

THE COLOURIMETRIC DETERMINATION  
OF TRACE ELEMENTS IN PYRRHOTITE

A

Thesis

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in Partial Fulfilment of the Requirements

for the Degree of

Master of Science

in the Department of Geology

of the University of Saskatchewan

by

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Written under the Supervision of



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## ABSTRACT

A sample of pyrrhotite, mechanically separated from its host rock, is dissolved in excess concentrated hydrochloric acid. Iron and any traces of copper present are oxidised by potassium chlorate.

The strength of the hydrochloric acid solution is adjusted to 8.0 Molar and the bulk of the iron is extracted with iso-propyl ether.

Traces of cobalt, copper, zinc, cadmium and residual iron are separated from lead and nickel by passing the extracted solution through a column containing Dowex 1-X10 - a strongly basic quaternary amine anion exchange resin. The traces are adsorbed as anionic chloro-complexes.

The adsorbed metal traces and residual iron are then separated one by one by elution of the resin with hydrochloric acid of diminishing concentrations.

The trace metals thus separated are determined quantitatively by simplified colourimetric techniques. The absorption of the coloured solutions is determined with a Beckman Model D.U. Quartz Spectrophotometer, corrected for reagent absorption and compared with the results obtained by using known quantities of the particular metal.

A sensitivity of 1 to 2 ppm., may be expected, with results accurate to  $\pm 10$  per cent at all but the lowest concentrations.

By making suitable chemical or ion exchange separations of the macro elements, the method may be extended to a variety of other sulphides and acid extracts from crushed rocks, soil samples and others.

Carefully purified reagents must be used throughout.

### ACKNOWLEDGMENTS

I am particularly indebted to the Saskatchewan Research Council, for the award of a Grant in aid of Research, which made this work possible.

I should like to acknowledge the help and suggestions of Dr. A. R. Byers, on the numerous occasions during the course of the experimental work, and for his constructive criticism during the preparation of this Thesis.

Credit for the original suggestion of using Ion Exchange, is due to Dr. R. L. Eager of the Chemistry Department, University of Saskatchewan.

I should like also, to express my thanks to Dr. R. A. Arnold, who kindly devoted his efforts to the preparation of some synthetic Pyrrhotite samples used in this work.

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## INTRODUCTION AND GENERAL CONSIDERATIONS

Originally, this project started by trying to determine Co and Ni in Pyrrhotite samples using an X-ray Fluorescent Spectrometer. However, preliminary experiments showed that limits of sensitivity of 10 ppm Ni and 50 ppm Co only, could be achieved due to the adverse concentration of Iron.

The possibility of using an Ion Exchange Resin to separate the bulk Iron, and thus improve the sensitivity was suggested by Dr. R. L. Eager, Associate Professor, Chemistry Department, University of Saskatchewan.

An investigation of the literature showed that it would be possible not only to separate the Iron, but possibly the Trace Elements from each other as well, thus making their determination by other methods, such as Colourimetry (which is basically more sensitive than X-ray spectrometry) as attractive proposition.

The present thesis describes the method devised for the determination of Ni, Co, Cu, Zn, Cd, and Pb in Pyrrhotite, while it is hoped to include results of its Geological application, together with consideration of such problems as sample preparation and contamination, as part of a Thesis at the Doctorate level.

Trace Elements and Trace Element Data - A Trace Element, for the purposes of this study, will be considered as one present in concentrations of up to 1000 ppm or so in a host mineral. From Geological considerations, it should be present as impurity within the host crystal structure, rather than as a discreet and theoretically separable mineral phase. However, until such times as adequate separation procedures for such material are available

or are proved necessary, much information as published, and much new data must be explained by the presence of "Trace Minerals" rather than "Trace Elements."

Limitations of Published Results - Trace Element studies are assuming a growing significance in Geological work, especially connected with mineral deposits. Yet a study of the published results concerning Sulphides especially, to my mind reveals the following three main limitations.

1. General lack of systematic data.
2. Lack of sensitivity for certain elements, or failure to give details of methods used or their sensitivities.
3. Invalidity of much of the data due to gross contamination.

The first limitation is probably in the main due to lack of suitable equipment. Most of the Trace Element work on mineral Sulphides has been carried out by Emission Spectrometry, which involves some expensive equipment.

The present method is no exception, yet it can be adapted to far simpler and less expensive apparatus, which Emission Spectrometry cannot.

Published results are often notably lacking in information on the method used, its accuracy and its sensitivity. Although it would be hard to improve upon some Emission Spectrometric sensitivities, others, particularly for Zinc and Cadmium, leave much to be desired, while the accuracy for many elements below the 10-20 ppm range is poor.

I regard gross contamination as being the most critical factor in successful interpretation of any Trace Element studies. Many of the published Trace Element concentrations are obviously due to contamination by separate mineral impurities or inclusions. In fact, this is often freely admitted by the authors! If, as is maintained by some Geologists,

the presence of such minerals as may form minute inclusions or exsolution bodies is not harmful, or indeed, is necessary for correct interpretation, then this is no handicap. If however, one regards any separate mineral phase in the host mineral as being a source of confusion or error in Trace Element work, and considers that actual lattice impurities are likely to provide more information, then it seems that much of the available data is of limited use.

Since it seems that the concentration of an element as a lattice impurity is likely to be limited in extent by exsolution of a separate phase, this focusses further attention on the difficult problem of clean mineral separations, as well as indicating the need for an accurate method for measuring the lower concentrations of the Trace Elements.

Available Methods and Results - Table I gives some figures for Trace Element sensitivities obtainable by different methods. The figures have been adjusted to the limits at which a  $\pm 10$  per cent error could be expected. The figures are somewhat conservative, as the limits of detectability (at a  $\pm 100$  per cent error) are 1/10 of these and no account of preliminary enrichments or separations is taken. Table II gives quoted sensitivities taken from published results for some common Sulphide minerals, obtained by Emission Spectrometry. A number of points are apparent:

I. The full sensitivity of Emission Spectrometry is not being attained or used. This is probably explained by the fact that the full sensitivity requires either more elaborate apparatus or more refined techniques, which in view of the extra trouble or expense, is not considered worth while.

TABLE I.

Trace Element Sensitivities - in p.p.m.

Element	Neutron Activ <sup>n</sup> *	Copper Spark	Graphite D.C.Arc.	Colourimetric
Mg	0.03	0.01	0.1	0.06
Al.	0.0005	0.1	0.2	0.002
Ti	-	0.1	-	0.03
V	0.00005	0.05	-	0.2
Cr	0.01	0.05	2.0	0.03
Mn	0.00003	0.02	0.2	0.001
Fe	0.45	0.5	0.2	0.05
Co	0.001	0.5	-	0.025
Ni	0.0015	0.1	4.0	0.04
Cu	0.00035	-	0.2	0.03
Zn	0.002	2.0	20.0	0.016
Pd	0.00025	0.5	-	0.1
Ag	0.0055	-	0.1	0.1
Cd	0.0025	2.0	4.0	0.01
Au	0.00015	0.2	-	0.1
Pb	0.10	0.05	0.2	0.03
Bi	~0.02	0.2	0.2	1.0 <sup>†</sup>
U	0.005	1.0	-	0.7

Values Selected from Meinke, W.W. (1955) - in 'Trace Analysis'  
- WILEY (1957) pp.626.

\* Using Oak Ridge L.I.T.R. Reactor - Other reactors may be  
less sensitive (approx X50)

† Probably a misprint, 0.01 seems more realistic.

TABLE II.

Trace Element Sensitivities for some Common Sulphide Minerals, taken from published Data - in ppm.

Element	Pyrite	Pyrrhotite	Arsenopyrite	Chalcopyrite	Galena	Sphalerite
Mn	5-100	10-100	10	10	1-10	1-100
Co	10-30	10-15	10-22	10	-	5-50
Ni	2-20	10-15	10-100	10-15	1-5	1-50
Cu	1-10	2-10	-	x	1-10	1-100
Zn	100	-	-	-	-	x
Ag	5-30	5-30	-	-	-	1-5
Cd	-	-	-	-	10-100	10-100
Sn	10	-	-	10	3-100	3-100
Pb	10	-	-	-	x	5-20
Bi	10-100	-	-	1-100	1-100	1-10

Values Selected from Fleischer, M., -Econ Geol. 50th. Ann. Vol. pt. II. pp

The gaps in the table may be taken as a Qualitative indication of the lack of published sensitivities or of results of any kind for the elements listed, up to 1955.

-The position has improved little since that date.

II. Colourimetric Methods are in most cases as good as or even decidedly better than Emission Spectrometry, and are surpassed only by Neutron Activation Methods.

III. This latter method obviously, requires expensive facilities and equipment which are not readily available, while Colourimetric methods potentially involve the least expense of any method.

Colourimetric Methods - Before looking at Colourimetric Methods more closely, it is necessary to consider this aspect: the desirability of increased sensitivity and accuracy at the lower concentrations has been mentioned, yet there is little evidence at present to suggest that mineral analyses for Traces correct to the nearest ppm. or sensitive to much less than 1 ppm. can have much Geological significance. Figures from 1 or 2 ppm. and up, with  $\pm 10$  per cent error will probably be adequate for most purposes.

It is clear from Table I that Colourimetric methods are more than adequate for this purpose. In fact, since their ultimate sensitivity is not required there is the possibility that techniques may be simplified somewhat.

Apart from the well established Geochemical Prospecting methods, and some procedures for Silicate Rocks, Colourimetric methods have been applied only in somewhat isolated instances to other Geological materials, particularly Sulphides.

The main objection to Colourimetry is that very few of the reagents used are specific, and most of them require often elaborate separations or complexing procedures to reduce the ratio of the Host constituents to the Trace Elements or to prevent their mutual interference. This is

time consuming; it introduces sources of chemical and mechanical error and may require the careful purification of reagents used, which themselves may often contain more of the Trace Elements than the sample to be analysed.

Ion Exchange Separations - The use of an Ion Exchange Resin in the present method is an attempt to eliminate lengthy separations. Indeed, the determination of six Trace Elements in one sample of Pyrrhotite without it, would be a most protracted process.

The method uses the fact that the adsorption of Anionic Chloro-complexes by the resin is highly dependent on the concentration of the supporting electrolyte, in this case Hydrochloric Acid. Thus an element may be passed through a column of resin or adsorbed at will by simply changing the Hydrochloric Acid concentration. The adsorbed ions may be separated from each other by selective elution with acid of the appropriate concentration. The result is a series of chemically simple solutions containing the individual Trace Elements, allowing maximum simplification of their Colourimetric determination.

Specifications of the Proposed Method - As a result of the foregoing general considerations, we may set down more precisely, the following desirable features which the method should aim to achieve:

1. Sensitivity - A detection limit of 1 or 2 ppm., (an error of  $\pm 100$  per cent at this limit is assumed).
2. Accuracy - Except near the detection limit, a general accuracy of  $\pm 10$  per cent or better, should be aimed at, with a high degree of confidence.

3. Range - The method should cover the expected Trace Element concentrations in the samples. Although high concentrations of Trace Elements, as mentioned, are probably due to impurities, the method should be able to handle these high values.

4. Simplicity - The method should be as concise and simple as possible, and involve a minimum of separations and expensive equipment. Although the Beckman Model DU Spectrophotometer at present in use, and the more sensitive equipment contemplated hardly fit this last condition, there are somewhat less accurate Visual Filter Photometers available at much less cost which would be good enough for routine application.

5. Sample requirements - The method should be applicable to small samples. This is important, as the difficulty of achieving a sufficiently pure separation may be considerable. Since it was originally intended to use this method on small Diamond Drill core samples, among others, a sample weight of 0.5 gms., was chosen as the basis of all calculations, and this value has been retained.

6. Versatility - The method should be capable of extension to other Trace Elements and Geological materials without difficulty.

These criteria will be discussed again later, in the light of the experimental results.

SOURCES OF INFORMATION

Four excellent Reference Texts which cover both the theoretical and practical aspects of the methods used in this Thesis, and from which many of the pertinent references were obtained, are listed below:

Samuelson, O. (1953) 2nd. Ed. "Ion Exchangers in Analytical Chemistry"  
Wiley & Sons.

Kunin, R. (1958) "Ion Exchange Resins" Wiley & Sons.

Sandell, E. B. (1959) 3rd. Ed. "Colourimetric Determination of Traces of  
Metals" Interscience Publishers Inc.

Yoe, J. H. & Koch, H. J. Editors (1957) "Trace Analysis" Wiley & Sons.

The displaceable ions conferring neutrality are known as 'Counter-Ions' and the resin is said to be in the 'Hydroxide Form' for example, if the Counter-Ions are OH' ions. Dowex 1-X10 is used in the Chloride form throughout this Thesis.

### Some Properties of Ion Exchange Resins

Capacity and Loading - The Capacity -C, is the number of equivalents of exchange sites per unit weight or volume of resin. It is conveniently expressed in milliequivalents per gram or ml. (meg/gm. or meq/ml.). The Capacity of Dowex 1-X10 equals 3.5 meq/gm. or 1.33 meq/ml. of wet resin. The value of C is used to estimate quantities of adsorbable materials and to calculate column sizes. The Loading -L, is defined thus:

$$L = \frac{a (A^{\pm a})_{(r)}}{C} \quad \text{-----} \quad 1$$

where a = charge on ion A and (r) denotes concentration in resin phase. The Loading has a very great effect on the selectivity. Generally, there are fewer complications to consider if a resin is used at a low loading.

Effects of the X-number. - The X-number strongly affects the swelling properties of the resin. Swelling increases with decreasing X-number and decreasing electrolyte concentration; it is very small for X=10 or more. The Capacity of the resin decreases with decreasing D.V.B., the Selectivity also decreases, since with greater swelling, the resin is more porous and larger ions may be admitted. However, equilibrium is more rapidly reached due to the increased porosity.

Effects of Particle Size - The particle size has a number of important effects; The smaller the particles, the more rapidly is equilibrium reached. Smaller particles reduce the 'channeling' whereby the solution flows through the middle of the pore spaces and packing irregularities without contacting the resin. The rate of flow of a solution through the pore spaces is however also reduced. The smaller particles have the advantage that, due to the capillary forces, no air enters a column when all of a solution has drained through. Air entering a column cannot be removed by adding more solution to the top of the column; it must be repacked. A plug of glass wool at the top of the column prevents this trouble if larger mesh resins are used.

Distribution Coefficient - This is the ratio of the concentration of the adsorbed species in the resin phase to its concentration in the liquid phase. It is designated as  $D$  if concentrations are expressed by weight, and as  $D_v$  if expressed as weight per unit volume. Fig. 1 shows a typical Adsorption Isotherm - note it is only linear at relatively low loading. Fig. 2 shows a typical 'Breakthrough' curve, obtained when a solution is passed through a resin column until saturation occurs, and the adsorbable ions appear in the effluent. The curve may be used to calculate  $C$ . If only a small volume of solution is added to the column, and the adsorbed ion then eluted, the band of ions passes through the column and traces out the characteristic Gaussian Elution curve, Fig. 3. The Elution Constant -  $E$ , which may be measured from such a curve, is defined as follows:

$$E = \frac{I}{V_{max}} \quad \text{or} \quad E = \frac{dA}{v} \quad \text{----- 2.}$$

Fig I. Adsorption Isotherm for Typical Ion-Exchange Resin.

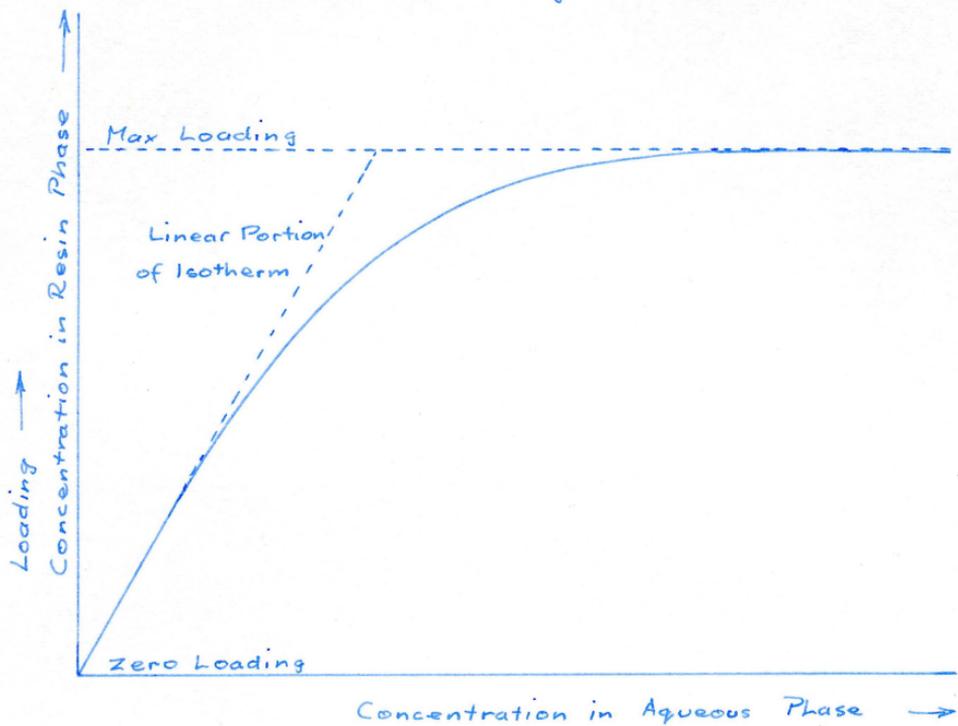


Fig 2. Typical Break-through Curve.

