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Ion exchange resins in steel analysis

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I O N E X C H A N G E R E S I N S

I N S T E E L A N A L Y S I S .

Thesis submitted for Master of Science Degree to the
N.S.W. University of Technology by F.M. HALL.

SUMMARY.

Using ion exchange resin techniques, a method has been devised for the quantitative separation and estimation of the metals Vanadium, Chromium and Molybdenum in steels.

The programme involved studying, on DE-ACIDITE "FF" anion exchange resin, the behaviour of the metals Iron, Tungsten, Vanadium, Chromium and Molybdenum when certain complexing agents were present; either in the original mixture or in the eluting solution.

The work established that:

- (a) strongly basic anion exchangers are most useful for the separations
- (b) the metals should be in their highest valency states in the solution because their anionic characteristics are then the most pronounced
- (c) complexing agents can be usefully employed either in the influent or as eluting agents

The method described separates Vanadium, Chromium and Molybdenum

- (a) from the other components of steel by absorption on DE-ACIDITE "FF" anion exchange resin
- (b) from each other by selective elution from the column with aqueous solutions of 0.7N sodium hydroxide, 8N hydrochloric acid and 1N hydrochloric acid respectively.

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CHAPTER 1.

ION EXCHANGE RESINS AND THEIR SCOPE IN ANALYTICAL CHEMISTRY.

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ION EXCHANGE RESINS.

1-4 A modern ion exchange resin is a high molecular weight organic polymer containing replaceable ionic groupings, these groupings being an integral part of the polymer structure.

Originally ion exchangers were natural substances such as cellulose, coal or zeolite sands. In 1935 Adams and Holmes improved upon the then synthesised resins, such as sulphonated coal, by reacting polyhydric phenols with formaldehyde and then these with sodium sulphite to give strongly acidic sulphonic acid groups.

To-day the polymeric form is usually prepared from styrene and divinylbenzene, highly crosslinked to render its solubility negligible. The more divinylbenzene employed the denser is the network and the less the swelling of the resin in water.

There are two methods of synthesising an ion exchange resin, one being when the ionic groups are made an integral constituent of the monomer prior to polymerisation, and the second when the ionic groups are introduced into the hard polymer structure. The former method gives the more homogeneous resin. Pepper (1) gave details of the preparation of such a sulphonated polystyrene - divinylbenzene resin, whilst Bauman (2) described the properties of this type of resin.

The extent of cross linking in the polymer affects

both the swelling properties of the resin and the size of the ions that may diffuse through the resin. It also affects the exchange capacity of the resin; that is the number of replaceable ions in the resin.

In cation exchange resins the active groups, such as sulphonic, carboxyl or hydroxyl are acidic, the sulphonic group being strongly acid, the carboxyl weakly acid and the hydroxyl weaker still. The formula of a cation exchanger in the hydrogen form may be represented by RSO_3H with the hydrogen ion the exchangeable ion. The hydroxyl groups present from the phenol used to prepare a resin possess reducing properties which can make them unsuitable for use with oxidising agents; also in anion exchangers this hydroxyl group may act as a ligand towards some metals, thus leading to cationic metal absorption by the anion exchanger. Phenol-formaldehyde type resins then are frequently unsatisfactory and this in part accounts for the development of the strictly mono-functional resins of styrene.

The active groups in anion exchangers are amino groups such as $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, or quaternary ammonium groups $-\text{NR}_3^+$. This latter group gives a strongly basic resin, the others a weak or medium strength basic exchanger.

All of the ion active groups tend to solubilize the resin - an undesirable feature. But by controlling the

degree of cross linking, an insoluble, yet sufficiently hydrophilic resin, can be prepared. Some hydrophilic property is necessary to permit diffusion of ions through the resin and so obtain maximum exchangeability.

CATION EXCHANGE RESINS.

1.2 The ionic character of cation resins is primarily determined by the active groups.

A simple method of examining these active groups is by titration of the exchanger, when all the exchange groups are satisfied by hydrogen ions. The exchanger may be considered an acid, and its titration, using an alkali as titrant, is analogous to a soluble acid.

For simple ions the exchange capacity of a cation exchanger, containing only the strongly acid sulphonic group, is independent of the pH of the solution as well as the nature of the exchangeable ions. If other weakly acid groups are present in the resin, as in sulphonated coals, the exchange capacity will increase with increasing pH due to these weakly acid groups.

The relative ease of replacement of the various cations is dependent on many factors; such as the charge on the ion, concentration, radius of the ion and hydration of the ion. However the following general statements are correct

- (a) For the alkali and alkaline earth cations the relative replacing power is in the order of increasing atomic number. For example $\text{Li} < \text{Na} < \text{K}$. In each group the charge on the ion is the same, the replacing power being dependent on ionic size which involves hydration effects.
- (b) the relationship between the different series follows the valence rule at low concentrations; that is the higher the valence the greater the displacement power.

Wicklander (3) found that concentration alters exchangeability, so much so that the order can be reversed. An explanation as to why this alteration occurs is the hydration theory, in which the difference between ion behaviour is attributed to the differences in the radii of the hydrated cations. It must be noted however that the number of water molecules surrounding each cation is not a fixed number, but varies with temperature and concentration. The exact value of the hydration radius is not known, but the relative activities of the various ions at any particular ionic strength may be used for estimating the relative exchange ability of the various ions. Boyd (4) has shown the relationship that exists between activities of ions and the ionic radii of the ions.

ANION EXCHANGE RESINS.

1.3

The ionic character of anion exchangers is also primarily determined by the polar groups. In studying anion exchangers one method is by titration with acid to give titration curves similar to those of the cation exchangers. The range of basicity covers strong, weak and very weak bases.

The relative ease of replacement of the various anions depends upon the polar group of the resin, valence, ionic size, concentration and strength of acid formed by the anion. The hydroxyl group is analogous to the hydrogen ion in cation equilibria and its ease of replacement varies with the basic strength of the anion exchanger itself. For example, in strongly basic resins, the hydroxyl ion exhibits a very low "exchange potential," whereas for weakly basic exchangers the hydroxyl ion exhibits a very high "exchange potential." Such differences in "exchange potential" merely reflect the degree of ionization of the various basic exchangers. The "exchange potential" of ions other than the hydroxyl ion depends more upon the nature of the ion than upon the anion resin itself and generally this exchangeability or "exchange potential" increases with valence. Kunin and Myers (5) give the following order of exchange for a weakly basic exchanger; hydroxide > sulphate

> chromate > citrate > molybdate > acetate > chloride > fluoride. For a strongly basic anion exchanger Kunin and Myers (6) found the same series to exist except for the hydroxyl ion, it now being the weakest replacing ion.

These series however, as in the case of cation exchangers, are not constant over a wide range of concentration and pH change, due to the difference in the activity coefficient - concentration relationships for any two ions (3). It is important to note that the ionization constant of the acid formed by each anion is not the important factor influencing its position in the absorption series, but if the ionization constant is very small the hydrolysis of its corresponding salt with the exchanger will be so great as to permit very little exchange. When then hydrolysis is small, valence and ion size become important factors.

The exchange capacity of a strongly basic anion exchanger is independent of the pH of the solution. The resin, a quaternary ammonium compound, has the form $\text{RN}(\text{CH}_3)_3^+\text{OH}^-$ and is completely ionized. On the other hand the other basic forms of anion exchangers, such as $\text{R NH}_3\text{OH}$ are only slightly dissociated due to hydrogen bonding with the hydrogen atoms of the amino groups. The hydroxyl groups are bound by this bonding process and

7.

compete for the protons in the group RNH_3^+ . This does not happen in the $\text{RN}(\text{CH}_3)_3^+$ ion.

Weakly basic exchangers do not possess a definite and constant maximum exchange capacity, although theoretically it is equal to the total number of amino groups contained in the resin. The working capacity depends on the total number of amino groups, and the fraction available at the pH of the experiment. The higher the basicity of the exchanger the less is its capacity dependent upon pH. Capacity also increases with increasing valence of the competing anion; thus $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HCl}$ whilst generally anion affinity decreases with decreasing acid strength; thus $\text{HCl} > \text{CH}_3\text{COOH} > \text{C}_6\text{H}_5\text{OH}$.

The process of anion exchange then on a weakly basic exchanger is subject to variables in the solution, but with strongly basic resins exchange is rapid due to the high dissociation of the resins. Quantitative exchange will occur only if the anion in the resin has a lower affinity for the resin than the anion in the solution, other effects such as concentration being neglected.

Gregor (7) has given the result of studies of selectivity of quaternary base anion exchangers towards univalent anions. In some systems the selectivity coefficients varied little with composition, such as in the

halide, acetate and nitrate pairs. But in other systems a marked difference was observed as in the thiocyanate, perchlorate, di- and tri- chloroacetate pairs.

RESINS AND THEIR USES.

1.4

The separation of electrolytes in a common solution by means of ion exchangers may be accomplished in several ways. Firstly, if the two ionic species are of opposite charge then either a cation or anion exchanger will give a ready separation. Secondly, ionic species of like charge may be separated in several ways. Depending upon differences between the ionic species in question, such as ionic radius, valence, or acidic or basic strength, these differences resolve themselves into a difference in "exchange potential" or exchange rate.

For example, large organic ions may be separated from small inorganic ions by using resins of certain pore size. The small ions can pass into the resin structure and be absorbed whilst the large ions are unable to penetrate the resin structure and can only be absorbed on the surface of the resin.

To separate two anions of different strength in the acid form, an anion exchanger can be selected whose basic strength is sufficient to neutralize only one of

these acids. However, often the differences between the two species are not sufficiently great to give a quantitative separation.

In this latter technique separations may be divided into two classes

- (a) separations on the absorption cycle, and
- (b) separations on elution of the absorbed mixture.

Two general methods for such utilization of exchangers are available, the first being a "batchwise" operation and the second a "column" operation. The batchwise operation is simple but inefficient as the number of consecutive operations necessary for a complete conversion varies with the equilibrium of the system.

The equilibrium

will require a considerable number of resin contacts whereas

requires but one. In the first equation, an equilibrium is established between hydrogen and sodium ions in both the resin and solution phases. In the second equation, the hydrogen ion is removed as water, so that only one contact with sufficient resin will cause the reaction to proceed to completion.

As most exchange processes are equilibrium reactions necessitating a continuous contacting of the

exchanger with fresh electrolyte, the column technique is widely used.

ION EXCHANGE IN ANALYTICAL CHEMISTRY.

1.5 The applications of ion exchangers to analytical processes may be classified as

- (a) Separation of interfering ions of opposite charge.
- (b) separation of ions from non-electrolytes;
non-electrolytes having no effect on exchange resins.
- (c) separations based on ionic size.
- (d) separations based on differences in basic or acid strength
- (e) separations based upon conversion of ions to opposite charge or to non-electrolytes by complex salt formation.

An example of (a) is given by Salmon (8) who separated phosphoric acid from vanadium IV and vanadium V by absorbing the vanadium ions only on a cation exchanger. A similar separation of cation and anion is given by Samuelson (9) in the analysis of phosphate rock ~~only~~. The cations are absorbed by the hydrogen form of a cation exchanger.

Gustavson (10)(11) supplies a very interesting example of (b). He showed that by means of both cation and anion exchangers, it is possible to determine the cationic chromium, the anionic chromium and the uncharged

chromium in a tanning liquor.

Davies and Nancollas (12) have exemplified (d) by using an anion exchanger to prepare a carbonate free sodium hydroxide solution. The carbonate ions are absorbed by a strongly basic anion exchanger.

An example of (e) is the separation of iron III from aluminium (13). When to a solution of these metals excess thiocyanate is added, the iron only is retained as a complex on an anion exchanger.

ION EXCHANGE EQUILIBRIA.

1.6

When an ion exchanger is brought into contact with an electrolyte solution, exchange takes place until equilibrium is reached. The concentrations in each medium have then assumed new values and a knowledge of the laws governing the distribution of ions is necessary in order to select optimum conditions in such a batch process. At present knowledge of conditions in the resin phase is very imperfect, but numerous theories, have been proposed.

The Donnan Theory is one such theory. When a sulphonic resin and a sodium chloride solution attain equilibrium, the following relationship holds between the ion activities in the resin phase(r) and those in the external solution(w).

$$\frac{a_{Hr}}{a_{Na r}} = \frac{a_{Hw}}{a_{Na w}}$$

In low concentration, equilibria between monovalent cations and hydrogen ions show good accord with the Donnan Theory, but data available fails to agree when divalent cations are used, even though consideration of activity coefficients improves the results.

The Donnan equation must give due consideration to activity coefficients, as different ions of equal valence are retained differently by the exchanger due to their respective activity coefficients. Lack of knowledge of activity coefficients is a drawback to the use of the Donnan equation.

The Mass Action Law can also be applied to equilibrium studies, for the thermodynamic equilibrium of the exchange reaction.

may be defined as

$$\frac{x_{Br}}{x_{Ar}} \cdot \frac{c_{Aw}}{c_{Bw}} \cdot \frac{y_{Aw}}{y_{Bw}} = K \frac{y_{Ar}}{y_{Br}} \dots\dots\dots(1)$$

Where x_{Ar} and x_{Br} are the equivalent fractions in the resin phase, c_{Aw} and c_{Bw} the ion concentration in the external solution, and y the activity coefficients. All quantities on the left side of equation (1) can be determined experimentally, and for convenience an apparent equilibrium constant K_a may be introduced and defined as

$$\frac{x_{Br}}{x_{Ar}} \cdot \frac{c_{Aw}}{c_{Bw}} \cdot \frac{y_{Aw}}{y_{Bw}} = K_a = K \cdot \frac{y_{Ar}}{y_{Br}} \dots\dots\dots(11)$$

Expressing concentrations instead of activities which is permissible in dilute solution then

$$\frac{x_{Br}}{x_{Ar}} \cdot \frac{c_{Aw}}{c_{Bw}} = Q \dots\dots\dots (iii)$$

Many authors (16)(17) have shown that K_a generally does not remain constant when the ratio $x_{Br} : x_{Ar}$ is varied, this indicating the resin phase cannot be considered an ideal solution. Samuelson (14) and Lowen (15) have shown that in general K_a is dependent on the ratio $x_{Br} : x_{Ar}$.

The Rothmund and Kornfeld formula (18) given by

$$\frac{x_{Br}}{x_{Ar}} \cdot \left(\frac{c_{Aw}}{c_{Bw}} \right)^p = K \dots\dots\dots (iv)$$

where K and p are empirical parameters is one which is most interesting and according to Walton (19) fits all data in the literature.

The differences in "exchange potentials" of ions can generally be attributed to differences in the activity coefficients in the resin phase and the K_a value may be regarded as a practical measure of the relative affinity of the ions for the exchanger. Two ions possess the same exchange affinity if $K_a = 1$. For ions of different valence the ion concentration in the resin phase affects the equilibrium and the equation for a monovalent ion A and a divalent ion D may be expressed as

$$\frac{x_{Ar}^2}{x_{Dr}} \cdot \frac{a_{Dw}}{a_{Aw}^2} = K_p \dots\dots\dots (v)$$

and this equation can be used as well as (iv) above for determining K values rather accurately in all cases of equilibrium.

ION EXCHANGE IN COLUMN OPERATION.

1.7

For analytical purposes the general procedure is to percolate the solution containing the ions through a fixed bed of ion exchanger packed in a long narrow column. The operation is usually downflow, the solution entering being known as influent and the solution leaving as effluent. Normally the exchanger contains but one exchangeable ion type whilst the influent may contain one or more ion types. Absorption of the desired ions is the first step, followed by washing, after which the exchanger contains the exchangeable ions as well as some of its original ions. The next step is elution or the process of removal of the absorbed ions from the column. Finally the resin is regenerated to the desired form in which it may again be used for absorbing ions. The total number of exchangeable groups in the column is conveniently expressed as milli-equivalents and denotes the total capacity of the column. Subsequent to capacity being attained the break-through capacity of the column is reached. For many reasons, such as particle size, rate of liquid flow, or resin packing, the break-through capacity is less than the total capacity of the resin column.

If the influent contains only one ion, absorption occurs right throughout the resin column until the breakthrough point is reached. If the influent contains more than one exchangeable ion a certain separation of the ions will be obtained since the various ions differ in their affinities for the resin. This principle is the basis of ion exchange chromatography.

Complexing agents can be usefully employed also, as a complex compound on being formed can retard or prevent the uptake of a certain ion. This effect is due to altering the nature and size of the charge on the ion under consideration. For example the problem in the ion exchange separation of the rare earth metals (20) is one of moving one of the cations out of a narrow absorption band at the top of the column at a more rapid rate than the others so that all or most of it is eluted before elution of a second cation begins. Greater column lengths assist this form of separation, but high yield must be balanced against speed in such a technique.

For elution in cation exchangers hydrochloric acid or sodium salts are commonly used. An example of the use of hydrochloric acid for a cation exchanger is the separation of sodium and potassium (21). As the potassium has a higher replacing ability, or a higher "exchange potential" than sodium the $\text{Na}^+ : \text{K}^+$ ratio in the

solution will increase as the desorbing solution moves downward.

Elution is also affected by acid concentration. Samuelson (22) studied the elution of potassium, copper II, aluminium and iron III ions to find a certain optimum concentration of hydrochloric acid as eluting agent. The value given is 3 to 4N acid for all ions examined. Higher acid concentrations may cause the formation of complex ions and may also shrink the resin causing a lowering in the rate of desorption.

If complexing agents can be present in the cation solution without interfering with the determination of the cations it may be practical to use a complexing agent as desorber. Such a technique was used by Samuelson (23) when removing iron III from a cation resin with ~~the~~ potassium oxalate.

The tetravalent metals zirconium, hafnium, niobium and thorium are very difficult to remove from a resin with hydrochloric acid as desorber (24). Therefore hydrochloric acid allows a separation of these metals from many others; oxalic acid subsequently removes these tetravalent metals.

Experimental data on break-through curves for anion-exchangers is rather meagre. Sussman, Nachod and Wood (25) however have shown that the shapes of the curves

are in principle the same as those of curves for cation exchangers.

TECHNIQUES OF ION EXCHANGE SEPARATIONS.

1.8

A significant advantage of ion exchange separations is that the accuracy of the final analysis is unaffected by working within a considerable latitude of safety in respect of exchanger, washing water, or eluant.

For analytical purposes column operation is the important technique, and an essential requirement of the resin itself is the absence of interfering reactions. The strictly monofunctional polystyrene types of resin generally meet this latter requirement. Reduction by the resin nevertheless does occur with all types of resins although the degree of reduction may vary both with the resin type and the redox potential of the electrolyte system. Runberg and Samuelson (26) found that reduction of the following oxidants occurs when left in contact with certain resins:- permanganate, chromate and molybdate. This is in agreement with the reduction of iron III, chromium VI and vanadium V experienced during the studies outlined hereafter.

