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GEOLOGY AND GEOPHYSICS

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SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY APPLIED TO ROCK ANALYSIS

by

J.R. Beevers

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CHELATE-FORMING COMPOUNDS

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SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROPHOTOMETRY APPLIED TO ROCK ANALYSIS

The information contained in this record was presented at the Geological Society of Australia Specialists Meeting held at the University of Adelaide from 23rd - 25th August, 1966. The session in which the paper was presented was called "Modern Methods of Rock Analysis for Constituent Elements".

INTRODUCTION

It is almost a century since the first systematic study of solvent extraction and the formulation of the distribution law by Berthelot in 1872. Atomic Absorption Spectrophotometry is a much younger technique having only just completed the first decade of its existence; the combination of the two has developed only in the last five years. The need for the combined technique arises in rock analysis for two essential reasons:

1. to separate small amounts of elements whose concentration is required, from much larger amounts of other elements which if present in the same solution would give rise to intolerable non-atomic absorption.

2. to increase the concentration of the element to be determined to a practical level so that a reasonable aborption is obtained. The technique therefore lowers the limit of detection.

THEORY OF SOLVENT EXTRACTION

The distribution of a species between an organic and an inorganic phase is given by the distribution ratio or partition coefficient (Pn)

$$\text{Pn} = \frac{\text{Total conc* in organic phase}}{\text{Total conc* in aqueous phase}}$$

* (more correctly activities rather than concentration)

The percentage of species extracted (%E) by the organic phase is related to the partition coefficient by the following

$$\%E = \frac{100\ \text{Pn}}{\text{Pn} + \left(V_w/V_o \right)}$$

Where Vo and Vw represents the volumes of the organic and aqueous phases respectively.

The relationship of %E to Pn is shown diagrammatically for Vw/Vo = 0.1, 1 and 10 in Figure 1. It is obvious that for the best extraction Vw/Vo should be low and Pn high. In practice, the ratio Vw/Vo varies between 1 and 10; values greater than 10 are usually avoided because of the mutual solubility of the two liquid phases. For an organic solvent that is less than 1% soluble in the aqueous phase, a ratio of up to 10 for Vw/Vo is a workable proposition. For good (> 90%) extraction, and Vw/Vo equal to 10, a partition coefficient of greater than 100 is necessary, and any complex that does not have such a favourable partition under these conditions is not considered very good for solvent extraction purposes. Ideally, one requires a complex that is insoluble in the aqueous phase and very soluble in the organic.

The above considerations have been made with the unstated assumption that the parameter Pn is constant, but this is by no means so. It varies with the concentration of the extractable species, with changes in the ionic strength of the solution (salting out) because of the changing activities of the species, and with changes in the mutual solubilities of the two solvent phases (brought about by changes in ionic strength including changes in pH). Provided the value of Pn is high, these changes occurring during an analysis will not seriously affect the value of %E. Changes in pH affect the partition, and hence %E, much more seriously because of the effect of pH on the stability of the complex and on the complexing agent itself, and this is dealt with more fully in a later section of this paper. Complications can develop also because of hydrolysis of the solvent when using esters for the solvent extraction of metal chelates from strongly acid solutions, but this is not dealt with further in this paper.

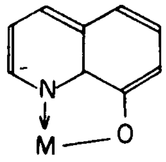
MECHANISM OF COMPLEX FORMATION

Complexing agents used in solvent extraction systems are many, but they may be conveniently grouped depending on the type of metal complex formed:

1. Inorganic compounds or ions e.g. halides

   $HgCl_2$, $FeCl_4^-$

2. Uncharged chelate compounds e.g. the metal chelate of 8 - hydroxyquinoline



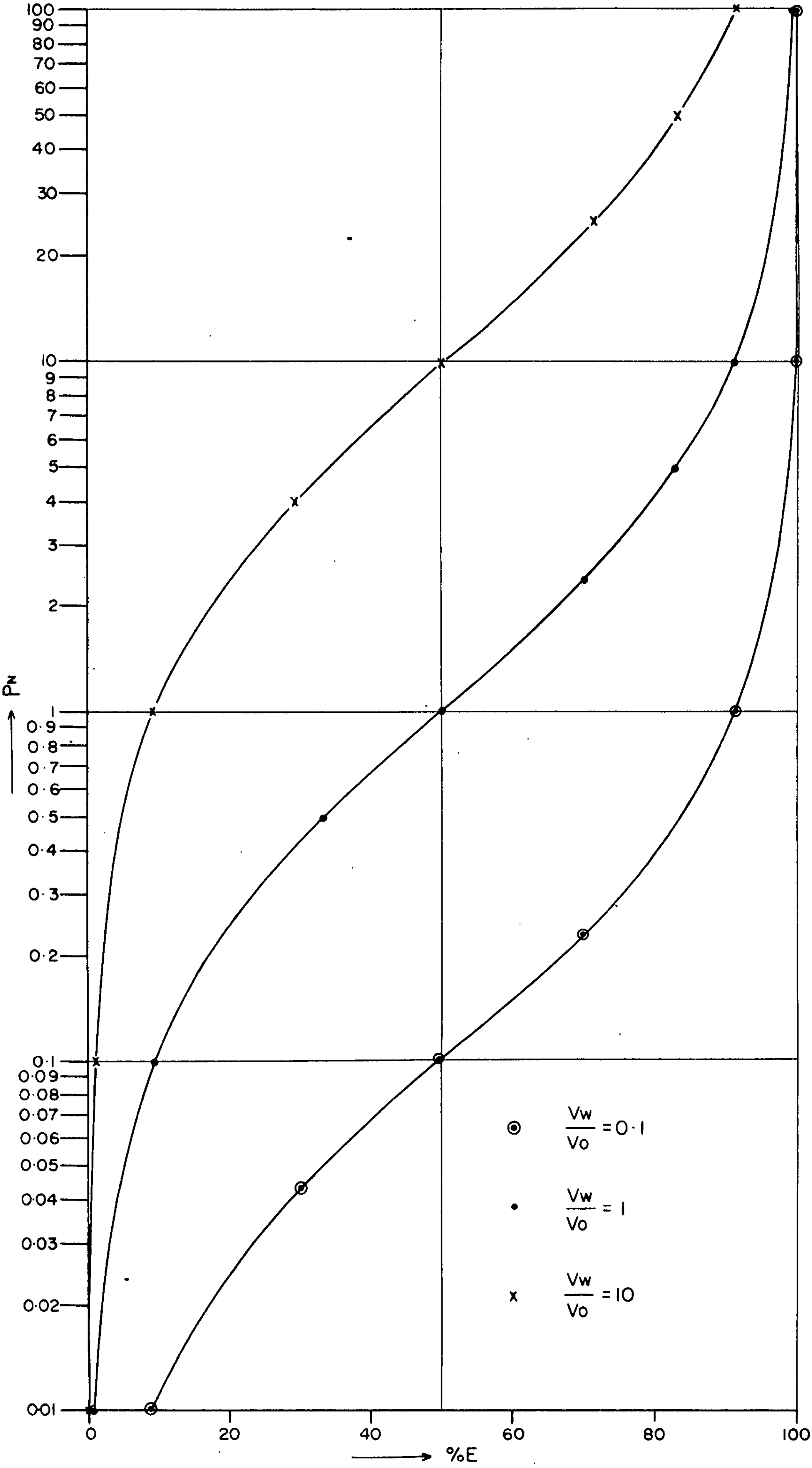
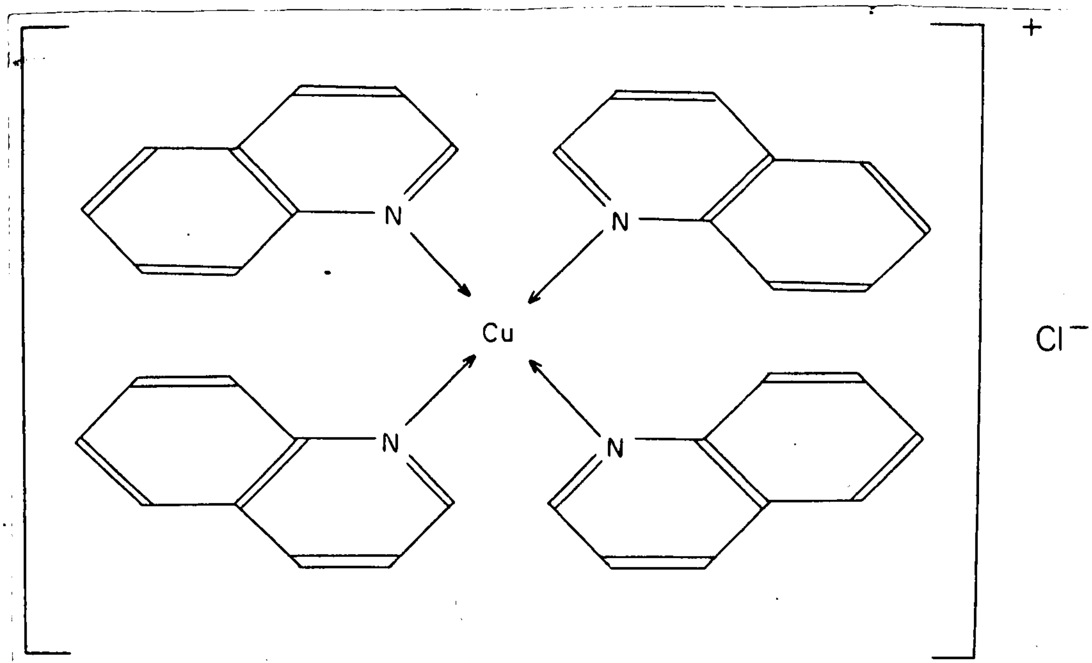


Fig. 1. Relationship between partition coefficient (PN) and extraction (%E) with various $\frac{Vw}{Vo}$ values

3. Cationic chelate compounds e.g. Cuprous biquinoline

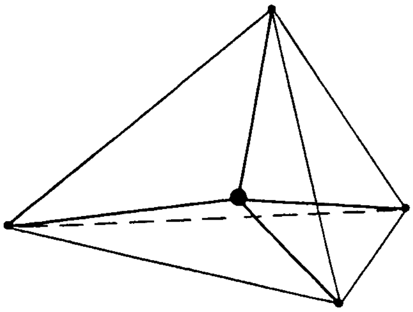


4. Anionic e.g. the perrhenate of the tetra-phenyl arsonium radicle.

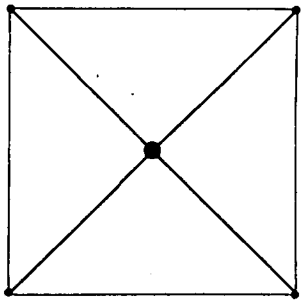
$$\left[(C_6 H_5)_4 As\right]^+ \left[Re\ O_4\right]^-$$

All four types are used analytically, but the second is by far the most important for the trace element analysis of geological materials, and only this type will be discussed further in this paper.

Most of our understanding of the formation of chelate compounds is due to Werner, who, in 1893 proposed the classical theory of coordination. He suggested that, in addition to its normal or primary valence, an element may possess a residual or secondary valence given a value known as the coordination number, usually 4 or 6. Elements with a coordination number of 4 have their coordinate valence linkages directed in space towards the points of a tetrahedron or square.