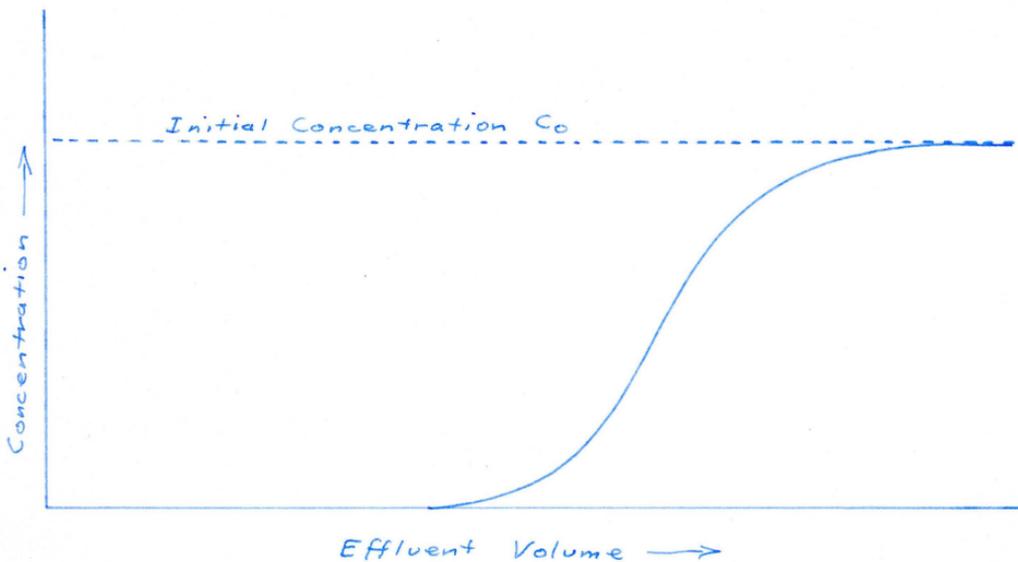
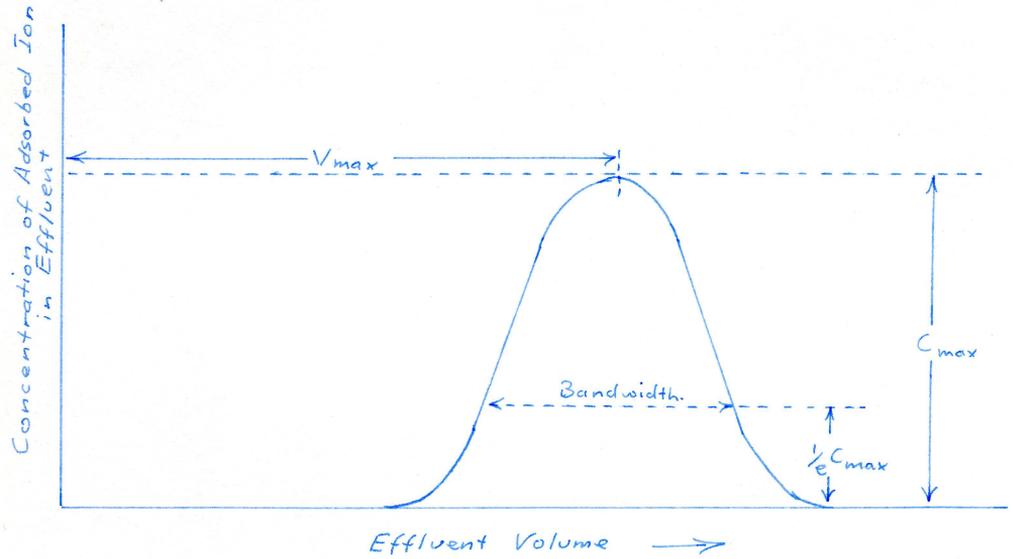
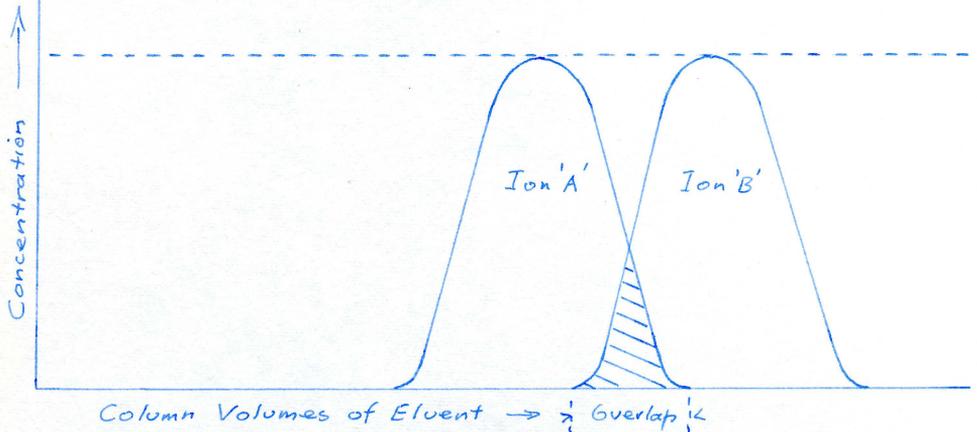


Fig 3. Typical Elution Curve



Note:  $E = \frac{1}{V_{max}}$ .

Fig 4. 'Degree of Overlap' - as a Measure of Sharpness of Separation of Equal Quantities of two Adsorbed Ions - 'A' & 'B'



Note: - If Overlap is zero, then separation is complete  
 - Shaded area as a fraction of either curve area is a measure of the amount of mutual contamination.

where  $d$  = distance the band moves down a column of cross-section  $A$  for a volume of eluant  $v$ .

It is easily seen that the following relations are true:

$$E = \frac{l}{(i + D_v)} = \frac{l}{(i + D_\rho)} \quad \text{----- 3.}$$

where  $\rho$  = density of resin and  $i$  = fractional interstitial volume - 0.45 gms/cc and 0.4 - 0.42 respectively, for Dowex 1 -X10.

Kunin (1958), Kraus, K. A. (1957), and Dow Chemical Co., (1958), all provide details of the measurement of these and other quantities.

### ION EXCHANGE THEORY

Introduction - A number of theories have been proposed to explain the action of Ion Exchange Resins. Some of these tend to be rather complex in detail, but some simplified concepts are highly useful, and for most purposes quite adequate for applying Ion Exchange techniques.

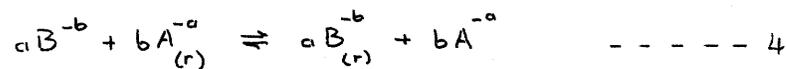
Theoretical Plate Theory - The basis of this theory is the likening of an Ion Exchange column to a distillation column. The diameter of the column at constant height controls the Capacity, while the height controls the effectiveness of an Elution separation.

The Effective Height of a 'Theoretical Plate' (E.H.T.P.) may be determined from Elution and Breakthrough curves. It is a variable, strongly dependant on the conditions, such as resin particle size and packing, flow rates, temperature, etc., It is smaller for smaller resin bead diameters. The separation of two ions is strongly dependent on the number of Theoretical Plates, and on the ratio of their respective Distribution Coefficients. The effectiveness of a separation may be conveniently expressed as the degree of overlap of the Elution curves for the two ions - Fig. 4. As the ratio of the  $D_v$  values for the two ions, called the Separation Factor -  $S$ , decreases, so the number of Theoretical Plates increases sharply for any given degree of overlap. In practical terms, the height of a column must be increased. It can be shown that for  $S \geq 2$ , a column need rarely be longer than 10 cms., even for a small overlap. It is obviously an allround advantage then, to make  $S$  as large as possible, for the column size can then be reduced and flow rates increased without risk of contamination. If one of the  $D_v$  values is  $\leq 1$ , then the separation will be very rapid, and the Elution curve will be

sharp, and the adsorbed ions will appear within a very few Column Volumes of effluent (Column Volume = Physical Volume of Column -  $\pi r^2 h$ ).

Application of the Law of Mass Action - A number of useful facts can be obtained by using the laws of Mass Action, with appropriate assumptions, when applied to Ion Exchange.

Assuming that an Ion Exchange Equilibrium may be represented thus:



where A and B are ions (in solution) with charges a and b, while (r) indicates the resin phase. Then from the Law of Mass Action -

$$K = \frac{(B^{-b})_{(r)}^a (A^{-a})^b}{(B^{-b})^a (A^{-a})_{(r)}^b} \times \frac{g_{B(r)}^a g_A^b}{g_B^a g_{A(r)}^b} = K_{AB}^{(')} \times C_{AB} \quad \text{----- 5}$$

where  $g$  = activity coefficient,  $( )$  = concentration of species,  $K^{(')}$  concentration or selectivity coefficient, and  $G$  = activity coefficient quotient.

Consider now the adsorption of an ion  $X'$  from a solution of Hydrochloric Acid, assumed to be completely dissociated - ie.  $H^+ + Cl'$ , we may then use stoichiometric concentrations -  $m$  - in Eq. 5. ie  $m_X = (X')$ ,  $m_{X(r)} = (X')_{(r)}$ , etc.

$$\text{Thus } D = \frac{m_{X(r)}}{m_X}$$

Assuming that  $G$  is independent of the concentration, then Eq. 5. becomes;

$$D_X m_{Cl} = \frac{K_{Cl,X}}{C_{Cl,X}} \times m_{Cl(r)} \quad \text{----- 6}$$

Now at low or trace loading, it may be validly assumed that  $m_{Cl(r)}$  is constant, hence Eq. 6. is a constant. Furthermore a plot of  $\log D$  vs.

log m will give a straight line of slope - 1, and if X has a charge of - b, and the eluting ion A a charge of -a, then it can be shown that -

$$D_x^a \cdot m_A^b = \left(\frac{K}{C}\right) m_{A(r)}^b \quad \text{----- 7}$$

- and a plot of log D vs. log m will be a straight line of slope -b/a.

One of the important conclusions to be drawn from this is as follows: since S, the Separation Factor for two ions is largely dependent on the ratio of their D<sub>v</sub> values, it follows from Eq. 7. that if they are of equal charge, their D<sub>v</sub> values will vary similarly with the electrolyte concentration, and hence S will be independent of it. The separation, if possible will depend mostly on K<sup>(<sup>1</sup>)</sup> - the Selectivity Coefficient.

However, this apparent lack of selectivity can be avoided by other means.

Adsorption of Negatively Charged Species - A large number of metals may be converted into -ve. charged complexes in acid solutions. This explains the apparent anomaly of using an Anion Exchange Resin in this Thesis for metal separations. Moreover, since these complexes vary in stability, species and charge with different supporting electrolyte concentrations, and from metal to metal, their adsorption may be made highly selective by choice of the electrolyte and solution concentration. It can be shown that for a metal which forms a series of negatively charged complexes, the value of D<sub>v</sub> is given by the product of the Selectivity of Coefficient K<sup>(<sup>1</sup>)</sup>, the ion fraction F<sub>x<sup>-a</sup></sub> and the supporting electrolyte Anion concentration in the aqueous and resin phases -

$$D = K^{(1)} F_{x^{-a}} \times \frac{m_{x(r)}^a}{m_x^a} \quad \text{----- 8}$$

- where  $X^{-a}$  represents the complex, and X the Anion of the supporting electrolyte.

The selectivity for a particular complex may be so great that it may be preferentially adsorbed even if F is very small - and consequently even if the element is present only in Trace quantities.

Criteria of Separations - We may at this stage summarize some points regarding separations.

1. Providing such complications as high loading are avoided, separations can be designed from prior experiments.
2. The Separation Factor S should be as large as possible and at any rate  $\geq 2$ . for a column height of 10 cms. or less.
3. D for the eluted ion must be  $\leq I$  for elution in practical times and with small eluant volumes.
4.  $D_v$  values for all but one ion may be made high and the one ion removed by passage of the solution.
5. The concentration of the medium may be changed progressively so that  $D_v$  values become I and the ions are removed successively.
6. The  $D_v$  value for the Trace ion may be made high, and only it adsorbed.

### SPECIFIC SYSTEMS OF ION EXCHANGE

The system for which most information is available is that using Hydrochloric Acid. It has been systematically studied for virtually every element and oxidation state by Kraus and Coworkers, (review 1956), using Dowex I. Fig. 5 shows the Distribution Coefficients plotted against HCl Molarity.

Several classes of curves may be pointed out:

1. A large number of elements are not adsorbed at any acid concentration, in other words, they do not form negatively charged complexes under these conditions. Notable among these are  $Ni^{++}$  and  $Al^{+++}$

2. For many elements,  $D_v$  decreases with the increased HCl. strength. These are mostly elements of the 2nd. and 3rd. rows of <sup>the</sup> Periodic Table, including those generally known to form strong Chloride complexes - eg. the Platinum Group. Some of these may be eluted with very strong acid - eg.  $Ag^+$ . Most of these are very difficult to remove completely once they are adsorbed.

3. A large number of elements show increasing  $D_v$  with increasing acid concentration, often with an intermediate maximum. These are mostly in the 1st. and 2nd. long rows of the Periodic Table. They may be adsorbed from strong acid, and eluted at successively lower concentrations.

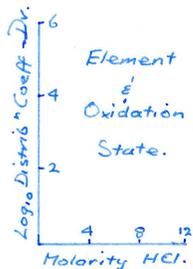
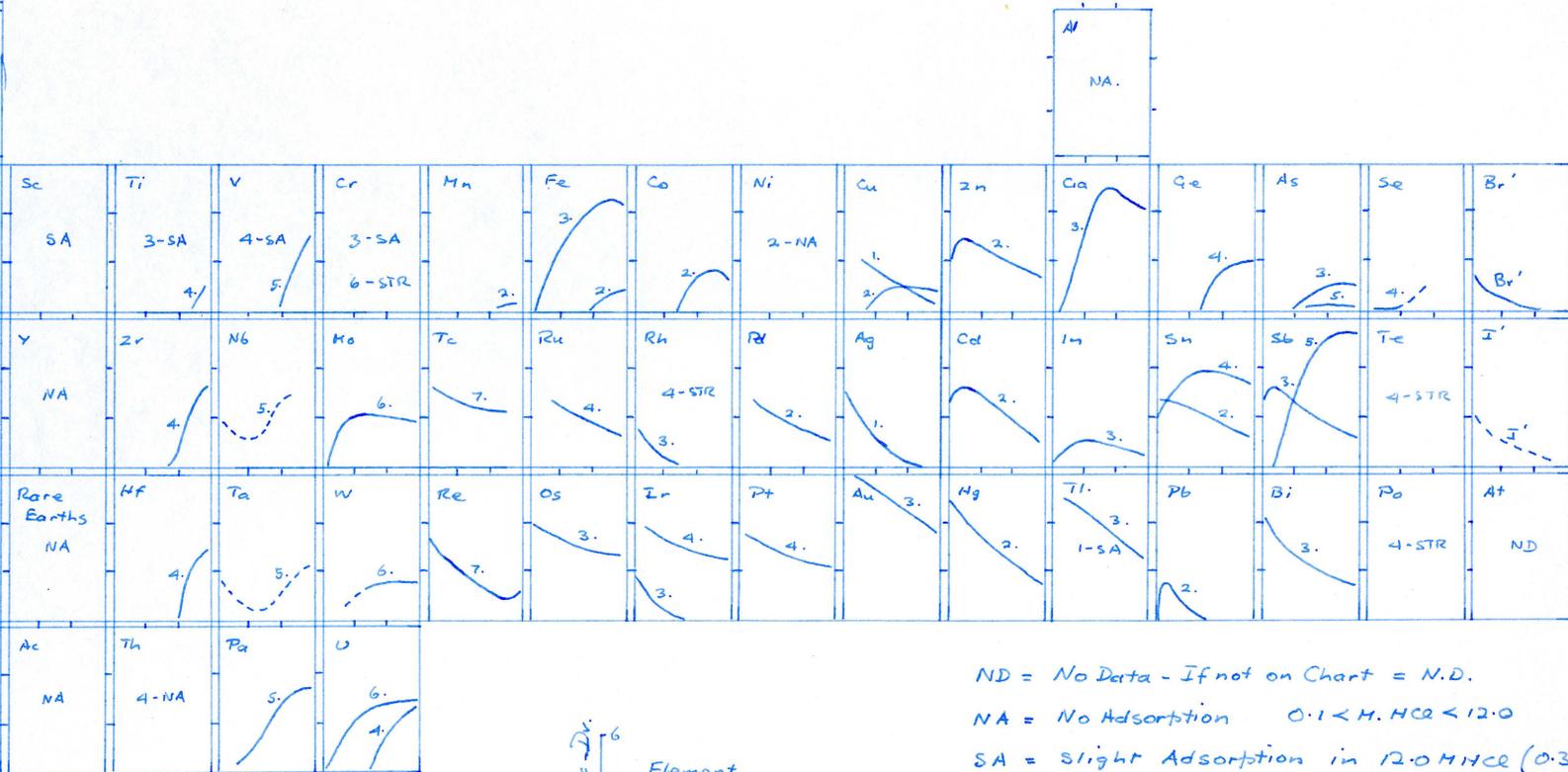
4. Some elements are adsorbed at all acid concentrations.

It is worth noting that due to Hydrolysis difficulties, some of the curves have been extrapolated.

The use of a resin with a different X-number may be expected to

Fig 5 - ADSORPTION OF THE ELEMENTS WITH DOWEX I.  
FROM  
HYDROCHLORIC ACID.

Li	Be
NA	NA
Na	Mg
NA	NA
K	Ca
NA	NA
Rb	Sr
NA	NA
Cs	Ba
NA	NA
Fr	Ra
NA	NA



ND = No Data - If not on Chart = N.D.

NA = No Adsorption  $0.1 < M.HCl < 12.0$

SA = Slight Adsorption in 12.0 M HCl ( $0.3 \leq D_v \leq 1$ )

STR = Strong Adsorption  $D_v \gg 1$ .

ex Kraus, K.A. & Nelson, F

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give similar results, with differences only in details. Thus X8 resin could be used instead of X10 if so desired.

The use with other systems will show more notable differences, depending largely on the stability of the complexes (if formed) compared to the stability of the Chloride complexes. It is not even safe to assume that results for one system will be even qualitatively similar to those using another system. Thus Bismuth is adsorbed at all concentrations of HCl. (see Fig. 11), but is readily eluted with dilute Sulphuric Acid. Use of these facts may be made occasionally in separations.