The hydrogen form of the cation exchanger is the most common form used. If hydrolysis can occur, the hydrogen form may be necessary. On the other hand with

organic compounds, other than the hydrogen form may be necessary to prevent precipitation of the organic acid on the resin. An example of this type of problem is a vanadate solution, which under acid conditions is a good oxidant of a resin, - Samuelson (27). Consequently the hydrogen form of the resin is undesirable as the vanadium IV formed by reduction is essentially cationic only in character, whereas vanadate is anionic.

The apparatus for column operation is quite simple. A long glass tube with a porous plug or plate at the bottom and a tap for control of flow rate, are the main requirements. It is preferable to keep the resin in the column under water at all times, due to its swelling properties and this may be achieved by keeping the column outlet above the level of the resin bed. Usually the operation for ion absorption is downflow, but elution may be downflow or counter-current. The advantage of counter-current elution is the avoidance of transporting the absorbate, or absorbed ions, through the whole column. A coarse resin gives a fast flow rate with a consequent decrease in break through capacity. Finely ground resins on the other hand tend to prevent normal flow of solution but improve resin capacity.

The effect of acidity can be generally formulated in that the separation can be quantitative if the sum of the

metal cation and hydrogen ions does not exceed the break-through capacity of the resin bed. This means it is advisable to maintain a minimum acidity in most solutions. An exception would be when a complexing agent, for example citrate, is being used, for addition of acid would then facilitate the absorption of metal ion by decreasing the citrate ion concentration and so allowing greater dissociation of the complex metal citrate.

In anion exchange techniques, the hydroxyl or chloride form of the resin is the most popular. If the entry of hydroxyl ions into the eluate is of no consequence, then the hydroxyl form is the easiest to prepare as regeneration of the resin is rapid with sodium hydroxide due to the "exchange potential" of the hydroxyl ion and the weakly basic character of many of the anion exchangers. However the use of a complexing anion, for example citrate, may be advisable as this anion can cause absorption of those metals which form an anionic complex with the complexing agent. Such a technique is convenient in separating metals which form complexes, from those which do not, without the presence of the complexing agent in the solution.

COMPLEX SALT INVESTIGATIONS.

1.9

Ion exchange resins offer great possibilities for the study of both composition and stability of complex

compounds. Such investigations can be carried out under equilibrium or non-equilibrium conditions, with the former the more important. The non-equilibrium method can only be used for strong complexes and then only gives qualitative data as to composition of the complex.

The simplest form of the equilibrium method is to shake a known volume of solution of known composition with a known weight of dry resin until equilibrium is attained and then to analyse the eluate.

In the study of complex systems, two properties of exchangers should be noted. The first is selectivity which appears both in the absorption of ions of different ionic charge and also in that of ions of the same ionic charge but of different hydrated ionic radius. The second property arises mainly from the Donnan membrane type of equilibrium which, as has been shown, prevails between the electrolyte solution and the resin. The selectivity leads to the preferential absorption of ions of higher ionic charge from dilute solution, but of ions of low ionic charge from concentrated solution; whilst for ions of the same ionic charge those of lower hydrated ionic radius are preferentially absorbed. The effect of the Donnan equilibrium is that with a cation exchanger, for example, the concentration of free ions of an anionic ligand will be very low in the resin phase, which will favour a shift

of the equilibrium in that phase towards complexes with fewer ligand groups.

In cation exchange equilibria the absorption of a cation M^{m+} by a cation exchanger in the hydrogen form is governed by the equilibria

where r denotes the resin phase, provided any anions present do not form complexes with the cation. Hence complex formation may be detected by an upset of this equilibrium.

The stepwise formation of a series of complexes between M^{m+} and a ligand group "L" will lead to complexes of the type ML , ML_2 ML_n and if "L" is neutral these will all be cationic. But if the ligand is derived from an acid some of the complexes will be neutral or anionic.

If some of the complexes are cationic then they will be absorbed by the cation exchanger together with the free cation and in such cases complex formation will be detected by the non-absorption of the neutral or acid group by the cation exchanger. Stokes and Walton (28), and Salmon (29) have reported results of this approach to the study of various complex systems.

These study methods are applicable only at low metal ion concentrations and a frequent problem encountered in applying such procedure is hydrolysis. In all of these studies it is necessary to carry out many experiments in

which the ratio of ligand to metal, the pH, the total salt concentration, and temperature are varied over a wide range of values.

Samuelson (30)(31) investigated the complex equilibrium in a solution of charged and uncharged complex to determine the free central group in the solution. The system contained cations AP^p and BQ^q and anions R and S where "p" and "q" are the charges on the respective ions. The only complexes are assumed to be of the type BS_n for a calculation of the complexity of the system B-S is possible only on the supposition that A and S do not give any complexes.

Analysis of the resin bound ion may be difficult, but analysis can be more simply effected on the aqueous solution provided the strong complex problem can be overcome.

The distribution coefficient, K_d^0 , in the absence of the complexing agent S, and the distribution coefficient, K_d , in the presence of the complexing agent S, are determined under identical conditions. The dissociation constant K_c of the complex BS_n follows from the Mass Action Law.

$$K_c = \frac{CB \cdot CS_n}{C \cdot BS_n}$$

Schubert and Myers (32) derived the following relationship between these quantities

$$K_c = \frac{C \cdot BS_n}{[(K_d^0/K_d) - 1]}$$

and a straight line should be obtained by plotting $[(K_d^0/K_d-1)]$ against concentration C_{Sn} on a log-log plot.

Gunther-Schulze (33) calculated the composition of the complex cations directly from the changes in composition of the aqueous solution. However Samuelson (34) pointed out that it is not possible to calculate the dissociation of the complex in the outside solution directly from the distribution of the ion between the resin and solution because ion concentrations in the two phases differ considerably.

Nevertheless a rapid evaluation of the relative merits of a complexing agent for separating cations can be made by measuring the ratio of the distribution coefficients in the presence of known concentrations of the complexing agent under controlled conditions (35).

However a general weakness in the use of exchangers for studying complexes is that equilibrium among the various species of the complex will slowly shift as one species is absorbed by the resin. Such a problem was observed by Adams (36) when studying complex chromium III salts.

Whilst absorption of a metal by a resin exchanger is affected by complex formation, so also is the desorption of a metal affected by complex formation. Genge and Salmon (37) compared various acid eluants by using the

metal form of the exchanger and, as desorber, different acids of different concentration or pH.

Complex formation can also be studied by anion exchange equilibria methods. Using the hydroxide form of the resin as an example and an anion A^{a-} where "a" is the charge on the anion, the following equilibrium system is eventually attained

where "r" denotes the resin phase.

Equilibria may also be established where complex anions are involved and the complex formation may be shown by the absorption of the metal grouping in the anion exchanger. Kraus and co-workers (38) used such methods to study the complex halides of numerous metals.

A theoretical treatment of the batch equilibrium method as applied to anion exchange studies has been proposed by Fronaeus (39). It applies to solutions of low metal ion concentration and constant ionic strength, but of variable ligand concentration.

Salmon (40) also has used a similar procedure in anion exchange equilibrium studies, his work being directed towards iron III and phosphoric acid, and aluminium and phosphoric acid.

The selectivity of ion exchangers can be an asset in the study of complexes. Knowing that selective

absorption may result in the strong absorption of a complex normally present in solution in low concentration, whilst a complex present in higher concentration may not be absorbed at all, an efficient separation may be obtained of a mixture of complex compounds. Thus if a complex ML^{x+} can be identified by cation exchange and a complex ML^{y-} by anion exchange and if the ligand "L" can be identified in terms of one of the anions of the polybasic acid from which it is derived, then the remaining complexes may be inferred even if not absorbed (41).

According to Vickery (42) a comparison of the efficiency of various eluants may be simply related to the overall stability constants formed by the metal ions and the desorber; however the stability series varies because of a factor influenced by the valency of the ions when ions of different valency are eluted.

Freiling (43) introduced the gradient elution theory to exchange methods of separation. Gradient elution is the use of a continuously changing eluant strength and allows the derivation of equations for the resulting peak locations and peak widths.

SOME APPLICATIONS OF EXCHANGERS TO METAL SEPARATIONS.

Perhaps the simplest, yet one of the most convenient applications of exchangers, is the separation

of interfering ions of opposite charge.

Salmon (8), for example, separated vanadium IV and vanadium V from phosphoric acid by absorbing the vanadium on a cation exchanger.

A method of determining sodium and potassium in the presence of vanadium has been devised by Samuelson (27). The vanadate solution was passed through an ammonium cation exchanger when all vanadate passes into the effluent. The sodium and potassium may then be eluted with hydrochloric acid.

An anion exchanger may be saturated with a complexing anion prior to metal ion absorption. Kielczewski (44) used this technique. He saturated an anion exchanger with phosphate ions and this resin form absorbed iron III but allowed copper, nickel and cobalt to pass into the effluent.

Yoshino and Kojima (45) used a cation exchanger to separate iron III and titanium IV. Both metals are absorbed on the resin and the iron is preferentially eluted with potassium cyanide. The titanium may be subsequently eluted with 10% sulphuric acid.

An anion resin was used by Hague and co-workers (46) for the separation of nickel, manganese, cobalt and iron in high temperature alloys. After solution and

removal of tungsten, silicon, copper and molybdenum, the solution was passed through an anion exchanger and the nickel, manganese and chromium were collected in the first fraction by elution with 9N hydrochloric acid. Cobalt was collected in a second fraction by 4N hydrochloric acid elution and the iron in a third fraction by 1N hydrochloric acid elution. This separation is based on chloro-complex formation.

Russell (47) has shown that tetravalent ions can be selectively eluted from a sulphonic acid resin by means of oxalic acid due to the strong complexes formed. Tri-, di-, and mono-valent ions can be separated by citrate buffers. At pH3 a 5% citrate solution displaces the trivalent species; at pH5 the remaining di-, and mono-valent cations are displaced from the column.

The results of a study of the elution behaviour of titanium, tungsten, molybdenum and niobium in various hydrochloric - hydrofluoric acid media have been published by Høgre (48). Titanium and niobium are easily separable under a variety of conditions; molybdenum and tungsten are also easily separable; but titanium and tungsten are difficult to separate effectively under all possible conditions.

Ferric iron was separated from aluminium (13) by absorbing the iron as a negatively charged ferric thiocyanate complex ion on an anion exchanger.

The separation of beryllium from aluminium is also possible by ion exchange methods according to Kakihana (49.) Using a phenol sulphonic acid type resin and a solution of less than 0.01N aluminium and beryllium the aluminium only should be absorbed.

Meloche (50) separated rhenium and molybdenum by passing a solution of perrhenate and molybdate through an anion exchanger and eluting the molybdate with 10% sodium hydroxide solution.

Molybdenum in ferromolybdenum was also separated by Usatenko and Datsenko (51) by passing the hydrochloric acid solution through a cation exchanger and eluting the molybdenum with 5% sodium hydroxide solution.

RESINS SELECTED.

For the experimental work of this paper one cation and one anion exchange resin were selected, namely ZEO-KARB225 and DE-ACIDITE"FF" respectively. Both resins are supplied by the Permutit Company Limited and have the following characteristics.

ZEO-KARB225 is a polystyrene resin crosslinked with divinylbenzene and containing only one active group, the sulphonic acid group. It is rapid in cation absorption and has the same total capacity at all pH values, namely approximately five milli-equivalents per gramm. It is closely crosslinked with a consequent lessening in capacity for ions larger than $(N Me_4^+)$.

DE-ACIDITE"FF" is a highly basic resin prepared also from polystyrene crosslinked with divinylbenzene. Its active group is the quaternary ammonium group (NR_4^+) and has a high capacity for such feeble ions as carbonate. Its capacity for absorption of strong and weak acids is fair, but its total capacity is less than that of the cation resin, namely approximately 2.5 milli-equivalents per gramm.

For the cation resin the type of reaction may simply be given as

whilst for the anion exchanger the reaction involved may be illustrated as

where R denotes the resin grouping.

CHAPTER 2

SOME ASPECTS OF THE CHEMISTRY OF THE METALS UNDER CONSIDERATION.

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IRON.

2.1

Iron is a transition element with more than one valence state, the di- and tri- valent states existing in solution. It readily forms complex compounds in solution in both valence states.

In the divalent state, iron gives a series of definite salts which are quite stable and the complexes involving this state have a co-ordination number of six for the cations but rarely six for the anions except in the ferrocyanides. The ammine complexes are rather unstable whilst only the fluorides and chlorides give complex halides. The salts of mono basic organic acids seem to be simple, but the salts of dibasic acids, such as oxalic acid, are complex.

COMPLEX SALTS OF IRON II .

The carbon complexes of iron II are confined to the cyanides which are of two kinds, the ferrocyanides $\text{M}_4[\text{Fe}(\text{CN})_6]$ and the pentacyano compounds $\text{M}_x[\text{Fe}(\text{CN})_5\text{X}]$. The ferrocyanide is very stable and most of the heavy metal derivatives give signs of increasing complexity due to polymer formation.

The nitrogen complexes contain up to ten ammonia groups per mole of iron II , but dissociate rapidly. However chelation increases stability so that the pyridine complex, $[\text{Fe}(\text{py})_4\text{Cl}_2]$, or the cyclic amines $[\text{Fe}(\text{en})_3]\text{Cl}_2$ are quite stable.

The oxygen complexes have as many as four organic molecules to one iron and the chelate derivatives of diketones and salicylaldehyde are readily made.

The "ato" compounds are relatively few and practically always four covalent.

The complex chlorides are of the types $M[Fe Cl_3]$, $M_2[Fe Cl_4]$ and $M_4[Fe Cl_6]$.

COMPLEX COMPOUNDS OF IRON $\overline{III}$.

Iron $\overline{III}$ has a much stronger tendency to form complexes than has iron $\overline{II}$. Stability is improved by covalent bonding and the resulting compounds are nearly all anions with co-ordination numbers of four and six.

Almost the only ferric salts that are not complex are those of the strongly oxy-acids such as nitric and perchloric acids.

The cyanide complexes are very similar in type and stability to those of iron $\overline{II}$, a typical compound being $M_3[Fe(CN)_6]$.

The affinity for nitrogen is very small although the organic amines, especially of pyridine and quinoline are more stable than those of ammonia.

Iron $\overline{III}$ on the other hand has a great affinity for oxygen and hence a strong tendency to react with alcoholic hydroxyl groups to form very stable compounds. The derivatives of mono basic carboxylic acid can be seen by their red colour to be complex although the structure and

even composition are frequently uncertain. Usually three iron atoms occur in the central grouping because the two oxygen atoms of one carboxyl group are too near to attach themselves to only one iron atom; but two or more carboxyl groups can be joined through two or more iron atoms to give an unstrained ring.

Of the "ato" compounds, the oxalato complexes are numerous and stable. There are two series, the di-oxalato, which are green-yellow in colour, and the tri-oxalato which are green and more stable. Mixed oxalato compounds also exist and are four covalent. Ferric chloride may be complex due perhaps to the instability of the shared sextet

- cl.
in Fe - cl. It is capable of forming ions of the type
- cl.

$[\text{Fe Cl}_4]^-$ and $[\text{Fe Cl}_6]^{3-}$.

Thiocyanate gives an intensive red colour with iron III. Ion exchange studies (56) have shown the thiocyanate complex to be cationic, but other ion exchange studies (13) have shown that there is an anionic ferric thiocyanate complex.

Ion exchange techniques have been found useful in both the analysis and study of iron solutions. By such techniques the complex ion of iron III sulphate has been studied (57). The distribution coefficient between the resin and solution and the effect of complexing agents were used

as a method for determining dissociation constants.

Again a separation of arsenic from iron was achieved by Yoshino (54) by passing a hydrochloric acid solution of these elements through a cation exchanger. Arsenite and iron were quantitatively separated but arsenate and iron were not.

Other means have also been used in studying iron complexes. Thoms and St. Clair (67) studied the relative stabilities of iron III complexes by spectral means. In increasing order of stability the complexes were cyanide, citrate, oxalate, acetate, phosphate, sulphate, chloride and nitrate.

Polarographic studies of the oxalate, citrate and tartrate complexes of iron II and iron III have been made by Lingane (64). Reduction from the ferrous to metallic state was observed in citrate solution at pH values above 11 and in tartrate solutions above pH6. He believes also that a hydroxo-citrato complex is formed in strongly alkaline citrate solutions.

Phosphoric acid has been used as an eluting agent for iron (59). Using cation exchangers, results suggested complex formation between ferric ions and phosphate ions with the iron having a high affinity for the resin, and the order of efficiency for the acids used as eluting agents was phosphoric acid > sulphuric acid > nitric acid = hydrochloric acid.

VANADIUM.

2.2

Vanadium is also a transition element. It displays variable valencies in its compounds and forms di-, tri-, tetra-, and penta- valent salts.

VANADIUM $\bar{V}$.

The anhydride, V_2O_5 , is amphoteric. It dissolves in acids to give salts generally of the type VOX_3 or VO_2X where "X" is a monovalent anion. The iso-electric point has been quoted at pH2.2 and the solution colour of yellow or orange is dependent on the M:V ratio with pH affecting the "V" concentration. This effect of pH upon colour intensity was personally experienced in this work whilst attempting the determination of vanadium $\bar{V}$ by colorimetric means. Graph $\bar{I}$ indicates maximum colour development, at 400 m U, of a solution of ammonium vanadate in sulphuric acid, with sodium hydroxide as pH adjustor, occurs in the pH range of 3.5 to 5.5 whilst above and below these values the colour of the solution fades.

The effect may be given as

Colourless vanadate + H^+ $\rightarrow$ coloured ion rapidly: coloured ion + OH^- $\rightarrow$ colourless ion slowly.

The complexes of vanadium $\bar{V}$ are not numerous and generally of the "ato" type or oxyhalide type such as $M^I[VO_2SO_4]$ or $M^I[VOF_4]$.

Curve of $\frac{M}{500}$ NH_4VO_3 solution at 400 m μ pH
against Transmittancy

VANADIUM $\overline{\text{IV}}$.

The oxide is only slightly acidic. Its normal salts are of the type VOSO_4 , generally blue, and very stable, whilst its complex salts are all "ato" compounds with a co-ordination number of six.

VANADIUM $\overline{\text{III}}$.

Its compounds are reducing agents and not normally existant in solution except in the form of complexes. The complexes are nearly all anionic with a co-ordination number of six, and no preference is shown for nitrogen over oxygen in such complex formation.

VANADIUM $\overline{\text{II}}$.

The salts are simple salts but strongly reducing to give the vanadium $\overline{\text{IV}}$ form. The few complexes it forms show a co-ordination number of 6.

STUDIES MADE ON VANADIUM COMPOUNDS.

Considerable study has been devoted to the salts of both vanadium $\overline{\text{V}}$ and vanadium $\overline{\text{IV}}$, as, due to their amphoteric natures and hydrolysis effects, the compositions are readily varied and hence react differently. For example, on an ion exchange resin the radicle VO^{+++} could react differently to the radicle VO_2^+ .

