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Gary Lee Latwesen
Iowa State University

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A SEPARATION SCHEME FOR THE ANALYSIS OF MULTICOMPONENT SAMPLES

by

Gary Lee Latwesen

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Dean of Graduate College

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INTRODUCTION AND LITERATURE SURVEY

In the last few years great advances have been made in the automation and computerization of gas chromatography, mass spectrometry and certain other instrumental analytical techniques. However, comparatively little has been done along these lines for chemical methods of analysis.

The selection of a plan for analysis of a multi-component sample requires an experienced, trained chemist. Even then the choice of methods may be inappropriate. Some chemists try to do almost everything using their favorite technique. Others use reference books which may be outdated, or they may pick a method almost at random and hope that it gives satisfactory results. All too often a method will not work well the first time it is tried on a particular sample. Minor difficulties are often encountered and the method will frequently work only after some modification. Therefore, the analysis of new or nonroutine samples is often slow and costly. Each new type of sample often becomes a research project in itself.

A more systematic approach to the analysis of analytical samples, particularly those of a nonroutine nature, is clearly called for. The aim of the present work is to provide at least a start in that direction. A systematic scheme for the separation of some 27 different metal ions by column chromatographic techniques is presented. Once each metal ion component of the sample has been separated, measurement by appropriate titrimetric, spectral or other method is easily accomplished. Sometimes the measurement method used will permit determination of two or more elements without mutual interference thereby reducing the number of separations required and simplifying the analytical process.

The literature dealing with methods of separation is quite extensive. In deciding on the type and order of separation to be employed in the present separation scheme, the following points were considered:

1) The separations should be quantitative with each element being either strongly retained by the chromatographic column or not retained at all.
2) The separations should be quick and the elution volumes small.
3) The solvents used must keep all elements considered in solution and should be easily volatilized if removal is necessary.
4) Sufficient information should be available to predict the behavior of many elements under the conditions used.
5) The sequence of steps should be such that a minimum of solvent modification is required.
6) Possible incompatible combinations of metal ions and solvent media should be avoided by a prior separation of the interferences.

The types and order of separations selected for the scheme for the most part fulfill these requirements very well. The first four columns all are designed to work in sample media of 8 M hydrochloric acid. Thus no change at all in the acid concentration is needed in going from one column to the next. Only after passing through the first four columns must the sample be evaporated to remove excess acid and reduce the volume of sample entering the fifth and last column. However, after passing through 2 or 3 columns, the volume of sample plus accumulated eluent is large enough in some instances that concentration by some means is necessary.

In general the columns used are small. This cuts down on the elution time and the volume of eluent. Yet the column capacities are sufficient to retain enough of the various metal ions for accurate titration (mostly with 0.02 M EDTA) of major sample constituents and atomic absorption spectrophotometric determination for minor constituents. The size of the columns can be varied according to the amounts of various elements likely to be present.

Sample size may be small. Accurate analyses are obtained on multi-component samples using only 40 to 50 mg samples. In some cases as little as 25 mg of sample is sufficient.

Few separation schemes are reported in the literature for handling complex mixtures. The classical precipitation methods are slow and cumbersome, often requiring considerable modification when applied to specific samples. Most recent schemes reported are applicable to the separation of various isotopes obtained by neutron activation. Here the emphasis is more often on speed of separation than on clean separations, resulting in some overlapping of metals from one group to the next.

Gebauhr (28,29) resolved more than 30 elements by combining activation analysis with a separation scheme employing various distillation and precipitation techniques. The emphasis here was on detection of trace impurities in small total amounts of sample. Recoveries were typically in the range 70 to 98 percent. Chalmers and Dick (8) have described a separation scheme for the systematic separation and determination of 19 elements by solvent extraction methods using cupferron as the complexing agent. Chalmers and Svehla (9) improved the scheme by extending its applicability to 27 elements. A disadvantage of the modified scheme is that no simple and reliable back-extraction procedure has been found for the cupferonates. It is necessary to destroy the cupferron complexes by treatment with sulfuric and nitric acids. Also, the procedure requires a number of evaporation and distillation steps, increasing the time required for completing the separation and contributing to sample loss. The recovery range for metals present in amounts of approximately 100 μg are typically 70 to 100 percent.