Better qualitative agreement would be expected in - say - Lithium or Ammonium Chloride systems, while HF, HBr and HI systems for example, may show some similarities. Mixed systems such as HCl-HF, or systems with complexing agents such as Cyanide, have been applied, but the data on these are scanty, and limited as a rule to special problems. The use of  $H_2SO_4$  and  $Na_2CO_3$  systems for the extraction of Uranium by Ion Exchange, is a familiar mineral dressing example.

The presence of traces of other Anions in an HCl. system for example, would not be of any consequence, unless the Anions complexed or precipitated the Trace Metals. Thus a certain degree of Anionic impurity may be tolerated.

Separation Schemes - The Data of Kraus and Coworkers (1956), developed in the first instance for the study of fission product separations, have been used by many people for their own separation problems where an advantage could be gained over conventional procedures. Usually however, only one element was required free from interfering ions or gross impurities. Thiers et al (1955) used Dowex I to separate millimicrogram

quantities of Cobalt in blood, from Iron, Copper and Zinc.

Kraus and Nelson (1956) gave a tentative table (Table #3), for the separation of a large number of elements, based on their work with Dowex I. They are careful to point out that it does not represent a tested scheme. It is based on theory and experiment and was intended as a basis for further work. Similar work on other systems or resins is notably incomplete, but Jentzsch and Pawlik (1956) give details for the separation of a number of elements and oxidation states from Hydrochloric Acid media using Wolfatit L 150 - a mixed base Quaternary and Tertiary Amine Anion Exchange Resin.

The suggested basis of Kraus and Nelson (1956) outlined in Table #3 has been followed in principle for the elements concerned here, but the Molarities of the acid have been modified somewhat, using the original publications as a source of the Adsorption or Elution curves, and data from other workers.

Further information on the data of Fig. 5 and Table #3 may be obtained from the following:

<u>Reference</u>	<u>Elements dealt with-</u>
Kraus, Nelson, and Smith, G.W. J. Phys. Chem. <u>58</u> II, (1954)	Non-adsorbable elements
Kraus, Nelson and Moore, G.E. J. Am. Chem. Soc. <u>75</u> 1460, (1953)	Mn, Fe, Co, Cu, Zn.
Moore, G. E., and Kraus, J. Am. Chem. Soc. <u>74</u> 843, (1952)	Ni, Co.
Nelson and Kraus J. Am. Chem. Soc. <u>77</u> 4508 (1955)	Ge, As.
Huffman, E. H. Lilly, R. C. and Iddings, G.M., J. Am. Chem. Soc. <u>73</u> 4474 (1951)	Nb, Ta.



- Kraus, Nelson and Moore, G.E.  
J. Am. Chem. Soc. 77 3972 (1955) Mo, W,V.
- Sasaki, Y.  
Bull. Chem. Soc. Japan 28 89 (1955) Te, Po.
- Kraus and Nelson.  
J. Am. Chem. Soc. 76 984 (1954) Au.
- Nelson and Kraus  
J. Am. Chem. Soc. 76 5916 (1954) Pb, Bi.
- Kraus and Moore, G.E.  
J. Am. Chem. Soc. 72 4293 (1950) Pa.



Information on Th, Cr, Fe, Cu, Zr, Tc, Ru, Rh, Ag, Cd, Sn, Sb, Hf, Re, Os, Ir, Hg, has not been published. Some details on Cd and Fe for example appear in Kraus and Nelson (1956), where further Bibliography may be found.

The adsorption curves of Co, Cu, Zn, Cd, and Pb are given in Figures 6-10, taken from the appropriate reference or redrawn as indicated from Elution Constant curves using Eq. 3.

Nickel shows no adsorption at any acid concentrations. With the exception of Lead, adsorption from a strong solution of Hydrochloric Acid is indicated, using the principles outlined earlier regarding the Separation Factor  $S$ , and the Distribution Coefficient  $D_v$ .

#### Adsorption and Elution Sequence Chosen-

1. Passage of Solution at  $M \geq 8.0$  (8.5 was used)

Adsorption of Co, Cu, Zn, Cd, and residual Fe (see later).

Effluent contains Ni, Pb, Alkali Metal Chlorides.

2. Elution with  $M 4.0$  HCl. Effluent contains Co.
3. Elution with  $M 2.0$  HCl. Effluent contains Cu.
4. Elution with  $M 0.5$  HCl. Effluent ~~contains~~ residual Fe.

Adsorption Curve - Cobalt.

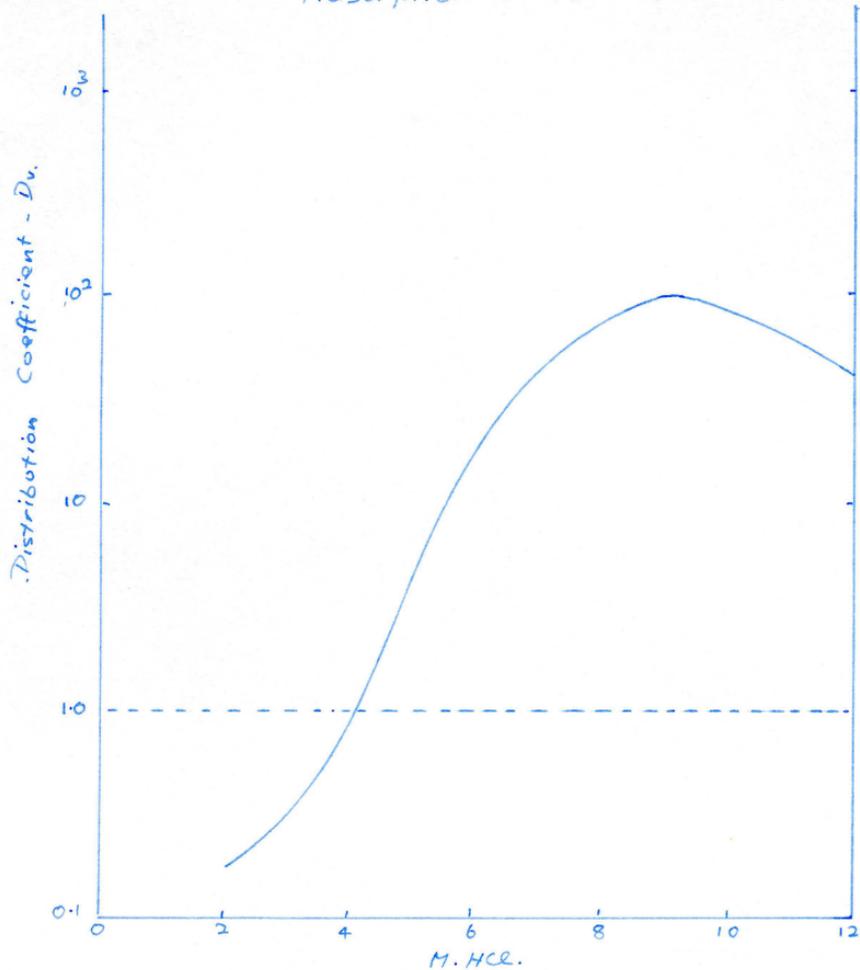
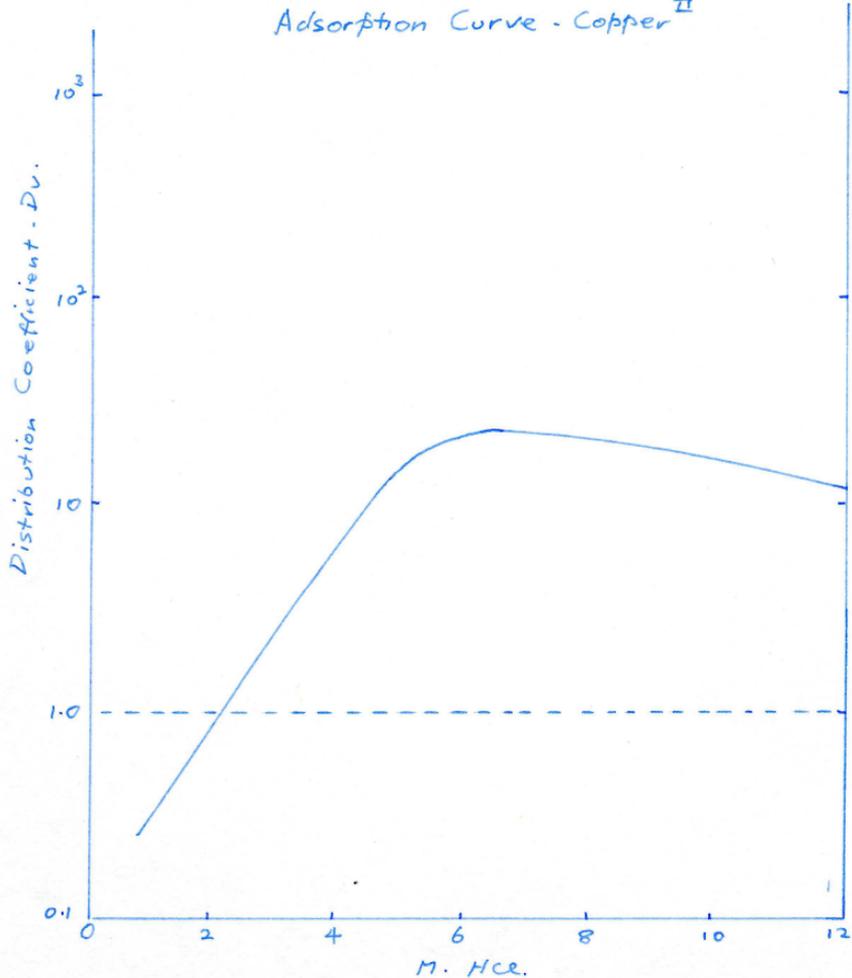


Fig 7.

Adsorption Curve - Copper<sup>II</sup>



Figs. 6 & 7. redrawn from Elution Constant Curves - from Kraus & Moore, G.E. J. Am. Chem. Soc. 75 1460 (1953).

Fig. 8.

Adsorption Curve - Zinc.

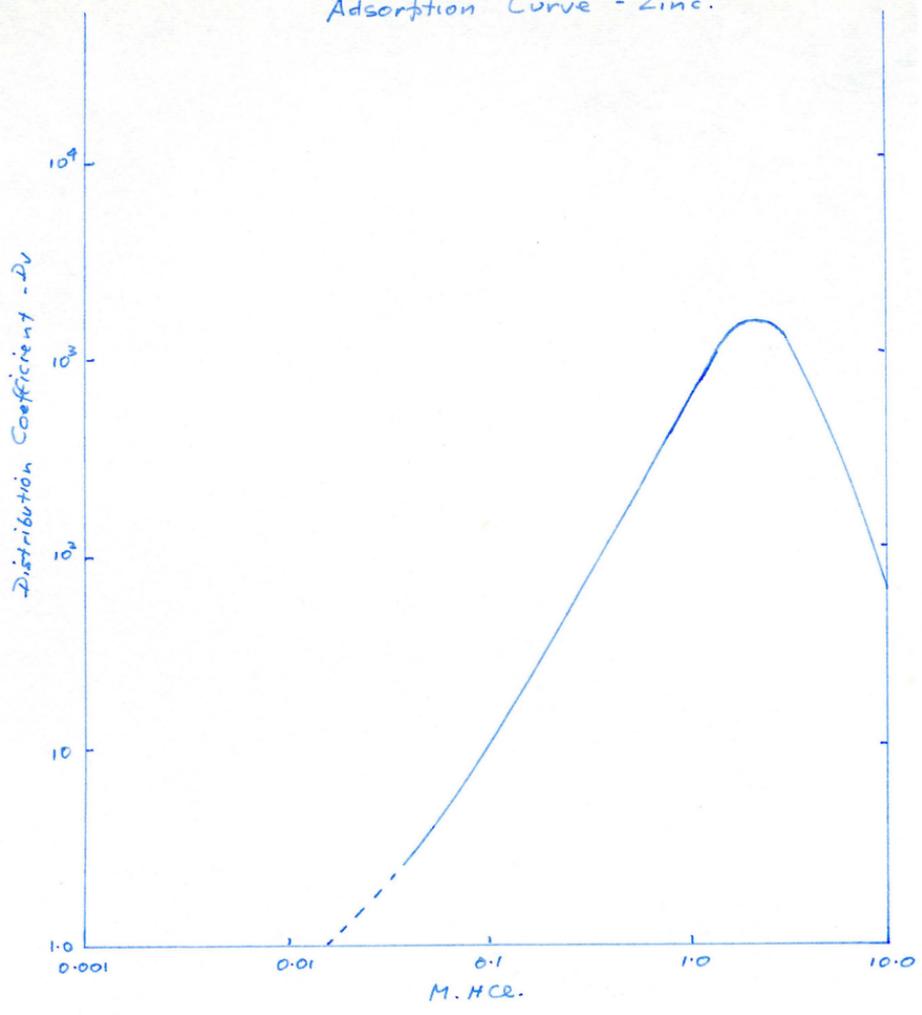
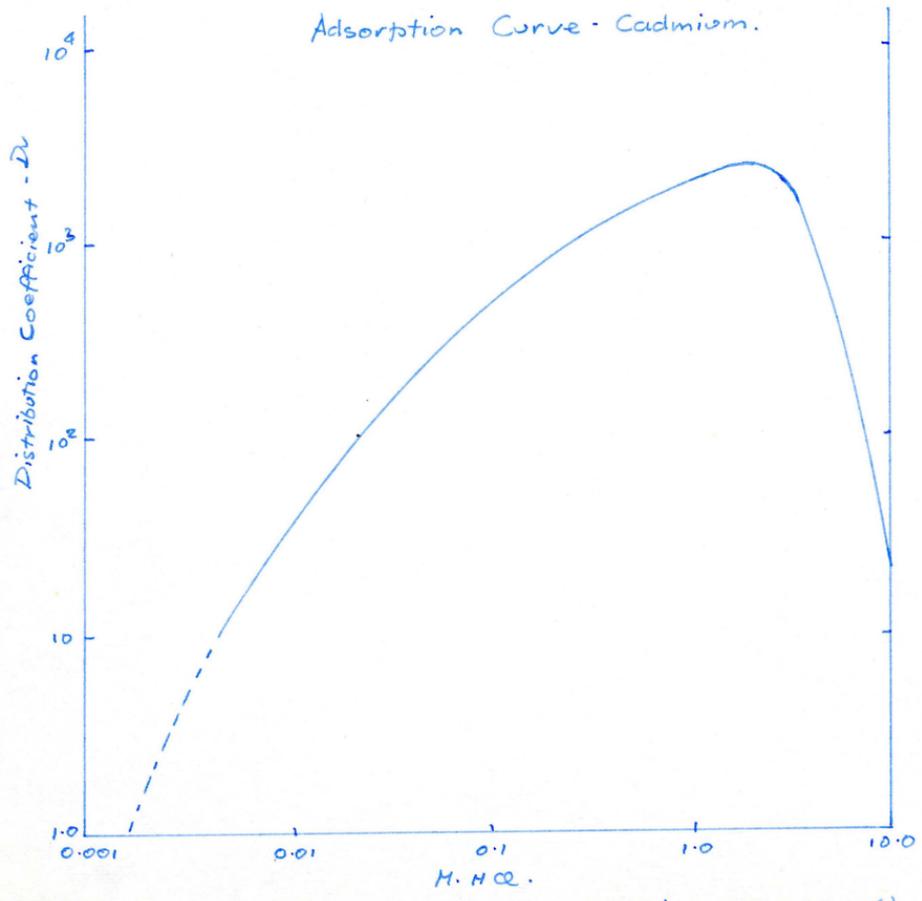


Fig. 9.

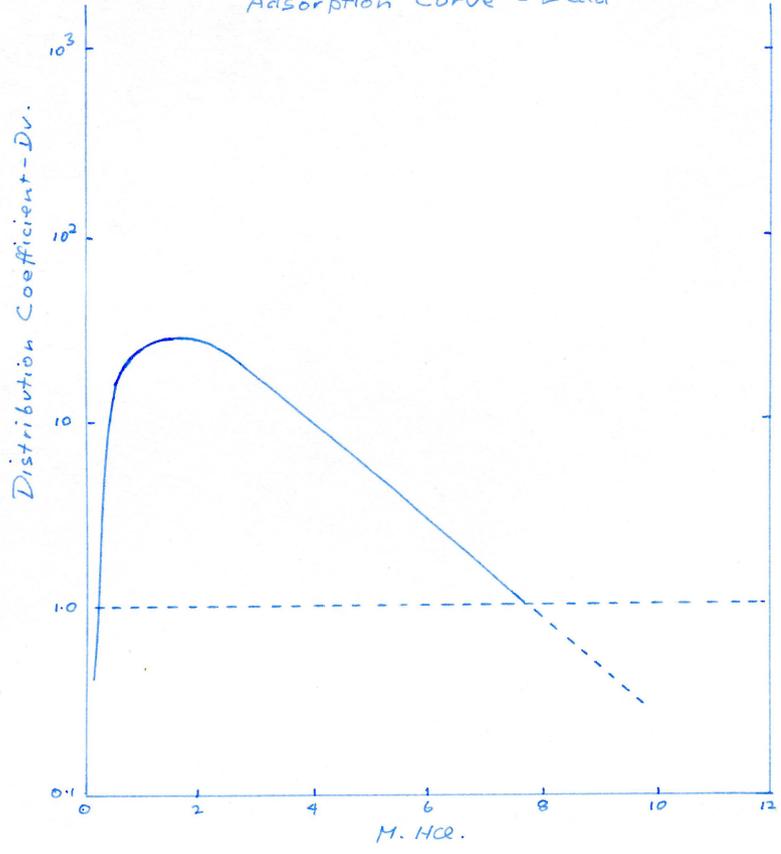
Adsorption Curve - Cadmium.