Carpenter (70) studied extensively the constitution of the vanadium $\overline{\text{V}}$ ion in acid solution, for Foerster and

Bottcher (71) had given evidence for the half cell reaction being

whilst Coryell and Yost (72), although postulating an ion $\text{V}(\text{OH})_4^+$, regarded vanadium V as existing predominantly as HVO_3 .

Ducret (73), because of conflicting data, used chemical means to study both vanadium V and vanadium IV in solution.

An ortho-vanadate solution was titrated with perchloric acid and the explanation offered is

Perhaps however the $\text{VO}_4^{\equiv}$ cannot exist in water hence

Thus the four stages of neutralization of ortho-vanadates are represented by

(i) neutralization of $[\text{OH}^-]$ ions formed by

(ii) the equilibrium

(iii) the condensation

Vanadium IV complexes with oxalate, citrate, tartrate and sulphate were also studied by Ducret. The oxalate raised the pH of precipitation of the vanadium and the stable complex was shown to contain the $[\text{VO}(\text{C}_2\text{O}_4)_2]^-$ ion. With tartrate ions a stable complex was formed when the vanadium IV to tartrate molecular ratio was 1:1. Two citrate complexes were observed, with one citrate molecule for one or two vanadyl ions. The citrate complexes were found more stable than the oxalate complexes but less stable than the tartrate complexes. The sulphate complexes were found to be poorly stable with a possible formula of $[\text{VO}(\text{SO}_4)_2]^=$.

Vanadium IV complexes with the halogens were found to be extremely unstable.

Using polarographic techniques Lingane (76) studied vanadium. Vanadium V gave a double wave, the first stage corresponding to a one electron reduction of the ion $[\text{V}(\text{OH}_4)]^+$ to the ion $[\text{VO}^{++}]$ and the second stage to a two electron reduction of the $[\text{VO}^{++}]$ ion to the $[\text{V}^{++}]$.ion.

Pecsok and Juvet (75), also by polarographic means, studied the behaviour of vanadium when complexed with ethylene diammine tetra acetic acid. They found that the diffusion

current constant of the vanadium $\bar{\text{V}}$ complex varied with pH, but that the vanadium $\bar{\text{IV}}$ complex gave an irreversible wave.

Kakihana (81) used vanadium $\bar{\text{V}}$ as an amphoteric electrolyte in cation exchange studies. The resin used was a phenol-sulfonic acid type containing more than one functional group. The conclusions were that vanadium $\bar{\text{V}}$ is fully absorbed by a hydrogen-hydrogen exchanger at all pH values of the influent, but that the vanadium quantitatively passed through the other resin forms if the pH of the influent was above 5.0.

MOLYBDENUM.

2.3 Molybdenum is also a transition element which gives rise to compounds of different valency, with six the most stable state.

Molybdenum trioxide (MoO_3) is the stable oxide, and gives molybdates of the type $\text{M}_2^1[\text{MoO}_4]$. Molybdic acid has a considerable capacity for condensation and polymerisation and unlike tungstic acid, is soluble in sulphuric acid, giving the "yl" sulphate such as MoO_2SO_4 .

Molybdenum $\bar{\text{V}}$ compounds are nearly always covalently bonded and the more important complexes are

- (i) the oxy-halides
- (ii) the cyanides
- (iii) the thiocyanates
- (iv) chelate organic derivatives

The chief type of (i) is $M_2^1[MoO Cl_5]$ where the magnetic moments correspond to one unpaired electron. In(ii) is exemplified the great stability of the eight co-valent cyanide complex of molybdenum $\bar{V}$. The molybdenum $\bar{V}$ thiocyanate complexes (iii) never have covalencies above six, but give a sensitive colour. The chelate organic derivatives (iv), such as the oxalate, are of the type $M^1[MoO_2(C_2O_4)]xH_2O$.

Molybdenum $\bar{IV}$ compounds are unstable and thus are restricted generally to the cyanides and a few "ato" compounds.

Molybdenum $\bar{III}$ compounds, such as $M_3^1[MoCl_6]$, are known with a co-ordination number of six. They are strong reducing agents.

Molybdenum $\bar{II}$ compounds exist in the polymeric form whilst the complexes are all derivatives of the dihalides by co-ordination.

Many techniques have been applied to the study of molybdenum compounds. For example Sussman (25) found molybdenum in ammonium molybdate to be completely anionic by its absorption on the chloride form of an anion exchanger. Recovery by sodium chloride elution was only qualitative, indicating strong absorption of the molybdate ion by the resin.

On the other hand Filippova (84) found that molybdenum as well as tungsten and antimony, could be quantitatively retained by cation exchangers of the sulphonic acid type. Desorption, based on their amphoteric character, may be obtained

by using an alkali solution.

An interesting effect reported (86), is that sulphonated ion exchangers absorb molybdenum weakly as do resins with both $[\text{SO}_3\text{H}]$ and $[\text{OH}]$ groups, whereas resins with a $[\text{CH}_2\text{SO}_3\text{H}]$ group are strong absorbers of molybdenum.

Ion exchange chromatography was used by Alimarin and Medvedeva (88) for determining molybdenum in steel. By using a cation exchanger and a sulphuric acid solution of the steel containing hydrogen peroxide, molybdenum, vanadium and tungsten were unabsorbed.

The constitution of aqueous solutions of molybdic acid and alkali molybdates was studied by Carpeni (90), who found that their composition depends on such factors as concentration, pH, and ionic strength. Below 3×10^{-4} molar however there exists only one species over the whole pH range, namely $[\text{MoO}_4^{=}]$.

Biswas (91) calculated reaction velocities for molybdic acid with tartaric, oxalic and citric acids and so obtained the comparative affinities for complex formation. The order given was oxalic $>$ tartaric $>$ citric, with the complex either unionized or anionic in character.

CHROMIUM.

2.4

Along with Molybdenum, Tungsten and Uranium, Chromium occurs in subgroup VIA of the Periodic Table and in solution displays several valencies, namely six, three and two.

Chromic acid, whilst impossible to isolate, is typical of the chromium VI compounds in solution. It contains $[\text{CrO}_4^{=}]$, $[\text{H}_2\text{CrO}_4]$, and $[\text{Cr}_2\text{O}_7^{=}]$ ions in equilibrium.

In the lower valence forms of three and two the chromium compounds may ionize as simple cations; but in the trivalent state the outstanding property is the power of complexing especially through nitrogen to give a co-ordination number of six.

Chromium VI gives acidic oxides only and whilst complex compounds may be formed, such as the halo-chromates, they readily hydrolyse with water.

Chromium III gives a hydroxide which is weakly acidic. Consequently the chromium is generally cationic except when a complex is formed with an anion carrying a charge greater than unity. For example the oxalate complex could be $\text{M}^3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ with the chromium in the anionic grouping.

Due to varying valency states, the anionic nature of the hexavalent state, and the diversity of complexes in the trivalent state, chromium has been extensively studied.

Gustavson (11) used a cation exchanger and an anion exchanger in series to isolate the cationic, anionic and neutral forms of chromium. However the weakness of the method is the shift in equilibrium existing between the three species due to flow rates.

Sussman and co-workers (25) have studied chromates by ion exchange methods. The explanation given of the desorption step of the chromate is that the primary, secondary and tertiary amines, of which the resin may be considered a mixture, are not such strong bases as the inorganic hydroxides used for desorption.

The desorption of an anion exchange chromate by a salt may be shown as

whilst by a base as

and whereas an excess of salt will shift equation (i) to the right, the excess of base will shift equation (ii) more completely to the right by furthering formation of the non-ionized base.

Sussman then attempted chromate recovery with the chloride, sulphate, carbonate and hydroxide of sodium, ammonium hydroxide and hydrochloric acid. All except the acid were effective, whilst the acid gave rise to substantial chromium III concentrations.

Gustavson (92) observed difficulties in the complete removal of chromium from resins when absorbed from complex solutions. He ascribed such difficulties to secondary reactions of the complex with the phenolic structure of the resin type used. Especially was it found that

absorption from a solution of hexa urea chromium III chloride was so strong that 1:1 hydrochloric acid had little elution effect.

A separation of chromium from nickel has been given by Lur'e and Filippova (84). The chromate is absorbed by an anion exchanger from solution of pH 1 to 12 and is eluted subsequently with 2% sodium hydroxide. Some chromium reduction was noted necessitating a final desorption with hydrochloric acid. The nickel is unabsorbed.

The structure of complexes of chromium were investigated by Thorstensen (103). For organic acids the order of increasing complex formation is given as formate, acetate, citrate and oxalate.

TUNGSTEN.

2.5 Tungsten occurs in subgroup VIA of the periodic table and displays varying valencies such as six, five and four.

The group valency of six is its most stable form and occurs in WO_3 the yellow trioxide insoluble in acids. The salts of tungstic acid, H_2WO_4 , have variable proportions of acid and base and can be classified as

- (i) normal tungstates M_2WO_4
- (ii) meta tungstates $M_2W_{14}O_{13} \cdot xH_2O$
- (iii) para tungstates $3M_2O \cdot 7WO_3 \cdot xH_2O$

Tungsten $\bar{\text{V}}$ compounds are generally confined to complex compounds, as indeed are the still lower valence forms.

COMPLEX COMPOUNDS OF TUNGSTEN.

Only two well defined series of complex cyanides are known. They are

- (i) $\text{R}_4[\text{W}(\text{CN})_8]$ containing tungsten $\bar{\text{IV}}$.
- (ii) $\text{R}_3[\text{W}(\text{CN})_8]$ containing tungsten $\bar{\text{V}}$.

Tungsten $\bar{\text{VI}}$ forms soluble complex ions with citric, tartaric, phosphoric and hydrofluoric acids due to chelate formation and polymerisation. The complexity of such compounds is exemplified in the hetero-poly-acids where there may be up to twelve WO_3 groups in the molecule.

Little work has been published on tungsten studies by ion exchange methods. However Samuelson and Runberg (26) have shown that a hydrogen cation exchanger is unsuitable for tungstate analysis although the ammonium form is satisfactory. The hydrogen form causes tungstic acid precipitations.

Ryabchikov and Lazarev (104) made a study of the absorption of vanadium and tungsten in relation to (a) the functional groups present in the ion exchanger chosen, (b) the solution acidity, and (c) the nature of the complex forming compounds present. The separation of vanadium and tungsten was achieved by using a hydrochloric acid solution of pH 1 containing hydrogen peroxide. The tungsten only was

absorbed by an anion exchanger and was subsequently eluted with ammonium hydroxide.

It is possible to use an anion exchanger to determine the total anion concentration in a solution. The free base of the resin is displaced by neutral ions in the solution and the effluent is titrated. Such a technique has been used (105) in studying tungstates, although consideration must be given to the fact that high molecular weight anions such as para-tungstates may not be absorbed by the resin.

The degree of hydrolysis of peroxy salts of tungsten have been examined by Rius and Rodriguez (106), whilst Kuan Pan (107) has studied the complex formation between tungsten and organic acids. In this latter study the tungsten was always found in the anion grouping.

CHAPTER 3

SOME ASPECTS OF THE CHEMISTRY OF THE COMPLEXING AGENTS SELECTED

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ETHYLENE DI-AMMINE TETRA ACETIC ACID (VERSENE).

3.1 This compound can give rise to four different salts by substitution of the hydrogen ions in the four carboxyl groups.

The tetra sodium salt is one of the most versatile complexing agents available.

It is very stable in solution, does not decompose in either acid or alkaline solutions, or at elevated temperatures, and it resists attack except from strong oxidising agents such as permanganate when it is slowly converted to a cyclic ureide.

The addition of mineral acid results in the formation of various acid salts. In the titration of the tetra sodium salt the neutralization equilibria may be given as

Versene reacts with both heavy metal and alkaline earth ions to form unusually stable soluble metal chelate compounds, with one mole of chelating agent for one mole of metal ion.

The extent to which complex formation occurs is generally expressed by the following complex formation constant K.

$$\text{and } K = \frac{[\text{MeV}^{n-4}]}{[\text{Me}^{+n}] [\text{V}^{-4}]}$$

A larger magnitude of K denotes a corresponding greater stability of the metal complex. For example for iron III $\log K = 25.1$ whereas for iron II $\log K = 14.2$.

The variation in solution pH affects the efficiency of versene complex formation. Two factors which must be considered are

- (i) dissociation of the metal chelate - low pH effect.
- (ii) Metal ion hydrolysis effect - high pH effect.

Referring to (i) an index of the efficiency of complex formation is given by the magnitude of the ratio of complex to uncomplexed free metal ions

$$\frac{[\text{MeV}^{n-4}]}{[\text{Me}^{+n}]} = K[\text{V}^{-4}]$$

The concentration of $[\text{V}^{-4}]$ is determined by the pH of the solution and a decrease in pH will decrease the concentration of the complexing species. Versene, therefore, complexes metallic ions most efficiently in alkaline solutions, but generally the complexing efficiency does not decrease appreciably until low pH values are attained.

Referring to (ii) a progressive increase in the $[\text{OH}^-]$ concentration results in an increased competition by these ions for the metallic cations and the tendency for formation of slightly soluble metal hydroxides is increased.

The overall process may be given as

$$\text{and } K_h = \frac{[\text{Me(OH)}_n] [\text{V}^{n-4}]}{[\text{MeV}^{n-4}] [\text{OH}^-]^n}$$

Thus an increase in $[\text{OH}^-]$ concentration would tend to shift the equilibrium to the right, that is give a precipitate of the metal hydroxide. Hence a loss of complexing efficiency results from increased pH values for certain metals. The effect of this hydrolytic effect is not constant. It varies with the characteristics of the metal ion concerned and is largely dependent upon the solubility product of the metal hydroxide.

The effect of hydrolysis on a metal versenate may be predicted from a knowledge of the complex formation constant K , and the solubility product, K_{sp} , of the metal hydroxide. Since

$$K_h = \frac{1}{K \cdot K_{sp}} \quad (\text{where } K_h \text{ is hydrolysis constant})$$

then if K_h is greater than one, the reaction above will proceed to the right, whilst if K_h is less than one, the reaction will proceed to the left. For example K_{sp} for ferric hydroxide is 10^{-36} , whilst K for the ferric system is 10^{-11} . Hydrolysis therefore is so great that ferric hydroxide precipitates in alkaline solution. Consequently the versene is an effective ferric ion chelating agent only in acid or neutral solution.

It might "a priori", be expected that the order of chelation of metal ions would be determined by the value of the complex formation constant. This would be true if only metal ions and versenate ions were involved in the equilibria. Actually however, the presence of precipitating anions and hydroxyl ions influence the order of chelation, in as much as they compete for the metal ion. Thus pH and the nature of the solution medium can vary the order of complexing.

As an example the formation constant for the ferric versenate system is much greater than that for the nickel versenate system. However due to hydrolysis ferric hydroxide is formed, but nickel remains effectively complexed, and so nickel is preferentially complexed in alkaline solution.

Schwarzenbach (61, 108) gave a list of the formation constants of various metals with versene. Some of interest are

<u>Metal Cation</u>	<u>Log of stability constants of 1:1 complexes; conc 0.1 M.</u>
V ⁺⁺	12.7
Fe ⁺⁺	14.3
V ⁺⁺⁺	25.9
Cr ⁺⁺⁺	24.0
Fe ⁺⁺⁺	25.1
Al ⁺⁺⁺	15.5
VO ⁺⁺	18.4

Martell and Calvin (69) in discussing the transition metal chelates gives the chelate of iron III as $\text{NH}_4^+ [\text{Fe}^{\text{III}} \text{ E.D.T.A. H}_2\text{O}]^{-1}$. Similarly they give the formula for the chromium III versenate as $\text{H}^+ [\text{Cr}^{\text{III}} \text{ E.D.T.A.}]^{-1}$.

Schwarzenbach, (109) from results based on potentiometric titrations, suggested that anionic complexes are formed between ethylene diamine $\text{N,N,N}^1, \text{N}^1$ tetra acetic acid and aluminium, chromium and iron in a 1:1 mole ratio; and contain one mole of co-ordinated water, which dissociates at pH 5-9 to give a hydrogen ion and a hydroxy complex ion $[\text{M}^{\text{III}} \text{ E.D.T.A. (OH)}]^{-2}$.

Schwarzenbach and Heller (60) have also shown that the iron II - versenate complex is stable and has a strong reducing property. The redox potential of the iron III - iron II - versenate system was found to be dependent on pH and this was taken as indicating the existence of different complexes at different pH values.

Whereas the normal mole ratio of metal to versenate is taken as 1:1 Pecsok and Sawyer (110) claim to have found molybdenum V and molybdenum IV complexes with two moles of versenate per metal atom.

OXALIC ACID.

3.2

Oxalic acid is a dicarboxylic acid, of formula

It is readily soluble in water and is a reducing agent. Due to the two carboxyl groups it has two dissociation constants, pK_1 and pK_2 being 1.2 and 4.2 respectively.

The heavy metal oxalates are generally insoluble in water, but many dissolve in solutions of the alkali oxalates by formation of oxalato complexes wherein each oxalate takes up two co-ordination positions through oxygen. Thus the type of compound formed has the form

The spatial arrangement about the central metal atom is octahedral.

The complex oxalato salts of iron III form two series, the di- and tri- oxalato. Whilst the iron can be entirely anionic it is possible that a compound of the form $\text{Fe}[\text{Fe}(\text{C}_2\text{O}_4)_3]$ can be formed. One value given for the stability constant of the iron III oxalato complex is $\log K_a = 10$. There are no genuine ferric salts of organic carboxylic acids like $\text{Fe}(\text{CH}_3\text{COO})_3$, and generally tri-ferric hexa-acido complexes occur, if anionic complexes, are not formed.

Lambling (62) has studied the oxalate complexes of iron III and his results showed several complexes to exist with the richest, the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{\text{III}}$ ion.

Babko and Dubovenko (63) have also investigated the iron III oxalate complex. At pH 1 or less, they found

the complex to be $[\text{Fe}(\text{C}_2\text{O}_4)]^+$, but with increasing oxalate concentration and increase in pH values to 2 the complex anion $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$ appeared. At pH 2.5 the anionic form predominated in the solution.

Aluminium like iron, forms complexes with dibasic organic acids. The dichelate $\text{M}[\text{Al}(\text{C}_2\text{O}_4)_2]$ and trichelate $\text{M}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ are known (111)(112).

Most complex salts of vanadium V have at least one oxygen atom covalently linked to the vanadium and nothing else. The most important are of the oxalate type, such as $\text{M}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot x\text{H}_2\text{O}$ and are very stable. Vanadium IV complexes can exist as open chain compounds or, as in the case of the oxalate, as ring compounds linked through one vanadium. There are two types of these oxalato complexes

Molybdenum V also forms oxalato complexes, the form being of the type $\text{M}[\text{MoO}_2(\text{C}_2\text{O}_4)] \cdot x\text{H}_2\text{O}$. (113).