A separation scheme for the determination of alkali metals, alkaline earths and rare earths in silicate materials has recently been reported by Murugaujan and co-workers (51). Cation-exchange and anion-exchange methods were employed using hydrochloric and nitric acids as eluting solvents to divide the elements into groups suitable for isotopic dilution analysis by mass spectrometry. The scheme will not accommodate all possible combinations of alkaline earth and rare earth elements, but where applicable, recoveries are in the range of 90 to 100 percent.

Blaedel, Olsen and Buchanan (2) reported a separation scheme by which more than 35 metallic radioelements were separated into six groups. The metals were sorbed onto a cation-exchange column and then eluted with a series of complexing eluents, each of controlled pH and ionic strength. Recoveries for most of the metals included in the scheme are greater than 90 percent. A separation scheme reported by Aubouin, Diebolt, Junod and Laverlochere (1) uses both anion-exchange and cation-exchange chromatographic columns to separate 38 elements. Various aqueous solutions of mineral acids were used as eluting solvents. The scheme has been coupled with activation microanalysis to determine impurities in very pure iron and for seawater analysis.

Moiseev, Kuznetsov and Kalinin (49) have reported an improved method for the activation analysis of silicon and silicon compounds by using a chromatographic separation scheme to extract and divide 27 microimpurities into groups. Chromatographic columns using anion-exchange resin, cation-exchange resin and also zirconium tungstate inorganic ion exchanger were used to perform separations. Mineral acids which could be easily removed after separation by means of evaporation were the primary solvents used as eluents. Typical recoveries ranged from 88 to 98 percent.

Several separation schemes have been developed for the determination of elements in biological material by activation analysis. A method devised by van den Winkel and co-workers (68) separates nine elements using two anion-exchange columns and various concentrations of hydrochloric, hydrofluoric and nitric acids. Recoveries were reported to be quantitative in most cases. Jervis and Wong (40) developed a sequential ion-exchange group separation scheme to aid in determining traces of metals in blood and other biological materials. After neutron activation, the radioelements were separated into groups by using three small anion-exchange and cation-exchange columns. Some components were sorbed onto the anion-exchange column from concentrated hydrochloric acid and eluted with acidic solutions of decreasing concentration. After evaporation, the metal ions in the initial eluate from the anion-exchange column were taken up on a cation-exchange column and eluted with various buffered solutions of complexing agents.

Recoveries were reported to be quantitative in most cases.

Samsahl and co-workers (57,59,60) have reported several separation schemes applicable to the determination of components in biological samples by activation analysis. Several recent reports (58,61) have described ways of automating the scheme devised. The separation scheme uses distillation, ion-exchange chromatography and extraction chromatography to separate up to 40 elements into 16 groups. Conditions have been established such that each group is sequentially sorbed onto a chromatographic column while the nonextracted elements pass through to another column. Reagents are added to the column eluates to change conditions so another group of elements can be sorbed by the next column in the sequence. The radioelements, once sorbed to the proper column, are not eluted for counting. Instead the resin bed is removed, mixed and used as the counting source. Recoveries for most of the elements in the scheme are reported to be greater than 90 percent.

THEORY OF COLUMN CHROMATOGRAPHY

Chromatography is a technique by which substances can be separated based on the difference in the rate at which each component of a mixture moves through a column. The column contains a stationary phase which may be a solid sorbent or a liquid partitioning agent on a solid support. Chromatographic separations are divided into classes according to the nature of the stationary phase and the mobile phase. The two types commonly used for inorganic separations are ion-exchange chromatography and liquid-liquid partition chromatography.

In liquid-liquid partition chromatography the extractive properties of the column are due to a solvent which is sorbed to the solid supporting material. By elution with a liquid that is immiscible with the sorbed solvent a mixture can be separated into its components if each species is extracted to a different extent into one of the two liquid phases. When the sorbed liquid is the polar or aqueous phase and the mobile phase is non-polar or an organic phase, the method is called liquid-liquid partition chromatography. When the procedure is reversed, sorbing the nonpolar solvent on the column and the polar solvent is used as the mobile phase, the method is called reversed-phase liquid-liquid partition chromatography. Because of the principles involved, both types of partition chromatography can be thought of as being related to liquid-liquid extraction.