Figs. 8 & 9. redrawn from Kraus, K.A. & Nelson, F. (1956)

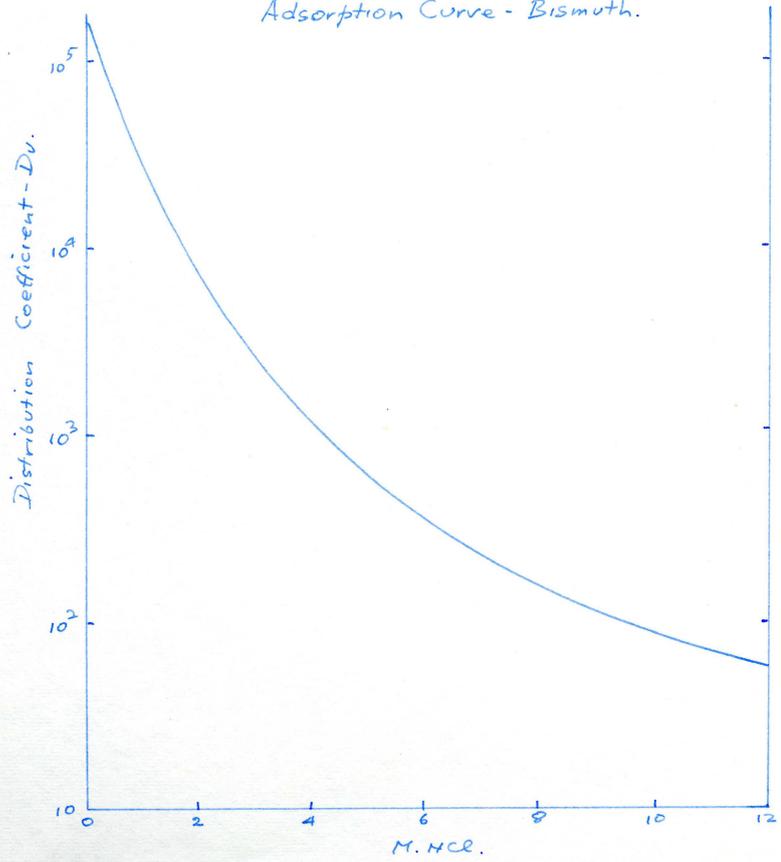
10.

Adsorption Curve - Lead<sup>++</sup>



11.

Adsorption Curve - Bismuth.



Figs. 10&11. Redrawn from Nelson, F, & Kraus, K.A. J. Am. Chem. Soc. 76 5716 (1954)

Note that the values of  $D_V$  for Zn, and Cd are still approximately  $10^2$  and  $10^5$  respectively.

5. Elution with M 0.01 HCl. Effluent contains Zn. Note that  $D_V$  for Cd. is approximately 35 even at this low acid concentration.

6. Elution with M 0.001 HCl or water. Effluent contains Cd.

An alternative separation of Lead is possible, as can be seen from the  $D_V$  curve: the initial passage of the bulk solution is made at M 6.0 HCl, when Lead is also adsorbed; it is then eluted at M 8.0, and the rest of the elements treated as above. Both of these possibilities were tried and found effective.

Adsorption of Hydrochloric Acid - One factor which must be allowed for in the calculation of the volumes of eluant required and the column sizes used, is that Hydrochloric Acid itself is adsorbed by the resin, especially at the higher concentrations (note colour change from buff to brown). Hence proper elution in the above scheme will not begin until the adsorbed acid concentration has adjusted itself to the lower eluting acid concentration. The practical effect is to increase slightly the volumes of eluant needed at the higher concentrations.

#### Practical Considerations

Column Design - Most Ion Exchange experiments are carried out using a simple column, plugged at the bottom to retain the resin. The early work of Kraus and Coworkers (1956) was carried out using relatively large columns, then later on with columns approximately 10 cms. long and 2 mm. in diameter, packed with a -200 mesh resin. From calculations of the weight of resin contained in such a column, it would theoretically

adsorb 0.3 milliequivalents, using 3.5 meq/gm. for the Capacity of the resin and  $i = 0.4$ . Allowing a safety factor of 2 for non optimum conditions, simple calculation shows that it should adsorb from 3mg of Iron, to about 15mg of Lead. Since only the Iron is likely to approach the milligram range, it is therefore the most critical, and for a 0.5gm. sample of Pyrrhotite (FeS) it can be calculated that a preliminary removal of at least 99 per cent of the Iron must be achieved to avoid overloading a column of this size.

This size (ie. 10cms. long and 0.2 cms. diameter) was used for much of the experimental work of this Thesis. However, since the larger mesh resin available (100-150 mesh) caused some packing irregularities and 'channeling', there was very little room for error in the Preliminary Iron separation. The column also gave a rather slow flow rate, despite the larger sized particles used, of only 1 ml. per 6 mins. (30 mins. for the average 5 mls. of effluent). Although this would not be a drawback in the staggered operation of several columns, it was a handicap for single operations.

Later full cycle experiments were carried out using a column 4 cms. long and 0.6 cms. I.D. The flow rate for this column was just under 1 ml. per minute. The Capacity of this column was greater, and so was the safety factor, yet it was found that the separations could be achieved with the same volumes of eluant as before, despite the increased Column Volume - presumably due to reduction of channeling.

It is proposed to use a column of this size, but with a smaller mesh resin (200 - 400) for future work, to give sharper elution bands and avoid air entering the resin.

Resin Pre-treatment - Since the resins tend to scavenge metallic ions from water and reagents during manufacture, and may contain unconverted Amines etc., some pre-treatment before use is usually needed. It may also be necessary to convert the resin to the correct form.

The sample of Dowex - I used, was shaken with Ethyl Alcohol and drained, and the process repeated until the resin had lost its objectionable Amine smell, rinsed with water to remove the alcohol, then in turn with concentrated Hydrochloric Acid (8M) and water.

After each elution cycle, the column was eluted with several 5 ml. portions of water, and reconditioned for the next experiment with Hydrochloric Acid of the appropriate concentration.

The reagents used for the conditioning and pre-treatment were specially purified, as were all reagents used for this work. (see Appendix).

### SAMPLE PREPARATION

Introduction - The manner of preparation of the samples for analysis is limited by the requirements for the Ion Exchange Separation, hence these requirements have been established first.

I do not propose to deal in any great detail with the initial separation of a Mineralogically 'pure' Pyrrhotite sample, since this will be the subject of future work. Regardless of Mineralogical considerations however, it will be essential to avoid contact with metallic objects, and possible metallic contamination at all stages. The basis of separation is expected to be somewhat as follows: Selected fresh fragments will be ground by hand in a Mullite mortar, to pass a 150 or 200 mesh silk screen, carefully separated on a Frantz Isodynamic Separator, followed by removal of dust and fines from the Pyrrhotite fraction by washing in Alcohol, and storage in plastic containers in a dessicator. Control of the purity of the separation will be by microscopic examination and grain counts of mounted representative samples.

Preparation of the Solution for Ion Exchange Separation - The solution of the Trace Elements to be separated by Ion Exchange should comply with the following conditions:

1. The elements must be in the correct oxidation state in a Hydrochloric Acid solution of the chosen concentration.
2. The solution must be freed from at least 99 per cent of the Iron of the original sample.
3. The solution should be free of any extraneous metallic impurities, and Anionic impurities should be present in only small amounts,

or absent completely. Some Alkali Metal Chlorides may be tolerated however.

4. The final solution volume should be small - 5 to 10 mls if possible - and as little chemical and mechanical loss as possible should be involved in its preparation.

Possible Methods - One apparent way to achieve most of the above criteria and which would be of general applicability to most Sulphides would be to carefully roast the specimen in a stream of dust-free air or Oxygen, and to dissolve the residue in concentrated Hydrochloric Acid. The objection to this is that at the temperature at which oxidation proceeds at a reasonable rate ie. > 350 to 400 C, there is the possibility of volatilization losses, more especially for Cadmium and Zinc. No detailed work was done on this problem, but the method may have to be used on some Sulphides, other than Pyrrhotite.

A wet chemical method was therefore used. The fact that Pyrrhotite will dissolve in Hydrochloric Acid was made the basis of the method used:



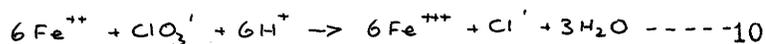
The sample was therefore dissolved in a slight excess of concentrated Hydrochloric Acid, and the solution boiled for a few minutes to promote solution and to drive off Hydrogen Sulphide.

The Iron, and any Copper present, must then be oxidised by an oxidising agent which will not conflict with condition #3 above. Moreover the excess reagent must be removable by means which also satisfy this condition.

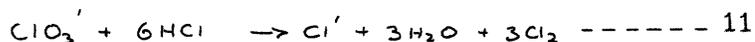
Of several possibilities, Potassium Chlorate was chosen as being the most convenient. A little Bromine was also added with the Potassium

Chlorate, to promote solution of any residue from the boiling with Hydrochloric Acid. Some Pyrrhotite samples left a little residue of Sulphur after the acid treatment, and the Bromine, while not causing complete solution of this residue, converted it from a grey colour, possibly containing 'locked' Sulphide grains, to a pure white colour. This small amount of residue did not apparently have any effect on the results, being filtered off without any difficulty.

The oxidation reaction is as follows:



- while the excess reagent was destroyed by heating with an excess of Hydrochloric Acid:



The Chlorine and any residual Bromine are driven off, and the solution volume reduced to 3 to 5 mls., by boiling, when the excess Hydrochloric Acid will be approximately 6M. (Constant Boiling Mixture).

The solution at this stage should be a rather syrupy dark red-brown liquid possibly containing a little Sulphur. The strength of this solution must then be made up to M8 by addition of approximately 5 to 10 mls. of Hydrochloric Acid of strength  $\approx$  9M. A final volume of 10 to 12 mls. of 8.5 M strength should be aimed at.

This solution was then extracted with isoPropyl Ether. From the data quoted in Sandell, (1959) - p. 45 et. seq., 99 per cent of Fe will be extracted at 6.0 M strength using di-Ethyl Ether, and > 99 per cent at M  $\approx$  8 using isoPropyl Ether. The latter method was chosen, and two extractions were made, to give an ample safety factor for the Ion Exchange

Separation. Almost complete extraction of the Iron cannot be made by repeated extraction, as the Extraction Coefficient decreases sharply with decreased Iron concentration.

Losses during the Solution Procedure - The procedure outlined above results in the partial or complete loss of a number of elements, a point which must be noted if it is ever desired to study these using this Thesis as a starting point.

All elements forming volatile Chlorides or Complexes will be to some extent removed during the boiling with Hydrochloric Acid. Notable among these will be Germanium (completely), Arsenic, Antimony (near complete loss) and such elements as Tin and Bismuth (partially). Many elements, such as Gallium, Gold, and Molybdenum etc. will be extracted by isoPropyl Ether, if present. According to Sandell, (ibid), a Trace of Nickel, approximately 0.2 per cent of Zinc and 0.05 per cent of Copper<sup>present</sup> will also be extracted. The extracted species is usually a Chloro-acid - eg. Chloroferric Acid,  $H FeCl_4$ .

Final Solution Procedure - The actual details of the solution procedure as adopted are as follows:

1. To the weighed sample ( 0.5 gm.) in a conical Pyrex flask add 5 mls. of 6.0 M HCl, and warm. After the initial reaction has subsided, bring the mixture to the boil.
2. If reaction is still sluggish, add another 2 or 3 mls. of 6.0 M HCl. and boil until approximately 5 mls. of liquid remain.
3. Add 5 mls. of 5 per cent  $KClO_3$  solution and a drop of Bromine or a crystal of Potassium Bromide.

4. Stand for a few minutes, then boil to drive off Chlorine and Bromine, and to reduce the volume of solution to 5 mls. or less. Any residue at this stage should be small in amount and white in colour (Sulphur). The evaporation is carried out with a small Polyethylene funnel in the mouth of the conical flask to prevent losses by splashing; allow the flask to cool somewhat.

5. Filter the liquid through a small Polyethylene funnel containing a small plug of glass wool, into a 60 ml Separating Funnel.

6. Wash the flask, funnel splash trap and filter plug with 10 mls. of 9 M HCl, in two 5 ml. portions, and add to the Separating Funnel.

7. Extract the solution with two 10 ml. portions of isoPropyl Ether, shaking vigorously for 2 minutes with each portion. Separate sharply. Transfer the extracted solution to an Ion Exchange Column.

Notes: Stages 1 to 4 should be carried out in a fume cupboard.

The extraction stage results in a little isoPropyl Ether dissolving in the acid solution. This appears to have no effect on the Ion Exchange Separation (no quantitative tests were made however). Some of the dissolved Ether separates out on dilution during the course of the Nickel and Lead determinations. Although it need not be a hindrance in the determination of these elements, it may be evaporated by passage of a stream of filtered air through the solution after the Ion Exchange stage.

## COLOURIMETRY

Introduction - Colourimetry is a rather loosely applied term used to describe the measurement of a substance after conversion into a strongly coloured compound.

The actual measurement of Colour may be more strictly speaking divided into the following fields:

1. Colourimetry - uses 'white' light and makes a comparison of the sample with a standard or standards.

a. Subjective - the observer judges the colour or hue (mixture of colours.)

b. Objective - the comparison is made by a photoelectric cell.

2. Spectrophotometry - uses a narrow band of wavelengths (ideally a 'single wavelength') - not necessarily in the visible spectrum. The fraction of light transmitted or absorbed is measured.

a. Subjective - the observer matches the intensity of sample and standards by mechanical means, eg. neutral wedge.

b. Objective - the transmission is measured by a photoelectric cell or cells. - see below -

Theoretical Considerations - The 'Colour' of a solution is usually measured by finding the percentage of light transmitted at a chosen Wavelength through the material concerned. If the Transmittance T is plotted against the Wavelength, the Transmission Curve is obtained. If the percentage of light absorbed is plotted in place of T, then the Absorption Curve results. The following relationship applies to very

weakly coloured solutions:

$$A = \log \frac{I_0}{I} = abc \quad \text{----- 12}$$

- where A = Absorbance, I = Intensity of the Transmitted Light beam, I<sub>0</sub> Intensity of Incident Light Beam, a = Absorptivity or Coefficient of Extinction, b = length of light path (in cms.) and c = Concentration of Coloured Species.

(Note: the usual convention regarding logarithmic bases is followed, ie. 'log' = log<sub>10</sub> and 'ln' = log<sub>e</sub>)

This relation is known as 'Beer's Law' although strictly speaking the Bouger-Beer law gives the relation between I and I<sub>0</sub> at constant b, while the Lambert Law gives the relation between I and I<sub>0</sub> at constant c, (see Sandell, 1959 p. 75).

If c is given in Moles/litre, then a = ε, the Molar Absorptivity or Molar Extinction Coefficient.

Since the definition of Transmittance T is given by -

$$T = \frac{I}{I_0} \quad \text{----- 13}$$

it follows from Eq. 12. that  $A = -\log T$  ----- 14

Sensitivity - The Sensitivity S of a colour reaction may be defined as the smallest detectable weight of substance (usually given in micrograms) which can be detected in a column of solution of unit cross-section (usually 1 cm<sup>2</sup>) as a highly coloured species. Note that no account of the length of the column b, enters this definition, hence the actual concentration c, of the unknown is immaterial. If as in many cases, b equals 1 cm., then the sensitivity in γ/cm<sup>2</sup> will be numerically equal to the concentration of the unknown in γ/cm<sup>3</sup> or ppm, if the density of the solution is 1 gm/cc.

It need scarcely be said that values of  $S$  should be qualified by exact conditions of determination, but it is often assumed that optimum conditions are implied for any particular colour-forming reagent.

The Sensitivity  $S$ , is controlled by two factors:

1. - the Intrinsic Sensitivity, which is proportional to  $\epsilon$ .
2. - the smallest difference in  $c$  which an observer can detect - with or without equipment.

Visual Sensitivity - This is largely controlled by probability, ie. the value of  $S$  is given at which it is highly probable that a (trained) observer can detect a difference (in colour) from a 'blank'. The error in  $c$  increases rapidly as this value is approached, but becomes somewhat constant, at  $\pm 10$  per cent, when  $c \geq 15s$  (approximately). Some Visual Sensitivities are given in Table 4.

Spectrophotometric Sensitivity - There are two other factors affecting Spectrophotometric Sensitivity:

1. The Wavelength  $\lambda$ , at which the determination is made. Curves of  $T$  or  $A$  vs. Wavelength  $\lambda$ , usually show one or more maxima or minima, and it is usual to select a Wavelength at which  $A$  is a maximum.
2. The Reproducibility of a measurement of  $T$ . This includes mechanical, scale reading and setting errors. The full utilization of the potential photoelectric sensitivity depends much on the instrument design, but, other things being equal, the photoelectric sensitivity will affect the general reliability of results, particularly at the lower concentration levels.

It is usual to assume that current instruments will detect a difference of 0.001 in  $A$ , which corresponds to 0.2 per cent  $T$  (more or

Table IX - Comparison of Some Visual and Spectrophotometric Sensitivities - in  $\mu\text{g}/\text{cm}^2$ .

Element	Reagent	Sens. <sup>y</sup>	
		Visual.	Spectro-Ph.
Al.	Aurintricarboxylate pH=5.5	0.01	0.002
Au.	p-Diethylaminobenzylidinerhodanine	0.05-0.1	0.01
Be.	Morin (fluorescence)	0.002	0.0005
Bi.	Iodide	0.5	0.006
Cd.	Dithizone	0.03	0.0014
Co.	Nitroso-R Salt	0.01	0.0019
Cu.	Diethyldithiocarbamate-Water	0.05	0.004
Fe.	o-Phenanthroline	0.05	0.005
Hg.	Titan Yellow	0.05	0.017
Mn.	MnO <sub>4</sub> <sup>-</sup>	0.1	0.027
Ni.	Bromine-Dimethylglyoxime	0.05-0.1	0.0092
Pt.	Iodide	0.5	0.05
W.	Thiocyanate - Stannous Chloride	0.3	0.013

Figures selected from Sandell-(1959)

Note: The Spectrophotometric Sensitivities are those corresponding to  $\text{Log} \frac{I_0}{I} = 0.001$ .

less), and hence sensitivities are usually quoted for the concentration of substance which will produce a change of  $A$  equal to 0.001. Some sensitivities on this basis are included in Table 4. Note the not-so-large gap between Visual and Spectrophotometric methods, and the generally high sensitivity of both methods in the light of the definition of a 'Trace Element' given earlier. That these  $S$  values are not usually achieved in practice is usually due to less elaborate methods or larger errors at other stages of the determination.