CITRIC ACID.

3.3

Citric acid is a tribasic hydroxy acid of formula

with four functional groups. Its pK values are approximately pK_1 3.1, pK_2 4.6 and pK_3 5.8.

It is an excellent complexing agent for metals such as iron and aluminium, with oxygen linkages. Many derivatives are known of both molybdic and tungstic acids with such oxy acids as citric acid. Citrate complexes of vanadium IV are also known; their form, as in the oxalato complexes, indicating the vanadium to be in the anionic grouping of the complex.

MANNITOL.

3.4 Mannitol is one of the polyhydric alcohols, in fact a hexahydric alcohol closely related to the simple class of sugars, the hexoses.

Its formula is

and is classified as a weak masking agent. Like other sugars, mannitol dissolves alkaline earth hydroxides and prevents their precipitation when bases are added to their salts. The resulting complex compounds are however quite unstable.

As ferric iron, and most of the higher valency metals have a great affinity for oxygen and hence a strong tendency to react with alcoholic hydroxyl groupings to give complex compounds, mannitol was chosen to check on the character of the metals used. For example, it is known that molybdic acid combines with sugars probably to form ring compounds, but no information has been found giving details of the type compound formed.

HYDROCYANIC ACID AND CYANIDES.

3.5 The cyanide group (CN) is found attached, by covalent bonding from either the carbon or nitrogen, to many metals. That is, its structure may be written as $-C \equiv N:$ or $:C \equiv N-$. There is also a possibility that the CN group is attached at both ends by covalent bonds; thus $-C \equiv N-$, and this may be the case in a number of metallic cyanides.

Many metallic cyanides redissolve in the presence of excess cyanide ions with the formation of the complex metallo-cyanide complex $[M^n(CN)_m]^{-(m-n)}$. In these complexes the co-ordination number "m" is greater than the electrovalency "n" of the metal, hence these ions carry a negative charge of (m-n).

There are many salts containing ions of the type $[M(CN)_6]$ the best known being the ferro- and ferri- cyanides; all are octahedral.

Molybdenum and tungsten are notable for forming complex octacyanides of the type $K_4^1[M(CN)_8]_2H_2O$. In the case of the molybdenum, the eight cyanide groups are arranged at the apices of a dodecahedron around the metal atom.

PERCHLORIC ACID.

3.6 Perchloric acid is a powerful oxidising agent of structural formula

55.

It can oxidise compounds to give per- compounds
or can form cationic complexes.

CHAPTER 4.

EXPERIMENTAL DETAILS USING THE METALS

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4.1 The following chapters 4 and 5 are devoted to the experimental work carried out in order to determine by what means the metals chosen could be separated.

Firstly the metals were studied individually for whilst certain information is available this may not agree with results obtained when using DE-ACIDITE"FF". Also not all these metals have been studied with all the eluting agents used. Where analogous results have been obtained by other workers they are quoted in the discussions following each table of results.

Secondly the metals were combined in solution and various methods were used to attempt their separation. Such combinations as these havenot been previously studied. References to similar separations have however been discussed.

In the analysis of a ferrous alloy it is not general practice to estimate iron. Thus the ideal separation by ion exchange techniques would be the absorption of all elements excepting iron. As the acidic character of an element increases with increasing valency, it may be possible to separate the metals under consideration, namely chromium VI, vanadium V, molybdenum VI and tungsten VI from iron III by the use of an anion exchanger. However it must be remembered that in the case of vanadium V the isoelectric point is at pH 2.2 whilst tungstic acid can precipitate from acid solution. In fact the higher the pH value of the solution, the greater is the assurance that the chromium, vanadium, molybdenum and tungsten are anionic in character in solution. Unfortunately iron III commences to precipitate at approximately pH 2 to 2.5 so that it is necessary to complex the iron to allow a sufficiently high pH value to be attained.

Iron III complexes essentially through oxygen and strongly with di- and tri- basic organic acids through chelate formation. Increasing pH in such cases will not only increase the stability of the complexes, but also aid formation of anionic complexes of iron. This would then allow absorption of iron by the anion exchanger. This effect excludes the use of di- and tri- basic acids.

The iron III derivatives of monocarboxylic acids, such as acetic acid, can also be seen to be complex from

their brown colour. The structure and even composition are uncertain, they being highly complex with more than one iron atoms in the molecule. This is because in monobasic acids the two oxygen atoms of one carboxyl group are too near together to attach themselves to one iron atom; but two or more carboxyl groups can be joined through two iron atoms to give an unstrained ring. The groups produced by the monobasic carboxylic acids may be of different kinds but of importance here is that in all cases the complex groupings containing the iron are all cationic.

By using acetic acid and an acetate buffer a cationic iron III complex is formed; this prevents iron absorption by the anion exchanger, whilst the pH of the solution may be raised sufficiently to allow absorption of the other metals without iron III precipitation.

Generally however the iron concentration is high in a ferrous alloy and pH may not be able to rise above 2.2 without precipitation occurring. Nevertheless it was found that by the use of mannitol, which gives a more stable iron III complex, the pH could be raised to a value whereby all metals with the exception of the iron III are in solution on anionic form. Alkaline conditions may be obtained with mannitol, but it was then found that some iron was absorbed by the anion exchanger.

Phosphoric acid must be absent as it causes precipitation of a complex phosphate at pH approximately 2 to 2.5.

Notwithstanding the success of this separation of iron, in the subsequent tables of attempted separations iron was included in small amounts to observe its effects in the absorption and elution steps.

Up to 25 ml of 0.1M iron solution could be separated from 5 ml of each of the other metals, whose strength is quoted on the following pages, at a pH value of approximately 2.5 to 3.0 when the sulphuric acid solution of all metal ions, was passed through the nitrate form of the strongly basic anion exchanger DE-ACIDITE"FF".

SOLUTIONS OF METALS EMPLOYED IN THE
EXPERIMENTAL WORK.

4.2 Ferric Iron.

48.12g of ferric ammonium sulphate per litre of very dilute sulphuric acid solution, the acid preventing hydrolysis with consequent iron precipitation. This is a 0.1M solution and 10ml contains 55.85 milli-grams of iron.

Vanadium.

11.7g of ammonium vanadate, NH_4VO_3 , dissolved in one litre of sulphuric acid by first mixing the vanadate with water, adding concentrated sulphuric acid till solution complete and then diluting with water. This is a 0.1M solution and 5ml contains 25.5 milli-grams of vanadium.

Molybdenum.

7.448g of molybdenum trioxide, MoO_3 , dissolved in a minimum of sodium hydroxide solution and diluted to one litre. 5ml aliquots of this 0.05M solution is equivalent to 24 milli-grams of molybdenum.

Chromium.

19.42g of potassium chromate made up to 1 litre with water. 5ml of this 0.1M solution yields 26 milli-grams of chromium.

Tungsten.

16.50g of sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), made up to one litre of solution with water to give a 0.05M solution. 5ml aliquots yields 46 milli-grams of tungsten.

Low concentrations of metal ions are used to avoid the possibility of attaining the break through capacity of the resin columns used.

METHODS OF ESTIMATING THE METALS USED
IN THE EXPERIMENTAL WORK.

4.3 Many estimations are necessary when studying absorption and desorption of metals on a resin. For example, after absorption of an ion it is necessary to elute with varying acid strengths or with a salt solution at varying pH values, and this means for each experiment numerous estimations.

Again, due to the complexing agents which can be used as possible desorbers, sensitive methods are required for the metal estimations.

Thirdly, reduction of the metal may occur and this factor has to be considered also in the estimations.

Fourthly, interference from other metal ions in the solution has to be overcome.

Upon consideration of these problems, the following methods were finally adopted

Iron - determined colorimetrically using an ammoniacal solution and thioglycollic acid.

- Vanadium - determined colorimetrically with hydrogen peroxide in 4N sulphuric acid. In certain cases evaporation to dryness was first necessary, for example in strong hydrochloric acid.
- Molybdenum - determined colorimetrically with stannous chloride and thiocyanate in dilute acid solution.
- Chromium - determined colorimetrically by firstly ensuring chromium VI present by alkaline bromine oxidation, removing excess of bromine with phenol, just acidifying with sulphuric acid and adding diphenyl-carbazide.
- Tungsten - A method described by Freund (115) was adopted. The tungsten solution is acidified with 10ml 36N sulphuric acid, cooled, 20ml 10N hydrochloric acid and 5ml 2M stannous chloride added and the solution heated. After cooling a yellow colour is developed by the addition of 10ml of 2M potassium thiocyanate. This method is satisfactory only for small amounts of tungsten, such as used in the subsequent experimental work.

It is pointed out that where possible colorimetric methods were employed, this being in view of the large numbers of estimations required.

These methods have been described by Sandell (114) and Welcher (115.)

All solutions used contained 5 ml of the above mentioned metal solutions in a volume of approximately 150 ml.

The columns employed were coarse tipped burettes containing about 20 to 25ml of resin, previously soaked for at least one hour in the appropriate regenerant. It was found that very fine resin tended to prevent the flow of solution unless pressure was applied. To prevent this, the burette contained a glass wool plug at the bottom, about 5ml of fine grain resin (-60 mesh) and then the remainder the coarser resin as supplied. Whilst the capacity of the column decreased with increasing particle size, the concentration of metal ions used, left a very high safety factor. Temperature control has little effect on this type of work and was not considered except in so far that solutions were always at room temperature. Flow rates, controlled by the burette tap, were varied depending on circumstances. For example, absorption is generally quite rapid thus allowing fast flow rates, whilst desorption can be very slow so that during elution steps flow rates were set at approximately 10 - 15 drops per minute. The volume of influent, besides flow rate, has a marked effect on desorption however.

It is desirable to keep a liquid cover over the resin to prevent resin shrinkage and air locks. The ideal arrangement for this would involve a gradient elution system which is limited in its scope and which involves large solution volumes. A convenient yet simple apparatus was

employed to minimise ~~on~~ air locks. This consisted of a flask fitted with a stopper and glass tube some two inches in length and cut angularly at the outlet end. The solution was added to the flask, which was then clamped in the upturned position with the glass tube inside the resin column. This provides a constant head of solution so long as solution is still available for resin contact.

As mentioned above, volumes of solutions can be an embarressment in ion exchange studies. In all the subsequent elutions 250ml were used and flow rates decreased below 10 - 15 drops per minute if necessary.

ELUTION OF METALS FROM THE ANIONEXCHANGER "DE-ACIDITE FF"

4.4 Faintly alkaline solutions of vanadate, chromate, molybdate and tungstate were added separately to the hydroxyl form of the ion exchanger. Due to hydrolysis iron could not be studied in these series.

The various eluting agents were used to study the possibility of selective elution of the absorbed anions and the results are given below in Tables I - VIII.

The metals were added individually.

TABLE I.

Elution of the individual metals after their absorption by the anion exchanger from weakly alkaline solutions. Hydrochloric acid is the eluting agent.

ELUTING ACID STRENGTH (H Cl)	% METAL ELUTED			
	VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
0.05N	8	--	Trace	--
0.1N	13	Nil	Trace	10
0.25N	83	Nil	10	--
0.5N	75	Nil	20	--
1.0N	90	Nil	60	--
2.0N	100	--	100	40
4.0N	100	100	Nil	--
8.0N	100	100	Nil	--
10.0N	100	100	Nil	50

REMARKS ON TABLE 1.

VANADIUM - elution was quite rapid with the effluent yellow or yellow-green indicating some reduction of vanadium $\bar{\text{V}}$ to vanadium IV . The results show that the quantitative vanadium elution is enhanced by higher acid strengths, which could be due to three factors, namely, increasing chloride ion concentration resulting in greater displacing power, secondly more pronounced vanadium reduction with increasing acid strength and thirdly cation vanadium $\bar{\text{V}}$ formation.

Kraus, Nelson and Smith (78) in their broad study of chloro complexes by ion exchange methods, have included both vanadium $\bar{\text{V}}$ and vanadium IV in published results. They showed that considerable absorption of vanadium $\bar{\text{V}}$ occurs in 12M hydrochloric acid but only slight absorption of vanadium IV and vanadium III . The absorbability of vanadium IV was studied over the range of 1 - 12M hydrochloric acid and in no region was absorption considerable. The resins were anion exchangers.

Salmon (8) found that certain exchangers reduced vanadium $\bar{\text{V}}$. Whereas it was previously assumed that reduction preceded absorption, Salmon found that only the absorbed vanadium was reduced after elution with for example 2N hydrochloric acid.

Whilst then Kraus has found chloro complexes of vanadium $\bar{\text{V}}$ to exist, they exist only in very strong hydrochloric acid. The results in Table 1 show no anionic vanadium complexes occur up to 10 N hydrochloric acid or if so formed

they are readily displaced by the chloride ion.

The results also indicate that hydrochloric acid is of use only in the desorption of vanadium even if reduction does occur, for at all acid strengths some vanadium is eluted.

CHROMIUM - stronger acid strengths elute chromium. As the effluent was green reduction obviously occurred. The results show a definite line of demarcation between acid strengths causing and not causing elution, and this effect could be due to increasing hydrogen ion concentration raising the redox potential of the chromium VI - chromium III system above that of the chloride - chlorine system with the consequential reduction of chromium VI to cationic chromium III. In the equation

$$E = E_o + \frac{RT}{nF} \ln \frac{[Cr_2O_7^{=}][H^+]^{14}}{[Cr^{3+}]^2}$$

$[H^+]$ is raised to the fourteenth power, and when the activity coefficient of 4M acid is given as 1.8 approximately at 20°C, "E" is increased substantially. Although the resin is itself a mild reducing agent, no chromium reduction was observed under alkaline conditions.

Whilst studying chrome tanning liquors, Gustavson (94) used basic chromium chloride solutions and both cation and anion exchange resins. He observed that in certain analyses chloride was retained on the cation exchanger, thus indicating the presence of positively charged chloro-chromium III groups. Such a type compound may have been formed in

Table I when using stronger acid although stronger acids do not favour the basic type of salt. Chloride analyses were not carried out.

Hamm and Shull (104) also studied chromium III chloride solutions, but this time by polarographic means. Fresh solutions were reduced at a half wave potential of -0.61V whereas aged solutions were reduced at a much more negative potential. The former value was proposed for the reduction of the $[\text{Cr}(\text{H}_2\text{O})_4 \text{Cl}_2]^+$ ion and the latter for the reduction of $[\text{Cr}(\text{H}_2\text{O})_6]^{+++}$ ion. However in both cases the chromium III ion is cationic. The effluents in Table I being green indicate no ageing of the chromium chloride complex and support the tetraquo compound formation.

MOLYBDENUM - using acid strengths up to 2N, elution efficiency increased with increasing acid strength. However above 4N acid strength no elution occurred and this result indicates the formation of an anionic chloro-molybdo complex.

Shemyakin (82) found molybdenum VI to be cationic in dilute hydrochloric acid solutions, but complex halides such as $[\text{Mo} \text{ VI } \text{O}_2\text{F}_4]^=$ are quite stable anionic complexes. Probably however this anionic chloro complex contains molybdenum V with a formula of the type $\text{M}_2^1[\text{Mo O Cl}_5]$ due to molybdenum VI reduction. Kraus (38) quotes maximum absorption for molybdenum from hydrochloric acid at an acid strength approximately 5 molar. To this value absorption

increases, but no significant variation occurs above this value.

Elution by hydrochloric/^{acid}was always slow and the effluent colourless.

TUNGSTEN - partial elution occurred at all acid strengths. Acidification of a tungstate gives colloidal tungstic acid and some of the colloid could be mechanically entrapped by the resin. If so this would account for the partial elution. The effluents on standing, especially those of stronger acid strength, slowly clouded up with yellow tungstic acid.

SUMMARY.

Tungsten prevents a clean separation of any of the metals when hydrochloric acid is the eluting agent. Neglecting tungsten however, it should be possible from these results, to separate vanadium and chromium from molybdenum by using 4N or stronger hydrochloric acid. Alternately by using 1N acid it should be possible to separate vanadium and molybdenum from chromium.

TABLE II.

Elution of the individual metals after their absorption by the anion exchanger from weakly alkaline solutions. Sulphuric acid is the eluting agent.

ELUTING ACID STRENGTH H_2SO_4	% METAL ELUTED			
	VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
0.05 N	25	--	--	--
0.1 N	25	Nil	Nil	10
0.25 N	95	Nil	--	--
0.5 N	90	--	Nil	15
1.0 N	90	Nil	5	--
2.0 N	95	--	--	25
4.0 N	100	20	80	--
8.0 N	100	--	--	--
10. N	100	100	80	25

REMARKS ON TABLE II.

VANADIUM - was eluted by the sulphuric acid at all strengths, with efficiency improving with increasing acid concentration. Some reduction of vanadium occurred especially with the more concentrated acid. The results show that sulphuric acid can only be used for desorbing vanadium. There are reputed to be vanadium $\bar{V}$ sulphato complex compounds and if so formed the results show they must be neutral or cationic in acid conditions, or otherwise readily displaced by sulphate ions.

CHROMIUM - elution occurred only at higher acid strengths and then due to chromium III formation. In this case however reduction must be due to the resin, as sulphuric acid is not a reducing agent. The chromium III sulphate formed must be neutral or cationic and, as it was green in colour, of the type $[\text{Cr}(\text{H}_2\text{O})_4\text{SO}_4]^+$.

Gustavson (95) found that in both dilute and concentrated solutions of $\text{Cr}(\text{OH})\text{SO}_4$ and in dilute solutions of $2\text{Cr}(\text{OH})\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ 92 - 100% of the chromium is cationic in a complex wherein two chromium atoms bind one sulphate group. But in concentrated solutions of $2\text{Cr}(\text{OH})\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$ only 36% of the chromium is cationic and 60% is uncharged.

Also in ion exchange studies on chromium Samuelson (96) observed that the separation of chromium and sulphate ions was incomplete except in the case of the violet hexa-aquo chromium III sulphate. For the green chromium III sulphate solutions some chromium passed through the cation exchanger and some sulphate was retained. This is explained by the fact that not all the chromium is cationic in the sulphato-chromium III complex.

From the results it would appear that if the green complex has been formed it is displaced by the high sulphate ion concentration.

MOLYBDENUM - elution is ineffective at low acid strengths, but much improved even though still slow, at higher acid strengths. Apparently no anionic complex is formed and the elution rate is slow because the "exchange potentials"

of the sulphate and molybdate ions are quite close. Kunin and Myers (5) found the "exchange potential" of sulphate greater than molybdate, but it is realised that these values are readily varied by other factors in the solution. Such a factor as concentration may explain the desorption of the molybdenum in Table II at higher acid strengths only.

TUNGSTEN - partial elution at all acid strengths due probably to the formation of colloidal tungstic acid. The effluent very slowly gives a yellow precipitate the rate increasing with increasing acid strength.

