (1958) and Riedel (1957) report that Fe can be separated from Zn, Ni and many other elements by extraction from 6N hydrochloric acid into MIBK. Work reported here shows that Ni is not extracted and Zn only slightly under these conditions.

Conclusion.

A comparison of extraction data obtained by discontinuous countercurrent liquid-liquid extraction with similar data obtained by batch extraction, for inorganic ions in the system cyclohexanone/3N hydrochloric acid showed that the former technique is a rapid and accurate method for determining extraction data. This conclusion is supported by comparison of data, obtained by this technique, with results obtained by other workers for metal ions in the system MIBK/hydrochloric acid. In view of this, the percent extraction of a number of metal ions into MIBK from hydrochloric acid, obtained by a combination of discontinuous countercurrent extraction and spectrographic analysis and reported here for the first time, can be taken as accurate.

(e) Investigations Into the Use of Discontinuous Counter-current Extraction for the Separation of Fe.

As mentioned above, attempts were made to use cyclohexanone as the organic phase in discontinuous counter-current extraction to separate Fe from the other elements extracted by this solvent from a rock solution 3N in hydrochloric acid. This was done by reducing the volume of the extract to 40 ml. and making this the first two organic phases on a discontinuous countercurrent apparatus in which the organic phase, cyclohexanone, passed over a series of tubes containing hydrochloric acid in varying concentration. The distribution pattern for a typical result is shown in Fig. 12. For this, the first ten tubes contained 3N hydrochloric acid, the next ten 1N hydrochloric acid and the remaining 30 tubes contained distilled water. It is clear from Fig. 12 that Fe was not separated from the other elements.

The possibility of using countercurrent extraction with MIBK as the organic solvent to separate Fe from the majority of the other elements was investigated. The distribution patterns of the elements Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi and Fe after 50 equilibrations on a countercurrent apparatus in which the two phases were MIBK and 6N hydrochloric acid is given in Fig. 13. It is clear from this, that none of these elements occur

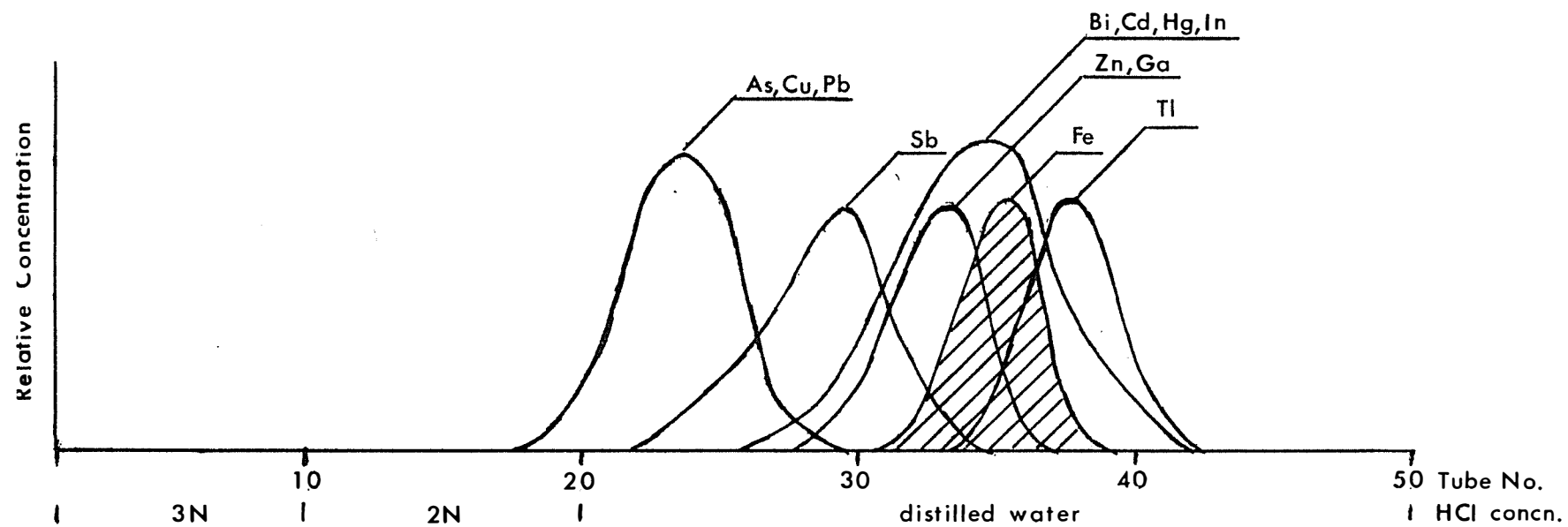


Fig. 12

Distribution curves for a number of elements after countercurrent extraction with cyclohexanone with varying concentration of hydrochloric acid in the aqueous phase.

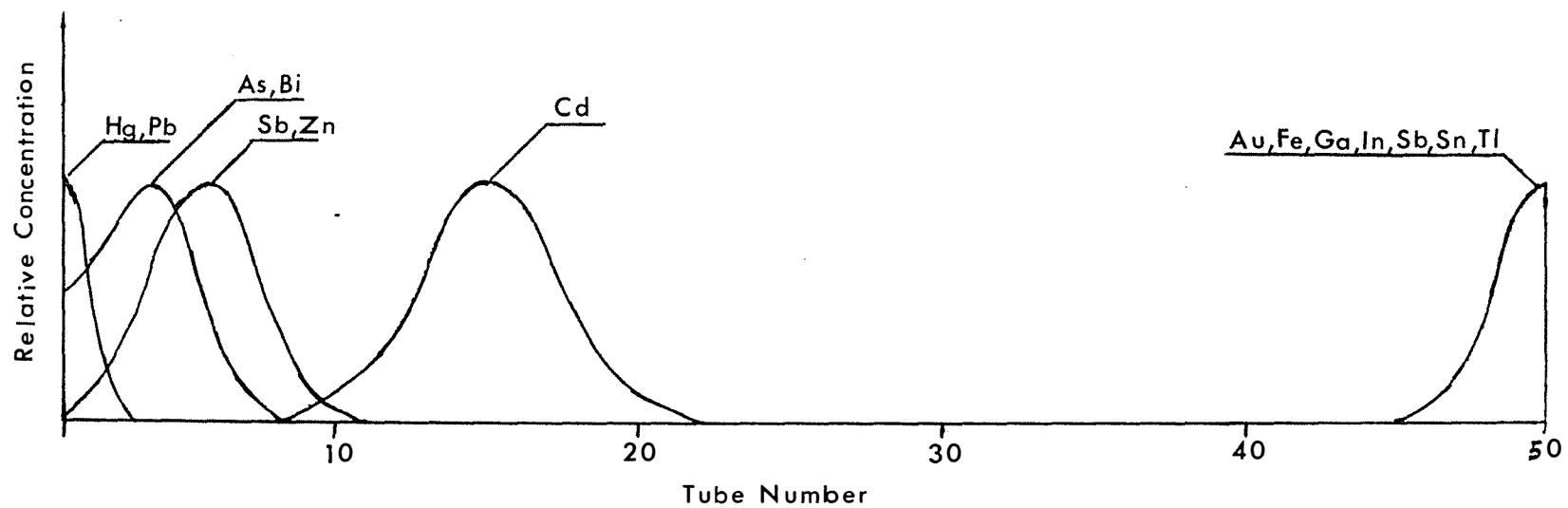


Fig. 13

Distribution curves for a number of elements after countercurrent extraction with methyl isobutyl ketone from 6N hydrochloric acid.

in significant amounts between tubes number 22 and 45 (approx.). If, therefore, in this region the aqueous phase could contain a reagent which would reduce the extraction of Fe to less than 20% without appreciably altering the extraction of any of the other elements, it would be possible to separate this element completely. Goto (1962) has shown that in a solution 6N in hydrochloric acid and 1M in NH_4CNS , Fe is only 17% extracted. Attempts were made to separate Fe from the rest of the elements by counter-current extraction with 6N hydrochloric acid and MIBK. Tubes number 28 to 38 contained 1M NH_4CNS in addition to 6N hydrochloric acid. However, before the solvent front reached the tubes containing the NH_4CNS (approx. 3 hours) the solution in them had turned a bright yellow. In this condition they did not give the characteristic red colouration with Fe^{3+} and on further standing formed a white precipitate. Investigations with this system were therefore not continued.