Spectrophotometer Operation - The section on Errors to follow will be clearer if the general principles and operating procedure for the Spectrophotometer are set out here. The Beckman Model D.U. consists essentially of a light source backed by a Condensing Mirror which reflects the light onto the Entry Mirror from which it is reflected through the Entry Slit into the Monochromator Housing (see Fig. 12). The light is focused by a Collimating Mirror into a Quartz Prism where it is refracted on entry, reflected off the silvered rear surface and refracted further on emergence from the Prism. The angle of incidence of the white light on the Prism is altered by rotating the Wavelength Selector. The refracted light is focused again by the Collimating Mirror onto the Exit Slit, where light of the chosen Wavelength emerges, passes through the specimen, and causes a current gain on striking the Phototube. The current gain is amplified and balanced on a Null-Meter by rotating the Absorbance-Transmittance control.

The first stage of the operation consists of setting up the desired Wavelength, and adjusting the Exit Slit width, Sensitivity and 'Dark Current Control' until there is no deflection on the Null-Meter.

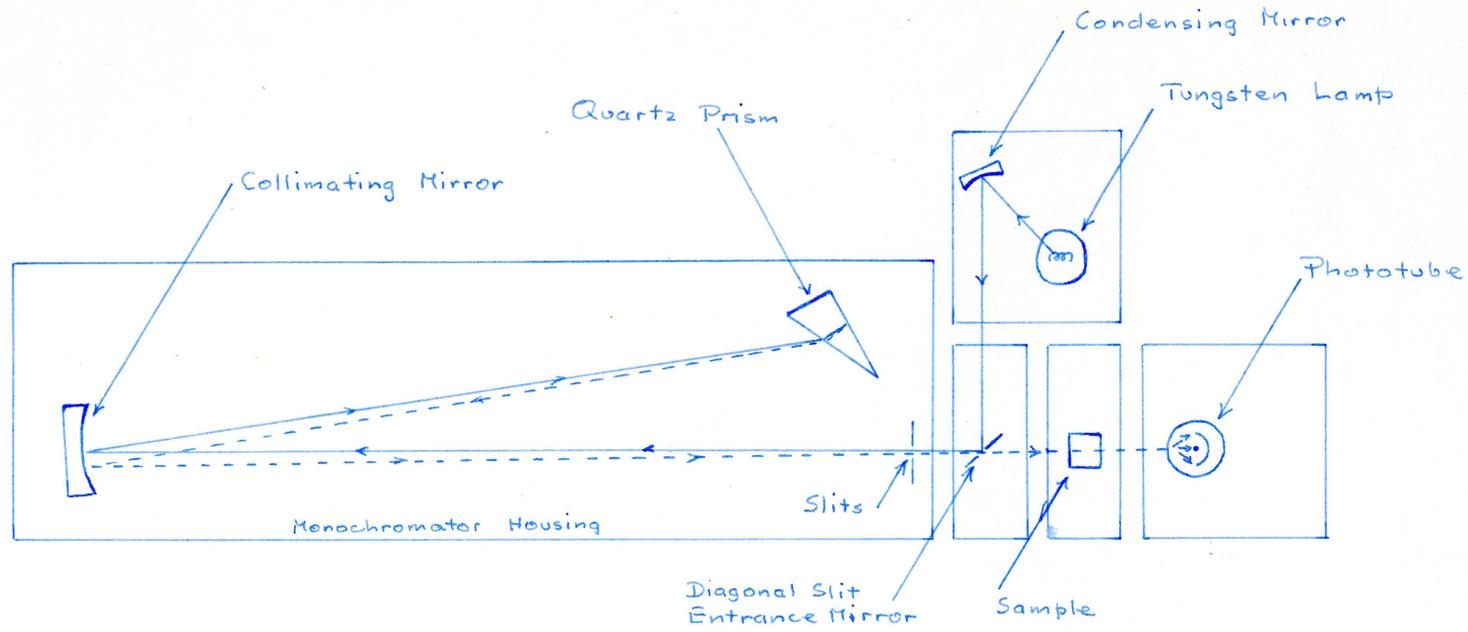


Fig. 12 - Optical System of Beckman Model D. U. Spectrophotometer.

from: Beckman Manual # 305.

This is necessary due, among other factors, to the fact that the output of the Tungsten Lamp and the response of the Phototube differ from Wavelength to Wavelength.

No direct determination of the Transmittance of the coloured solution is possible, since it must be held in a transparent container, which has its own Transmittance, as well as reflection and refraction effects. The solvents and any other dissolved substances will also contribute to the total Absorbance.

Thus it is usual to determine the Transmittance of the sample against a pure solvent or reference standard (often water) in an identical cell, after this standard has been adjusted to read  $T = 100$  per cent. This method then compensates subsequent readings for the cell effects. (see also p.36).

The full operating procedure is given in Appendix 6.

Errors in Spectrophotometry - It may be helpful at this stage to define these facts concerning Errors:

Errors may be Random or Systematic.

Random Errors affect the Reproducibility of the results - ie. the Precision.

Systematic Errors affect the proximity of the results to the truth - ie. the Accuracy.

Both Precision and Accuracy may be implied by the general term Reliability - Grideman, (1952).

Further consideration of equation 14 -  $A = -\log T$ , provides some useful information on Precision, as follows:

by differentiation w.r.t.  $T$  -

$$\frac{dA}{dT} = -\frac{\log e}{T} \quad \text{-----15}$$

by dividing by A and substituting from Eq. 14.

$$A \frac{dA}{dT} = - \frac{\log e}{AT} = \frac{\log e}{T \log T} = \frac{1}{T \ln T} \quad \text{--- 16}$$

ie.

$$\frac{dA/A}{dT} = \frac{1}{T \ln T} = F \quad \text{--- 17}$$

- where F = 'Error Function', and is, in words, the 'fractional deviation' in A divided by the 'absolute deviation in T' -

A plot of F against T gives the curve known as the Twyman-Lothian function, (see Fig. 13).

Now let  $\sigma_G$  = standard deviation of a Galvanometer reading.

$\sigma_T$  = Standard deviation of a Unit of Transmittance on the 0-100 per cent scale.

$\sigma_t$  = standard deviation of Actual Transmittance T, on the 0- 1.0 scale.

$\sigma_A$  = standard deviation of A.

We may then make the following assumptions, and derive some practical value from the Twyman-Lothian curve:

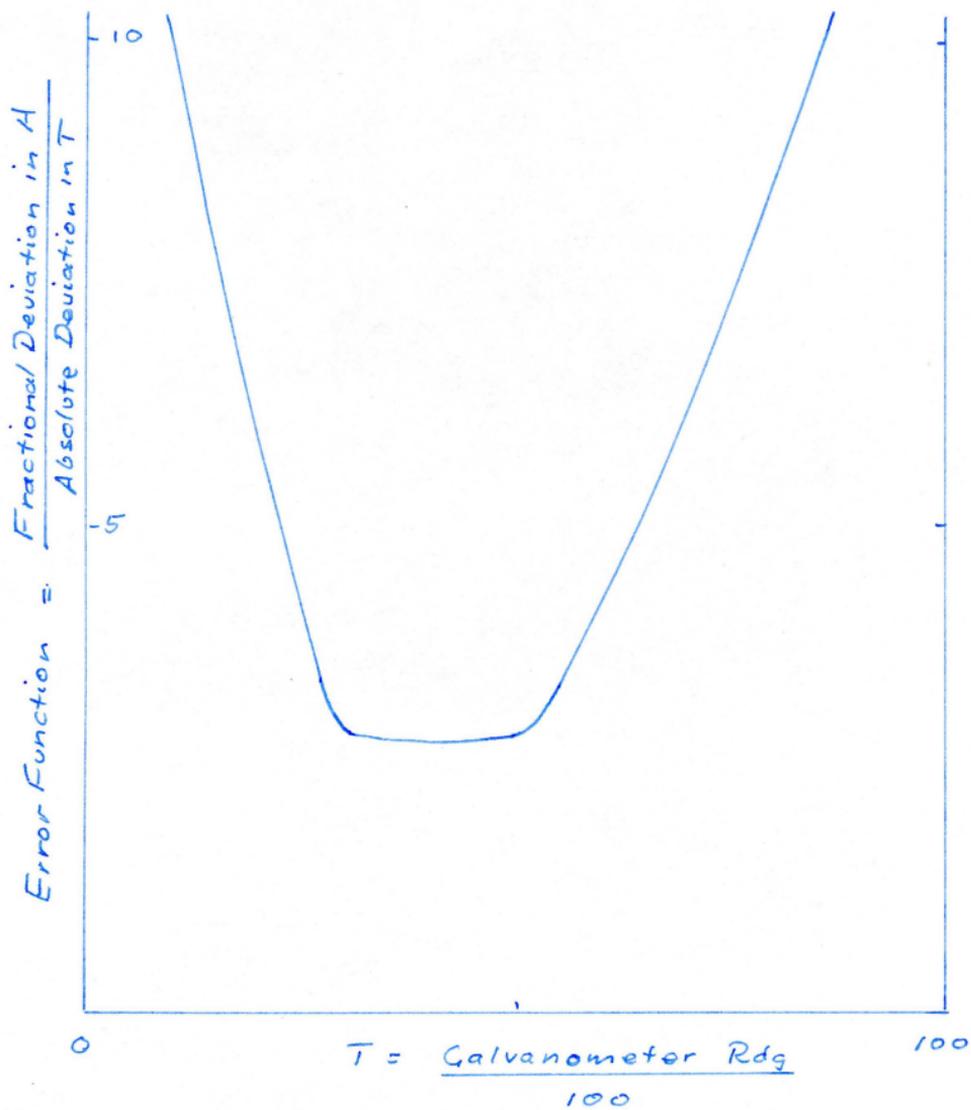
1.  $\sigma_G$  is uniform at all points of the scale.
2. That the 0-100 per cent Transmittance scale is an exact linear reflection of 0-1.0 Transmittance, and in particular that

$$\sigma_G = 100 \sigma_T \quad \text{--- 18.}$$

3. That the 'trim' of the Galvanometer scale is perfect when the sample solution is being measured - ie. it is assumed that there are no mechanical or other 'setting errors' or in other words that  $\sigma_t$  is the only operative error.

How much these assumptions are valid in practice depends on instrument characteristics. According to Grideman (1952), assumptions

Fig. 13. Twyman-Lothian Function  
(idealized)



1 and 2 are generally true for most instruments, but assumption 3 is strongly dependent on the constancy of the 'Dark Current' - which in turn depends much on the quality of the power supply unit. Assumption 3 is open to doubt from other considerations too.

Given these assumptions, we may now validly substitute  $\delta A$  for  $dA$ , and  $\delta t$  for  $dT$  in Eq. 17. -

ie. 
$$\frac{\delta A/A}{\delta t} = \frac{1}{T \ln T} = F. \quad \text{----- 19}$$

Now let the error in setting the Dark Current to zero on the Galvanometer scale be  $z \delta t$ , and the error in setting the Unit Transmittance point (100 per cent T) on the Transmittance scale to  $u \delta t$ , where  $z$  and  $u$  are arbitrary numerical factors. These errors will of course contribute to the uncertainty of the estimate of T for the Sample, in addition to that covered by  $\delta t$  alone.

Furthermore they will be dependent on T thus:

Source of Error	Effect on estimate T of the Sample
Reading of Sample Transmittance	$T \pm \delta t = T \pm p.$
Setting of Zero Transmittance	$T(1 \pm T)z \delta t = T \pm q.$
Setting of Unit Transmittance	$T \pm Tu \delta t = T \pm r.$

If it is assumed that these three errors are completely independent of each other, then their joint contribution to the total error of T is  $\sqrt{p^2 + q^2 + r^2}$ . Hence the final estimate of T is, by expansion:

$$T \pm \delta t \sqrt{T^2(z^2 + u^2) - 2Tz^2 + z^2 + 1} \quad \text{----- 20}$$

We may now modify the Error Function F, by substituting this revised function of  $\delta t$ , for  $\delta t$  in Eq. 19.

ie. 
$$\frac{\delta A/A}{\delta t \sqrt{T^2(z^2 + u^2) - 2Tz^2 + z^2 + 1}} = \frac{1}{T \ln T} \quad \text{----- 21}$$

$$\text{but } F = \frac{\epsilon A / A}{\epsilon t}$$

$$\text{therefore it follows that } F = \frac{\sqrt{T^2(z^2+u^2) - 2Tz^2 + z^2 + 1}}{T \epsilon u T} \quad -22$$

It will be noted that this is the Twyman-Lothian function if  $z = u = 0$ .

F is infinite for  $T = 0$  or  $1$ , but has an intermediate minimum when

$$f'(F) = 0 -$$

$$\text{ie. when } \epsilon u T = \frac{T^2(z^2+u^2) - 2Tz^2 + z^2 + 1}{Tz^2 - z^2 - 1} \quad - - - - - 23$$

(the differentiation is straight forward and the working has therefore been omitted). To find optimum conditions it only remains to substitute likely values of  $z$  and  $u$ . The minimum always lies between 2.7 and 4.8 for  $z$  and  $u$  values up to 2.0. This corresponds to values of  $T$  between 0.27 and 0.52 (ie. 27 per cent and 52 per cent). Since the Error Curves are rather flat in this region, approximately 30 per cent - 50 per cent is the optimum working range even if  $z$  and  $u$  are not exactly known. This range is also recommended in good working practice even if the assumptions made at the beginning of this section are not completely valid, as the nature of the curves will cover slight departures from validity.

It should be emphasized that the above working does not affect the Accuracy of the results, but only the Reproducibility. In this particular work, the reproducibility of the colour measurement is probably of more importance than the accuracy attainable with the Spectrophotometer, since the accuracy is liable to be controlled by the stages before the actual colour measurement.

Practical Considerations - A number of more practical factors enter into the use of the Spectrophotometer.

Band Width - The dispersion of the Quartz Prism is non linear with Wavelength. This means that the Spectral Slit Width transmitted by the Exit Slit varies with Wavelength, and is in fact, smallest in the Ultra-violet and Infra-red regions. Hence, since some of the Absorption Maxima used in Colourimetry are rather sharp, it is important to keep the Exit Slit width to a minimum, in order to approach as nearly as possible the ideal 'Single Wavelength'. This also has the advantage that the Phototubes may be operated at higher sensitivities on the reduced intensity of the transmitted light beam. Due to diffraction and other aberrations however, the effective Slit Width tends to a constant value  $\approx 0.03$  mm. - as the actual Slit Width is decreased. Further reduction of the Slit Width serves largely to reduce the Intensity of the transmitted light.

Dispersion data for the Beckman Model D.U. are given in the Beckman Manual #305.

Cell Effects - A number of important factors must be described in connection with the Absorption Cells.

It is obvious that, apart from dictating the volume of solution used in a determination, the Cells will add their own contribution to the Absorption recorded at any particular Wavelength. The Cells supplied by the Manufacturers consist of 'Matched Sets' - usually of four Cells. These are guaranteed to be matched within certain limits of Light Path Length and Transmittance at a stated Wavelength. In the case of the Cells supplied by Beckman Instruments Inc., these tolerances are 2 per cent Transmittance at  $320 \text{ m}\mu$ , and 0.5 per cent Light Path Length.

In routine work, it is seldom necessary to make the small corrections for Light Path Length and Cell Absorption. However, in more precise

work it may be necessary to calibrate each Cell at every Wavelength used, and for every different solvent used, as well as correcting for the Light Path Differences.

In this Thesis no corrections were made to any of the results which will be set out later, although the Cells were calibrated and corrections worked out for a few results to see the magnitude of the effect. As expected, the corrections were too small to justify their inclusion in the results at this level. With a more sensitive Photomultiplier, and with more refined techniques, these corrections should be applied as standard procedure. The calibrating procedure is set out in the Beckman Manual #305.

The Cells, when in use, are an integral part of the Optical train of the Spectrophotometer, hence they must be handled and cleaned with the appropriate care. The method frequently advocated for filling and emptying Cells, and for rinsing out with solvent or solution by means of a pipette was found to be tedious and decidedly inefficient, especially since the determinations involve changes from aqueous solutions to organic solvents. It was found more practical and far quicker to empty each Cell after use, and rinse out with one or two strong jets of deionized water from a wash bottle. The outside optical surfaces were wiped dry with lens tissue, and the Cell was dried by placing in an oven at 100°C for a few minutes. The dried Cells were placed in the Cell Holder and allowed to cool before filling again. This method was found effective for both aqueous and organic solutions, and allowed preparation to take place for the subsequent determinations while the Cells were drying. Water-Alcohol-Ether washing and drying was also found effective.

In the Beckman Model D.U., there is part of the Wavelength Scale which is covered by both the Red-sensitive and Blue-sensitive Phototubes. The same solution may not give the same Transmittance values with each tube, due to enhanced errors near the working limits of each tube. Provided the instrument is in normal working order, these errors will be reproducible, and thus they can be allowed for by the use of Working Curves. Changes in the magnitude of these and other errors, or in other words, failure of the instrument to reproduce readings, is frequently an indication that the Phototube concerned is nearing the end of its life - (M. Mallard, Personal Communication.)

This is of some importance, since the instrument may in all other respects appear to be functioning normally.

## COLOURIMETRIC REAGENTS

Introduction - A good Colourimetric Reagent should show the following three desirable properties:

1. Sensitivity - The Trace Element should produce a very strongly coloured compound with the reagent. The more strongly coloured the compound is, then the less Trace Element will be needed to produce a given colour density. In other words, the reagent will be more sensitive, other things being equal. Some reagent sensitivities for the appropriate ions have been given earlier.