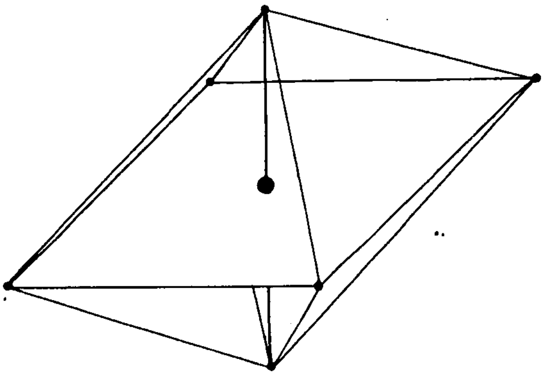


(a) Tetrahedron



(b) Square

Those elements with a coordination number of 6 have their co-ordinate valence linkages directed in space towards the points of an octahedron

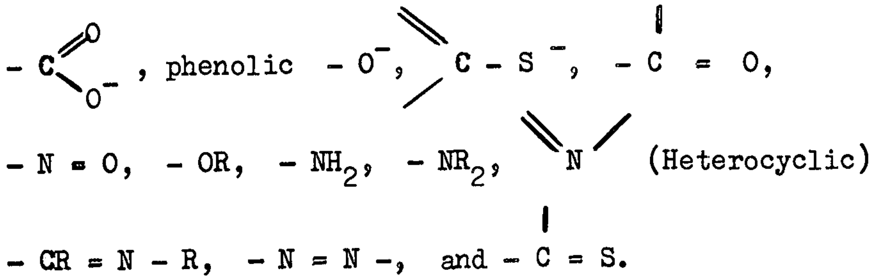


(c) Octahedron

The coordinate bonds are formed between two elements by the sharing of a pair of electrons, both of which are provided by one of the elements in the coordination group.

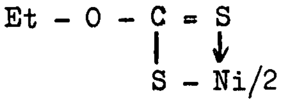
Organic reagents that form chelate inner complexes are generally weak acids e.g. dithizone, 8-hydroxyquinoline and cupferron. Metal chelates are formed from such compounds by replacement of the acidic hydrogen by the metal; and a second functional part of the base, which is in a favourable position to form generally a stable 5 or 6 membered ring, donates two electrons to form a coordinate link between it and the metal, e.g. the metal 8-hydroxy quinolate shown previously (p2).

Complexing agents or ligands are usually anions or neutral molecules possessing groups of the following types:



Both neutral and charged species can donate electrons to form the coordinate bond with an element, and where an unchanged complex results the number of charged species forming such bonds must be equal to the valency of the element forming the complex. Werner's theory tells us that either 4 or 6 coordinate linkages are possible in chelate compounds. Where one, two or three positions in the coordinating shell are occupied by functional groups in the same molecule or ion, the coordinating ligand is called either mono, bi or tri-dentate, respectively.

As mentioned previously, 5 or 6 membered rings are generally the most stable. However, the size and orbital direction of S atoms permits 4-membered rings in complexes of dithio acid derivatives, such as the nickel complex of Xanthic acid.



$$\begin{array}{lcl}\mathrm{Et-O-C} & = & \mathrm{S}\\ \qquad\qquad\ | & & \downarrow\\ \qquad\qquad\ \mathrm{S} & - & \mathrm{Ni/2}\end{array}$$

The possibility of inner complexes or chelates forming arises whenever the acidic and donor groups are favourably situated in the molecule. Chelate compounds are not formed unless the functional groups are favourably situated spatially. If the coordination number of the central atom is more than twice its charge, then H_2O may occupy the free positions in the coordination sphere. In fact, one may look on the formation of chelates and complexes as the replacement of solvent molecules, usually water.

EFFECT OF pH IN SOLVENT EXTRACTION OF CHELATES

Because chelate systems are formed partially by replacement of hydrogen atoms in the ligand molecule, pH will be of great importance in chelate formation.

Consider the reaction between a ligand molecule LH and a metal M, of valence n, in the aqueous phase

$$n\ \mathrm{LH} + \mathrm{M}^{n+} \rightleftharpoons \mathrm{ML}_n + n\mathrm{H}^+$$

The equilibrium constant can be written

$$K_{ML} = \frac{[MLn]\,[H^+]^{n}}{[M^{n+}]\,[LH]^{n}} \qquad \text{\_\_\_\_\_\_\_\_\_\_(1)}$$

Similarly for the ligard molecule we can write

$$K_{HL} = \frac{[L^-]\,[H^+]}{[HL]} \qquad \text{\_\_\_\_\_\_\_\_\_\_(2)}$$

The partition coefficient (P_{N}) of the chelate between the two liquid phases, is related to the extraction by the following relation:

$$\%E = \frac{100\,P_{N}}{P_{N} + (Vw/Vo)} \qquad \text{\_\_\_\_\_\_\_\_\_\_(3)}$$

The formation of hydroxyl complexes by hydrolysis cannot be overlooked particularly in solutions of high pH. Nor can the formation of other complexes be overlooked, e.g. chlorides and sulphates. These ions might be present as a result of the attack on the rock sample, or in some cases, be added as masking agents to minimise the interference of a foreign ion.

From these relationships (1) to (3), one can develop a very useful relationship between %E, n and pH. Neither time nor space permits me to develop the relationship here, but for interested persons, it is developed fully in "Solvent Extraction in Analytical Chemistry" by Morrison & Freiser (Ref. 4). The relationship is:

$$\log \%E - \log\ (100 - \%E) = \log K^* + npH \quad - (4)$$

Where K* is a term dependent on all conditions in the system other than n and pH, and including terms to account for inorganic complexing anions, hydrolysis etc. mentioned previously.

This can be rearranged to

$$pH = \frac{1}{n} \log \frac{\%E}{(100-\%E)} - \frac{1}{n} \log K^* \qquad \text{\_\_\_\_(5)}$$

This equation represents a family of symmetrical sigmoid curves with the position of each along the pH axis dependent only on the magnitude of K^*, as shown in Fig. 2. The pH value at %E = 50, has been designated as $pH_{\frac{1}{2}}$, and its value is equal to $-\frac{1}{n}\log K^*$. The difference in the $pH_{\frac{1}{2}}$ values of two species in a specific system is a measure of the