From Table 21 it is clear that, of the elements considered in Part II with an extraction of greater than 95% into MIBK from 6N hydrochloric acid, only Ga, Sn, Tl, Au and Fe were better than 60% extracted into the same solvent from 2N acid. All the other elements were less than 30% extracted in the latter system. Of the five elements well extracted from 2N hydrochloric acid, Ga, Sn and Fe are less than 10% extracted by the same solvent

from 0.5N acid while Au and Tl are still extracted better than 95% in this system. Using these large differences in extraction properties in the three different acid concentrations it should be possible to design an extraction system that, in theory, (with the exception of Sn and Ga) can separate Fe from all the other elements extracted by cyclohexanone from 3N hydrochloric acid solutions.

The distribution of a solute in the various fractions of a countercurrent extraction system is governed by a binomial function. If a sufficiently large number of transfers are made, the binomial function approximates very closely to the "normal" or Gaussian function. Under these conditions, after Craig and Craig (1956), the number of the tube (r) containing the maximum concentration of a given solute after n transfers is given by (4.3). The spread of solute over the tubes follows a normal distribution with standard deviation (s) given by:

$$s = (nD)^{\frac{1}{2}} / (1+D) \quad (4.5)$$

Using equations (4.3) and (4.5), it is therefore possible to calculate the approximate distribution of a solute on an extraction train in which the concentration of the ligand varies in different parts of the train, provided the extraction data for all conditions met on the train are known.

The distribution of the elements Au, Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb, Bi and Fe after 70 trans-

fers on a discontinuous countercurrent extraction apparatus in which the aqueous phase in the first 20 tubes was 6N hydrochloric acid, the next 40 tubes containing 2N hydrochloric acid and the remaining 10 tubes containing 0.5N acid, was calculated using equations (4.3) and (4.5) and the data from Table 21. The theoretical distribution is shown in Fig. 14 together with the distribution obtained after 70 equilibrations of a solution containing all the elements listed above. These elements were dissolved in 6N hydrochloric acid and placed in the first tube of the extraction apparatus, the aqueous phase being as described above.

As a solute moves along the extraction train it spreads out over a number of tubes. Accordingly when the solute arrives at a point in the train where there is a sudden change in acid concentration in the aqueous phase it is not located in one tube only, but spread out over a number of tubes. It is therefore not possible to calculate the distribution of the solute on the extraction train accurately after the solute has passed such a point and a number of approximations must be made.

In view of these approximations, the agreement between the theoretical and experimental distributions, as shown in Fig. 14, is very satisfactory. In the theoretical calculations allowance was made for the two

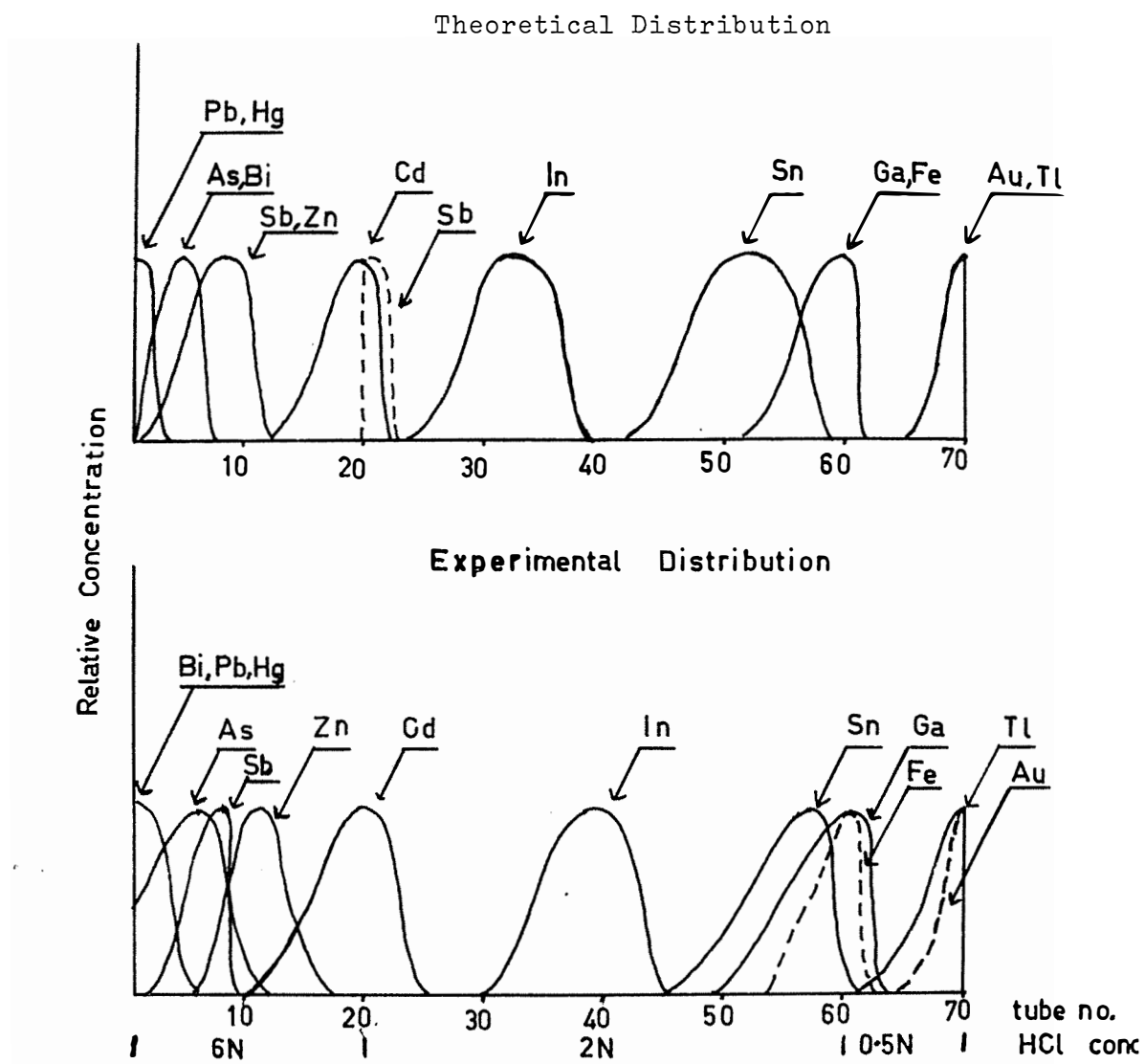


Fig. 14

Theoretical and experimental distribution curves for certain elements after countercurrent extraction with methyl isobutyl ketone with varying concentrations of hydrochloric acid in the aqueous phase.

valence states of Sb. In the experimental work, only the peak corresponding to the species with lower extraction was found. The distribution patterns of In and Sn are displaced further along the train than expected from calculations. This is most probably due to the fact that after the solvent front, saturated with 6N acid, reached tube number 20, redistribution of the acid between the two phases occurred with a consequent rise in acid concentration in the first tubes containing the 2N acid and a corresponding change in the extraction characteristics of these elements.

From Fig. 14 it would appear possible to separate Fe completely from a large number of elements using a discontinuous countercurrent extraction apparatus with MIBK as the organic phase and appropriate changes in hydrochloric acid concentration in the aqueous phase.

PART V

THE DETERMINATION OF BISMUTH, CADMIUM, GALLIUM,
LEAD AND ZINC IN SILICATE ROCKS.

(a) The Development of Quantitative Procedures.