SUMMARY.

As in Table I tungsten prevents a clean separation of any of the metals. The only possible separation offered by these results is the removal of vanadium with very dilute sulphuric acid, tungsten being neglected.

TABLE III.

Elution of the individual metals after their absorption by the anion exchanger from weakly alkaline solutions. Phosphoric acid is the eluting agent.

ELUTING ACID STRENGTH H_3PO_4	% METAL ELUTED			
	VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
0.05 N	25	--	--	--
0.1 N	20	Nil	Nil	Nil
0.25 N		Nil	--	--
0.5 N	38	--	Nil	--
1.0 N	50	Nil	--	--
2.0 N	45	--	Nil	Nil
3.0 N	67	Nil	--	--
4.0 N	97	Trace	10	--
8.0 N	100	10	20	Nil

REMARKS ON TABLE III.

VANADIUM - the results indicate that at slow rates with large volumes of eluting agent, a quantitative elution of vanadium is possible. There is no evidence of anionic complex formation and the reason for slow elution is because the phosphoric acid is weak thus restricting ionic concentrations and their effects on "exchange potentials."

Matsuo and Iwase (79) used phosphate ions to separate vanadium and molybdenum. Both metals were absorbed by a cation exchanger from a solution of pH2 and the molybdenum only was eluted by sodium phosphate (pH9) solution. The vanadium must then be cationic in the presence of phosphate ions, and is subsequently removed from the cation exchanger by 3N hydrochloric acid by displacement.

CHROMIUM - is only eluted by strong phosphoric acid solutions due no doubt to the fact that the phosphate ion concentration is insufficient to raise the "exchange potential" of the phosphate above that of the chromium VI. Kunin and Myers (5) quote the phosphate "exchange potential" below that of chromate and the results contained in Table III agree with their finding.

MOLYBDENUM - only a qualitative elution was obtained and this only at higher acid strengths. The phosphate "exchange potential" is just above "molybdate" (5) and hence concentration effects become important especially with phosphoric acid. This is shown in the results in Table III. Also Matsuo and Iwase (79) found phosphate (pH9) eluted molybdenum from a cation exchanger, this indicating the anionic character of molybdenum in alkaline media even with phosphate ions present and the higher "exchange potential" of the phosphate ion.

TUNGSTEN - no elution occurred due to either the lower "exchange potential" of the phosphate under the operating conditions or the formation of a complex phosphate of tungsten where the tungsten is in the anionic grouping. Complex phosphates are known and have been referred to earlier especially in relation to their anionic character.

SUMMARY.

From these results it appears possible to separate vanadium from chromium, molybdenum and tungsten by using dilute phosphoric acid. No other separation appears feasible. Nevertheless the vanadium elution is not rapid.

TABLE IV.

Elution of the individual metals after their absorption by the anion exchanger from faintly alkaline solutions. Oxalic acid and oxalates, 0.1 Molar, are the eluting agents.

FORM OF INFLUENT	pH OF INFLUENT	% METAL ELUTED			
		VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
Oxalic acid	2.0	Nil	Nil	Nil	Nil
Sod.Oxalate	6.5	69	--	--	50
Sod.Oxalate	10.8	100	Nil	Nil	100
Sod.Oxalate	12.0	100	Nil	Nil	100
Amm.Oxalate	8.4	45	--	--	100
Amm.Oxalate	9.5	76	--	Nil	100
Amm.Oxalate	10.2	--	Nil	Nil	--

REMARKS ON TABLE IV.

Oxalic acid itself causes no elution of any metal. Either the "exchange potential" of the oxalate ion is too low or anionic oxalato complexes are formed. The former explanation is favoured due to the low oxalate ion concentration in a solution of the acid, and the effect of hydrogen ions on complex formation.

VANADIUM - elution efficiency with sodium oxalate increased with increasing pH, that is with increasing oxalate ion concentration. With ammonium oxalate the same general increase was noted, but the elution was less efficient.

The question whether hydroxyl ions cause elution must be considered, even though the minimum of excess alkali was used. But ammonium oxalate elutions were more efficient than ammonium hydroxide alone and the same applied to sodium hydroxide and sodium oxalate. Thus elution can be ascribed to oxalate ions displacing vanadate ions or to a neutral or cationic complex being formed. The cationic or neutral complex is not the normal form of such a complex when excess oxalate ions are present - rather the complex could be anionic due to the co-ordination number of the vanadium and the charge on the oxalate ion. Under the operating conditions then, oxalate displaces either the vanadate or complex vanadium oxalate ion due to "exchange potential" variations.

Complex compounds of oxalate and vanadyl ions were studied by physico-chemical methods by Zolotavin and Kalugina (74). They showed the existence of a compound $[\text{VO}(\text{H C}_2\text{O}_4)_2]^\circ$ but suggested the presence of an ion $[\text{VO}(\text{H C}_2\text{O}_4)]^+$. Neither compound would be expected to be present in the experimental work of Table IV however due to the excess of oxalate ions. However if present such groupings containing vanadium would be eluted but the studies in this work could not prove their existence. On the other hand a typical oxalato complex of vanadium V is of the type $\text{M}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2]$ whilst for vanadium IV is of the type $\text{M}_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ in which case the vanadium is anionic. These latter types are favoured under the experimental conditions used and if present are eluted by "exchange potential" variations.

CHROMIUM - was not eluted by the oxalate at any pH value. Either the oxalate "exchange potential" cannot be made sufficiently high to elute the chromium or an anionic oxalato - chromium complex is formed which is very stable and very firmly absorbed by the resin. Whilst chromium VI was added no doubt this complex is a chromium III compound.

In fact subsequent elution of the chromium by other agents was very difficult. The deep violet colour of the chromium complex moved only slowly down the column under the influence of a sulphurous - sulphuric acid mixture. Especially was this acid elution slow after the ammonium oxalate elutions and it appears then that ammonium ions enhance the stability of the oxalato complex by becoming a ligand in the central grouping. The reducing acid effluents were green in colour.

Gustavson (94) found that in passing a solution of $\text{Na}[\text{Cr}(\text{C}_2\text{O}_4)_2]$ through a cation exchanger no uptake of chromium occurred, although by varying solution conditions some uptake could be achieved. The complex then is very stable and anionic in character.

Adams (97) found also that sodium oxalate reduced cationic chromium to a non-cationic form whilst Chambard and Grall (98) showed by ion exchange means that oxalate additions reduced the percentage of cationic chromium absorption. The non-cationic chromium was non-ionic for the lower oxalate levels and anionic at the higher levels.

Further studies of chromium complexes in relation to their cationic, non-ionic and anionic forms were carried out by Grall (99) using the ions formate, oxalate and sulphate, and the results showed the various forms of the chromium.

The stability of the chromium oxalato complexes has been shown by Shuttleworth (102). On boiling a chrome alum solution with oxalic acid and sodium oxalate, the sulphate was displaced from the anionic chromium complex. The complexes of up to four moles of oxalate per mole of Cr_2O_3 were found stable to heat and upon titration with alkali took up two additional hydroxyl groups. With sodium oxalate present penetration continued up to six moles when the complex was saturated.

Both the results found and the data quoted agree that the chromium is anionic when oxalate ions are in excess and that the complex is very stable. The difficulty in elution may be due also however to an attachment to the resin through the quaternary ammonium grouping serving as a bridge.

MOLYBDENUM - was not eluted by oxalate ions at any pH values, that is by any oxalate ion concentration. The problem indeed was the eventual molybdenum elution after the attempted oxalate elutions. Either the "exchange potential" of the molybdate is very much higher than that of the oxalate, or a very stable and strongly attached oxalato-molybdo complex has been formed. In either case the oxalato complex must be anionic with a high net charge on the anionic grouping.

Souchay (89) established the formulae of various complexes of molybdenum under varying pH conditions and mole ratios. Such formulae as $[\text{Mo O}_3(\text{C}_2\text{O}_4)^-]$ for oxalato molybdate and $[\text{Mo O}_3(\text{C}_4\text{H}_4 \text{O}_6)^-]_n$ for tartrato-molybdate were established. In all cases the molybdenum was in the anionic grouping.

Both the experimental data and the quoted literature, show the molybdenum to be anionic in character in the presence of oxalate.

TUNGSTEN - both sodium and ammonium oxalates gave a rapid quantitative elution of the tungsten, efficiency increasing with increasing alkalinity. As tungsten almost invariably occurs in the anionic grouping of a compound, the oxalate ions must displace tungstate ions due to the low exchange potential of the latter. The anionic character of the oxalato-tungstate complex which could form has been demonstrated by Kuan Pan (107) who indicated a formula such as $[\text{R} - (\text{COO})_2\text{WO}_2]^-$.

Realising also the tendency of tungsten to form such hetero-poly acids as quoted above the elution may be due to the ionic size of the anionic tungsten grouping being too large for the resin.

SUMMARY.

A separation of vanadium and tungsten from chromium and molybdenum appears possible using an alkaline sodium oxalate solution as eluting agent.

TABLE V.

Elution of the individual metals after their absorption by the anion exchanger from faintly alkaline solutions. The disodium salt of ethylene diammine tetra acetic acid and more basic forms of the versenate, 0.1 Molar, are the eluting agents.

FORM OF INFLUENT	pH OF INFLUENT	% METAL ELUTED			
		VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
Sod.Versenate	4.5	Nil	Nil	Nil	Nil
Sod.Versenate	7.5	40	Nil	Nil	50
Sod.Versenate	11.5	100	Nil	Nil	100
Amm.Versenate	5.5	Nil	Nil	Nil	Trace
Amm.Versenate	8.0	50	Nil	Nil	25
Amm.Versenate	11.0	85	Nil	Nil	100

REMARKS ON TABLE V.

The disodium salt of ethylene diammine tetra acetic acid did not elute any of the metals.

VANADIUM - elution efficiency increased with increasing alkalinity, whilst as in the oxalate elutions, sodium versenate was more efficient than ammonium versenate. The stability of versenate complexes generally increases with increasing pH to give complexes of the form MeV^{n-4} , where "Me" is the metal ion, "V" the versenate and "n" the valency of the metal ion, and in which the metal is always in the anionic grouping. If such a complex is formed with vanadium then its "exchange potential" is low as it is readily displaced by versenate ions.

However in a polarographic study of vanadium Pribil (77) found that versene did not complex vanadium $\bar{V}$ in ammoniacal solution. This being so the vanadate ion is simply displaced by the versenate ions.

CHROMIUM - was not eluted by versenate ions at all and this could indicate the formation of a strongly bound anionic chromium-versenate complex. Upon addition of versenate the resin containing the absorbed chromium turned a deep purple colour which showed little or no moving front during elution. The front however moved under the influence of a sulphurous-sulphuric acid wash and the elution thereby obtained is due to (a) reduction to chromium III and/or (b) alteration of the stability constant of the complex due to hydrogen ions. Point (b) is favoured as the purple colour on the resin indicates the chromium was reduced on the resin by either, or both, the resin and versenate. As with all versenate complexes the chromium would be in the anionic grouping, and this was found to be so. The strength of bonding to the resin could be due to co-ordinate linkaging between the chromium and the amine grouping of the resin.

MOLYBDENUM - was not eluted at any pH by the versenate, this indicating the formation of a strongly bound stable complex with molybdenum in the anion grouping. Coupled with the non-elution of chromium it would appear that the versenate ion has a low exchange potential.

TUNGSTEN - whilst not eluted at the lower pH values of the versenate solution, it was slowly eluted by the alkaline versenate solutions. As oxalate rapidly eluted the tungsten, it again can be assumed that versenate has a low "exchange potential." The versenate-tungsten complex, if formed, must then be displaced by the higher versenate concentrations.

SUMMARY.

Alkaline versenate solutions could be used to separate vanadium and tungsten from molybdenum and chromium by leaving the latter two on the anion exchanger.

TABLE VI.

Elution of the individual metals after their absorption by the anion exchanger from faintly alkaline solutions. Citric acid and various citrates, 0.1 Molar, are the eluting agents.

FORM OF INFLUENT	pH OF INFLUENT	% METAL ELUTED			
		VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
Citric acid	2.4	Nil	Nil	Nil	10
Sod.Citrate	5.5	Nil	Nil	Nil	75
Sod.Citrate	11.0	100	Nil	Nil	100
Sod.Citrate	12.2	100	Nil	Nil	100
Amm.Citrate	4.0	30	Nil	Nil	5
Amm.Citrate	7.5	45	Nil	Nil	25
Amm.Citrate	10.0	60	Nil	Nil	40

REMARKS ON TABLE VI.

VANADIUM - was eluted only by alkaline citrate solutions, efficiency increasing with increasing pH. The sodium citrate was also more efficient than the ammonium citrate. This elution can be ascribed as due to two possibilities; firstly by the formation of a cationic citrate complex and secondly the displacement of the anionic vanadium whether complexed or not. The first is not favoured due to the high charge on the citrate ion generally leading to anion formation. Samuelson (80) too found that vanadium IV is eluted from an anion exchanger by citrate ions. In the second case displacement is favoured as

the "exchange potential" of the citrate increases with increasing pH due to both an increase in concentration and an increase in charge on the citrate ion because of the three pK values for citric acid.

An interesting observation was that the top portion of resin, containing the absorbed vanadium, turned red upon contact with citric acid, but not with citrate solutions. The red colour however slowly turned green indicating vanadium IV formation by reduction. The red colour could indicate formation of an unstable vanadium V citrate complex. Vanadium V complexes are greatly influenced by the presence of hydroxyl groups, one of which occurs in citric acid. In alkaline solution the hydrogen of the hydroxyl group is replaced by an equivalent of the co-ordinating metal ion. The stability of the complex is dependent on the number of hydroxyl groups and thus it would not be expected that the citrate complex would be very stable. The reduction of vanadium V is proof of this relative instability.

CHROMIUM - was not eluted at all by citric acid or citrates. A strongly bound anionic complex is obviously formed. The top portion of resin turned violet upon addition of the citrate indicating chromium reduction and the chromium was only slowly eluted with sulphurous-sulphuric acid as a green solution. This elution must be due to a decrease in the stability of the complex by hydrogen ions and the displacement of the anionic complex by sulphate ions. The "exchange potential" of the trivalent citrate ion cannot be

sufficiently high to displace the strongly bound chromium complex.

By conductometric means Shuttleworth (100) obtained curves of chrome alum solutions boiled with citrate solution. For a mole ratio of 1:1, the disappearance of the three carboxyl groups and the formation of a complex with one acidic group attached was indicated. The use of two or more moles of citrate per mole of chromium gave complexes with four carboxyl and two hydroxyl groups co-ordinated to each chromium atom. The results indicate a double five or six membered ring structure with two carboxyl and one hydroxyl groups from each citrate molecule and these results support the concept that ionization of an acidic hydroxyl group must precede stable co-ordination with chromium. Hydroxy acids therefore may be expected to penetrate more readily into a basic chromium complex.

In a broad study on trivalent metal ions Bobtelsky (101) showed chromium III citrate complexes to exist in several forms depending on mole ratios.

The experimental data and these references both indicate a stable chromium citrate complex, wherein the chromium is anionic, when excess citrate ions are present.

MOLYBDENUM - was also not eluted under any operating conditions, this showing the formation of a strongly bound anionic complex with a high "exchange potential" value. Sodium hydroxide subsequently eluted the molybdenum but only

slowly.

Pecsok and Parkhurst (87) in determining molybdenum in steel made use of the anionic molybdo citrate complex formation. By reducing the chromium, vanadium and manganese to stable cations and adding citrate to keep the molybdenum in solution all but the molybdenum were absorbed by a cation exchanger.

TUNGSTEN - was slightly eluted by citric acid and effectively eluted by alkaline citrate solution. The elution was not as rapid as in the cases of oxalate and versenate, and this could indicate (a) citrate has not as high an "exchange potential" as oxalate or versenate; or (b) the citrate complex if formed, is more firmly held by the resin than the oxalate and versenate complexes. As mentioned earlier high polymer citrate complexes of tungsten can be formed, but in this case the extent of polymerisation has not prevented some tungsten absorption.

SUMMARY.

A sodium citrate solution will elute vanadium and tungsten, but can make the subsequent elution of chromium and molybdenum especially the latter, somewhat slow.

TABLE VII.

Elution of the individual metals after their absorption by the anion exchanger from faintly alkaline solutions. Sodium hydroxide was the eluting agent.

STRENGTH OF NaOH	% METAL ELUTED			
	VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
0.05 N	Nil	Nil	Nil	Nil
0.1 N	10	Nil	Nil	Nil
0.25 N	15	Nil	Nil	Nil
1.0 N	45 - 100	Nil	Trace	5
2.0 N	60 - 100	Nil	50 - 100	20
4.0 N	100	Nil	100	80
8.0 N	--	Nil	100	100
10.0 N	100	Nil	--	--

REMARKS ON TABLE VII.

VANADIUM - elution efficiency was dependent on both alkali strength and flow rates. The variable results for 1 N and 2 N alkali are explained by variable flow rates.

When vanadium was absorbed as the vanadate ion its charge could vary from one to three, as in the ions VO_3^- and $\text{VO}_4^{=}$, and as explained under the Chemistry of Vanadium. The fact that elution occurred at lower hydroxyl ion concentrations indicates that the hydroxyl ion has a very much higher "exchange potential" than the vanadate ion and/or that the charge on the vanadate ion is low.

The fact that little or no vanadium was eluted by very weak alkali shows that in the oxalate, versenate and citrate solutions, elution was due to these anions and not to the slight excess of hydroxyl ions.

CHROMIUM - the fact that chromium was not eluted by the sodium hydroxide shows that chromium, as chromate, is very strongly held by the resin and its "exchange potential" is very high. A slow frontal movement of chromium was however observed when using 10 N alkali. Normally hydroxide ions are quoted as having the highest "exchange potential" of any anion, and if this be so it is possible that the chromium is linked to the resin through the amine functional grouping.

The chromium was subsequently eluted quite readily with sulphurous-sulphuric acid to give a green effluent containing chromium III.

These results are at variance with those of Lur'e and Filippova (84) who eluted chromate from an anion exchanger with 2% sodium hydroxide. The resin types used appear to offer an explanation for such conflicting results.

MOLYBDENUM - was slowly eluted by sodium hydroxide, efficiency increasing with increasing alkali concentration, due to concentration effects on "exchange potential" values.

Fisher and Meloche (50) also have eluted molybdate with sodium hydroxide, as a means of separating molybdenum and rhenium. Both perrhenate and molybdate were absorbed

from an alkaline solution by the hydroxide form of a strongly basic anion exchange^r but molybdate only was eluted with 10% alkali. The authors however admit to a very slow separation technique.

Previously a separation (85) of these two elements had been obtained by adjusting the solution pH to 4 - 8 in order to obtain the greatest difference in absorption coefficients. The less strongly absorbed molybdate was then eluted with a sodium hydroxide - boric acid buffer solution of pH 8.35, but incompletely so according to Fisher (50).