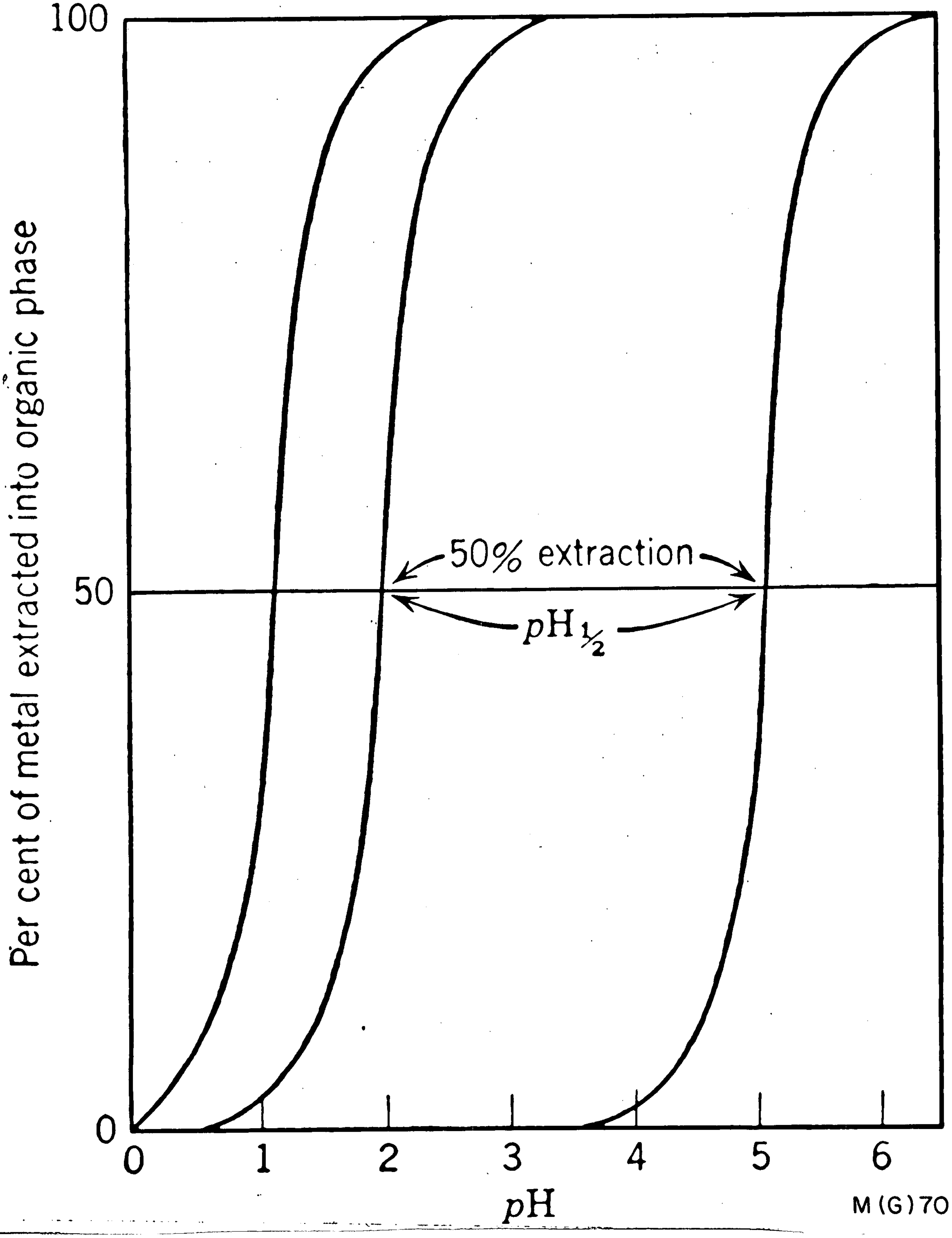


Fig. 2. Shows relation between pH and %E for the equation (5) shown in text.

separability of these two species. Looking at the separability another way, we can consider poor extraction to be represented by E%= 1, and good extraction to be represent by %E = 99. Substituting these values for %E in equation (5) we get

$$pH_1 = \frac{1}{n} \log \frac{1}{99} - \frac{1}{n} \log K^*$$

and

$$pH_2 = \frac{1}{n} \log \frac{99}{1} - \frac{1}{n} \log K^*$$

$$\therefore \Delta pH = \frac{4}{n}$$

In other words, for a divalent metal ion, the range between 1% extraction and 99% extraction is covered by two pH units. This fact is widely used in practise in the separation of metal ion chelates, and buffer systems are generally used in solvent extraction work in order to control pH carefully.

For the separation of two metal ions we depend essentially on the stability constant of their complexes and the partition of the complexes

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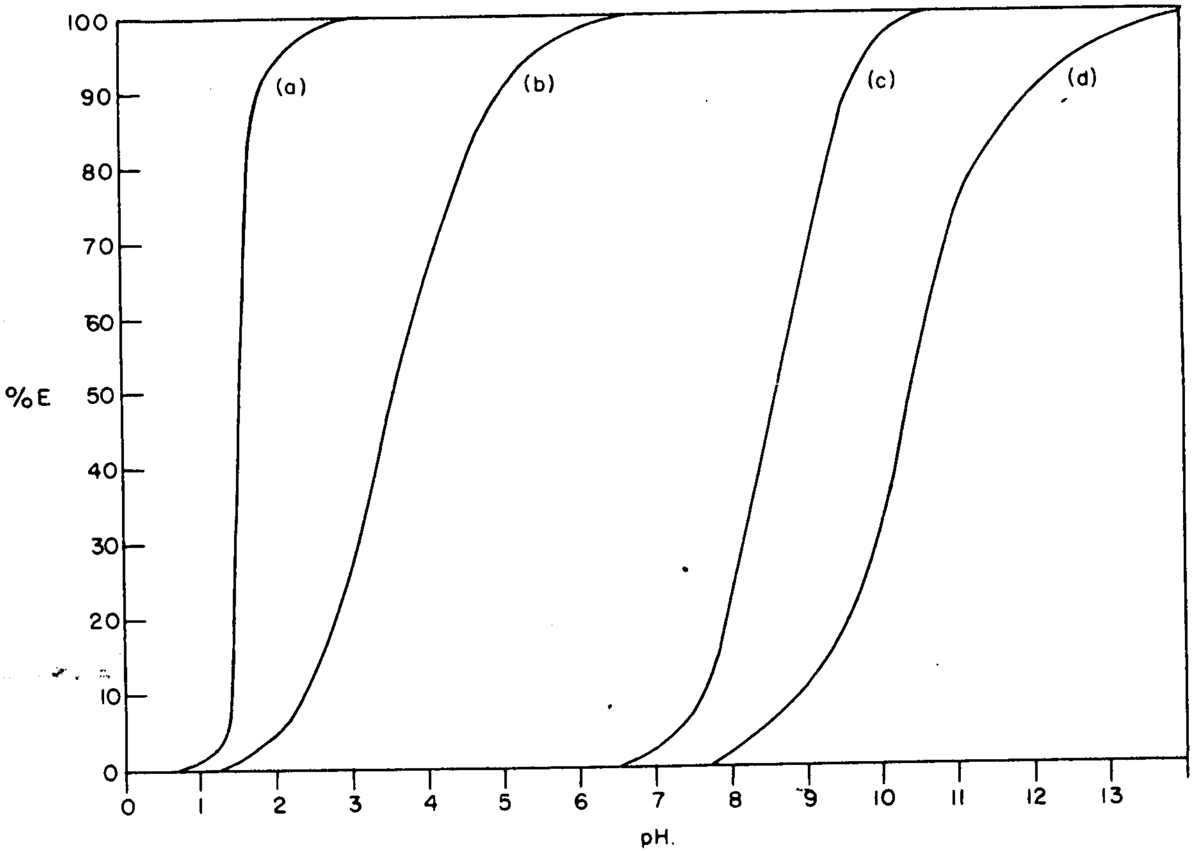