(1) Dissolution of rocks:

Rocks to be examined were first crushed in a carefully cleaned percussion mortar and ground to below 100 mesh in an agate mortar and pestle. Dissolution was achieved by the following modification of the method of Brooks (1960). Twenty grams of the finely ground rock were weighed into a teflon beaker and made into a paste with 5 ml of aqua regia. To this was added 25 ml. of "Analar" hydrofluoric acid followed by a further 20 ml of aqua regia. The mixture was taken to dryness on a hot plate and the residue transferred to a borosilicate beaker followed by 25 ml of concentrated hydrochloric acid, 75 ml of distilled water and 25 ml of concentrated sulphuric acid. The solution was evaporated and heated to remove all fluoride and sulphate ions. The residue was boiled with 200 ml of 3N hydrochloric acid and 1 ml of bromine. The solution was decanted from any residue and the latter transferred to the teflon beaker where it was taken to dryness with 25 ml of hydrofluoric acid. The residue from this was mixed with 25 ml of concentrated hydrochloric acid, and transferred to the borosilicate beaker. To this was added 75 ml of distilled water and 25 ml of concentrated sulphuric acid. The mixture was again heated to remove excess sulphate. The residue was boiled with a further

300 ml of 3N hydrochloric acid and 1 ml of bromine and the two hydrochloric acid solutions combined. In most cases this treatment was sufficient to completely dissolve the rock. Occasionally however, a small residue remained after this treatment. Spectrographic analysis of the residue for cations showed the presence of Ca, Mg and Al while chemical analysis for anions showed that the only one present was the sulphate ion. The residue was therefore a mixture of Ca, Mg and Al sulphates and since this contained no detectable amounts of trace elements it was discarded with no further treatment.

(ii) Separation of Fe after batch extraction with cyclohexanone.

As discussed in Part II (d), preliminary investigations showed that the conditions most suitable for extracting trace elements from a rock solution also caused Fe to be extracted. In Part III (b) this extraction was shown to be almost complete. Because of the very complex spectrum of Fe and its relatively high concentration in silicate rocks, it is desirable to either prevent the co-extraction of Fe or separate it from the other elements after extraction. In Part IV (e) a scheme using discontinuous countercurrent extraction with MIBK as the organic phase and hydrochloric acid in varying concentrations as the aqueous phase was developed. This

scheme was theoretically capable of separating Fe from most other elements except Sn and Ga and was tested as follows: A 3N hydrochloric acid solution of 20 g of a granite-gneiss from the Charleston area, New Zealand, was chlorinated and extracted with cyclohexanone which had been pre-equilibrated with 3N acid. The volume of cyclohexanone was adjusted until both phases had the same volume. The organic phase was separated and taken almost to dryness on a rotary evaporator at 100°C under vacuum. When all that remained of the organic phase was a tarry residue from the cyclohexanone, this was dissolved in MIBK which had been pre-equilibrated with 6N hydrochloric acid. An equal volume of the latter was then added to redissolve any precipitated inorganic material. The two phases were then mixed, chlorinated and placed in the first two tubes of the previously described countercurrent apparatus. With the exception of these, the first twenty tubes on the extraction train contained an aqueous phase of 6N hydrochloric acid. The next 40 contained 2N acid and the last ten 0.5N acid. After 70 equilibrations the contents of the tubes, in groups of ten, were then taken to dryness, in the presence of 20 mg of NaCl, ashed at 450°C, and arced. The elements found present in each fraction are given in Table 22 together with the weight of sample in each fraction (after correction for the added NaCl).

Table 22

Elements Found in the Various Fractions after Discontinuous Countercurrent Distribution between MIBK and Varying Strengths of Hydrochloric Acid.

Element	Tube number*						
	1-10	11-20	21-30	31-40	41-50	51-60	61-70
acid conc.	6N	6N	2N	2N	2N	2N	0.5N
weight of residue (gms)	0.042	0.029	0.020	0.079	0.181	0.061	0.049
Ag	1	1	1	1	1	1	1
Bi	1	—	—	—	—	—	—
Cd	1	1	1	—	—	—	—
Cu	1	1	1	1	1	1	1
Fe	—	—	—	1	3	3	1
Ga	—	—	—	1	2	2	1
In	—	—	—	1	1	1	—
Mn	3	3	3	—	—	1	1
Mo	1	2	2	2	2	2	1
Pb	3	1	1	—	—	1	2
Sb	—	**	**	—	—	—	—
Sn	3	3	3	1	1	2	3

* The numbers 1,2,3 in the table correspond to increasing relative concentrations of the element and were estimated visually.

** Indicated the possible presence of an element but the spectral line was so weak that it could barely be seen.

From this it is clear that the technique was capable of separating Fe from any elements that occurred in the first thirty tubes only. The total bulk in these tubes was approximately one fifth of the total residue after extraction. However, so much Fe was present in the original rock solution that it was distributed in large quantities over the remaining 40 tubes. The theoretical and experimental distributions shown in Fig. 14 give the

distribution of the elements in terms of relative concentrations and not absolute values. Therefore, if one element is present in large excess it will be distributed over more tubes than shown in Fig. 14. In the distribution of the cyclohexanone extract of the granite-gneiss, Fe was present in far higher concentrations than any of the other extracted elements.

Another factor to be considered is that in this system the first few tubes of the organic phase did not contain pure MIBK but a solution in MIBK of the tar from the cyclohexanone residue. Because of this, the distribution on the extraction train under these conditions differed from that when pure MIBK was used. In view of this, the agreement between the preliminary work and results obtained in practice is very satisfactory.

As can be seen from Table 22, the distribution for Sn was not at all similar to that obtained in the preliminary work. Furthermore the element was spread out over all the tubes in the extraction train. This was most probably a consequence of the presence of the cyclohexanone tar and also of Sn impurities in the reagents. A large Sn blank was found in the residue after evaporation of the Analar-grade acid used throughout this study. The relatively uniform presence of Cu, Ag and Mn was also due to impurities in either the reagents or electrodes.

Because of the unfortunate effect of the high

Fe concentration, the separations originally envisaged when using discontinuous countercurrent extraction were not possible and the extraction train was modified as follows:-

The aqueous phase in the first twenty tubes was 6N hydrochloric acid and the next ten tubes contained 2N acid. No aqueous phase was present in any of the other tubes. After evaporation as before, a cyclohexanone extract of a rock solution was dissolved in 6N hydrochloric acid and MIBK and was placed in the first tubes on the discontinuous countercurrent apparatus. Seventy equilibrations were then carried out, MIBK being the organic phase. The conditions used were therefore exactly as before except that there was no aqueous phase in the last forty tubes. The contents of the extraction train were split into two fractions: (a) those in the first thirty tubes, and (b) the contents of the remaining tubes. These two fractions were taken to dryness, ashed and arced. Portions of the resultant spectra are shown in Fig. 15. From this it is clear that the majority of the Fe is in the second fraction and almost complete separation has been achieved.

(iii) Spectrographic techniques.