2. Selectivity - Ideally the reagent should react with only one ion, or at least, produce a strongly coloured species with only one ion. The reagent is then said to be Specific for that ion. If a reagent, as is usually the case, is not Specific, then it is obviously of little value if the other reacting ions are also present in the sample. Thus the majority of Colourimetric Reagents require varying amounts of preparatory work to eliminate or reduce the effects of the interfering ions.

3. Stability - Both the reagent and the coloured species formed should be stable, or stable enough to give reproducible results under stated conditions.

A number of other factors which may be of importance will suggest themselves to the reader. For example, the reagent should not be too highly coloured itself, and its coloured compounds should have Adsorption maxima different from those of the pure reagent. It should react under a fairly wide range of conditions such as pH. and concentration, and should not react with any other substances such as acids, salts, etc., which might also be present in the sample solution. Factors such as cost and availability may also be important.

Reagent Purity and Blank Determinations - Whether or not a reagent is Specific, if it is as Sensitive as is usually desirable, then precautions must be taken to eliminate or compensate for any reacting Trace Element present in the reagents used. It is quite commonly the case that the purest commercially available solvents and reagents contain more Trace Element than the sample to be analysed. Consequently the further purification of virtually all reagents used is the rule rather than the exception.

Full details of all purification procedures adopted in this Thesis, will be found in Appendices 2 to 5.

Despite purification, there is still the problem of residual Trace Elements to be considered, since it is not always possible to purify all reagents to below the limit of detection of the Colourimetric method, particularly if large volumes of solvents or digesting acids are involved before the final step. Also, because of this residual Trace Element problem, Absorbance readings are likely to vary if volumes or weights of reagents are altered at all - say to accommodate a larger sample - quite apart from the contribution due to the sample itself. To allow for this factor, it is usual to run 'Blank' determinations. This entails carrying a determination right through the entire procedure, but without the sample, using the exact weights and volumes of reagents and solvents, and to determine the Absorbance as if a sample had been used. A reading will be obtained, which will be the sum of the Absorbance due to the reagents and the residual Trace Element. This value - the 'Blank' - is then subtracted from subsequent determinations with actual samples, when the difference, if any, will be due to the Trace Element from the sample itself.

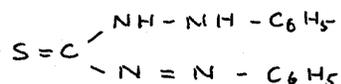
It may be possible to convert the Blank reading into a concentration of Trace Element, but this is tedious and for the most part not necessary. There is no rigid ruling about when, or how many Blanks should be made. It depends on the determination in question, and the accuracy involved. Blanks should be carried out for every batch of reagents or solvents, and for each Trace Element concerned, and this should be repeated when any fresh solutions are made up, or when volumes or concentrations of reagents are altered in any way. It is rarely necessary to run a Blank to go with each actual sample determination, unless highly unstable reagents or solutions are being used, in which case it would be better to change to another method to avoid this tedious procedure.

It is customary to run a blank for each day's work, or for each batch of samples. If however the constancy of the Blanks from day to day indicate little change or deterioration in the reagents due to storage, then less frequent Blanks may be run. This was the case in many of the determinations involved in this Thesis. Even a stock solution of Dithizone, supposed by some Authors to be highly unstable when kept at room temperature, showed only slight changes in Absorbance readings and Blank determinations over a period of five months. In this connection, extra time and effort taken in the initial purification stages, will often more than pay for itself in the stability of solutions and time saved through less frequent Blank determinations at a later stage.

Colourimetric Reagents Used - Much of the theoretical detail to follow is based on the very complete information given by Sandell (1959). Fur-

ther information, and a very complete Bibliography will be found therein under the appropriate headings.

Dithizone: Dithizone, or more fully Diphenylthiocarbazone -



- is one of the most valuable reagents available for many Colourimetric determinations. There is a considerable volume of literature dealing with it and its applications to Trace analysis - (see Sandell p. 139 et. seq.)

Under suitable conditions, Dithizone will react with the following metals: Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cd, In, Sn, Te, Pt, Au, Hg, Tl, Pb, Bi, and Po.

This is at once a source of versatility and also of considerable interference troubles. Frequently elaborate separation and complexing procedures are entailed with the use of Dithizone in normal Colourimetric methods.

Dithizone is a dibasic acid, insoluble in acid solutions, but soluble in organic solvents and in basic solutions, when it forms a soluble salt. The solutions in organic solvents are an intense green in colour, and these are usually used in the 'Solvent Extraction' type of determination. Carbon Tetrachloride and Chloroform are the most common laboratory solvents used, but White Spirit, Xylene, Toluene etc, are often used in field applications.

Dithizone reacts to give a Primary (Monobasic) extractable Internal Complex with the Metal ions. A secondary (Dibasic) complex may also be formed in some cases. The varying conditions of pH, acid or base strength, the varying stability of the complexes, and the use of complexing agents, form the basis of the many determinations possible with Dithizone.

The pH. is usually the most critical factor in a Dithizone determination, with acid or base strength often important too. The pH. for optimum extraction and optimum reaction may not be the same, while the limits within which reaction or extraction may take place also vary considerably from metal to metal.

Stability of Dithizone - Dithizone has a number of properties undesirable in a Colourimetric reagent, the most serious of these being its very rapid oxidation under certain conditions. It is oxidized atmospherically, especially under the influence of light, while Ferric ion for example, oxidizes it readily in basic solutions. The first product, Diphenylthiocarbadiazone, can be reduced easily to Dithizone again by mild reducing agents, but further oxidation products are permanent. Both Dithizone and the Dithizonates especially, are light sensitive. Thus Dithizone solutions must be stored in the dark, and all Dithizonates determined without delay. Dithizone solutions are decidedly sensitive to impurities, not only metallic but also organic. These may inhibit Dithizonate formation - eg. in Copper determinations.

However, in spite of these adverse properties, Dithizone is capable of giving consistent and reliable results. The successful use of Dithizone depends, as many workers have pointed out, upon the careful and thorough purification of all solvents and reagents. The same 0.01 per cent (w/v) stock solution of Dithizone in Carbon Tetrachloride, stored in a foil-covered Pyrex bottle, was used for this Project over a period of five months. 0.001 per cent working solutions prepared from this stock solution showed very little variation in Transmittance or Blank Absorbance over this period. A 0.001 per cent solution gave the same Transmittance reading after 24 hours, and showed an increase of 1.5 per cent T. after 7 days

(measured at 530 m $\mu$ ). Carefully purified Carbon Tetrachloride was used for both stock and working solutions - see Appendix 2 and 3.

Determination of Individual Elements - Some of the essential conditions for the determination of Lead, Copper, Zinc and Cadmium will now be set out. The step-by-step procedure will be given later.

Appendix 1.

Lead - The solution containing the Trace Lead may also contain Nickel, and any of the ions which are not adsorbed at this acid strength, if present. Of these, Silver, Manganese, and Nickel also react with Dithizone. The optimum pH. for the extraction of Lead Dithizonate using a Carbon Tetrachloride solution of Dithizone is 10.8, according to Mathre (quoted in Sandell 1959). It appears that little error will result if the extraction is made between pH. 10.5 and 11.5. The addition of Potassium Cyanide will effectively prevent interference from Nickel, Silver or Manganese, if present. The solubility of Lead Dithizonate in Carbon Tetrachloride is rather small, hence any sign of a pink precipitate upon extraction with the Dithizone solution must be watched for. The difficulty may be overcome by taking a smaller aliquot of the solution for the determination. Further difficulties may be encountered due to the fact that Lead is an extremely common Trace impurity in many reagents. Reagents for Lead determinations should be carefully purified.

Copper - The solution containing the Copper should contain no other Trace Element. Thus the Copper may be determined under optimum conditions - in dilute acid solution = 0.1M (HCl) for a Carbon Tetrachloride solution of Dithizone. Above 0.1M acid strength, reaction is slow, and may be incomplete. The purity of the Carbon Tetrachloride is also very important.

Zinc - The solution containing the Zinc should contain no other Trace Element. The Eluting acid strength must be accurate, as slow or incomplete Elution will result if the strength is too high, and Cadmium will be eluted if the strength is too low. Zinc reacts readily in both weakly acidic or weakly basic solutions. Extraction at pH.5.5 was used, since a buffer of this pH. was available from the Cobalt determination.

Cadmium - The solution containing the Cadmium will also be free from contaminating ions if the Elution is carried out correctly. Cadmium reacts readily with Dithizone, especially in basic media. Most published procedures utilize a high pH. for extraction, chiefly for the purposes of separating Cadmium from interfering elements. A faintly alkaline medium was chosen. The solubility of Cadmium Dithizonate in Carbon Tetrachloride is not very great, but this should not be a handicap, since what little data there are concerning Cadmium in Sulphides suggests that the concentration levels are very low.

Dimethyl Glyoxime - The Dioximes are the only reagents finding serious use for the determination of Nickel, Dimethyl Glyoxime being the most popular. It forms a deep wine-red solution or a pink precipitate of Nickel Dimethyl Glyoximate with Nickel ions.

Several procedures for the Quantitative determination of Nickel with Dimethyl Glyoxime are available, some of them largely empirical. The method for the determination of Nickel on the solution resulting from the Ion Exchange Separation presented in fact, far more difficulties than the remainder of the determinations, and I am still not entirely satisfied that it could not be improved. The chief objection at present is the large dilution factor and the consequent reduction in accuracy.

The methods available are briefly as follows:

1. Extraction of the Nickel Dimethyl Glyoximate complex from slightly acidic to fairly basic media (pH. range 4 - 11) with Chloroform, followed by the determination of the Absorption of the extract at a near Ultra-violet Wavelength.
2. As above - but with extraction of the Nickel from the Chloroform extract with dilute acid at  $\text{pH} < 4$  and determination as Nickel Dimethyl - Glyoximate in strongly basic solution in the presence of Bromine as oxidizing agent.
3. As for #2 above, but using Potassium Persulphate as oxidizing agent. Methods #2, and #3 may be made without a prior extraction in the absence of certain interfering ions.
4. The High Alkaline procedure of Oelschläger (1955a) - using Ammonium Persulphate as oxidizing agent. This was the procedure finally adopted.

Most of the difficulties arose from the fact that final determination required a strongly alkaline medium, while the Nickel Sample solution was strongly acidic (8M in HCl). Procedure #1 was tried and gave erratic results due to precipitation of Sodium Chloride on addition of the Alcoholic solution of Dimethyl Glyoxime called for. The Alcohol lowered the solubility of the Sodium Chloride formed during the neutralization, enough to cause it to precipitate. The precipitate, apart from transferring itself in part to the extract as finely divided crystals which caused Absorbance errors, also seemed to 'seed' some Nickel precipitation, especially in the stronger Nickel solutions, as recoveries at higher Nickel concentrations were very low. This could be remedied by making an adequate dilution, but only at the expense of accuracy. A preliminary separation of the Nickel complex from the

diluted solution, as in procedures 2 or 3, was also tried, to avoid a large dilution factor. This made the method somewhat lengthy, and therefore subject to more mechanical errors, and the results obtained were not as accurate as desired. One objection to procedures 1 to 3 is the use of Chloroform at some stage or another. Chloroform is relatively volatile, and errors are liable to arise due to change in the concentration of the Chloroform solution due to evaporation.

The High Alkaline procedure of Oelschlager has the advantage of using a solution of Dimethyl Glyoxime in Sodium Hydroxide solution, thereby avoiding the problem of the precipitation of Sodium Chloride attendant with the use of Alcoholic solutions. Ammonium Persulphate is used as oxidising agent, to reduce the colour development time of the complex from 30 minutes (using Potassium Persulphate) to less than 10 minutes. The method is free from interference by Manganese - which may be present - in small quantities. Manganese hinders the reaction (and Chloroform extractions) by causing the oxidation of Nickel, - Oelschlager (1955b). None of the other elements possible in the Nickel bearing solution interfere.

Nitroso-R Salt - 'Nitroso-R' is one of a number of substances (chiefly Napthalene derivatives) containing the grouping =  $\begin{array}{c} \text{C} - \text{C} = \\ | \quad | \\ \text{NO} \quad \text{OH} \end{array}$  = which give strongly absorptive red chelates with divalent Cobalt. Nitroso-R salt is water soluble, giving a yellow solution. Both the solution and the chelate are slightly light sensitive, but the solution is stable indefinitely in the dark.

Determination of Cobalt - Cobalt reacts quantitatively with Nitroso-R in neutral or slightly acidic media. The reaction will not take place at pH. < 2.5 or > 8, and is sluggish between these values unless the

reagents are heated. Adjustment of the pH. for optimum reaction is therefore very important. In the method adopted, the M 4.0 Hydrochloric Acid solution containing the Cobalt is neutralized to the end-point of Phenolphthalein (pH 8.2) and then an Acetate buffer of pH. 5.5 added. This gave a resulting pH. of about 6 - 6.5 which is about the optimum. All the difficulties encountered in the Cobalt determination were due to incorrect pH. adjustment - usually as a result of 'overshooting' the end-point during the neutralization. If no colour change (to an orange or reddish hue) occurs on addition of the Nitroso-R solution, it would be advisable to check the pH. by testing the mixture with a small fragment of Universal Indicator paper and adding more buffer if necessary. The Cobalt solution should contain no other interfering metals.

## RESULTS

Introduction - As mentioned previously, Working Curves must be prepared to relate the Absorbance of the final coloured solution to the amount of Trace Element present, before the procedures can be applied to the actual specimens. The important point is that the experimental procedure employed for the preparation of the Working Curves should conform as closely as possible to the conditions of an actual determination. If however, with this proviso in mind, the Working Curve determinations involve as few as possible of the stages of the full procedure, then they may be used as a check on the accuracy of the earlier stages. For example, in this Thesis, the Working Curves were prepared using solutions corresponding as closely as possible to those resulting from the Ion Exchange Separation. Thus the results may be used to check the efficiency of the Sample Solution procedure and the Ion Exchange Separation.

Accuracy of the Working Curves - Since the Working Curves will be used to interpret all subsequent work, it is obviously of considerable importance to ensure that they are accurate or to have some idea of their errors. As mentioned, Beer's Law applies only to very dilute solutions, and has other limitations, therefore it cannot be assumed that a graph of Absorbance vs. Concentration of Trace Element will necessarily be a straight line. Instrumental errors already discussed, and the Absorbance of unused reagents and other materials in solution all affect the validity of the Law. Much useful information on this point may be obtained from the literature, and the limits to which Beer's Law holds are often quoted with the experimental procedures - eg. in Sandell (1959).

The reproduction or reliability of a determination will also affect the Working Curves, and this is usually in fact, the limiting factor in the accuracy of a Colourimetric method, including this one. The best way to get a quantitative idea of this error is to perform sufficient replicate determinations, plot the Working Curve statistically and determine the probable Error by calculation.

As the emphasis in this Thesis was placed on developing the method, and since more accurate equipment is contemplated for future work, no complete program of analyses for the Working Curves was made at this stage.

However, the Nickel determination was selected for more detailed study, partly because it is a more important determination, and partly because the abundance of Literature on Dithizone methods have established the quite remarkable accuracy which they are capable of. As a useful check on such problems as Instrument Drift, contamination etc., the duplicate analyses were carried out some 3 months after the first set of experiments, and using a different set of reagent solution. There was no significant trend or variation between the two sets.

Standard Solutions - Standard solutions containing known amounts of Trace Elements were prepared - see Appendix 4. - and diluted as required for the Working Curve determinations. It is worth noting that precise weighing of the chemicals for the preparation of these solutions is not necessary, since even as much as a 2 per cent error in weighing, for example, might mean a solution contains 49 or 51 ppm. instead of 50 ppm. This is scarcely of any consequence at this stage.

The Working Curve determinations were carried out on known amounts of Trace Element from a Standard Solution made up into a solution of exact volume and acidity etc., as would be obtained from an actual Ion Exchange separation. The determination was then carried out exactly as set out in Appendix 1.

A Blank must be carried through the determination, and all results corrected for the Absorbance of the Blank. In this work, the mean Absorbance of two Blanks was used.

The Working Curves obtained for the Six Trace Elements are given in Figures 14 to 20. It need scarcely be emphasized that they are appropriate only for the procedure as given, and for the equipment and instrument settings used. Only experience or testing will show whether small changes in the procedure or the reagent quantities will have a significant effect on the Absorbance of the coloured solution at the chosen Wavelength, and therefore require a new Blank determination or Working Curve. It will be noted however that the concentration of the Trace Element is plotted in  $\mu$ /ml. of solution or extract for which the Absorbance was recorded, so that the actual ppm. for the sample may be calculated for varying sample sizes or solution aliquots used.

A few illustrations of the errors which may arise from altering the quantities of the active reagents or the conditions of the determination are given in Table 5.

Reliability of the Ion Exchange Separation - The value of the method proposed in this Thesis is strongly dependent on the reliability of the Ion Exchange Separation. If the recovery of the Adsorbed ion is incomplete but reproducible, then a correction factor may be applied to all results.

Table 5. Illustration of Errors Resulting from Changes in Set Procedure

Element	$\gamma$ Added	Determination	$\gamma$ Found
Ni	10.0	using 0.3 mls Ammonium Persulphate	9.8 $\gamma$
Ni	10.0	" 0.5 mls " "	10.4
Ni	10.0	" 0.7 mls " "	11.2
Ni	75.0	Absorbance measured after 1 min	42.5
Ni	75.0	" " " 5 mins	70.2
Ni	75.0	" " " 10 mins	76.5
Ni	75.0	" " " 20 mins	78.4
Ni	20	failed to mix before adding D.M.G.	11.0
Co	25	Eluted with M 5.75 HCl.	1.0
Cu	25	" " M 3.0 HCl	6.2

Table 6. Recoveries of Adsorbed Ion from Ion Exchange Column.