Fig. 3. Extraction of the 8-hydroxy quinolate of copper into chloroform in the presence of various masking agents

(a) No masking agent
(b) 0·01 M tartaric or oxalic acid
(c) 0·01 M EDTA
(d) 0·01M nitrilo tri-acetic acid

quinolate in the presence of nitrilo triacetic acid. Tartaric, oxalic, EDTA and nitrilo triacetic acid are classed as masking agents for the formation of copper 8-hydroxy-quinolate. Their function, as can be clearly seen is to progressively increase the pH at which the complex is extracted, and this can be used for instance to effect a separation of copper from molybdenum. For the system containing 8-hydroxyquinoline and EDTA, the dissociation constants of these compounds are such that up to pH 7, the concentration of free EDTA ions is so much greater than the concentration of free 8-hydroxyquinolate ion, that the formation of the EDTA complex takes place in preference to the formation of the 8-hydroxy-quinolate. Above pH 9, the 8-hydroxyquinolate of copper is completely extracted even in the presence of EDTA because the stability of the copper 8-hydroxyquinolate is so much greater than the stability of the copper EDTA complex. This change is brought about because of the different values of the dissociation constants of the complexing agents and the different values of the stability constants of the complexes.

pH is certainly the best single control of a solvent extraction system that we have, but the use of masking agents, in addition to pH control, enables us to make systems more selective.

For a masking agent to be truly successful it is necessary that the element that has been masked should be soluble in the aqueous phase and not co-extracted into the organic. This particular aspect is not so critical when AAS is to be used for subsequent analysis because absolute separation is not essential; co-extraction should be kept to a minimum however, as non-atomic absorption can occur even in the organic phase if the concentrations in this phase are too high. In order to ensure that a masking agent does not give complexes soluble in the organic phase, one should be chosen that possesses an unco-ordinated hydrophilic group in the molecule after complex formation. Chelate forming agents that are used for extracting particular elements because the chelate is insoluble in water, can be converted to masking reagents by introducing a grouping that renders the chelate water soluble; the sulphonic acid grouping helps to increase solubility in water because this radical has lone pairs of electrons that can form hydrogen bonds with water e.g., Ferron can be formed from 8-hydroxy-quinoline. For a substance to be water-soluble it must either possess co-ordination water in its structure or possess groupings that can interact with H_2O molecules through hydrogen bonding.

ORGANIC SOLVENTS

For an organic solvent to be useful in both the solvent extraction stage, and in the AAS flaming, the following conditions make for the ideal.

1. The densities of the two phases (aqueous and organic) are sufficiently different for the two phases to separate easily and quickly.

2. The two phases do not emulsify easily.

3. The mutual solubilities of the two phases are small - for

the organic phase to be less than 1% soluble in the aqueous phase is usually sufficient.

4. The metal complex, whether it be ionic or uncharged, shall partition very favourably in the organic phase.

5. The organic solvent shall be suitable for introduction into the flame of the A.A.S. In this regard there are four very important points to note:

   (a) the solvent shall not extinguish the flame

   (b) the solvent shall not burn with a sooty flame

   (c) the solvent shall not have a low flash-point for safety reasons

   (d) the solvent shall not have too high a viscosity otherwise the aspiration rate will be much reduced.

It is not necessary that the solvent support combustion; after all water does not support combustion and this is the solvent most eommonly introduced into the flame. Moreover, when the solvent does support combustion a luminous flame is not always undesirable even though a smoky flame is. For instance the best conditions for Cr analysis from aqueous solution are a rich, highly luminous flame and an air/acetylene fuel.

In addition to the desirable properties of a solvent listed above, the choice of solvent depends very much on the chelate to be extracted.

There are two main groups of solvents:

(1) Non-polar e.g., CCl_4

(2) Polar - mainly oxygen bonding types e.g. amyl acetate

Chloroform, although a polar solvent, does not co-ordinate strongly to metal complexes and hence is usually classed with carbon tetrachloride. It cannot however, be used in AAS work because it burns with a smoky flame, as does benzene. It has been found that carbon tetrachloride can be introduced into the air-acetylene flame with virtually no change in flame characteristics and certainly no change in flame absorption compared to the flame free of this compound. The fact that CCl_4 can be introduced successfully into the flame is very fortunate because much of the work carried out using solvent extraction techniques to date (usually spectrophotometric) and reported in the literature has been using non-polar solvents, particularly carbon tetrachloride. It should be possible therefore to use much of the information gathered using CCl_4 and subsequently spectrophotometry, and apply this directly to AAS.