The above work showed that it was possible to separate Fe from many of the elements extracted with it

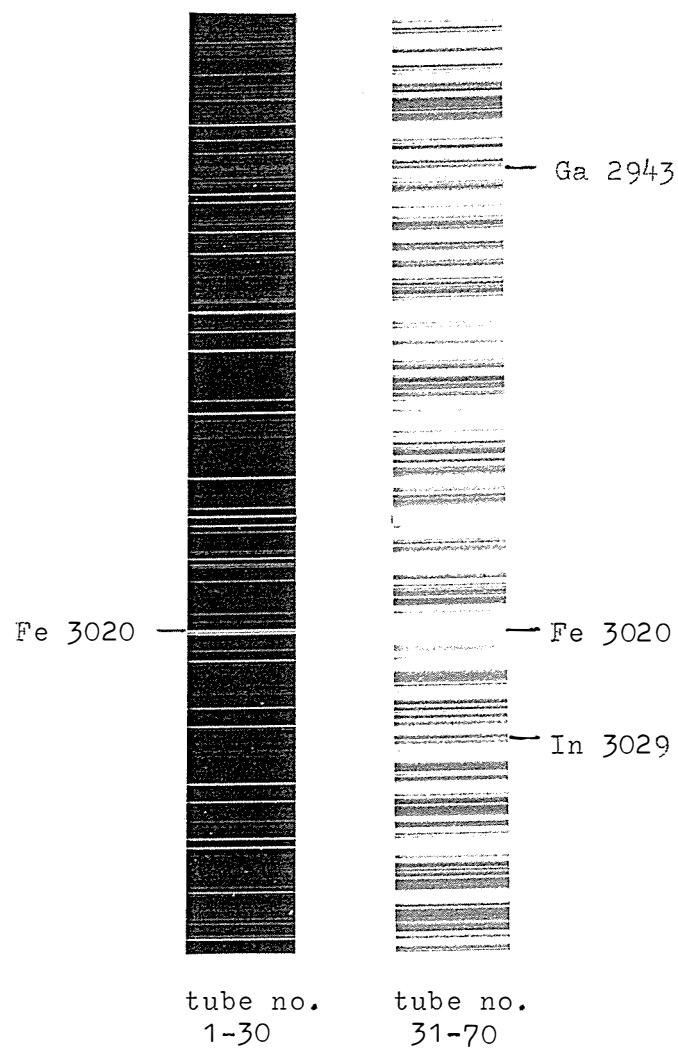


Fig. 15

Spectra of fractions obtained from countercurrent distribution of a rock extract.

by cyclohexanone from a rock solution. It was envisaged that subsequent to the use of batch extraction and countercurrent separation, the elements present would be analysed spectrographically. Suitable internal standards were therefore necessary. Inspection of Table 22 showed that Ag, Cu, Mn, Mo, Pb and Sn occurred at almost every point on the extraction train and therefore none of these could be considered as an internal standard. It is also clear that Ga, In and Tl occur in the last forty tubes only, so that any of these would be suitable as internal standards for elements occurring in tubes number 1-30. If ashing at 450 °C is to be necessary to remove the last of the cyclohexanone tar, Tl cannot be used as an internal standard since it volatilizes below this temperature. It was therefore decided to investigate Ga and In as possible internal standards for the elements occurring in the fraction comprising the first thirty tubes of the extraction train after separation of Fe. Of those considered in this study, the elements that occur in this fraction are As, Bi, Cd, Hg, Pb, Sb and Zn. The use of Ga or In as possible internal standards for these elements was investigated. The method used was that outlined in Part III(b) and the spectrographic operating conditions were those given in Table 16. The coefficients of variation for the appropriate line pairs are given in Table 23.

Spectral lines used were:- As 2860; Bi 3067; Cd 3261;
Ga 2943; In 3039; Sb 2877 and Zn 3345.

Table 23

Coefficients of Variation of Certain Line Pairs.

Element	Coefficient of Variation	
	Ga	In
As	18.6	7.4
Bi	18.3	18.0
Cd	17.3	13.9
Sb	18.5	16.5
Zn	14.4	16.7

The In 3039 line was used instead of the stronger In 3256 because of Mn interference with the latter. Neither Pb or Hg was studied. The former occurred at both ends of the extraction train and therefore could not be determined in the spectrographic analysis of the separate fractions. Mercury compounds are volatile and it was considered unlikely that any of this element would be in the rock solution after the treatment required to dissolve the specimen. It is clear from Table 23, that In is, in general, a more suitable internal standard than Ga. However further investigation showed the presence of an Fe line coincident with this line. Brooks and Cohen (personal communication) have found that this Fe line interferes to quite a marked extent with In 3039 so that in material containing relatively high Fe concentrations this line cannot be used with confidence.

Discontinuous countercurrent separation effectively removed the bulk of the Fe from the fraction of the rock extract in which the elements considered above occurred. However, a very small quantity of Fe was found present in this fraction in sufficient concentration to cause interference with In 3039. Because of this, it was decided to use Ga as an internal standard for the above five elements.

The elements Au, Ga, In and Tl all occurred after tube number 30 in the extraction train. If these elements were to be determined spectrographically, then, in view of the necessity for ashing at 450°C, Tl could not be determined. Also, since this is the fraction containing Fe, enrichment will not be sufficient to determine Au. The use of Cd as an internal standard for Ga and In was investigated. A matrix consisting of equal parts of NaCl and Fe_2O_3 was mixed with the above three elements and eleven replicate arcings made using the conditions of Table 16.

The intensities and intensity ratios for these elements are shown in Fig. 16. Because of Fe and Mn interference with In 3039 and In 3256 respectively, In 4511 was used. The other spectral lines were Ga 2943 and Cd 3261. The coefficients of variation for the line pairs In/Cd and Ga/Cd were 13.5 and 17.7 respectively. While these intensity ratios are not highly reproducible it was considered that the precision would nevertheless be satisfactory for the purposes of the investigation.

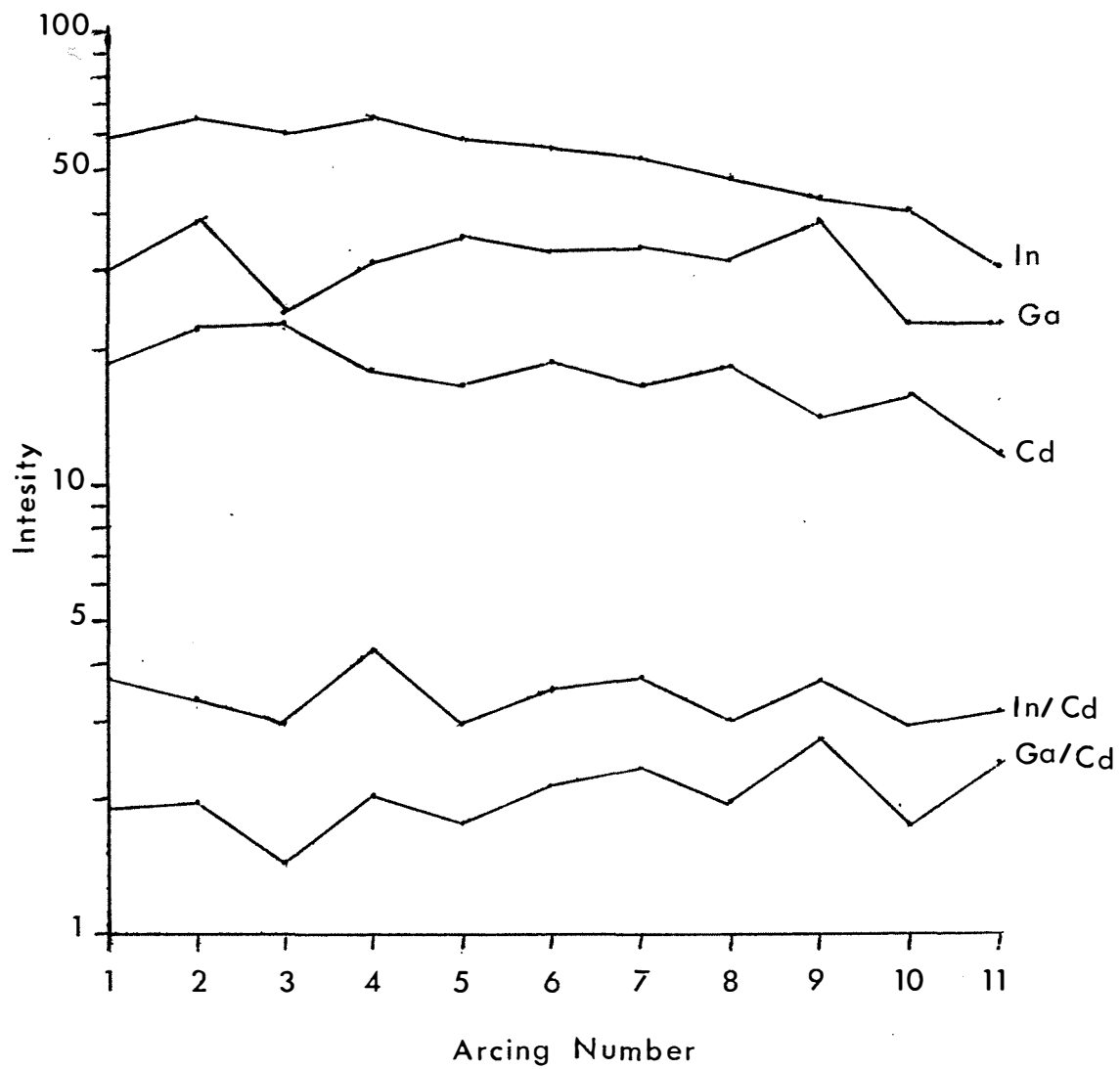


Fig 16

Line intensities and intensity ratios for determining the reproducibility of Cd as an internal standard for the spectrochemical determination of In and Ga.