Adsorbed Element	Separate tests		% Found	Mixture of Ions		% Found
	$\gamma$ Added	$\gamma$ 'Found'		$\gamma$ Added	$\gamma$ Found	
Ni	30 $\gamma$	29.2	97	40.0	43.0	108
Pb	10	10.6	106	15.0	13.9	89
Co	15	16.2	93	60.0	57.5	96
Cu	7.35	6.75	92	20.0	18.9	95
Zn	9.75	9.10	93	4.0	3.75	94
Cd	8.12	8.78	108	4.0	4.58	114

Fig 14.

Nickel Working Curve (Low Concs)

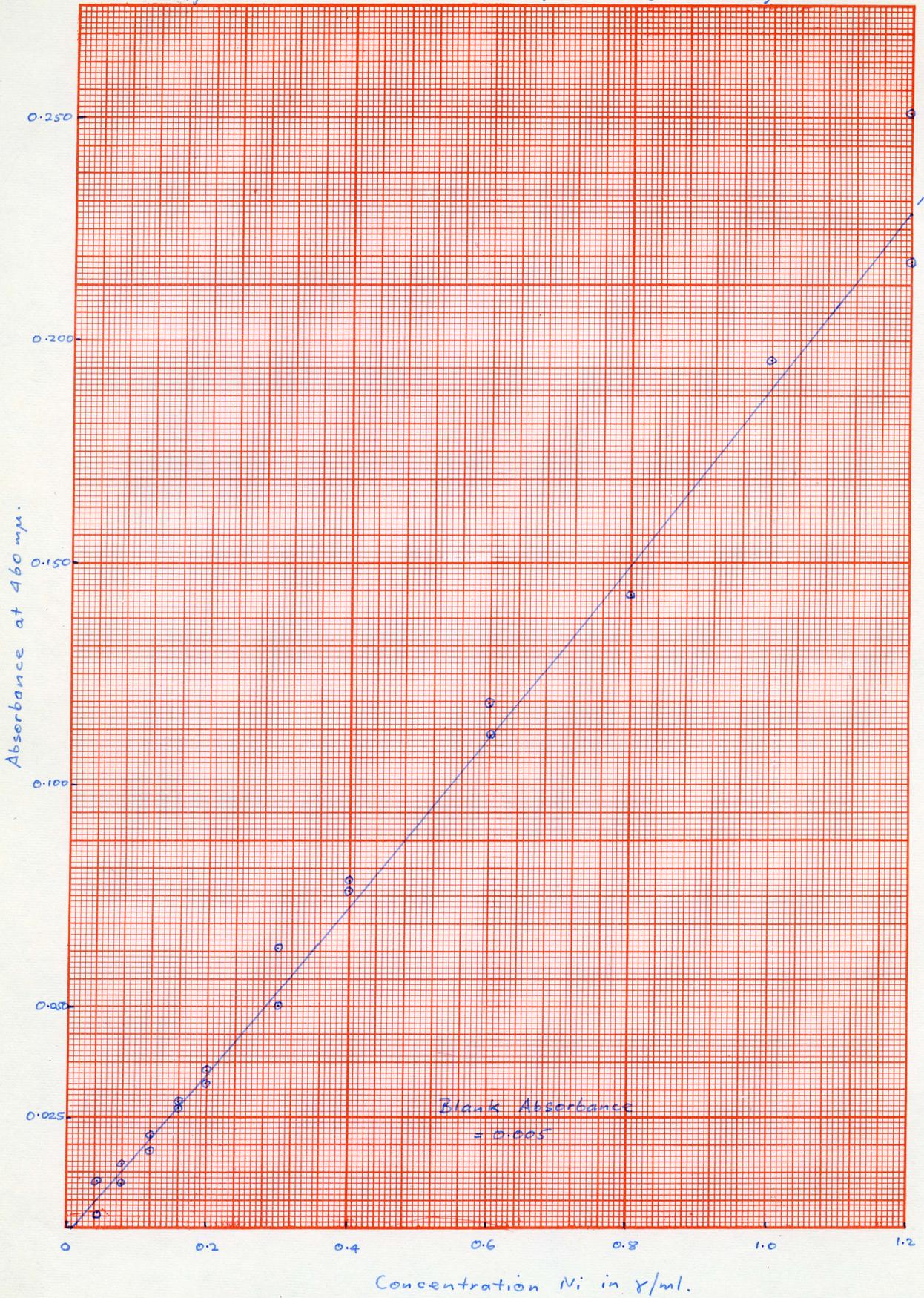


Fig. 15. Nickel Working Curve (High Concs).



Fig. 16. Lead Working Curve.

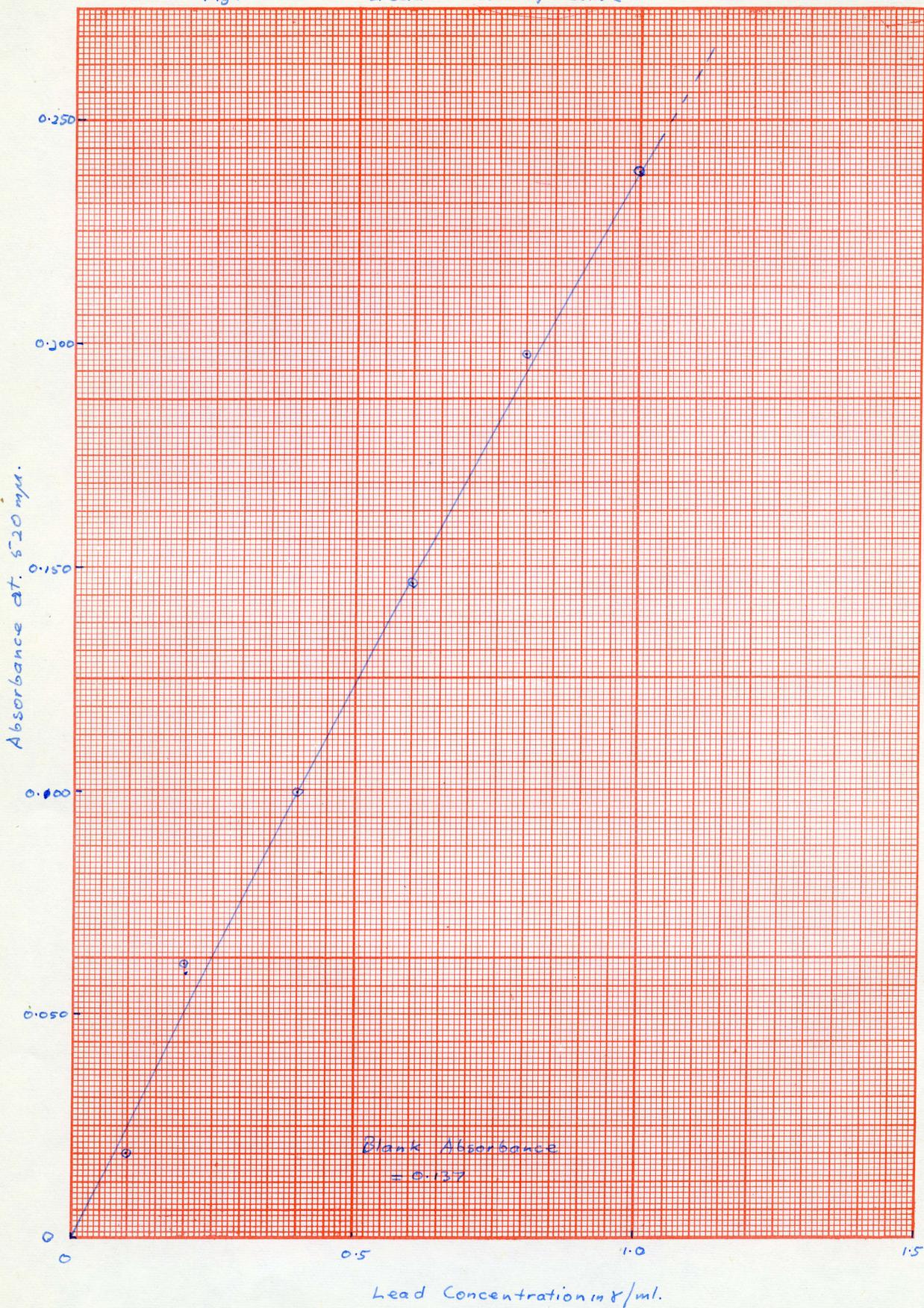


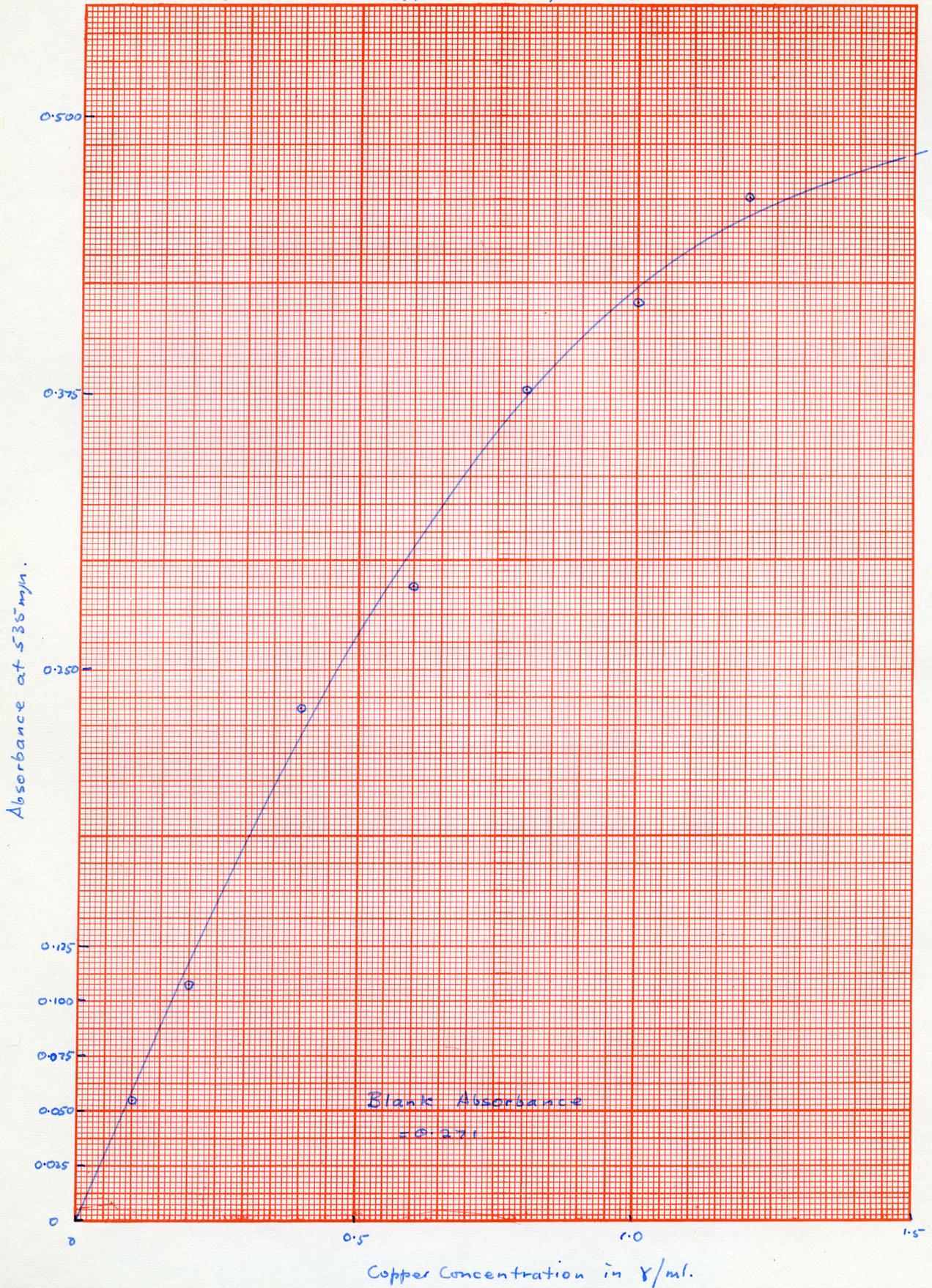
Fig 18.

Cobalt Working Curve



Fig 18.

Copper Working Curve



To face p. 51.

Fig. 19.

Zinc Working Curve

Absorbance at 530 m $\mu$ .



Blank Absorbance  
= 0.374.

Zinc Concentration in g/ml.

To face p. 51.

Fig. 20.

Cadmium Working Curve



The effectiveness of a separation has been discussed earlier, and it was shown that a separation could be worked out from Distribution curves, and its effectiveness calculated given certain data. However, although the separations used in this Thesis may be considered as quantitative, the recovery requires some further thought.

The Literature is singularly deficient of any systematic data on the recovery of Adsorbed ions. Most workers comment only upon wide departures from quantitative recovery, clearly regarding quantitative recovery to be the rule under optimum conditions. The work of Kraus and Coworkers (1956) upon which this Thesis is based was conducted with a view to separating radioactive isotopes, and radioactive tracers were used extensively to check on the efficiency of their separations. Except where elements 'tail' badly, or are difficult to remove from the resin, elution with the appropriate strength acid was usually found to be sharp, and recovery quantitative, since no residual radioactivity was recorded. The quantities of material were, however often in the milligram range, although many of their experiments were carried out with microgram quantities.

Other information is scanty, but Thiers et al. (1955) record a 95 per cent recovery of Cobalt from Dowex 1. The quantities involved were in the millimicrogram range. The theory of Ion Exchange, to a first approximation, and the results of other workers summarized in review articles and references - eg. Kraus and Nelson (1956), and Trace Analysis (1957), indicate that submicrogram quantities may be handled satisfactorily by Ion Exchange. It was therefore assumed for this work that recovery could be considered quantitative within the somewhat larger

limits arising in the other stages of the determinations.

This proposition was checked on each ion individually, and upon mixtures of the six ions involved, and found to be true. The results obtained are shown in Table 6.

These limited experiments clearly do not preclude the possibility of quite a significant departure from quantitative recovery, but it would be rather protracted to get accurate figures with the method as it stands. This matter will be checked upon with the new equipment and Ion Exchange Columns.

Analysis of Synthetic Pyrrhotites - A neat way to check the reliability of the method proposed in this Thesis would be to analyse Synthetic Pyrrhotites containing known amounts of the Trace Elements and to compare the observed results with the known values.

Since the raw materials, particularly the Iron, could be expected to add some impurities, a 'Blank' pyrrhotite would have to be prepared and analysed and the results corrected for the Blank. This however clearly presupposes that the method will be more or less accurate. This anomaly must be accepted however, since it would be very difficult to get an analysis of the Blank, accurate enough for testing purposes by any other means.

Some analyses of Synthetic Pyrrhotites, kindly prepared by Dr. R. G. Arnold, were attempted, but it was found that the method of introducing the Trace Elements into solution was unsatisfactory. A solution made up of a mixture of known volumes of Standard Solutions was carefully evaporated on the charge in a Silica tube. This left a certain quantity of solid salts, some of it deposited on the walls of the tube.

It was apparent from visual inspection after the synthesis, that a deposit still remained on the walls of the tube, and this was confirmed by the analyses, which showed recoveries of Trace Elements much below those added, in most cases, instead of higher, as would have been expected - (Note: The 'Blank' impurities would tend to raise the total Trace Element content).

It is intended to prepare subsequent Standard Pyrrhotites by first preparing a 'Master' Sulphide - from Iron, Sulphur and "Trace" Elements added as weighed quantities of metals, and to 'dilute' a carefully selected and weighed sample of this by fusion with a 'barren' Pyrrhotite charge to bring the introduced metal concentrations down to the ppm. range. This method will also avoid introduction of unwanted phases from metallic salts.

DISCUSSION OF RESULTS

Introduction - Earlier, (p.5) some desirable specifications of the method were set out, and it remains now to consider how well the results obtained so far fulfil these requirements.

Sensitivity and Accuracy - Table 7. gives a summary of some relevant information. The Absolute Sensitivity is that given for an Absorbance of 0.001 (taken from Sandell - 1959). It was found that values of T could often be reproducibly interpolated to 1/10 per cent, and rarely varied more than 1/5 per cent from the mean value. The Sensitivity corresponding to an Absorbance of 0.002, has been calculated from the linear portions of the Working Curves (low concentration portions), and may be regarded as the conservative limit obtainable with the present equipment, since it corresponds to 0.5 per cent T at the higher T values. Using the Dilution Factor - the factor by which the Trace concentration must be multiplied to equal the Sample Trace concentration in ppm - and the Sensitivity for A = 0.002, the 'Detection Limit' may be calculated, and is a conservative limit of detection which could be approached if the remainder of the procedure were perfect.

An accurate value cannot be given to the Practical Detection Limit without more detailed work, since it must take into account the deviation of the plotted points from the mean curve. However, I have included my considered estimate of the Practical Detection Limit, at which a  $\pm 100$  per cent error might be expected with the method as it stands.

The values for Copper, Zinc and Cadmium may be considered adequate, but the values for Nickel, Lead and Cobalt - mostly as a result of the large dilution Factors - leave something to be desired.

However, the method as it stands will cover a wide range of Trace

Table 7. Sensitivities and Dilution Factors

Element	"Absolute" Sens. $A=0.001 - \gamma/cm^2$	Calculated Sens. $A=0.002 - \gamma/cm^2$	Dilution Factor	"Detection Limit"	Estimated Detection Limit
Ni	0.0042	0.0115	250	2.88 ppm	3.0 ppm
Pb	0.0019	0.0083	250	2.08 "	2.5 "
Co	0.0019	0.0040	250	0.950 "	1.5 "
Cu	0.0022	0.0036	50	0.180 "	1.0 "
Zn	0.0016	0.0036	50	0.180 "	1.0 "
Cd	0.0014	0.0036	50	0.184 "	1.0 "

Element concentrations, as was intended, and modifications may be made to the sample size and solution aliquots used, to effect an immediate improvement in the Detection Limit. Thus a 1gm. Sample and 10ml. aliquots throughout would result in Detection Limits  $1/4$  of those quoted. This would be more than adequate for the present purposes.