All the solvents listed in Table 1 can be successfully introduced into the air-acetylene flame; it is sometimes necessary to reduce the acetylene flow to avoid a luminous flame, but none of them burn with a smoky flame. The table is by no means exhaustive, but it does include a representative of each of the chemical groups generally used in solvent extraction work, and most chelates will dissolve in one or more of them.

	Sol'y in H_2O
2 : 6 Dimethyl 4-Heptanol	$<0.05\%$
n - Butyl Ether	0.03%
Amyl Acetate	0.2%
iso-Butyl Methyl Ketone	1.8%
Carbon Tetrachloride	0.08%

TABLE 1. Solvents useful for solvent extraction followed by AAS.

Choosing a solvent for extraction of a particular chelate is still mostly empirical, but, consistent with the suitability for flaming, the following points are important.

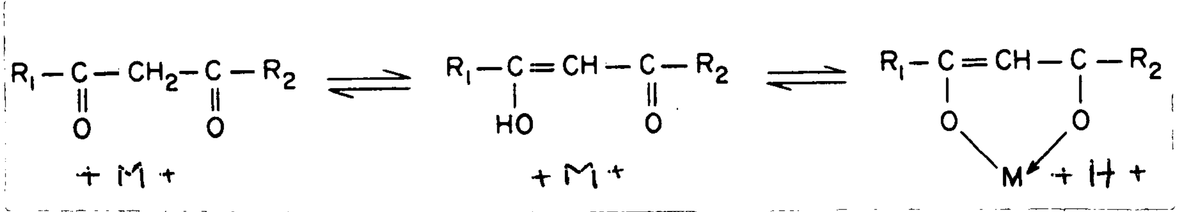
(1) the chelates can be expected to be excellently soluble in the non-polar solvents if the molecule contains no free acidic or basic groups (free acidic and basic groups in this case include those forming inner complexes through auxiliary valencies).

(2) a similarity in chemical composition between the chelate and the organic solvent can be taken as a good indication that the chelate will be soluble in that solvent. Solvation helps to secure this similarity. Fiegl and co-workers have taken this to the limit and showed that most inner complex salts seem to be soluble in melts of their particular complex formers (Fiegl et al., 1943).

(3) if the co-ordination sites of the element to be extracted are incompletely filled, a solvent that is capable of co-ordinating to the metal ion (and displacing the co-ordinating water molecules) will be expected to be useful for extraction in that system. Such solvents are those containing oxygen, e.g. alcohols, esters, ketones and ethers. Non-polar solvents are of little use in such systems.

CHELATE-FORMING COMPOUNDS

(a) B-Diketones



The best known member of this group is acetyl acetone ($R_1 = R_2 = CH_3$). It is useful for macro extractions because its chelates are soluble in organic solvents to the extent of gm/litre rather than the more usual mgm/litre. It is particularly effective for Al^{3+} and Fe^{3+} and CCl_4 is a good solvent. As it is a liquid at normal temperatures it may be also used as the solvent for the extraction of the chelates, but this is undesirable when a large ratio Vw/Vo is required because its solubility in water is about 17 gm/100 ml at 25°C.

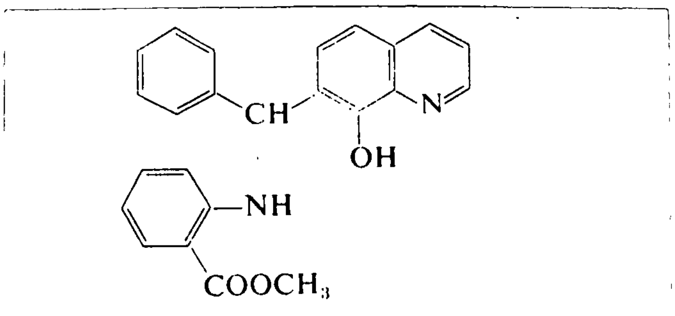
When R_1 = Benzyl and R_2 = Methyl, the product is benzoyl acetone; it is found to be more specific than acetylacetone because the values of the partition coefficients for the chelates are higher.

When $R_1 = R_2$ = Benzyl, the product, dibenzoyl methane, gives chelates whose partition coefficients are very high because of the hydrophobic nature of the two benzene rings.

(b) 8-hydroxyquinoline and derivatives

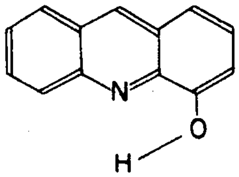
Chelating agents belonging to this group are commonly called "oxines". They are generally non-selective reagents, reacting with most elements, but they can be made partially selective by variations of pH and by using masking agents. They are generally used dissolved in non-polar solvents; partitions coefficients and stability constants are known for many metal oxines.

More selective reagents can be made from 8-hydroxyquinoline by introducing a large organic grouping into the 7 position, for example 7 -[α - 10 - carbomethoxy anilino benzyl] 8-hydroxyquinoline.



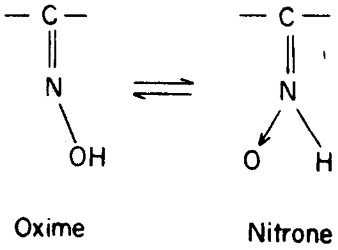
Because of steric hindrance this compound does not react with tri and tetra-valent metal ions, but only with divalent ones. Thus it can be used to extract divalent metal ions in the presence of Fe^{3+} and Al^{3+}.

Another derivative of oxine which can be used for the quantitative extraction of Cu, Ni, Co and Zn is neo-oxine or 1-Hydroxy acridine.

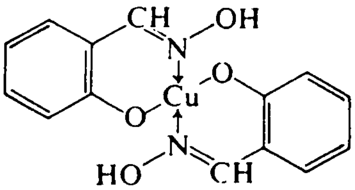


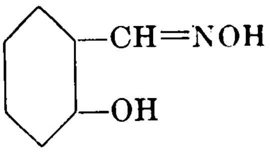
(c) Oximes

The oximes are characterised by the >C = N - OH group, which exists in two tautomeric forms



Chelation apparently takes place from the oxime form as examplified in the best known chelating reagent of this type, salicyl aldoxime, shown here with the copper chelate.