Sodium hydroxide then is a slow eluting agent for molybdenum, and effective only in solutions greater than 1 Normal in strength.

TUNGSTEN - elution improved with increasing hydroxyl ion concentration due to this effect on the "exchange potential" of the hydroxyl ion. The charge on the tungstate ion is normally greater than one whilst the condensation tendency of tungstates could mean a large ionic radius. If this be so tungstate absorption would be slow and its elution slow also. Thus of the factors involved in "exchange potential" values, tungstate is favoured by ionic size and ionic charge, but gradually the hydroxyl ion is favoured by concentration increase.

SUMMARY.

Almost all strengths of sodium hydroxide eluted vanadium, molybdenum and tungsten, leaving in the case of this

particular resin, chromium still absorbed, to be subsequently eluted with reducing acid.

However the elution of molybdenum was very slow.

TABLE VIII.

Elution of the individual metals after their absorption by the anion exchanger from faintly alkaline solutions. Ammonium hydroxide was the eluting agent.

STRENGTH OF NH ₄ OH	% METAL ELUTED			
	VANADIUM	CHROMIUM	MOLYBDENUM	TUNGSTEN
0.5 N	10	Nil	Nil	Nil
1.0 N	15	Nil	Nil	--
2.0 N	10	Nil	--	Nil
3.8 N	20	--	Nil	Nil
7.6 N	20	--	--	--
10 N	25	Nil	Nil	Nil

REMARKS ON TABLE VIII.

Being a weak base, with a resulting low hydroxyl ion concentration, no elution was expected by ammonium hydroxide. This was found to be so except for vanadium in which case some elution occurred when using very slow flow rates. This partial elution of vanadium is indicative of the vanadate ion having a low "exchange potential", for the concentration factor has lowered the "exchange potential" of the hydroxyl ion.

The subsequent elution of chromium with reducing acid was found to be slow. This shows that the ammine complex is more strongly bound to the resin, and more stable, than the aquo complex, which would be present

prior to the addition of ammonium hydroxide.

Sussman (25) has also found that ammonium hydroxide will elute vanadium. When passed through the chloride form of an anion exchanger ammonium meta-vanadate was absorbed and subsequently substantially eluted with 2-8 M ammonium hydroxide.

Ryabchikov and Lazarev (104) also found that tungsten, after absorption by an anion exchanger from a oxidised acid solution, was eluted with ammonium hydroxide. The results of Table VIII do not agree with this finding, but it was later found that large volumes of ammonium hydroxide at slow flow rates could cause slight elution of tungsten.

SUMMARY.

Ammonium hydroxide slowly elutes vanadium and large volumes of reagent would be required for a quantitative elution. However it is then possible that some tungsten would also be eluted. Chromium and molybdenum are unaffected by ammonium hydroxide.

4-5

Studies on the absorption of various complexes of the metals, iron, vanadium, chromium, molybdenum and tungsten by the anion exchanger and their elutions using various strengths of hydrochloric acid. The metals were added individually

Columns of the hydroxyl form of DE-ACIDITE "FF" were prepared by washing the resin with sodium hydroxide. To the columns were then added solutions containing (a) known volumes of the above metal solutions, (b) various complexing agents in excess to ensure complete complexing of the metal, and (c) acid or base to adjust pH values.

Elution technique with the hydrochloric acid was:- to the columns to which alkaline metal solution had been added elution order was successively weak to stronger acid. Such results are in the "A" Tables. To the column to which acid metal solution had been added elution order was successively strong to weak acid. The results obtained are in the "B" Tables.

The purpose of this series of studies was to determine acid strength effects in chloro-metal complexing and the effect hydrogen ions could have in lowering the stability constants of the metal complexes when formed.

Absorption of individual metals in presence of oxalic acid or oxalate and their subsequent elution with hydrochloric acid. [Individual elutions were employed.]

TABLE IX A

% METAL ELUTED BY ACID

METAL	INFLUENT pH	%METAL IN EFFLUENT	0.5 N	2.0 N	5 N
Fe	4.9	Nil	Trace	Trace	Trace
Mo	10.1	Nil	Nil	70	Nil
V	9.5	Nil	90	90	--
Cr	9.9	Nil	50	70	--
W	10.0	Nil	30	30	--

TABLE IX B

% METAL ELUTED BY ACID

METAL	INFLUENT pH	%METAL IN EFFLUENT	10 N	5 N	2 N
Fe	2.0	Nil	Nil	Trace	Trace
Mo	2.2	Nil	Nil	Nil	45 (60)
V	1.9	Nil	100	70	Nil
Cr	2.1	80	20	--	--
W	2.2	Nil	10	Nil	--

REMARKS ON TABLE IX.

IRON - precipitates at higher pH values due to hydrolysis. However the iron was absorbed from faintly acid solution and its subsequent elution was difficult. The stability constants of the iron III - oxalato complex are given at 10 and 18 (log K_a) which is apparently sufficiently high to prevent cation iron formation due to hydrogen ion suppression of the complex.

It is however also known that an iron III chloro complex is formed in strong hydrochloric acid solution. Thus even if high acid strengths effect the oxalato complex the chloro complex formed should not be, and was not eluted.

This then would explain the failure to elute with both strong and weak acid for in the former case the anionic chloro complex is formed whilst in the latter case the oxalato complex remains.

Samuelson and Djurfelt (55) have studied the effect of acetate and oxalate ions on numerous cations. Using a cation exchanger the iron was absorbed from an acetate solution but not from an oxalate solution. This shows the iron to be anionic in the oxalato complex and agrees with the experimental results of Table IX.

MOLYBDENUM - was absorbed by the resin from both acid and alkaline solutions and was eluted by dilute acid. As in Table I where molybdate was eluted with hydrochloric acid, dilute acid caused molybdenum elution this indicating, in this case, a low stability for the oxalato complex if

formed. Also as in Table I strong acid caused no elution this indicating the formation of the anionic chloro-molybdenum complex.

Elution however was always slow indicating that molybdenum compounds have a rather high "exchange potential" due to charge and/or ionic size.

The most stable oxyhalo complexes of molybdenum in its penta- and hexa- positive states are the fluoro complexes such as $[\text{Mo O}_2 \text{F}_4]^=$ and $[\text{Mo OF}_5]^=$ and apparently similar chloro complexes exist although not so stable.

VANADIUM - was absorbed from both faintly acid and alkaline solutions and quite readily eluted by all acid strengths.

If an oxalato complex is formed its stability constant must be low and as seen earlier vanadium compounds have a low "exchange potential." Both these effects explain the elution of the vanadium over all acid strengths.

The effluents were blue or blue-green indicating some reduction to vanadium IV by the oxalate, hydrochloric acid, or resin, or a combination of these three factors.

Oxalic acid contains no hydroxyl groups. As a result vanadium oxalato complexes would not be expected to be very stable. The experimental results agree with certain polarographic studies that the complex is weak.

CHROMIUM - was completely absorbed only from alkaline solution. In acid solution the redox potential of the chromium system is increased and its failure to be absorbed is due to cationic chromium III formation by reduction. Elution was obtained with dilute acid whereas previously (Table I) the chromate itself was eluted only by strong acid. This must be due to (a) chromium reduction by the oxalate especially upon addition of the acid, (b) formation of a complex, (c) lowering of the stability constant of the complex due to hydrogen ions and (d) displacement of the chromium III compound by the acid. The oxalate reduction is the important reaction in this case.

The dilute acid effluents were violet, indicating an aquo chromium III complex, whilst the strong acid effluent, green in colour, indicated a chloro-chromium III complex. However in neither case would the chromium be in an anionic grouping as the former gives cationic chromium and the latter, at best, a neutral grouping.

TUNGSTEN - was absorbed by the resin under both faintly acid and alkaline conditions and was slowly eluted by all acid strengths. No doubt the formation of colloidal tungstic acid could account for both the uptake from acid solution and the slow qualitative elutions. A similar effect was obtained in Table I results.

Tungsten, like molybdenum, can form complex halides or oxyhalides such as $[W O_2 F_4]^-$. If such a

chloro complex is formed it was displaced by the acid, for the tungsten is in the anionic grouping. Also however a polymeric form could exist, realising the condensation properities of tungsten, and if so the ionic size could be too large for the resin pore size.

A slow settling out of a yellow precipitate in the effluents showed, nevertheless, eventual tungstic acid formation.

If oxalato complexes of tungsten do form then these results show them to be relatively unstable.

SUMMARY.

Concentrated acid eluted tungsten qualitatively and slowly, chromium rather slowly and vanadium quite readily, but caused no elution of iron and molybdenum.

Dilute acid had a very faint elution effect on iron and quite an appreciable elution effect on molybdenum, vanadium, chromium and tungsten.

Thus the concentrated acid technique offers a separation of chromium, tungsten and vanadium from iron and molybdenum.

100.

TABLE X.

Absorption of the individual metals in the presence of versene or versenate and their subsequent elution with varying hydrochloric acid strengths. In this table elutions were successive, that is for one absorption step two or three elution steps were carried out. Table "A" gives increasing acid strength results and Table "B" decreasing acid strength results.

In the ideal case the sum of the elution and effluent values should come to 100%.

TABLE X A.

METAL	pH OF INFLUENT	% METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			0.5 N	2.0 N	5 N
Fe	4.0	Nil	50	50	---
Mo	10.7	Nil	40	55	---
V	9.9	Nil	85	10	---
Cr	10.2	Nil	10	10	20
W	10.6	Nil	Trace	Trace	5

TABLE X B.

METAL	pH OF INFLUENT	% METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			10 N	5 N	2 N
Fe	2.4	100	---	---	---
Mo	1.9	Nil	Nil	Trace	80
V	1.8	Trace	100	---	---
Cr	1.9	20	75	Trace	---
W	1.9	15	40	Trace	Trace

REMARKS ON TABLE X.

IRON - the hydrolysis constant for the hydroxide of iron III is greater than the stability constant of the iron III versenate complex. Hence due to precipitation the use of alkaline solutions was prevented.

From more strongly acid solution the iron was not absorbed by the resin, this showing the effect hydrogen ions have on the formation of the iron III - versenate complex. However as the pH of the solution rose the versenate ion concentration increased with the resultant formation of the anionic versenate complex which was absorbed by the resin.

The absorbed iron was eluted quite readily by dilute acid. Whilst strong acids were not used it would be expected that elution would not occur due to the formation of the anionic iron III chloro complex.

In the studies of iron to prevent the possible effect of hydrolysis due to liberated hydroxyl ions from the

resin, it would be preferable to use, not the hydroxyl form, but rather the chloride or similar form of the resin exchanger.

The iron elution indicates a low value for the stability constant of the complex versenate, and a previously quoted value is $\log K_1 = 25.1$. This value would be suppressed by hydrogen ions according to the law of mass action, for versene, is a weak acid.

In ion exchange studies such as these one drawback to the use of versene is the crystallization of the acid from acid media. This effect caused considerable blockage of the columns.

MOLYBDENUM - was absorbed by the resin from both acid and alkaline versenate solution, and as before, was eluted by dilute acid because of hydrogen ion effects on both the molybdo-versenate complex and the versene itself. Again no elution occurred with strong acid due to the formation of the anionic chloro-molybdo complex.

VANADIUM - was absorbed by the resin from both acid and alkaline solution, but was readily eluted by all acid strengths. Complexes, if formed, then are very weak. Some vanadium IV was formed due to reduction by either the versene, resin, or the effect of hydrogen ions on redox potential values.

The iso-electric point for vanadium has been quoted at pH 2.2. It may be assumed then that the pH value of the acid solution was raised by the hydroxyl ions of the

resin to a value above 2.2. In later cases when a nitrate form of the resin was employed only partial absorption of vanadium occurred if the pH was below 2.2 and this supports the argument relating to hydroxyl ion neutralization of the hydrogen ions in the influent.

The value $\log K = 18.7$ is given for the VO^{++} ion with versene but hydrogen ions would lower this value considerably.

CHROMIUM - was only partially absorbed from acid solution and then readily eluted with strong acid. However quantitative uptake occurred from alkaline solution and dilute acid was an inefficient eluting agent. In Table V it was found that versenate did not elute chromium, and these results further indicate the formation of a stable chromium-versenate complex, which is affected by hydrogen ions due to formation of the undissociated acid versene.

TUNGSTEN - was not quantitatively absorbed from acid solution, due no doubt to colloidal tungstic acid formation. Elution by all acid strengths was also only qualitative due to tungstic acid formation.

If a tungsten-versenate complex is formed it is very unstable and most susceptible to hydrogen ions.

SUMMARY.

An acid solution, with versene present, does not permit iron absorption. In itself this is desirable and

iron, being the major constituent in steel, is not required for analysis. However from such solution conditions chromium and tungsten are only partially absorbed.

Neglecting iron due to hydrolytic effects the other metals were absorbed from alkaline solution but hydrogen ion effects on stability constants cause a general elution of the metals and no separations. The only possible separation would be of tungsten, chromium and vanadium from molybdenum by using strong acid, and subsequently eluting molybdenum with dilute acid. In this case the versene itself serves no specific purpose.

TABLE XI.

Absorption of the individual metals in the presence of citric acid or citrates and their subsequent elution with varying hydrochloric acid strengths. As in Table X elutions were successive and the sum of elution values should add up to 100%. Table "A" gives increasing acid strength results and Table "B" decreasing acid strength results.

TABLE XI A.

METAL	INFLUENT pH	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			0.5 N	2 N	5 N
Fe	10.5	Nil	80	20	--
Mo	10.2	Nil	10	80	Trace
V	9.8	Nil	80	20	--
Cr	10.1	Nil	10	20	20
W	10.0	Trace	30	30	10

TABLE XI B.

METAL	INFLUENT pH	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			10 N	5 N	2N
Fe	2.2	Nil	80	20	--
Mo	1.9	Nil	Nil	Trace	80
V	2.0	100	Nil	Nil	--
Cr	1.9	15	85	Nil	--
W	2.0	Nil	60	20	--

REMARKS ON TABLE XI.

IRON - was absorbed from both acid and alkaline solutions and readily eluted by all acid strengths. The absorption from acid solutions indicates a very stable complex ($\log K = 11.8$). However elution with 10 N acid was unexpected and not in agreement with studies by Samuelson and Sjöberg (58). They absorbed iron and aluminium on the citrate form of a resin, eluted the aluminium with 10 N hydrochloric acid and the iron with 1 N acid. A possible explanation for this variance is the dilution effect on the hydrochloric acid due to resin neutralization (the resin was in the hydroxyl form) and the formation of the triprotic citric acid from the citrate salt. Alternatively the chloride ions from the acid may have displaced the anionic citrate complex due to "exchange potential" variations and if this be so then the citrate complex must be more stable than the chloro complex.

Lanford and Quinan (65) have studied the reaction between iron III and citric acid and claim the reaction to be $\text{Fe}^{+++} + \text{H Cit}^{-2} \rightleftharpoons \text{Fe (H Cit)}^{+}$ when the ratio of iron to citrate is unity. Whilst this assumption may be correct it is not proven by the ion exchange studies both carried out and referred to.

Nevertheless Babtelsky and Jordan (66) found various iron III citrate and tartrate complexes to exist and the formulae they postulate show the complexes to be both cationic and anionic depending on the mole ratios involved.

MOLYBDENUM - was absorbed from both acid and alkaline solutions and was slowly eluted by acid below 5 N ~~in strength~~. This again shows the formation of a stable anionic molybdo-chloro complex, and the relative instability of the molybdo-citrate complex.

VANADIUM - quantitatively passed through the resin when in acid solution. The pH of the solution was below 2.2, the iso-electric point for vanadium, and non-absorption showed no anionic citrate complex to have been formed under the solution conditions used.

However absorption was quantitative from alkaline solution and elution quite rapid with dilute acid.

The effluent containing unabsorbed vanadium was blue and the acid elutions yellow-green, both colours being due to some vanadium reduction. But findings by Salmon (8) do not agree in respect of the unabsorbed vanadium, for he observed no reduction of vanadium without absorption. However conditions in the two cases were at variance even though both acidic. In this work it is possible the vanadium reduction is due to an increase in redox potential brought about by the high hydrogen ion concentration.

These results furthermore are in agreement with those in Table VI wherein no citrate complex was believed to be formed.

CHROMIUM - was only partially absorbed from acid solution but the elution of the absorbed chromium was quite rapid with 10N acid. Both the partial absorption and elution

indicate a reduction of the chromium in acid solution. Quantitative absorption occurred from alkaline solution but the elution was slow. This is in agreement with previous chromium elutions and is indicative of the strong absorption of the chromium whether absorbed as chromate or citrate complex.

TUNGSTEN - was absorbed by the resin and eluted by all acid strengths. The colloidal character of tungstic acid, as discussed earlier, accounts for the inefficient tungsten elution, for with an acid eluting agent causing colloid formation, even though very slowly, the resin can hold the tungsten by means other than as a true ion exchanger.

SUMMARY.

An interesting separation of some of the metal ions listed above when citrate ions are present, was devised by Samuelson and Schramm (53). They saturated an anion exchanger with anions capable of complexing with the metals to be removed from the solution. Thus iron III and vanadium IV were quantitatively retained by the citrate form of the resin and were subsequently eluted with 1 N hydrochloric acid. An interesting observation in this work was that chromium III ions were not absorbed by the resin under the operating conditions.

From an acid citrate solution it should be possible, from the results obtained, to separate vanadium from iron, molybdenum and tungsten. No satisfactory separations appear possible from the alkaline solutions.

TABLE XII.

Absorption of the individual metals in the presence of potassium cyanide and their subsequent elution with varying hydrochloric acid strengths. Elutions were successive in each table and the sum of elution values should add to 100%. Table "A" gives increasing acid strength and Table "B" decreasing acid strength results.

TABLE XII A.

METAL	pH INFLUENT	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			0.5 N	2 N	5 N
Fe	2.4	100	--	--	--
Mo	11.8	Nil	15	30	10
V	10.9	50	50	Nil	--
Cr	11.6	Nil	10	10	--
W	11.1	Nil	10	10	--

TABLE XII B.

METAL	pH	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			10 N	5 N	2 N
Fe	1.7	100	--	--	--
Mo	1.9	Nil	Nil	10	55
V	1.9	100	Trace	--	--
Cr	1.9	Nil	90	10	--
W	2.1	Trace	40	10	10

REMARKS ON TABLE XII.

IRON - as iron precipitated in alkaline solution only acid solutions were used, from which no iron was absorbed. Apparently solution conditions did not favour the formation of a ferricyanide wherein the iron is anionic. If however a ferricyanide was formed, it was displaced from the resin by cyanide ions due to the high "exchange potential" of the cyanide ion. This "exchange potential" would not be varied greatly by concentration in this case as the cyanide concentration was not great.