If it is known or suspected beforehand that low concentrations of the Trace Elements are present in the sample, then it would be quite easy, by taking maximum aliquots, to obtain Dilution Factors of 20 or 25 for Nickel and Lead, and 10 for the remaining elements, using a 0.5 gm. Sample.

It should be noted in passing that an error of 10 per cent for example, in a determination will result in a 10 per cent error in the final answer when multiplied by the Dilution Factor, regardless of its value. The larger Dilution Factor will, however, impose a greater stress on the correct reading of the Working Curves, particularly at their lower limits. In this case, it would be easier to calculate the answer from the measured Absorbance and the Slope of the linear portion of the curve, which can be measured more accurately.

Range and Sample Requirements - As has been mentioned above, the range of Trace Element concentrations covered by the Working Curves can be extended simply by changing the solution aliquots or the Sample size used in the analysis. The former expedient should be adequate for any low concentrations to which Geological significance could be attached. It will be noted too, that the Working Curves for the two elements most likely to occur in very high concentrations in Pyrrhotite - namely Nickel and Cobalt - do cover wide concentration ranges. In the case of Nickel, the high concentration curve is applicable even at levels which will cause nickel to precipitate

temporarily as Hydroxide during the determination. The Cobalt curve could be similarly extended, but the solutions obtained at high Cobalt concentrations have very low Transmittances.

Simplicity and Versatility - The number of steps involved in any determination has been kept to a minimum due to the unique simplicity of the Ion Exchange Separation and the solutions of the Trace Elements which result. Minor savings in the relatively small number of reagents and solutions needed, have been effected by duplication in more than one determination where possible. The result is a method which compares favourably with other possible methods, for simplicity. A little careful planning of technique, plus the use of such aids as automatic pipettes, could well make this method compare favourably in speed too, with other methods, especially in view of the potential accuracy of the results.

The versatility of the method will be dealt with more fully in the next section.

EXTENSION OF THE METHOD TO OTHER ELEMENTS AND MATERIALS

Introduction - The extension of this method to other elements and Geological materials offers numerous possibilities. Summarized very briefly, the requirements which should be met are as follows:

1. For other elements - the Distribution characteristics should be used to isolate the desired element, if possible free from any other elements. This will allow a colourimetric determination in its simplest form.

2. For other materials - the macro elements must first be removed, either by using their Distribution characteristics if possible, or by making a chemical separation. It may be possible to perform some Colourimetric determinations in the presence of certain macro constituents.

3. To minimize the number of preliminary experiments, the quantity of non-adsorbed materials, particularly Alkali Chlorides, and any other Anionic impurities introduced by the adaptation should be kept to a minimum. If this is not possible, a series of tests will have to be run to find what effect, if any, the presence of these Anionic impurities will have, and to adjust Adsorption and Elution Acid strengths accordingly.

Other Elements - The number of elements determined by this method could easily be enlarged, altered or reduced, as the requirements demand. Enlargement of the number determined in a single sample would tend to make the entire procedure rather tedious, and would offer no advantage over a good Emission Spectrometric method, except perhaps for one or two elements having low Emission sensitivities.

Reduction of the number of elements determined will obviously speed the procedure without in any way decreasing its accuracy; the reverse might well be the case. As an example, suppose that only information on Zinc and Cadmium was required. In this case, Adsorption of both elements

from 0.5 M. Hydrochloric Acid would be followed by Elution with 0.01 and 0.001 M. Hydrochloric Acid to give solutions containing Zinc and Cadmium respectively, free from all other elements and capable of precise determination. No Iron separation need be made in this case, since it will not be Adsorbed. It would be difficult indeed to separate these two elements quantitatively from Pyrrhotite by any other method.

Other Sulphides - The problems of extending the method to other Sulphides involve getting the mineral into a Chloride solution without forming high concentrations of other Anions, especially Sulphate, and removing the macro metal or metals. Since few of the common Sulphides are soluble in Hydrochloric Acid, a simple Oxidising Fusion, eg. with a Peroxide/Carbonate mixture might be resorted to, followed by solution in Hydrochloric Acid. The effects of the high concentrations of Alkali Metal Salts would then have to be checked.

Consider now the application to some of the more common Sulphides:

Pyrite  $\text{FeS}_2$  - Pyrite is insoluble in Hydrochloric Acid. The best treatment in this case would be to heat the sample gently in a 'closed' tube to drive off Sulphur and to treat the residue as for Pyrrhotite. Little loss of Trace Elements should result since the temperature required is not high.

Chalcopyrite  $\text{CuFeS}_2$  - Chalcopyrite would be one of the more difficult Sulphides to handle, since removal of Copper as well as Sulphur would also be required. The Sulphur could be removed in part by heating in a closed tube and the residue could then be dissolved in Hydrochloric Acid. In view of the difficulties of removing the Copper chemically or of determining Trace Elements in its presence, it might be better to use a larger Ion Exchange Column, and to handle the Copper in the normal Elution sequence. A 0.5 gm.

sample would provide some 5.5 meq. of Copper which would be adsorbed by 3 gms. of resin at 50 per cent loading. This could be fitted into a column 1 cm. in diameter and 13 cms. long - not an unduly large size. However the 50 per cent loading might cause difficulties unless very slow flow-rates are used. It would be possible to increase the column size - and decrease the loading - still further, and still be able to work with Elution volumes of the order of 25 mls.

Galena PbS - Galena is stable in most acid environments, therefore an Oxidising Fusion seems to offer the best possibilities in this case, followed by solution of the melt in Conc. Hydrochloric Acid. Lead Chloride is insoluble in dilute Hydrochloric Acid, but forms a soluble Chloride Complex in strong acid which would be unadsorbed by the Ion Exchange Resin.

Sphalerite ZnS - Sphalerite is soluble in Hydrochloric Acid, but the Distribution Curve for Zinc does not lend itself to any simple Ion Exchange removal. If handled in a large column, it would have to hold about 6 gms. of resin at 50 per cent loading for a 0.5 gm. sample.

Arsenopyrite FeAsS - Arsenopyrite could best be brought into solution after an Oxidising Fusion. It will be noted that Arsenic is one of the elements extracted by isoPropyl Ether, from a Hydrochloric Acid solution, hence the volume of Ether used for the normal Iron extraction need only be increased to accommodate the added load.

Application to other Geological Materials - It is readily apparent that the method could be applied to any Geochemical work involving a cold or hot Hydrochloric Acid extraction - such as stream sediments or soil samples.

However, inspection of Fig. 5 shows that none of the common rock-forming Cations - Na, Mg, Al, K, or Ca - is Adsorbed from Hydrochloric Acid

as an Anionic Chloro-complex by Dowex 1. Thus the possibility of using this method for the determination of Metallic Traces in Silicate Rocks can be seen.

The method could be applied without a preliminary Iron separation, to the Hydrochloric Acid extractable Metals from pulverized rocks, and with an Iron separation, to the Acid soluble material from simple fusions. In this latter case, a few trial experiments would be needed to determine the effects of the relatively large quantities of unadsorbed Anionic impurities.

Adsorption from HCl-HF media have also been worked out, indicating possibilities with rocks which have been treated with Hydrofluoric Acid, but considerable experimentation would be required to put this on a practical basis.

### CONCLUSIONS

A method for the Determination of six Trace Elements in Pyrrhotite has been put on a practical basis, using the unique properties of Ion Exchange to effect chemical separations of the elements.

An indication of the possible accuracy and detection limits has been given, and means of improving these described.

Although the original aims of this Thesis have been realized, to my mind this is not the most important result of this work which has emerged: the use of Ion Exchange, as outlined in the preceding section, could quite easily become a very powerful tool for Trace Element work on a great variety of materials of Geological interest.

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See also References p.18.

APPENDIX I.

Analysis of the Trace Solution (Iron Removed)

- Condition Ion Exchange Column with 2 mls. of 8.0 M. HCl. Discard effluent.
- Pass Trace Solution through the Column and collect the effluent in a 25 ml. Pyrex flask.
- Wash Column with 2 mls. 8.0 M. HCl, and add effluent to the flask. Make up to 25 mls. with water.
  
- Nickel - Transfer 5 ml. aliquot to a 25 ml. flask.
  - Neutralize with 10 M. NaOH soln. (Universal Indicator Paper)
  - Add 1 ml. in excess.
  - Cool if needed.
  - Add 0.30 mls. 10% Ammonium Persulphate soln.
  - Add 2.0 mls. 2% Dimethyl Glyoxime in 1 M. NaOH soln.
  - Mix and stand for 10 minutes.
  - Dilute to mark, mix and determine the Transmittance at 460m.
  
- Lead - Transfer another 5.0 ml. aliquot to a 25 ml. flask.
  - Neutralize to Phenolphthalein with 10 M. NaOH soln.
  - Transfer 5.0 mls. neutralized solution to separating funnel.
  - Add 5.0 mls. pH. 10.8 Ammonium Citrate - Ammonia buffer
  - Add crystal of Potassium Cyanide.
  - Add 5.0 mls 0.001% Dithizone in CCl<sub>4</sub>
  - Shake vigorously for 1 minute.
  - Separate and measure the Transmittance of the CCl<sub>4</sub> layer at 520 m $\mu$ . without undue delay.
  
- Elute Column with 5.0 mls. 4.0 M. HCl. Collect Eluate in 25 ml. flask.
  
- Cobalt - Dilute to mark.\*
  - Transfer 5.0 ml. aliquot to 25 ml. flask.\*
  - \* Neutralize carefully to Phenolphthalein with 10% NaOH soln.
  - Add 5.0 mls. 10% pH. 5.5 Acetic Acid - Sodium Acetate buffer.
  - Add 0.50 mls. 0.2% Aqueous Nitroso-R Salt soln.
  - Boil for 1 minute.
  - Cool in dark.
  - Dilute to mark and determine the Transmittance at 420m $\mu$ .
  
- Elute Column with 5.0 mls of 2.0 M. HCl. Collect Eluate in 25 ml. flask.
  
- Copper - Dilute to mark.
  - Transfer 5.0 ml. aliquot to separating funnel.
  - Add 5.0 mls 0.001% Dithizone in CCl<sub>4</sub>
  - Shake vigorously for 2 minutes.
  - Separate and measure the Transmittance of the CCl<sub>4</sub> layer at 535m $\mu$ . Avoid evaporation.

- Elute Column with 5.0 mls. of 0.5 M. HCl. and discard Eluate (contains residual Iron). Repeat with second portion of acid (10 mls. in all)
- Elute Column with 5.0 mls. of 0.01 M. HCl. Collect Eluate in 25 ml. flask.

Zinc

- Dilute to mark .
  - Transfer 5.0 ml. aliquot to separating funnel.
  - Add 5.0 mls. of 10% pH. 5.5 Sodium Acetate - Acetic Acid buffer.
  - Add 5.0 mls. 0.001% Dithizone in CCl<sub>4</sub>
  - Shake vigorously for 2 minutes.
  - Separate and measure the Transmittance of the CCl<sub>4</sub> layer at 530m $\mu$ . Avoid evaporation.
- Elute Column with 5.0 mls. of 0.001 M. HCl or water. Collect Eluate in 25 ml. flask.

Cadmium

- Dilute to mark.
- Transfer 5.0 mls. aliquot to separating funnel.
- Add 2 or 3 drops of dilute Ammonium Hydroxide soln.
- \*- Add 5.0 mls. 0.001% Dithizone in CCl<sub>4</sub>
- Shake for 1 minute.
- Separate and measure the Transmittance of the CCl<sub>4</sub> layer at 520m $\mu$ .
- \*- Avoid any delay from this stage onward.

Notes: - Pyrex apparatus should be used throughout.

- The sequence of operations must be followed as set out above, but steps marked \* (Cobalt determination) may be omitted. Other changes, such as the size of aliquots taken may be altered as indicated in the Text, when corresponding Blanks should be run to ensure maximum accuracy.

APPENDIX 2.

Preparation of Organic Solvents

Carbon Tetrachloride - Reflux the Reagent grade material with 10% NaOH for two hours, decant and shake for 5 minutes in a separating funnel with 10% Hydroxylamine Hydrochloride. Wash with water, separate sharply and dry overnight with Calcium Oxide. Distil from a little fresh Calcium Oxide, discarding the first few mls. of distillate.

To recover, separate the contaminated solvent from any aqueous phase and shake with 10% of its volume of conc. Sulphuric Acid. Separate and wash the solvent with water to remove acid, then treat as for the Reagent material.

Ethyl Alcohol - Dry overnight with Calcium Oxide, then distil from a little solid Potassium Hydroxide.

isoPropyl Ether - Treat daily as follows: Shake with a tenth of its volume of 2% Potassium Permanganate in 2 N. Sulphuric Acid. Repeat twice. Shake with 10% Sodium Sulphite solution, then wash thoroughly with 1:1 Hydrochloric Acid.

To recover, wash with several portions of water until the Ether layer is colourless. Wash with 10% Sodium Hydroxide and finally with water and return to stock.

APPENDIX 3

Preparation of Other Reagents

Water - Distilled water was further purified by Ion Exchange, using the column described by Kunin (1958) for this especial purpose.

Hydrochloric Acid - Pure HCl gas was prepared by dropping Reagent grade conc. HCl into conc. H<sub>2</sub>SO<sub>4</sub>. The mixture was heated when the reaction became sluggish. The gas was dissolved/<sup>in</sup>cooled purified water until a strength of approx. 9 M. was attained.

Ammonium Hydroxide - Solutions of Ammonium Hydroxide were prepared by dissolving pure NH<sub>3</sub> gas from a heated Reagent grade NH<sub>4</sub>OH in purified water.

Dithizone - Dithizone is ordinarily pure enough for most purposes if a 0.01% solution in CCl<sub>4</sub> gives only a faintly yellow coloured layer on shaking with an excess of pure dilute NH<sub>4</sub>OH. If the CCl<sub>4</sub> layer is a strong yellow, or pink, then the Dithizone may be purified by recrystallization from Chloroform, or by any of the methods given in Sandell (1959).

Acetic Acid-Sodium Acetate buffer pH. 5.5 - To a 10% solution of Sodium Acetate, add 'Glacial' Acetic Acid carefully, checking the pH. with a Universal pH. meter, until a pH of 5.5 is attained.

Ammonium Citrate-Ammonia buffer pH. 10.8 - To a 10% solution of Ammonium Citrate, add conc. Ammonia until a pH. of 10.8 is attained.

APPENDIX 4.

Preparation of Standard Metal Solutions.

Standard 0.01% solutions of the Metals were prepared from Reagent grade chemicals as follows:

- Nickel - Dissolve 0.405 gms. of uneffloresced  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in a litre of water.
- Lead - Dissolve 0.160 gms. of  $\text{PbNO}_3$  in a little dilute  $\text{HNO}_3$  and dilute to 1 litre.
- Cobalt - Dissolve 0.404 gms. of uneffloresced  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in a litre of water.
- Copper - Dissolve 0.1965 gms. of clear  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in a litre of water.
- Zinc - Dissolve 0.100 gms. of Zinc metal in 1:1  $\text{HCl}$  and make up to 1 litre with water.
- Cadmium - Dissolve 0.228 gms. of  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  in 1 litre of water.

These solutions must be stored in Polyethylene containers.

APPENDIX 5

List of Reagents Required

Ammonium Hydroxide - concentrated and dilute

\* "" Persulphate - 10% solution.

Buffers - pH. 5.5 and pH. 10.8 - see Appendix 3.

Dithizone - 0.01 % w/v in  $\text{CCl}_4$  stock solution. Prepare 0.001 % working solution as required.

Dimethyl Glyoxime - 2% solution in 1.0 M. NaOH.

Hydrochloric Acid - required in the following Molarities:

9.0, 8.0, 6.0, 4.0, 2.0, 0.5, 0.01, and 0.001. Prepare from strongest acid by approximate dilution, check by accurate titration and adjust if necessary.

Nitroso-R salt - 0.2% w/v in water.

Potassium Bromide

\* "" Chlorate - 5% in water.

" Cyanide

Sodium Hydroxide - 10 M. and 10%.

Solutions marked \* should be stored in Pyrex containers, the remainder should be stored in Polyethylene containers.

The following reagents may be required in the course of purification or recovery work:

Calcium Oxide, Chloroform, Hydroxylamine Hydrochloride,

Potassium Permanganate, Potassium Hydroxide, Sodium Sulphite,

Sulphuric Acid.

For purification of made-up solutions, see Sandell (1959), especially pp569-573.

APPENDIX 6

Notes on Spectrophotometer Operation.

Stepwise Operating Procedure:

- Turn Selector Switch to CHECK.
- Turn on Tungsten Lamp and Battery Power Regulator.
- Rotate the Charge Adjust to zero the ammeter needle.
- Allow to warm up for 1 hour.
- Set desired Wavelength.
- Select desired phototube and load resistor.
- Insert standard and sample cells in holder and place in cell compartment.
- Position standard in light beam with positioning knob.
- Rotate the Dark Current Control to zero the null meter.
- Turn Shutter on.
- Roughly zero the null meter by adjusting the Slit Width.
- Accurately zero the null meter with the Sensitivity Control.
- Turn Shutter off.
- Position sample in light beam.
- Turn Selector Switch to 1.0 or 0.1 if the Transmittance is less than 10%
- Turn Shutter on.
- Zero the null meter with the Transmittance control and note reading.
- Turn Shutter off and position next sample, repeat measuring procedure.

Notes: It was found more satisfactory to allow a warm up period of two hours since slight changes in the output of the accumulator caused some Dark Current drift during the first hour or more.

The equipment was operated with an external 'C' battery pack composed of cells from 6 volt lantern batteries. This resulted in far more stable operation than would be possible with tiny short-life batteries recommended. See Cecchini, L.P. and Eicher, M. - Anal. Chem. 25 534 (1953), and notes by Stenius, A.S. op. cit. 1527, for further information.