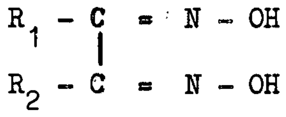




Nickel and palladium are the two metals most suited to solvent extraction by this reagent.

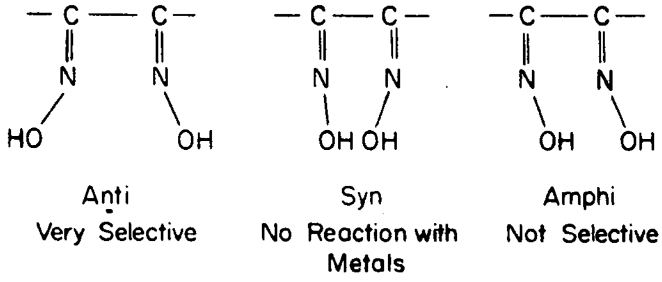
(d) α-Dioximes

These are a much more useful and interesting group of compounds than the monoximes. They have the general formula

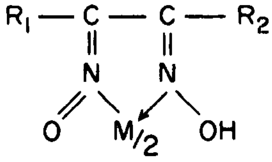


$$\begin{array}{l} R_1 - C = N - OH \\ \qquad | \\ R_2 - C = N - OH \end{array}$$

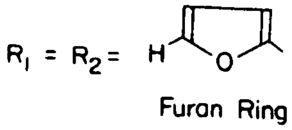
When $R_1 = R_2 = Me$ in this structure, we have the best known of the dioximes, dimethylglyoxime. The dioximes exist in three stereoisometric forms



As with the monoximes, tautomers exist for the dioximes of the oxime-nitrone forms as shown under oximes. With the dioximes however, chelation apparently takes place through the nitrone form, to give chelates of the form



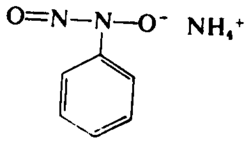
Probably a reagent of this type better than dimethylglyoxime is α-Furildioxime. In the general formula above

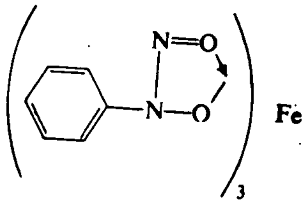


Its value lies in its greater solubility in water than the dimethylglyoxime and hence is available in greater quantities in the aqueous phase for chelate formation. Furthermore, the metal chelates are less water soluble.

(e) Nitroso Aryl Hydroxylamines

One of the best known chelating reagents used in inorganic analysis belongs to this group. It is cupferron, discovered by Baudisch in 1909. Its formula and that of the chelate with Fe(111) are:



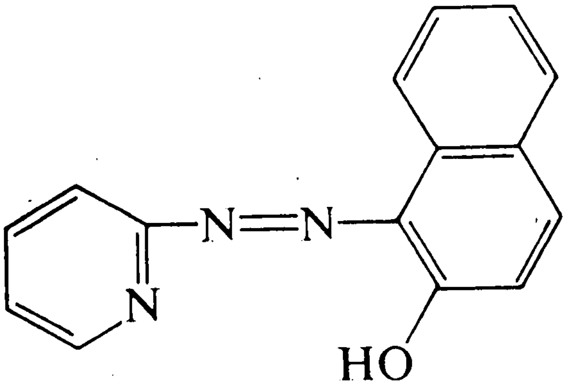


Cupferron is similar to 8-hydroxyquinoline in its capacity to form chelates with a number of metal ions. Non-polar solvents are generally used for the extraction of metal cupferrates, but amyl acetate can be used.

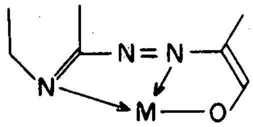
When the phenyl group is replaced by a naphthyl (to form neocupferron) a greater precipitating sensitivity is achieved.

(f) Azo Compounds

Compounds containing the azo grouping form an important group in solvent extraction work. They are primarily dye-stuffs or indicators because of the intensive colours developed with metals or with changes in pH. One well-known example is 1 - (2 - Pyridyl azo) 2 naphthol, commonly called PAN.



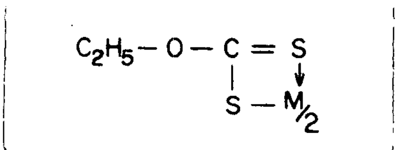
The bonding is probably of the form to give two 5-membered ring systems.



With a bivalent metal ion having 6-fold coordination, two such molecules of PAN form an uncharged octahedral complex, lacking hydrophilic groups, and which is therefore insoluble in water. Increasing the size of the aromatic part of the molecule or substitution of non-polar groups in the ring, gives reagents that are more selective and the corresponding chelates are more soluble in the organic phase.

(g) Thio-acid derivatives

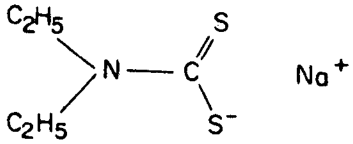
Sulphur is much less effective than oxygen in hydrogen-bond formation so that replacement of O by S in compounds of otherwise the same structure leads to a lower solubility in water. Nitrogen, on the other hand shows only slightly less tendency to form hydrogen bonds than oxygen. For this reason, complex forming reagents containing sulphur atoms are very popular in solvent extraction work because they partition very favourably in the organic phase. The size and orbital directions of the sulphur atoms permits 4 membered rings to be formed through two sulphur atoms, e.g. the nickel chelate and the xanthate ion.

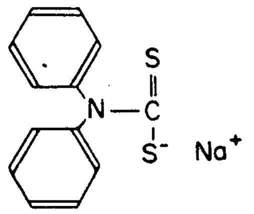


$$C_2H_5-O-\underset{\underset{S\,-\,M/2}{|}}{C}=\underset{\downarrow}{S}$$

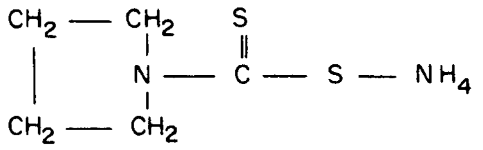
The metals showing the strongest tendency to form chelates through the sulphur atom are Cu, Ag, Au, Hg, As, Sb, Pt, Pd, Cd, Ni, Co, Mn, Ti. This group contains many of the elements commonly determined in silicate rocks. and it is not surprising that sulphur-containing liquids are widely used in rock analysis.