After separation by discontinuous countercurrent extraction and heating to remove the cyclohexanone tar, the fraction containing Ga and In consisted principally of Fe_2O_3 . Arcing this residue gave a complex spectrum (due to the Fe) with a high background. This was reduced by mixing this residue 1:1 with NaCl. Addition of more NaCl reduced this even further but prevented the determination of Ga and In by lowering their concentrations too much. The rate at which Fe, Ga, In and Cd evaporated from a matrix of 1:1 NaCl: Fe_2O_3 was obtained and is shown in Fig. 17. The spectrographic conditions were those given in Table 16. The time required for complete volatilization of these elements coincided with the end of the characteristic Na emission in the arc. In all further work arcing was stopped at this point to minimise Fe emission and to reduce background.

(iv) Final procedure:

Ten g. of the rock were dissolved in 3N hydrochloric acid as described above. This solution was chlorinated by bubbling Cl_2 gas through until saturated, and was then extracted with cyclohexanone which had been pre-equilibrated with 3N acid. The amount of cyclohexanone was adjusted so that at equilibrium the two phases were of equal volume. The organic layer was separated and taken almost to dryness on a rotary evaporator at 100°C under vacuum.

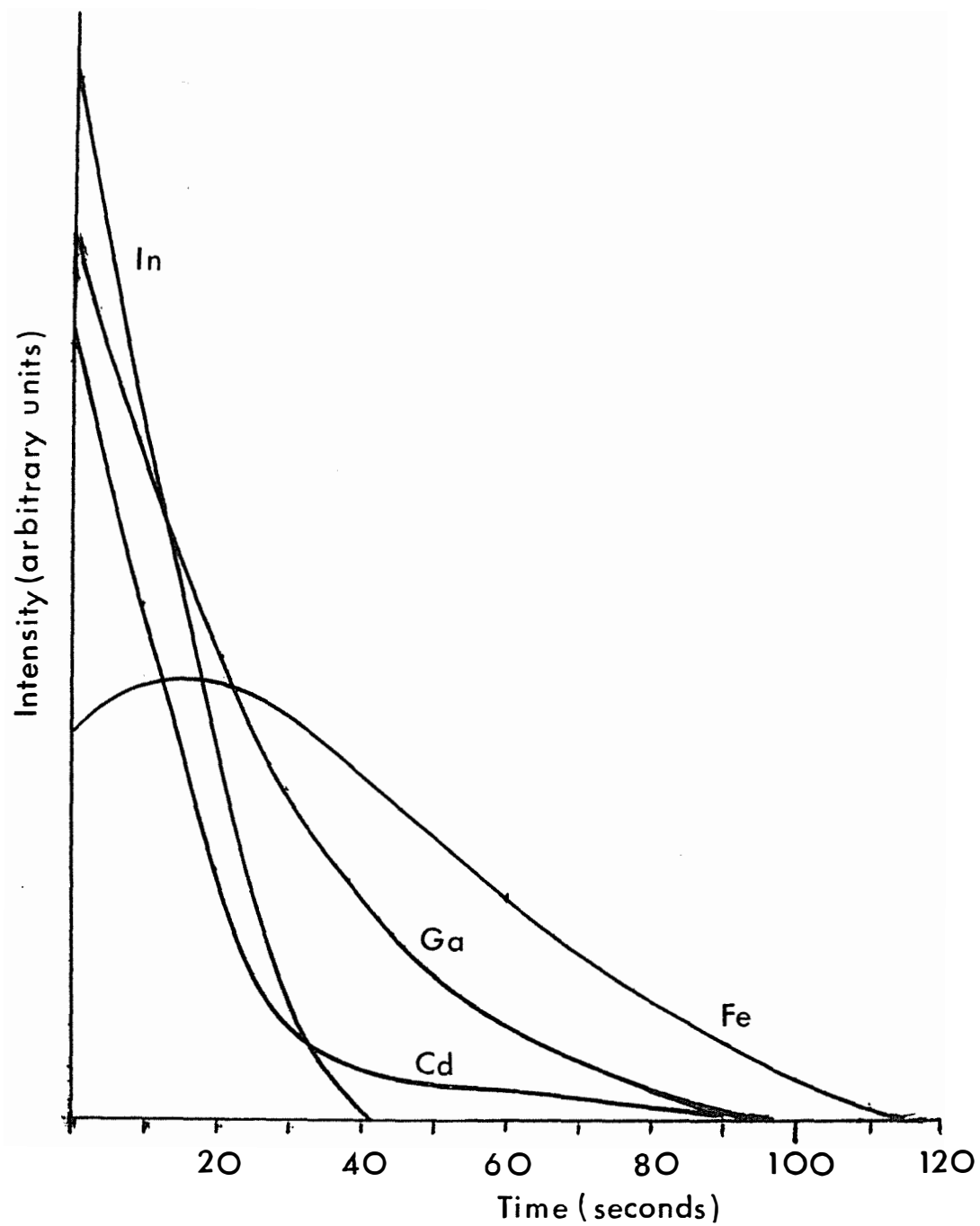


Fig. 17

Volatilisation curves for Ga, In, Fe and Cd from
a $\text{Fe}_2\text{O}_3/\text{NaCl}$ matrix.

This procedure reduced the formation of the cyclohexanone tar to a minimum. The residue from this evaporation was dissolved in pre-equilibrated MIBK and 6N hydrochloric acid. The volumes of both phases were adjusted to 40 mls and the mixture chlorinated to ensure complete oxidation. The phases were separated and the acid layer was made the aqueous phase in the first two tubes of a counter-current distribution apparatus; the next 18 tubes contained 6N hydrochloric acid which had been pre-equilibrated with MIBK. The next 10 tubes in the extraction train contained 2N hydrochloric acid which had also been pre-equilibrated with MIBK. The organic layer obtained above comprised the first two fractions of the organic phase travelling along the extraction train. The organic phase was MIBK which had been pre-equilibrated with 6N hydrochloric acid. Since the phases in the first two tubes were already in equilibrium, the equivalent of two inversions had already taken place and a further 68 equilibrations were carried out.

The material in the apparatus at the end of the separation, was divided into two fractions. Fraction 1 contained all the material in tubes number 1 to 30 and fraction 2 all in the remaining tubes. To fraction 1, 20 mg of NaCl and 1 ml of a Ga internal standard solution were added and the mixture taken to dryness. Fraction 2 was mixed with 1 ml of a Cd internal standard solution and

taken to dryness. The residue from both fractions was ashed at 450°C. The material from fraction 1 was loaded directly into an electrode and arced while that from fraction 2 was mixed 1:1 with NaCl before arcing.