Working on the basis that a higher valence or higher weight anion will displace the already absorbed anion from an anion exchanger Sussman (25) removed iron from a potassium ferrocyanide solution and subsequently recovered it by resin regeneration with dilute sodium hydroxide solution.

Samuelson (52) also used the anionic property of ferricyanide to separate iron from the alkali metals. The iron only, passed through a cation exchanger.

These references support the supposition above that in the experimental work of Table XII no ferri or ferrocyanide was formed.

MOLYBDENUM - was quantitatively absorbed from both acid and alkaline solutions and slowly eluted by dilute acid but not at all by strong acid due to chloro - complex formation. This is further proof of the stability of the chloro complex. If a cyano complex has formed its

reactions in the ion exchange studies were no different to the molybdenum solution alone. However no colours developed on addition of cyanide so that apparently conditions did not favour cyano complex formation.

VANADIUM - was not absorbed from acid solution, this showing that cyanide has no effect on the iso- electric point for vanadium. It was not expected to form a complex however as vanadium V co-ordinates essentially through oxygen to give "ato" type compounds.

Surprisingly however only partial vanadium absorption occurred from alkaline solution. It would not be expected that a cationic complex would form as the tendency to complex is low and the cyanide ion would tend to give an anionic complex. Either the ionic size of the anion formed is too large for the resin lattice or the cyanide ions having a high "exchange potential" have been preferentially absorbed by the resin column. Elution of the absorbed vanadium was efficiently obtained with dilute acid, as has been the case in all previous vanadium elutions.

CHROMIUM - was absorbed from both acid and alkaline solutions and readily eluted with 10 N acid and slowly with dilute acid. The stability of the cyanide complex, if formed, would be reduced by hydrogen ions as hydro- cyanic acid is a weak acid. This could explain the elution of the chromium if the cyano complex were formed. However it may be assumed from earlier discussions on hydrochloric acid

elutions of chromium that the metal is eluted through its reduction to the stable chromium III state by the strong acid.

TUNGSTEN - was absorbed by the resin and slowly eluted due to colloidal tungstic acid formation. The presence of cyanide appeared to have no effect on the tungsten as the results for tungsten with and without cyanide were similar.

Doubtless colloidal tungstic acid was present, in all cases involving acid solution, but absorption occurred because the solutions were freshly prepared and coagulation had not become effective.

SUMMARY.

The presence of cyanide did not seem to cause any alterations to the results obtained when no cyanide was present. This in some cases would be because solution conditions had not favoured cyano complex formation.

TABLE XIII.

Absorption of the individual metals in the presence of perchloric acid and perchlorate and their subsequent elution with varying hydrochloric acid strengths. Elution results are cumulative.

TABLE XIII A.

METAL	pH INFLUENT	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			0.5 N	2 N	5 N
Fe	2.2	100	--	--	--
Mo	9.5	100	--	--	--
V	10.0	100	--	--	--
Cr	10.0	100	--	--	--
W	10.1	100	--	--	--

TABLE XIII B.

METAL	pH INFLUENT	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			10 N	5 N	2 N
Fe	1.1	100	--	--	--
Mo	1.0	100	--	--	--
V	1.3	100	--	--	--
Cr	1.1	80	Trace	10	--
W	1.3	25	40	30	--

REMARKS ON TABLE XIII.

It is generally considered that perchloric acid complexes, if formed, are cationic and these results are further proof of this contention.

Evidence of a complex between iron III and perchlorate ions has been given by Sutton (68) even though hitherto it had been assumed that perchlorate ions form no complexes. Whilst the results of Table XIII do not disprove Sutton's findings of a complex, they show most clearly the cationic character of iron in perchloric acid solution.

The partial uptake of chromium from acid solution could be due to a mutual reduction between the chromium VI and perchloric acid.

TABLE XIV.

Absorption of the individual metals in the presence of mannitol and their subsequent elution with varying hydrochloric acid strengths. Elution results are cumulative and the order in each Table is from left to right.

TABLE XIV A.

METAL	pH INFLUENT	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			0.5N	2 N	5 N
Fe	11.4	50	50	--	--
Mo	11.0	Nil	80	15	Trace
V	10.9	Nil	50	50	--
Cr	10.8	Trace	Trace	Trace	--
W	11.1	Nil	5	20	20

TABLE XIV B.

METAL	pH INFLUENT	%METAL IN EFFLUENT	% METAL ELUTED BY ACID		
			10 N	5 N	2 N
Fe	1.5	100	Nil	Nil	--
Mo	1.5	Nil	Nil	5	20
V	1.7	100	--	--	--
Cr	1.7	100	Trace	--	--
W	1.6	Trace	20	20	--

REMARKS ON TABLE XIV.

IRON - was not absorbed from acid solution and only partially absorbed from alkaline solution. The fact that hydrolysis causes no precipitate of iron under alkaline conditions indicates the formation of a complex whilst the results show the iron to be wholly cationic in acid solution and partly cationic and partly anionic under alkaline conditions. The 50% absorption could indicate the complex to be of the iron ferrate type wherein half the iron is cationic and half anionic.

Dilute acid rapidly eluted the iron absorbed from alkaline medium.

MOLYBDENUM - the results were similar to previous molybdenum studies, namely quantitative absorption, slow elution with weak acid and no elution with strong acid. The mannitol formed a very weak complex with the molybdenum, if a complex was formed at all.

VANADIUM - a complex if formed, was unstable, for the vanadium results were similar to those of previous Tables, both in absorption and desorption.

CHROMIUM - was not absorbed from acid solution indicating the formation of a cationic or neutral chromium - mannitol complex. In the previous studies, chromium was partially absorbed from acid solution, so that the result in Table XIV shows the formation of a complex with the chromium in the cationic grouping. Dilute acid only slowly eluted the chromium absorbed from alkaline solution this showing the strong absorption of chromium

by the resin.

The results suggest that hydrogen ions permit reduction of the chromium and the formation of the cationic chromium III - mannitol complex, whereas in alkaline media the chromium is not reduced and hence absorbed. Table I shows the difficulty of eluting chromate alone from the resin when using dilute hydrochloric acid.

TUNGSTEN - gave the expected results in that absorption occurred from a freshly prepared acid solution and alkaline solution, and partial elution was obtained by all acid strengths. The mannitol caused no variation to the results obtained when using tungsten alone.

SUMMARY.

Mannitol is a masking agent and gives rise, according to these results, to cationic complexes of iron and chromium under acid conditions. As such it may be a useful agent in assisting in the separation of some of the metals involved.

Referring to the results obtained only molybdenum and tungsten were absorbed from an acid solution and their selective elution should be possible using 10 N acid for tungsten and 1 N for molybdenum. Nevertheless it is more desirable to absorb the chromium and vanadium also, and so use only one ion exchange column and one absorption step.

Unfortunately iron is partly absorbed from alkaline mannitol solution and whilst all the other metals are absorbed

a separation from iron would be difficult, if at all possible.

Thus the acid solution offers the only possibilities for further investigations.

CHAPTER 5.

EXPERIMENTAL DETAILS USING THE COMBINED

METALS IN SOLUTION.

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5.3 Elution of the metal complexes with hydrochloric acid	
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Absorption and Elution of the Metals when added to the resin mixed in the one solution.

5-1 This series of studies was carried out in the light of the previous studies, to observe whether the presence of more than one metal would cause variations in results.

Realising also that the hydroxyl form of the resin can cause difficulties, this series employed two forms of the resin, namely the hydroxide and chloride forms. Whereas solution pH values are not affected by the chloride resin, a disadvantage of this type is the slowness of regeneration. This feature has been referred to earlier under "Resins and their Uses."

The first section of the series was carried out as follows:- 5 ml each of vanadium $\overline{\text{V}}$, molybdenum $\overline{\text{VI}}$, chromium $\overline{\text{VI}}$ and tungsten $\overline{\text{VI}}$ were taken, the solution made faintly alkaline and added to the resin. Elutions were then attempted with versene and versenate, oxalic acid and oxalate, and citric acid and citrate. Iron was not studied due to its precipitation during preparation of the influent solutions.

The "A" Tables refer to the hydroxide form of "DE-ACIDITE FF" and the "B" Tables to the chloride form of the same strongly basic resin. The strengths of eluting agents were 0.1 molar with pH adjustments with sodium hydroxide.

After the attempted elutions with increasing alkaline solutions both 1 N and 10 N hydrochloric acid were finally used as desorbers. In the "B" Tables the acid also served as a regenerant.

Thus the elution values given in the Tables are cumulative, that is the sum of the values given for any metal should add up to 100%. The reason for the successive elutions was that if a metal were eluted at pH₄ approximately then its elution would also occur at higher pH values. Hence from these results can be seen any possible selective elutions as well as the minimum pH values necessary for elution. The results of this first section, Tables XV to XVII, may be compared to the results in Tables I to VIII.

The second section of the series, Tables XVIII to XIX, may be compared to Tables IX to XIV for 5 ml each of the metals including iron III and the appropriate complexing agent were added to the resin columns at varying pH values. Selective elution was then attempted with varying strengths of hydrochloric acid. In the "A" Tables, that is the hydroxide form of the resin - elution strengths increased from 1 N to 10 N acid, whilst in the "B" Tables, or chloride resin form, elution strengths decreased from 10 N to 1 N.

TABLE XV.

5.2 Absorption of the combined metals from alkaline solution by the hydroxide and chloride resin forms and their elution with versene and hydrochloric acid. The elution results are cumulative.

TABLE XV A.

METAL	% METAL ELUTED BY				
	VERSENE			HCl	
	pH 4.5	pH 9.5	pH 12.3	1 N	10 N
Vanadium	Nil	30	65	Trace	Nil
Molybdenum	Nil	15	15	65	Nil
Tungsten	Nil	30	40	20	10
Chromium	Nil	Nil	Nil	15	85

TABLE XV B.

METAL	% METAL ELUTED BY				
	VERSENE			HCl	
	pH 4.5	pH 6.8	pH 12.4	1 N	10 N
Vanadium	Nil	Nil	100	--	--
Molybdenum	Nil	Nil	10	80	5
Tungsten	Nil	Nil	40	35	25
Chromium	Nil	Nil	Nil	20	80

REMARKS ON TABLE XV.

The separation of chromium from the other metals is the only possible separation, but slow flow rates would be necessary for the quantitative elution of molybdenum. As distinct from Table V some molybdenum was eluted by the alkaline versenate solution, whilst as distinct from Table I some molybdenum was eluted by strong hydrochloric acid. In the case of the acid this slight elution could be due to dilution effects on the acid or the failure to completely remove the molybdenum previously carried down the column by the weak acid.

The versenate elution is however more difficult to explain, but could be due to the formation of a compound containing more than one metal in its structure. For example telluro molybdic complexes are known as are molybdo-phospho-tungstate complexes, and their formation is due to the power of condensation and polymerisation of molybdenum, not only with itself, but with a variety of other acids. Also both molybdenum and tungsten form hetero-poly-acids and a compound containing both metals could conceivably exist.

The different resin forms caused no variations in the results.

TABLE XVI.

Absorption of the combined metals from alkaline solution by the hydroxide and chloride forms of the resin and their elution with oxalate, and ^{with} hydrochloric acid.

TABLE XVI A.

METAL	% METAL ELUTED BY				
	OXALATE			HCl	
	pH 8.0	pH 11.9	pH 12.2	1 N	10 N
Vanadium	60	35	Nil	--	--
Molybdenum	25	75	5	--	--
Tungsten	30	60	5	Trace	--
Chromium	Nil	20	60	20	--

TABLE XVI B

METAL	% METAL ELUTED BY				
	OXALATE			HCl	
	pH 8.1	pH 11.7	pH 12.2	1 N	10 N
Vanadium	90	10	Nil	--	--
Molybdenum	50	50	Nil	--	--
Tungsten	50	50	Nil	--	--
Chromium	Nil	25	20	50	5

REMARKS ON TABLE XVI.

At pH 8 approximately it should be possible to elute vanadium, molybdenum and tungsten leaving chromium on the resin to be subsequently eluted with acid. However oxalate offers no selective elution of the eluted metals.

The different resin forms gave no significant variations in result, but this was to be expected when adding an alkaline solution of the metals.

In Table IV neither chromium nor molybdenum was eluted by oxalate. The explanation for the results of this Table XVI then must be the formation of compounds with more than one metal in its structure and the displacement of such compounds due to "exchange potential" differences.

The elution rates of chromium and molybdenum were slow.

TABLE XVII.

Absorption of the combined metals from alkaline solution by the hydroxide and chloride forms of the resin and their elution with citrate and hydrochloric acid. As in Table XVI the elution results are cumulative.

TABLE XVII A.

% METAL ELUTION BY

METAL	CITRATE SOLUTION			HCl	
	pH 5.8	pH 6.2	pH 12.2	1 N	10 N
Vanadium	10	90	--	--	--
Molybdenum	10	70	20	Trace	--
Tungsten	Trace	50	25	10	--
Chromium	Nil	Nil	20	40	40

TABLE XVII B.

% METAL ELUTION BY

METAL	CITRATE SOLUTION			HCl	
	pH 5.4	pH 8.6	pH 12.2	1 N	10 N
Vanadium	Nil	85	10	--	--
Molybdenum	Nil	50	50	5	Trace
Tungsten	Nil	50	40	10	--
Chromium	Nil	5	5	75	20

REMARKS ON TABLE XVII.

The only separation possible is that of chromium from vanadium, molybdenum and tungsten. It was noted however that elution from the hydroxide resin was easier than from the chloride resin. This would be due to pH increase in the eluting solution due to hydroxide displacement from the resin.

The results in Table VI showed neither chromium nor molybdenum was eluted by any citrate solution. Hence the elutions in this case must be due to complex formation involving more than the one metal in the compound. Especially would this be so for molybdenum whose elution was quite efficient.

TABLE XVIII.

5.3

Hydrochloric Acid Elutions of the versene complexes of the metals when all metals are present in the one solution.

TABLE XVIII A.

% METAL ELUTED BY HCl

METAL	INFLUENT pH	METAL IN EFFLUENT %	1 N	2.5N	5 N	10 N
Iron	1.2	100	--	--	--	--
Vanadium	1.2	25	45	20	--	10
Chromium	1.2	40	5	5	--	50
Molybdenum	1.2	Nil	Nil	5	--	Nil
Tungsten	1.2	20	20	10	--	50
Iron	4.0	90	10	--	--	--
Vanadium	4.0	Nil	90	5	--	Trace
Chromium	4.0	Nil	20	20	--	60
Molybdenum	4.0	Nil	25	5	--	30
Tungsten	4.0	Nil	25	5	--	70
Iron	10.4	iron precipitates from solution.				
Vanadium	10.4	60	20	15	--	Trace
Chromium	10.4	Nil	20	5	--	70
Molybdenum	10.4	Nil	10	Trace	--	Nil
Tungsten	10.4	40	10	15	--	50

NOTE - hydroxide form of the resin used with acid strength of eluting agent increasing.

TABLE XVIII B.

% METAL ELUTED BY ACID

METAL	INFLUENT pH	METAL IN EFFLUENT	10 N	5 N	2.5N	1 N
Iron	1.1	100	--	--	--	--
Vanadium	1.1	50	35	10	--	5
Chromium	1.1	60	30	5	--	Nil
Molybdenum	1.1	Nil	10	30	--	60
Tungsten	1.1	10	50	40	--	Trace
Iron	3.8	100	Trace	--	--	--
Vanadium	3.8	Nil	80	20	--	Nil
Chromium	3.8	Nil	10	Trace	--	Trace
Molybdenum	3.8	Nil	5	5	--	90
Tungsten	3.8	Nil	80	10	--	10
Iron	10.7	iron precipitates from solution.				
Vanadium	10.7	40	45	15	--	Nil
Chromium	10.7	Nil	20	10	--	Nil
Molybdenum	10.7	Nil	Nil	Nil	--	85
Tungsten	10.7	20	70	10	--	5

NOTE - chloride form of the resin used with acid strength of eluting agent decreasing.

REMARKS ON TABLE XVIII.

These results may be compared with those in Table X.

IRON - as in Table X was not absorbed from acid solution, this being due to hydrogen ion effects on the stability of the complex as well as the lowering of the versene solubility. Higher pH values could not be used because of hydrolysis of the iron.

VANADIUM - contrary to expectations, was not quantitatively absorbed from alkaline solution. However elution was rapid. The vanadium should be anionic but may not have been absorbed due to the influence of other anions, with "exchange potentials" in excess of the low value for the vanadium ion, preferentially being absorbed by the resin. In effect if this be true, the total anion concentration exceeded the total exchange capacity of the resin. Slight absorption of vanadium occurred from acid solution but this is due to either localised pH values exceeding 2.2, the iso-electric point for vanadium, or the formation, in part, of an anionic complex.

CHROMIUM - as in Table X was not quantitatively absorbed from solutions of low pH value, but was readily absorbed from alkaline solution and faintly acid solution. Also as in Table X some elution occurred at all acid strengths but efficiency increased with increasing acid concentrations. As discussed earlier this increased efficiency is due to hydrogen ion effects on the redox potential of the chromium system.

The violet colour of the effluents showed reduction of chromium to have occurred, and a complex to have formed.

MOLYBDENUM - was always quantitatively absorbed, as before, but in this case some molybdenum was eluted by 10 N hydrochloric acid. An explanation given under Table XV could also apply in this case, namely the formation of a molybdo complex containing more than one metal, and its displacement by chloride ions.

TUNGSTEN - was, as always, difficult to quantitatively absorb and elute in the presence of acids due to colloidal tungstic acid formation. Qualitative absorption from alkaline solution must also be due to complex formation.

SUMMARY.

These results are not as decisive as those obtained when studying the individual metals. The results point to polynuclear complex formation involving more than one metal in the compound, due to both less effective absorption and easier elution of the metals.

The following conclusions however may be drawn:-

- (a) versene and versenate were ineffective for the ion exchange separation of the metals considered.
- (b) iron is cationic or neutral in the presence of versene in acid solution. Anionic character increases with increasing pH.
- (c) the chloride form of the resin gave similar results to the hydroxide form of the resin. Obviously pH

- (c) variations due to hydroxyl ion displacement were unimportant in the solutions chosen.
- (d) acid solutions offered little prospect for metal separation due to partial absorption of chromium, molybdenum and tungsten.
- (e) absorption was satisfactory from faintly acid solutions but as shown for iron the pH must be carefully controlled.
- (f) hydrochloric acid alone was not an effective selective eluting agent.

TABLE XIX.

Hydrochloric Acid Elutions of the Citrate Complexes of the metals when all metals are present in the one solution.

TABLE XIX A.