Derivatives of dithiocarbamic acid are widely used in solvent extraction work. The simplest is the sodium salt of diethyldithiocarbamic acid which has the formula shown below. It gives water-insoluble precipitates with all those metals forming insoluble sulphides. Unfortunately, the reagent is very unstable in acid solutions, the rate of decomposition being directly proportional to the hydrogen-ion concentration. However, some other dithiocarbamates are far more stable under acid conditions, for example





Di Benzyl Ammonium Dithio Carbamate

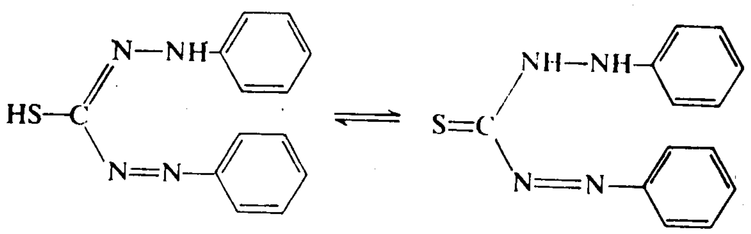


Ammonium Pyrrolidine Dithio Carbamate

Marshall (1965) used sodium diethyldithiocarbamate for a multi-element solvent extraction technique and found it quite satisfactory for the determination of a few micrograms of copper, lead and nickel in the presence of milligrams of ferric iron, masked by citrate at pH 7. Cobalt was not extracted.

(h) Dithizone

An account of chelating agents, however brief, would not be complete without a mention of dithizone. It is a popular colorimetric reagent for many elements and contains the azo grouping in addition to the S atom. It exists in tautomeric forms and it is most likely that chelation with metals takes place from the keto form.

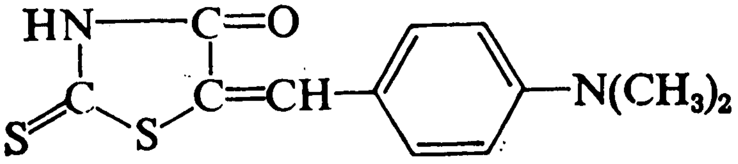


The reagent is not sufficiently specific to be of much use in solvent extraction work applied to the trace element analysis of silicate rocks, although it can be made fairly selective by judicious use of masking agents and variations of pH. A great drawback to its use in rock analysis is its instability in the presence of Mn (11) or Fe (111). The metal dithizonates are excellently soluble in many organic reagents.

Summary of Chelating Reagents

The foregoing list of chelating agents is by no means exhaustive, but it gives an idea of the variety of compounds that can be used for solvent extraction work. The majority of these are of the non-specific type and could be used for multi-element extraction.

Most analytical methods involving chelating agents depend on spectrophotometric methods of analysis and in most cases, quite specific conditions have to be obtained for accurate analyses. Such specificity is not required when AAS is used for the final determination of the extracted metal chelate. For example, p - dimethylaminobenzal rhodanine does not provide a specific method for the determination of gold in the presence of large amounts of iron, copper, silver etc., when spectrophotometric methods of analysis are used. When AAS is used for the analysis of the organic phase the method becomes quite specific and this has been used as the basis for the determination of gold in geological materials (Beevers, 1967).



AAS therefore permits a specific method of analysis to be developed from a non-specific reagent. Perhaps many chelating reagents have been discarded in the past because of their non-specificity. One wonders now how many such reagents could be used to give specific methods if AAS is used in the final analysis. This line of investigation could well be highly profitable.

General Comments on Rock Dissolution

The biggest problem in the study of trace elements in silicate rocks by solvent extraction/AAS is to get the rocks, with included trace elements, completely into solution. Because of the unavoidable inclusion of trace elements in the fluxes, fusion techniques as a preliminary to getting the sample into solution are not very satisfactory, and acid attacks are generally to be preferred. It may be possible to use the lithium tetraborate fusion technique as used in the X-ray fluorescence method for major element analysis, but I have not yet tried it and I don't know if anyone else has either. The HF/H_2SO_4 digestion technique is not completely satisfactory because the following minerals remain undecomposed: Andalusite, Kyanite, Sillimanite, Corundum, Tourmaline, Rutile, Garnet, Zircon and Spinel (Hoops 1964). It would appear that for complete decomposition of a silicate rock, an HF/H_2SO_4 attack, followed by a fusion (generally alkaline, but sometimes acid) of the residue is necessary. In this way, a minimum of flux is required, and the introduced trace elements are kept to a minimum. It is, of course, imperative in all solution trace element work to run blanks concurrently with the sample attack.

For complete of sulphide minerals I have found that a perchloric acid attack, taken to fuming in the later stages, is good for the solution of most trace elements in copper, zinc and iron sulphides. This method of attack is not good when Sb, Bi and Ag are being sought, because silver is lost as the insoluble silver sulphate, and Sb and Bi require complexing anions such as chloride to prevent hydrolysis in acid media less than about 2N. For the decomposition of lead sulphide, a straight hydrochloric acid attack is recommended, and at no stage must an oxidising acid be introduced into the system, otherwise sulphate is produced from sulphide with consequent precipitation of lead sulphate and occlusion or co-precipitation of trace elements.

Trace element analysis of rocks and minerals by solution methods obviously has its problems. As we have seen, some of these are overcome by the combined solvent extraction/AAS technique. The physical methods of analysis that are now available such as X-ray fluorescence, optical spectrography, neutron activation and mass spectrometry are sometimes more suited and more desirable to the problems in hand. There is obviously a place for all these methods of analysis, and the choice one often has to make is not for the most desirable, but for the one that is most economical. In this latter respect AAS, with or without solvent extraction, is often the choice.

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