Two series of working curves were prepared for matrices corresponding to fractions 1 and 2. Those for fraction 1 were prepared by duplicate arcings of known amounts of the elements As, Bi, Cd, Sb, Zn in NaCl together with 1 ml of the Ga internal standard solution. Those for fraction 2 contained the elements Ga and In in a 1:1 mixture of Fe_2O_3 and NaCl together with 1 ml of the Cd internal standard solution. Duplicate arcings were made for this fraction also. Using the same procedure as outlined in Part III (b), the concentration of trace elements found in the rocks was obtained. The spectrographic conditions were the same as used in the study of the lake waters and are given in Table 16.

(v) The use of atomic absorption techniques.

Although the technique of atomic absorption spectrometry has been used extensively in the last decade, very little use has been made of it in geochemical analysis. The theory of the technique is comprehensively discussed by Walsh (1961), while Gilbert (1963) and David (1964) give extensive reviews of applications and developments respectively. Trent and Slavin (1964) have determined

the major elements in the standard granite, G-1 and diabase, W-1 (Fairbairn et al., 1951) by atomic absorption spectrometry. Billings et al. (1964, 1965) have determined certain major and trace elements in geological material by this technique. It has also been applied to the determination of Ag in PbS concentrates (Rawling et al., 1961), Fe, Mn, Ni, Zn and Cu in sea water (Fabricand et al., 1962), Cu in sea water (Magee and Rahman, 1965), Na and Mg in carbonaceous rocks (Rubeska et al., 1963, 1965), Cu and Zn in silicates (Bett, 1964) and Sr in rock phosphate (David, 1962).

At the conclusion of the experimental work detailed in the preceding sections, an atomic absorption spectrometer became available at this laboratory. It was therefore decided to investigate whether extraction from 3N hydrochloric acid solution into cyclohexanone followed by analysis of the organic extract by atomic absorption spectroscopy would provide a rapid and simple method for the analysis of trace elements in rocks.

Of the elements considered in this study, the only ones for which geochemical applications of atomic absorption have been made are Zn and Cd (Bett, 1964; Billings and Adams, 1964). Enrichment by solvent extraction prior to analysis by atomic absorption has been used in the past. Almost invariably however, the elements have been extracted by ammonium pyrrolidine dithiocarbamate

into MIBK. It was therefore considered worthwhile to investigate whether the cyclohexanone/hydrochloric acid extraction system developed here, could be a useful alternative as an enrichment technique for atomic absorption analysis.

Ten grams of rock were dissolved in 3N hydrochloric acid as described previously and oxidised by saturation with chlorine gas. The solution was then extracted with cyclohexanone which had been pre-equilibrated with 3N acid. The volume of cyclohexanone was adjusted so that the ratio of the volumes of the organic to aqueous phases was 1:5. The organic phase was separated, filtered to remove any residual droplets of water and aspirated into the flame of a Techtron AA-3 atomic absorption spectrophotometer. The elements studied and the operating conditions are given in Table 24. Working curves were prepared by diluting stock solutions of the elements in cyclohexanone saturated with 3N hydrochloric acid.

Table 24

Operating Conditions for Atomic Absorption Spectrometry.

Element	Wavelength Å	Slit Width μ	Lamp Current (in A).
As	1937	300	12
Bi	2230	50	6
Cd	2288	150	4
In	3040	50	6
Mn	2795	100	10
Sb	2176	100	10
Tl	2768	200	4

Flame air/acetylene, nonluminous.
 Air pressure 15 psi.

The light of the absorbance path through the flame was adjusted to give maximum absorption for each element.

The hollow cathode lamps were made by Spectral Atomic Lamps Inc., Sydney.

(b) Results and Discussion

The concentration of the elements Bi, Cd, Ga, Pb and Zn in a suite of 28 rocks is given in Table 25 together with semiquantitative data for In. Table 26 gives the locality details of the rocks studied. Results for the individual elements are discussed separately.

Gallium, In and Zn were determined by the solvent extraction procedure using countercurrent distribution for the separation of Fe with subsequent spectrographic analysis. Cadmium, Pb and Bi were determined by atomic absorption analysis of the cyclohexanone extract of solutions of the rocks.

Table 25

Concentrations of Certain Metals in Silicate.

No.	Rock type	Ga	Zn	Pb	Cd	Bi	In**
Standard Rocks							
1.	Granite, G-1	*	22	44	0.17	2.1	*
2.	Sulphide, CAAS	8	281	192	0.78	11.2	m
3.	Syenite, CAAS	*	160	138	0.35	6.2	*
4.	Diabase, W-1	*	130	11	0.40	6.8	*
New Zealand Rocks							
5.	Granite-gneiss	8	138	11	2.0	8.1	h
6.	Granite-gneiss	19.5	94	*	*	*	l
7.	Gneiss	15.5	—	*	*	*	l
8.	Biotite-granite	18	—	*	*	*	m
9.	Ignimbrite	16.5	—	*	*	*	m
10.	Andesite	25.5	232	15	0.72	9.4	m
11.	Porphyritic-horn- blende-andesite	38	280	5.6	0.68	—	m
12.	Porphyritic-horn- blende-andesite	38	152	2.7	0.18	9.5	m
13.	Gabbro	29	—	14.3	1.18	18.2	m
14.	Olivine basalt	21.8	242	11.9	2.26	9.1	m
15.	Peridotite (wehrlite)	4.3	116	4.7	0.73	7.8	m
16.	Dunite	2.5	130	5.7	0.16	13.0	—
17.	Serpentine	0.9	146	10.3	0.80	11.3	m
Antarctic Rocks							
18.	Vida granite	11.2	130	3.5	0.18	—	—
19.	Vida granite	11.2	4.6	8.8	0.07	—	l
20.	Vida granite	27.5	84	—	0.06	—	m
21.	Microgranite	*	*	10.8	0.07	—	*
22.	Microgranite	22	116	7.3	18.8	—	—
23.	Granite, xenolith in part	17	657	9.1	0.38	9.5	m
24.	Granodiorite	*	*	8.3	0.27	—	*
25.	Lamprophyre	15.1	412	7.4	0.82	—	m
26.	Ferrar dolerite	*	*	59	0.69	7.4	*
27.	Basalt	9.2	261	11.9	1.05	13.6	m
28.	Peridotite	59	296	8.8	0.86	7.8	—

— below detection limits

* not examined

h, m, l indicate high, medium and low relative concentrations of In respectively.

Table 26

Locality Details of Selected Rocks Used for the Investigation.

No.	Rock Type	Locality
Standard Rocks		
1	Granite, G-1	Westerley, Rhode I, U.S.A.*
2	Sulphide, CAAS	Falsonbridge, Ont., Canada.**
3	Syenite, CAAS	Bancroft Area, Ont., Canada.**
4	Diabase, W-1	Centerville, Va., U.S.A. *
New Zealand Rocks		
5	Granite-gneiss	Charleston, Westland.
6	Granite-gneiss	Buller Gorge, Westland.
7	Gneiss	Milford Track, Westland.
8	Biotite granite	West Coast, Westland.
9	Ignimbrite	Maraetai Dam , Waikato.
10	Andesite	Crater area, Mt. Egmont, Taranaki.
11	Porphyritic-horn- blende-andesite	Paritatu, New Plymouth, Taranaki.
12	" "	" " "
13	Gabbro	Southend, Longwood Range, Southland
14	Olivine basalt	Auckland.
15	Peridotite (wehrlite)	D'Urville Is., Nelson.
16	Dunite	Dun Mountain, Nelson.
17	Serpentine	Upper Takaka Valley, Nelson.
Antarctic Rocks.		
18	Vida granite	Middle Taylor Valley, above Lake Bonney.
19	Vida granite	Near Lake Vida, Victoria Valley
20	Vida granite	Upper Taylor Valley
21	Microgranite dyke	Lower Taylor Valley, Mt. Coleman.
22	Microgranite dyke	Lower Taylor Valley, Mt. Coleman.
23	Granite, xenolith in part	From near contact, Pluto Peak, Lower Taylor Valley.
24	Granodiorite	Lower Taylor Valley, near Commonwealth Glacier.
25	Lamprophyre	Taylor Valley.
26	Ferrar dolerite	Middle Taylor Valley.
27	Basalt	Black Is., near Mt. Nubian, McMurdo Sound.
28	Peridotite	Between Suess and Canada Glaciers, Taylor Valley.