METAL	pH	% METAL ELUTED BY ACID				
		% METAL IN EFFLUENT	1N	2.5N	5 N	10 N
Iron	1.0	75	20	Trace	--	--
Chromium	1.0	20	5	Trace	5	Trace
Molybdenum	1.0	Nil	30	40	20	Trace
Vanadium	1.0	45	55	--	--	--
Tungsten	1.0	Nil	--	70	20	10
Iron	4.5	25	75	Trace	--	--
Chromium	4.5	Nil	Trace	20	25	10
Molybdenum	4.5	20	30	35	10	10
Vanadium	4.5	Nil	100	--	--	--
Tungsten	4.5	Nil	20	60	10	10
Iron	10.4	10	90	Nil	--	--
Chromium	10.4	Nil	Nil	5	35	15
Molybdenum	10.4	40	20	30	10	10
Vanadium	10.4	45	60	--	--	--
Tungsten	10.4	30	40	25	5	Trace

NOTE - hydroxide form of the resin used with strength of acid eluting agent increasing.

TABLE XIX B.

% METAL ELUTED BY ACID.

METAL	pH	% METAL IN EFFLUENT	10 N	5 N	2.5 N	1 N
Iron	1.1	85	Trace	5	5	--
Chromium	1.1	20	Nil	Trace	Nil	Nil
Molybdenum	1.1	20	Trace	10	40	30
Vanadium	1.1	70	30	Nil	--	--
Tungsten	1.1	Nil	10	90	Trace	--
Iron	4.0	50	40	5	10	--
Chromium	4.0	Nil	10	Nil	Nil	Nil
Molybdenum	4.0	20	10	25	40	Trace
Vanadium	4.0	Nil	100	--	--	--
Tungsten	4.0	Nil	50	50	Trace	Nil
Iron	10.9	15	70	10	5	--
Chromium	10.9	Nil	10	Trace	Trace	Nil
Molybdenum	10.9	60	10	15	30	--
Vanadium	10.9	80	20	--	--	--
Tungsten	10.9	40	55	10	Trace	--

NOTE - chloride form of the resin used with eluting agent decreasing in acid strength.

REMARKS ON TABLE XIX.

These results may be compared to those in Table XI, the variation being that in Table XI the metals were studied individually.

IRON - the effect of pH on the formation of the various citrate complexes is shown by the tendency towards anionic iron formation with increasing pH. Surprisingly however quantitative absorption did not occur from alkaline solution as was the case in Table XI. As the iron III citrate complex is anionic another complex must have formed, and the elution of the absorbed iron with 10 N hydrochloric acid is further proof of such a contention.

CHROMIUM - was absorbed from all but solutions of very low pH value. This is in agreement with previous findings, as are the elution results, in that all acid strengths caused some elution even though in a most inefficient manner. Elution with dilute acid was more effective in the hydroxide resin than was the strong acid elution on the chloride resin. Either the chromium is more firmly absorbed by the chloride resin or the strong acid makes it difficult to elute with weak acid. It could well be that the strong acid causes reduction of the chromium and the chromium III is then able to complex with the citrate ions initially absorbed by the resin.

MOLYBDENUM - the failure to achieve quantitative absorption was unexpected in view of earlier results. Also unexpected

in relation to Table XI was the slight elution by 10 N acid. The reason, regarding complex formation, has been suggested on previous pages, but of interest here is the tendency for decreasing absorption with increasing pH. This would seem to indicate that the formation of the complex is dependent on pH.

VANADIUM - the absorption of vanadium by the hydroxide resin from acid solution can be attributed to pH rise due to liberated hydroxyl ions of the resin. The failure to obtain quantitative absorption from alkaline solution was unexpected, and as with molybdenum, can be attributed to complex formation. Alternately the total anion concentration of the influent was greater than the total exchange capacity of the resin and due to its low "exchange potential" vanadium was not absorbed. As the pH of a citrate solution rises the charge on the citrate ion increases and this, along with concentration, increases the "exchange potential" of the citrate ion. This argument could also apply to the molybdenum, iron and tungsten.

TUNGSTEN - the unexpected result was the failure to obtain quantitative absorption. The arguments put forward for vanadium are applicable here also. Elution was again qualitative by all acid strengths due to colloidal tungstic acid formation.

SUMMARY.

Whilst it has been suggested that partial absorption could be due to total anion concentration of the influent, it

does not mean that such was the case; for knowing approximately the exchange capacity of the resin and the low concentrations of metals used the total exchange capacity of the resin taken should have exceeded by a safe margin the total ionic concentration.

This being so then the results show that the presence of citrate ions in no way assists in the separation of the metals due to complex formation involving more than one metal or of a size too great for the resin structure.

The results in Tables XVIII and XIX offered no incentive to attempted separations by the use of other complexing agents; so no further tests of this nature were carried out.

Whilst it has been suggested that the reasons for only qualitative absorption are complex formation the technique of column exchange with ion exchange resins is of little assistance in determining the nature of such complex compounds.

APPENDIX

This appendix relates to apparent inconsistencies between the following Tables.

- (a) IV and XVI wherein oxalate elutions of the individual and combined metals respectively were attempted.
- (b) V and XV wherein versenate elutions of the individual and combined metals respectively were attempted.
- (c) VI and XVII wherein citrate elutions of the individual and combined metals respectively were attempted.

It must be noted that the results in Tables IV, V and VI are not cumulative, whereas the results in Tables XV, XVI and XVII are cumulative.

The metals concerned, Molybdenum and Chromium, were further examined individually, in the presence of each other, and when Vanadium and Tungsten were present.

The results are given in the following Tables and were obtained by absorbing the metals, as outlined in Chapter 4, and eluting with the solutions quoted in each Table.

TABLE A.

The metals quoted were eluted by sodium versenate, citrate or oxalate from the DE-ACIDITE"FF" column, used in its chloride form for the metal absorption. The results given were obtained in separate experiments and consequently are not cumulative.

<u>Metal</u>	<u>Eluting Agent</u>	<u>pH</u>	<u>% Metal Eluted</u>
Mo	Citrate	6.0	Nil Mo
Mo	Citrate	10.5	10% Mo
Mo	Oxalate	6.2	Trace Mo
Mo	Oxalate	8.8	25% Mo
Mo	Versenate	5.8	Nil Mo
Mo	Versenate	9.0	10% Mo
Cr	Citrate	6.0	Nil Cr
Cr	Citrate	10.5	5% Cr
Cr	Oxalate	6.2	Nil Cr
Cr	Oxalate	8.8	Trace Cr
Cr	Versenate	5.8	Nil Cr
Cr	Versenate	9.0	Nil Cr
Mo,Cr,V,W	Citrate	6.0	15 Mo, Nil Cr
Mo,Cr,V,W	Citrate	10.5	30 Mo, 10 Cr
Mo,Cr,V,W	Oxalate	6.2	15 Mo, 5 Cr
Mo,Cr,V,W	Oxalate	8.8	70 Mo, 15 Cr
Mo,Cr,V,W	Versenate	5.8	Nil Mo, Nil Cr
Mo,Cr,V,W	Versenate	9.0	10 Mo, NilCr

TABLE B.

The metals quoted were eluted by sodium citrate (i) and sodium versenate (ii) from the DE-ACIDITE"FF" column, used in its chloride form for the metal absorption. The results obtained are cumulative.

B (i)% METAL ELUTED BY CITRATE

<u>Metal</u>	<u>pH 5.7</u>	<u>pH 6.0</u>	<u>pH 10.6</u>	<u>pH 11.0</u>
Mo	Nil	Nil	40	40
Cr	Nil	Nil	20	25
Mo,Cr,V,W	5 Mo Nil Cr	10 Mo Trace Cr	75 Mo 25 Cr	10 Mo 50 Cr

B (ii)% METAL ELUTED BY VERSENATE

<u>Metal</u>	<u>pH 8.8</u>	<u>pH 9.0</u>	<u>pH 10.9</u>	<u>pH 10.8</u>
Mo	Trace	30	40	30
Cr	Nil	Nil	Trace	20
Mo,Cr,V,W	10 Mo Nil Cr	30 Mo Trace Cr	50 Mo 25 Cr	10 Mo 55 Cr

REMARKS. The elutions of Chromium in Table A compare favourably with those in Tables IV, V and VI. The elutions of molybdenum are however at variance with those in Tables IV, V and VI in that some molybdenum was eluted.

The explanation could be that, due to variations in experimental conditions, such as column height and contact time of the eluting agent, reduction of the metal occurred and/or a greater frontal movement of the metal was obtained.

The elutions of the combined metals in Table A nevertheless gave higher elution values than the individual metals. This would be due to the chromatographic absorption of the metals on the resin whereby the metals are absorbed at different levels. For example if chromium were absorbed preferentially to molybdenum, then the molybdenum would need to move a shorter distance to the end of the column from the solution of combined metals than from the molybdenum solution alone.

This chromatographic effect is well illustrated in Table B. The absorbed metal ions must have moved down the resin column under the effect of the previously lower pH solutions, for at approximately the same pH value, higher percentages of chromium and molybdenum were eluted in Table B than in Table A.

CHAPTER 6.

ION EXCHANGE RESINS IN STEEL ANALYSIS.

		Page
6.1	Possible methods of separation of the metals.	141
6.2	A method of separating and estimating in steel.	144
	(a) Vanadium	
	(b) Chromium	
	(c) Molybdenum	

6.1 From the findings given in Tables I to XIX the following observations can be made.

- (a) Vanadium can be readily eluted.
- (b) Tungsten can be readily eluted.
- (c) Molybdenum whilst eluted by the various alkaline solutions is not eluted by very weak sodium hydroxide solution, nor by rather concentrated hydrochloric acid.
- (d) Chromium is difficult to elute except by reduction to chromium III.

Thus in order to obtain a separation of these metals in a single sequence of operations, it would be necessary to elute vanadium and tungsten first followed by molybdenum and chromium.

A separation of molybdenum and chromium is readily obtained by

- (a) eluting chromium with 8N or stronger hydrochloric acid and molybdenum with dilute hydrochloric acid.
- (b) eluting molybdenum with alkaline versenate and chromium with sulphurous acid.

The separation of vanadium and tungsten however was not possible with the reagents selected. The following list briefly summarizes the attempted separations.

- (1) 0.25N sodium hydroxide slowly eluted vanadium
- (2) 0.5N sodium hydroxide eluted vanadium more readily but also eluted up to 10% of tungsten
- (3) 1N sodium hydroxide readily eluted vanadium but also eluted some tungsten and commenced to slowly elute molybdenum
- (4) 0.5M phosphoric acid eluted vanadium but also some tungsten and chromium
- (5) 1M phosphoric acid eluted vanadium and some tungsten and chromium
- (6) Versenate, pH 8.3, eluted traces of vanadium only
- (7) Versenate, pH 10-11, eluted vanadium, tungsten and slowly some molybdenum
- (8) Citrate, pH 6-9, eluted vanadium, tungsten and molybdenum. More alkaline citrate also eluted some chromium
- (9) Oxalate, pH 9-10, eluted at least some of all four absorbed metals
- (10) 8N ammonium hydroxide gave traces of vanadium and up to 20 - 30% of tungsten

None of these attempted separations gave a separation of vanadium and tungsten. Whilst greater than 0.5N sodium hydroxide caused rapid elution of vanadium, phosphoric acid elution was very slow.

Tungsten was partially eluted by all reagents but in no case was a quantitative desorption obtained.

Neglecting tungsten, the following separations have been shown possible

- (1) (a) elution of vanadium with 0.6N sodium hydroxide
- (b) elution of chromium with 8N hydrochloric acid
- (c) elution of molybdenum with 1N hydrochloric acid
- (2) (a) elution of vanadium with 0.6N sodium hydroxide
- (b) elution of molybdenum with versenate pH 10-11
- (c) elution of chromium with sulphurous - sulphuric acid

In separation (2) the molybdenum elution was rather slow, whilst in (1) all separations were readily obtained.

From these findings various combinations may be applied, but in all cases vanadium must first be eluted. An objection to the versenate elution step is the subsequent crystallization of the acid upon adding the hydrochloric or sulphurous acid for chromium elution.

Hence the technique adopted for the certificated steels used was method (1) above.

The certificated steels chosen for the analyses had the following composition:-

<u>ELEMENT</u>	<u>NO. 1</u>	<u>NO. 2</u>	<u>NO. 3</u>
Vanadium	0.82%	1.02	0.30
Chromium	3.32	4.08	2.50
Molybdenum	0.55	0.40	0.50
Tungsten	16.12	18.05	10.02

<u>ELEMENT</u>	<u>NO. 1</u>	<u>NO. 2</u>	<u>NO. 3</u>
Nickel	0.43	0.09	2.84
Cobalt	4.35	0.11	--
Manganese	0.22	0.33	0.30
Tin	--	0.025	--
Carbon	0.71	0.73	0.28

and the details of the separation technique adopted are as follows:- 0.5000g or 1.000g of the steel was dissolved in 20ml 4N sulphuric acid. A few drops of concentrated nitric acid were then added and the solution digested for at least one hour. After filtering off the insoluble matter and the precipitated tungsten, 5ml 1N silver nitrate was added to the filtrate followed by a few drops of 5% potassium permanganate solution and some 2g of ammonium persulphate. The solution was then boiled for five minutes (with further addition of persulphate if the permanganate colour had not developed) and 15ml 1N sodium chloride added to destroy the silver catalyst. A further twenty minutes boiling was then used to destroy all permanganate colour. After cooling, the solution was filtered, 1g mannitol and 2g ammonium acetate added and the solution made up to approximately 200ml. The pH was then adjusted, by dropwise additions of concentrated ammonium hydroxide, to a value of 2.5 - 3.0 using a Phillips type GM4495 pH meter. The deep brown colour that develops served as a useful guide to the volume of alkali required.

The solution was next added to the nitrate form of the strongly basic anion exchanger DE-ACIDITE"FF." Approximately 25ml of the resin was lightly packed into a burette and converted to the nitrate form by passing a sodium nitrate solution down the column. To maintain a constant head of solution, so long as solution was still available for resin contact, the solution of steel was poured into a suitable flask fitted with a stopper and glass tube some two inches long and cut angularly at the outlet end. The flask was clamped in the upturned position with the glass tube inside the resin column.

The flow rate during absorption was in the order of 10-15 drops per minute. After all solution had passed through the column, the resin was washed several times with water.

The next step was the elution of the absorbed metals Vanadium, Chromium and Molybdenum.

The air bubbles were first removed by exerting air pressure down the column by means of rubber bellows, and then 200ml 0.6N sodium hydroxide were introduced into the column by means of the upturned flask. The flow rate was in the order of 5-10 drops per minute. The resin was again washed with water and the filtrate and washings made up to 250ml and reserved for the Vanadium estimation.

After again removing air locks 200ml 8N hydrochloric acid were passed through the resin at 5-10 drops per minute

and the filtrate made up to 250ml and reserved for Chromium estimation. No water wash was carried out in this step in order to avoid a premature elution of molybdenum.

Finally the Molybdenum was eluted with 200ml of 1N hydrochloric acid. This volume was then adjusted to 250ml.

ESTIMATION OF THE METALS.

VANADIUM. The 250ml of sodium hydroxide solution was filtered to remove the traces of iron which may have been carried through the resin column. 50ml of the solution were then taken, 11ml 36N sulphuric acid added to correct the final acidity to 4N, the solution cooled and 2.5ml 3% hydrogen peroxide added. After adjusting the volume to 100ml the vanadium was determined spectrophotometrically at 450mu using a Unicam SP400 spectrophotometer. The standard solution was prepared by dissolving 0.2340g NH_4VO_3 in 1 litre of dilute sulphuric acid and taking 5ml, 10ml, and 15ml aliquots, adding 10ml 36N sulphuric acid plus 2.5ml 3% peroxide to each and adjusting the volume to 100ml.

CHROMIUM. 5ml of the 250ml 8N hydrochloric acid solution were taken and made alkaline with 2N sodium hydroxide. 1ml of Bromine water was then added and the solution boiled for 10 minutes. A few crystals of phenol were next added, the solution cooled, and made just acid with sulphuric acid. Finally 1ml of a 0.25% solution of diphenyl carbazide in a 1:1 mixture of acetone and water was added, the volume adjusted to 200ml and the Chromium estimated spectrophotometrically at 540mu using a Unicam SP400 spectrophotometer. The standard chromium solution was prepared by dissolving 0.1942g K_2CrO_4 in 1 litre of water, taking 1ml, 2ml and 5ml aliquots and treating as for the unknown chromium.

MOLYBDENUM. 25ml of the 250ml 1N hydrochloric acid solution were taken and neutralized with ammonium hydroxide. Then 5ml 10N hydrochloric acid were added, plus 4ml 10% potassium thiocyanate and finally 2-3ml 10% stannous chloride solution in 2N hydrochloric acid. After adjusting the volume to 100ml the molybdenum was estimated at 475mu, within fifteen minutes, using the spectrophotometer referred to above.

The standard molybdenum solution was prepared by dissolving 0.4416g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in 1 litre of water, and taking 2ml, 3ml, 5ml and 10ml aliquots.

The standards were prepared as the unknowns except that 1ml of 1% ferric iron solution was added prior to the thiocyanate addition. No iron was added to the unknown solutions because traces of iron held by the resin were eluted by the 1N acid and not by the 8N acid.

RESULTS OF ANALYSES.% VANADIUM.

<u>NO. 1 (0.82%)</u>	<u>NO. 2 (1.02%)</u>	<u>NO. 3 (0.30%)</u>
0.80	0.98	0.28
0.78	0.92	0.28
0.74	0.96	0.30
0.82	1.00	0.32
0.80	0.98	0.30
0.80	1.00	0.28
0.82	0.96	0.24

% CHROMIUM.

<u>NO. 1 (3.32)</u>	<u>NO. 2 (4.08%)</u>	<u>NO. 3 (2.50%)</u>
3.30	4.00	2.46
3.18	3.88	2.50
3.28	3.94	2.40
3.34	4.06	2.46
3.20	4.06	2.44
3.38	4.10	2.48
3.30	3.98	2.54

% MOLYBDENUM.

<u>NO. 1 (0.55%)</u>	<u>NO. 2 (0.40%)</u>	<u>NO. 3 (0.50%)</u>
0.56	0.36	0.48
0.48	0.34	0.52
0.50	0.40	0.46
0.56	0.42	0.50

150.

% MOLYBDENUM CONT.

<u>NO. 1 (0.55%)</u>	<u>NO. 2 (0.40%)</u>	<u>NO. 3 (0.50%)</u>
0.54	0.40	0.44
0.50	0.36	0.44
0.48	0.38	0.52

These results may then be summarized as follows:-

<u>ELEMENT</u>	<u>SAMPLE NO.</u>	<u>MEAN %</u>	<u>PROBABLE ERROR</u>
Vanadium	1	0.79	0.02
Vanadium	2	0.97	0.02
Vanadium	3	0.29	0.02
Chromium	1	3.28	0.05
Chromium	2	4.00	0.05
Chromium	3	2.47	0.03
Molybdenum	1	0.52	0.02
Molybdenum	2	0.38	0.02
Molybdenum	3	0.48	0.02

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