*(Fairbairn et al., 1951)

**(Canadian Association for Applied Spectroscopy, 1961)

Gallium

The first major study on the geochemical behaviour of this element was reported by Goldschmidt and Peters (1931). Shaw (1957) has reviewed all work on Ga undertaken prior to 1957. Because of the similar size and charge of Al and Ga, the Al/Ga ratio was believed to be relatively constant (Nockolds and Mitchell, 1948) but more recent work has shown that this ratio decreases in successive differentiates (Borisenok, 1959; Borisenok and Tauson, 1959; Borisenok and Zlobin, 1959; Borisenok and Skukor, 1960).

Rooke (1964) has also shown that the Al/Ga ratio is not constant in a series of acid igneous rocks. She has shown that the best relationship is between Ga and $\text{Na}/(\text{Al} + \text{Fe}^{3+})$. All the above data show a relative enrichment of Ga in the later differentiates accompanying the increase of Al in these rocks. This trend is apparent in the data reported here, with the basic and ultrabasic rocks having a generally lower concentration of Ga than the acidic rocks. The Ga concentration of 57 ppm in the Antarctic peridotite is exceptionally high for this rock type. The values of 4.3 and 2.5 ppm Ga in the New Zealand peridotite and dunite are similar to values reported by Shaw (1957) and Borisenko (1963) for these rock types. No Ga figures for serpentine appear to have been reported previously and the value given here of 0.9 ppm is of the order expected for such a mineral.

Of the four standard rocks only the CAAS sulphide was examined for Ga and the value of 8 ppm obtained

is within the range of values reported by Weber (1965) and close to the mean of 13 ppm.

Zinc

In his recent estimate of crustal abundances of the elements Taylor (1964) calculated the average concentration of Zn to be 70 ppm with 100 and 40 ppm in basalts and granites respectively. This is lower than the value of 80 ppm obtained by Sandell and Goldich (1943) but higher than the estimate of 40 ppm made by Clarke and Washington (1924). Wedepohl (1953) using a double-arc technique, obtained values of 118 and 45 ppm respectively for the concentration of zinc in basic and acidic rocks. Assuming a 1:1 proportion of basic to acidic rocks (Taylor, 1954) this gives an estimated abundance of 80 ppm Zn which is slightly higher than that of Taylor.

Zinc has an ionic radius very similar to those elements in the magnesium-iron group and therefore tends to replace Fe and Mg in the ferromagnesium minerals, so concentrating in the more basic rocks. While the values reported here are, on the average, slightly higher than would be expected from those of other workers, they show this trend quite clearly. These higher values could be purely regional, since Rader et al., (1963) have shown large local variations in Zn concentration for basalts from the same area.

The exceptionally large amount of Zn in the

Antarctic granite-xenolith could possibly be associated with the relatively high concentration of this element in Lake Hoare nearby. The comparatively high concentration of Zn in the lamprophyre could be associated with the presence of the ferromagnesian minerals present in these rocks.

Zinc was estimated in all four standard rocks. The value reported for G-1 is much lower than that recommended by Fleischer (1965) but within the range of concentrations reported by the latter. The value for W-1 is higher than that recommended by Fleischer. The agreement of the values for the CAAS syenite and sulphide with those reported by Weber (1965) is considered to be very satisfactory.

Lead:

The first estimate of the abundance of Pb was made by Clarke and Steiger (1914). They suggested a value of 7.5 ppm but later workers showed this to be low. Clarke and Washington (1924) gave an estimate of 20 ppm as the average amount of this metal; von Hevesy (1932) found 16 ppm Pb while Sandell and Goldich (1954) reported an average of 14 ppm Pb in 54 North American rocks. The most recent estimate of the crustal abundance of Pb is that of Taylor (1965) who recommended a value of 12.5 ppm based on basalt and granite concentrations of 5 and 20 ppm respectively (Turekian and Wedepohl, 1961).

Lead is both chalcophilic and lithophilic and

because of the similarity of the radius of Pb^{2+} with K^+ , tends to concentrate in the later fractions of magnetic differentiation. Sandell and Goldich (1943) reported that the lead content of a series of volcanics rose from 8 to 20 ppm going from olivine basalt to rhyolitic obsidian. Wedepohl (1955) reported a similar trend which is also reflected in the data for the granite G-1 and the diabase W-1. The former contains 49 ppm Pb in contrast to 8 ppm Pb in the latter. Gavrilin and Pevtsova (1963) reported an opposite trend apparent in the intrusive phases of the Kzyl-Ompul massif with Pb enriched in syenites relative to granites.

The values for the concentration of Pb in the suite of New Zealand and Antarctic rocks as reported here, show no discernable trend. Sahama (1945) has shown that granites of southern Lapland have Pb contents ranging from 9 to 27 ppm. Putman and Burnham (1963) have also shown that minor element composition varies as much within one rock type as between different rock types. The difference between the concentration of Pb in granite and basalts is relatively small (Turekian and Wedepohl, 1961) so that the number of samples considered here may not be sufficient to show any trend.

With the exception of the value reported here for the CAAS syenite, the agreement between the recommended values for Pb in these rocks (Weber, 1965; Fleischer, 1965)

is very satisfactory. The value reported here for Pb in syenite is probably too low.

Cadmium:

Relatively little data are available in the distribution of Cd in igneous rocks. The first estimate of the abundance of this element was made by Washington and Clarke (1924) who suggested a concentration of from 0.1 to 1 ppm. based on indirect evidence. Goldschmidt (1938) has estimated also indirectly, a value of 0.5 ppm. The earliest reliable estimates are those of Preuss (1941) who gave concentrations of 0.2 and 0.02 ppm for acid and basic rocks respectively, and Sandell and Goldich (1943) who estimated concentrations of 0.14 and 0.19 ppm for these rocks respectively. Vincent and Bilefield (1960) have given values of 0.36 and 0.11 ppm for the concentration of Cd in acid and basic rocks whereas Brooks and Ahrens (1961) have estimated concentrations of 0.06 and 0.11 ppm Cd in acid and basic igneous rocks respectively. Brooks et al. (1960,1961) reported a higher Cd content in basic rocks than in acidic rocks. While this was originally suggested as due to substitution of Cd^{2+} for Ca^{2+} (Sandell and Goldich, 1953; Goldschmidt, 1954) this has been shown to be unlikely (Brooks and Ahrens, 1961).

The data for Cd reported here are higher than any reported previously for similar material, but the trend

for increased Cd in the more basic rocks is readily apparent, especially in the Antarctic rocks. The value of 18.8 ppm for the Antarctic microgranite is exceptionally high, especially in view of the low Cd concentration in a similar rock from the same area. Sandell and Goldich (1943) estimated the Zn/Cd ratio to be 500. The author's figures average about 550 which is close to that of Sandell and Goldich but lower than that suggested by Mookherjee (1961) and Rankama and Sahama (1950).

It has been possible to determine Cd quantitatively in the four standard rocks. While the Cd reported here for G-1 is relatively high compared with values reported by Fleischer and Stevens (1962), the value for W-1 is considered to be very satisfactory. No value for Cd in the CAAS sulphide has been reported previously. The only other value for Cd in the CAAS syenite was determined by atomic absorption spectrometry (Weber, 1965) and is considerably higher than that reported here. In view of the Zn concentration of approximately 200 ppm in this rock, the value reported here is most probably a better estimate of the Cd concentration than that quoted by Weber.

Bismuth:

The first direct determinations of Bi in silicate rocks were reported by Brooks et al. (1960) although Ehmann and Huizenga (1959) had determined Bi in 5 chondrites. The former suggested a magnitude of 0.2 ppm

Bi in the earth's crust based on the analysis of 19 rocks. Brooks and Ahrens (1961 a) in an analysis of 44 African rocks confirmed this magnitude and, assuming a 2:1 acid-basic rock ratio, suggested a crustal abundance of 0.17 ppm. This latter work appears to be the only definitive study on the abundance of Bi in silicate rocks. It was originally assumed that a $\text{Bi}^{3+} - \text{Ca}^{2+}$ substitution could take place in apatite (Goldschmidt, 1954) but there appears to be no evidence for this (Brooks and Ahrens, 1961 a). The latter showed a very strong enrichment of Bi and Tl in the earth's crust and Brooks (1961) has shown an apparent correlation between Bi and Tl.

The values for Bi reported here are more than a factor of 10 greater than those reported by other workers and are unlikely to be accurate estimates of the Bi content of these rocks. These values were obtained by atomic absorption spectroscopy and there is the possibility of interference from some other element. This possibility was investigated but no conclusive evidence was obtained.

The values for the Bi content in the four standard rocks as reported here appear to be too high. The data for G-1 and W-1 are an order of magnitude greater than all data reported by Fleischer (1965) and Fleischer and Stevens (1962). The mean of all estimates of Bi in the CAAS sulphide is 5 ppm (Weber, 1965) as compared with 11.2 ppm reported here. The only two values reported for the

CAAS sulphide are 0.25 and 5 ppm (Weber, 1965). The value reported here for this rock is in satisfactory agreement with the second of these determinations.

Other elements:

It was not possible to obtain reproducible results for the spectrographic determination of In so that semiquantitative data only are presented in Table 24. Both In and Tl were examined by atomic absorption spectroscopy but could not be detected in any of the samples. Although Mo could be detected using this latter technique, the values obtained were very low, due to Fe interference (Mostyn and Cunningham, 1966; David, 1961) and are not reported. When using atomic absorption spectrometry of the cyclohexanone extract for studying the rocks, absorption corresponding to As and Sb was detected but the values for the concentrations thus obtained were so high that the absorption must be attributed to interference. It was not possible to find the source of this interference.

PART VI

CONCLUSIONS

AND

CRITICAL EVALUATION

From the study undertaken and reported in this thesis it has been demonstrated that solvent extraction provides a satisfactory method for enriching trace elements in geological material prior to spectrographic analysis and/or analysis by atomic absorption spectrometry. The cyclohexanone/hydrochloric acid system developed here is not very satisfactory for material containing a high or relatively high concentration of Fe, due to co-extraction of this element with the trace elements. Under these conditions it is necessary to separate the Fe after extraction and prior to spectrographic analysis. This has been accomplished relatively satisfactorily by the use of liquid-liquid, discontinuous, countercurrent solvent extraction with the methyl isobutyl ketone/hydrochloric acid extraction system. If the material is to be analysed by atomic absorption spectrometry, it is not necessary to separate the Fe previously, provided that this element does not interfere in the determination.

However, the use of the cyclohexanone/hydrochloric acid extraction system coupled with spectrographic analysis provides a perfectly satisfactory and rapid technique for the determination of trace elements in material containing relatively low concentrations of Fe, as has been demonstrated in the study of the Antarctic lake waters.

Since both batch extraction and discontinuous countercurrent liquid-liquid extraction have been used

extensively in the work reported here, it may be advantageous to compare the relative merits of the two systems.

In this study, discontinuous countercurrent extraction has been used for the separation of interfering elements after batch extraction. When large volumes are to be extracted, batch extraction is more satisfactory than countercurrent distribution because of the limitation on the number of the tubes which may be occupied by the solution of the sample in the latter technique. Other advantages of batch extraction in comparison with countercurrent techniques are:

- (i) speed,
- (ii) the simplicity of the equipment required,
- (iii) the smaller volumes of solvents involved.

If a substance is present in a concentration such that only moderate enrichment is required for its determination but is interfered with by some other material, then countercurrent extraction is very useful. In this case it is often possible to separate either the material to be analysed or the interfering substance by the use of this method. Cohen, Brooks and Reeves (1966) have separated U and Fe from Be and the rare earths in uranium minerals by the use of this technique. If, however, very high enrichment factors coupled with separation of co-extracted species are required, then batch extraction used in conjunction with countercurrent distribution is invaluable.

A very valuable function of discontinuous counter-

current extraction, especially when coupled with spectrographic analysis is the ability to determine simultaneously the extraction characteristics of a large number of elements in a solvent system.

The three principal methods of enrichment prior to spectrographic analysis are solvent extraction, ion exchange and co-precipitation. If enrichment procedures are to be used, it is desirable to concentrate the trace elements into as small a volume as possible, thereby gaining maximum enrichment and correspondingly greater sensitivity. Since co-precipitation generally involves precipitating the trace elements in conjunction with one of the more abundant elements present, enrichment is not as high as can be obtained by either solvent extraction or ion exchange. These two latter techniques are therefore preferable if maximum sensitivity is to be obtained.

Ion exchange enrichment techniques have been applied to the spectrochemical determination of trace elements in silicate rocks. Ahrens, Edge and Brooks (1963) have published a comprehensive scheme for silicate analysis based almost exclusively on the use of ion exchange prior to spectrographic analysis. Brooks (1960) has studied the adsorption of the chloro-complexes of a number of metals on to an anion exchange resin from hydrochloric acid and applied this to the spectrochemical determination of trace elements in silicate rocks. The work reported

here was an extension of the above study into the solvent extraction of similar systems. It is therefore possible to make tentative comparison of the two enrichment techniques when used prior to spectrographic analysis.

As an enrichment technique, solvent extraction has a number of advantages over anion exchange:-

- (i) The equipment required for solvent extraction is simpler than that required for ion exchange. In the system studied here, the use of a countercurrent extraction apparatus was necessary to enable Zn to be determined in silicate rocks. This is a consequence of the solvent and ligand used and such sophisticated equipment is not necessary for all extraction systems. For example, Brooks (1961) and Brooks and Ahrens (1961 b) have determined In and Tl in silicate rocks by extraction of their iodo-complexes into ethyl ether with spectrographic analysis. Any Fe that was coextracted was separated by a second extraction so that the technique was essentially a simple one.
- (ii) Purification is much simpler for solvent extraction than for ion exchange, it being much easier to remove elements from a solvent by distillation than by elution from a resin.
- (iii) Solvent extraction is at present more versatile, in that a wider range of solvents and ligands are available compared with ion exchange. However, the variety of resins available is increasing with the development of

chelating resins (Schmuckler, 1965). The use of non-aqueous solvents as eluting agents for ion exchange resins is also increasing the versatility of this technique.

(iv) It is often difficult to remove a very strongly bound element from an ion exchange resin. In solvent extraction this can frequently be overcome by evaporation of the solvent. The use of organic solvents as eluting agents may overcome this problem to a certain extent in ion exchange.

(v) Solvent extraction is generally more rapid than ion exchange; only minutes being required for the former whereas it may take hours to effect complete elution from a column.

The major disadvantages of solvent extraction as an enrichment procedure compared with ion exchange are:

(i) it is often advantageous to be able to selectively elute elements from an ion exchange resin. This normally cannot be done with solvent extraction unless discontinuous countercurrent distribution systems are to be used. The apparatus required for the latter technique is far more sophisticated than that required for ion exchange so that two of the principal advantages of solvent extraction, viz. simplicity and speed are lost.

(ii) In general, distribution coefficients are considerably higher for ion exchange resins than for comparable solvent extractions systems.

If a solvent extraction system could be developed that is capable of separating the trace elements in a solution of a silicate rock from all the macro-elements, then this system, coupled with spectrographic analysis, would provide a very powerful tool for trace element determination in geochemistry.

The work reported in this thesis was an attempt to find such a system. In that it proved possible to determine a number of trace elements in material containing only minor amounts of Fe and certain elements in material containing relatively high concentrations of Fe, it was successful.

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