Two popular theories explaining the behavior of chromatographic columns are the plate theory and the kinetic theory. The plate theory, first introduced by Martin and Synge (48), is strictly valid only for the discontinuous processes such as counter-current extraction and is only an approximation for a continuous process such as chromatography. In a continuous process, true equilibrium is never attained. The kinetic theory is based on a continuous flow concept and has been described by numerous workers. It is extensively discussed in a recent work by Giddings (30). Although the plate theory is not strictly valid, it is the simplest to grasp and leads to a less difficult mathematical treatment of the chromatographic process. From a practical standpoint the plate theory serves as a useful concept for interpreting chromatographic column behavior and will be described in somewhat greater detail.

Because equilibrium is not attained on a chromatographic column, a plate can best be defined as that region in which the average concentration of the solute in the two phases is the same as that which would be attained if the solute were actually in equilibrium with the two phases within the region. The length of the column in which this equilibration occurs is called the HETP (height equivalent to a theoretical plate). The HETP can be thought of as an efficiency parameter which expresses the degree of spreading that occurs as the solute band travels along the column. This spreading results from a number of sources: 1) flow velocity inequalities caused by inconsistencies in column support particle size and column packing inhomogeneities, 2) molecular diffusion in the longitudinal direction and 3) nonequilibrium of solute between the two phases. The nonequilibrium, or sorption-desorption kinetic factor, is the most important and largely determines whether or not high-resolution and high-speed chromatography are possible. All three of these phenomena give rise to Gaussian spreading of the solute zone and therefore a Gaussian shaped elution curve as the solute is eluted from the column. From this curve, it is possible to calculate the total number of theoretical plates (n) for a specific column using the equation

$$n = 16\left(\frac{V_R}{w}\right)^2 \qquad (1)$$

where (w) is the width of the curve found by extending tangents from the inflection points of the elution curve to the base. V_R is the elution volume of the maximum concentration of the solute or retention volume. The retention volume (V_R) can be calculated using the equation

$$V_R = V_m + DV_s \qquad (2)$$

if the mobile phase volume (V_m), the stationary phase volume (V_s) and the distribution coefficient (D), defined as the ratio of the concentration of solute in the stationary phase over the concentration of solute in the mobile phase, are known. Once the number of theoretical plates has been calculated from Equation 1, and the column length has been determined, it is possible to calculate the HETP.

There are two reasons why Equation 1 is not completely valid. First, it has been assumed that the distribution coefficient (D) is independent of solute concentration. This is not strictly true under real conditions. Second, under chromatographic conditions equilibrium of solute between the two phases is never attained. Glueckauf (31) has taken these points into consideration and formulated a new equation for the number of plates in a chromatographic column,

$$n = 8\left(\frac{V_R}{\beta} \right)^2 \qquad (3)$$

where β represents the width of the elution curve at the point of concentration c equal to c_{max}/e which is equal to $0.368c_{max}$ and V_R again is the retention volume. This equation gives a somewhat better value for the number of theoretical plates in a column, but it too is in error in that it assumes an infinitely small initial sample volume.

An ion-exchange resin is a rigid polymer matrix which contains exchangeable cations or anions. In ion-exchange chromatography the solute ions in the mobile phase can be exchanged for ions of like charge on the resin. The characteristic difference between sorption and ion-exchange chromatography is that for ion-exchange the process is stoichiometric. Every ion which is removed is replaced by an equivalent amount of another ionic species of the same charge. The process is reversible and at trace solute concentrations, can be assumed to obey a linear distribution isotherm. The same theories that apply to partition chromatography can therefore be used for ion-exchange chromatography. Here again, the plate theory has the same limitations as it did for partition chromatography. Because of its simplicity and usefulness, however, it is frequently used to interpret ion-exchange column behavior.

Equation 2 for determining the retention volume (V_R) can also be applied to ion-exchange columns. However, in ion-exchange chromatography slightly different terms are used. The modified equation assumes the following form:

$$V_R = X(D_V + \epsilon) \qquad (4)$$

where V_R is the retention volume, X is the resin bed volume, D_V is the volume distribution coefficient and ϵ is the volume fraction of free liquid in the column, referred to as the void fraction. The product $X\epsilon$ corresponds to the term V_m in Equation 2. It is easier experimentally to determine weight distribution coefficients (D_W) where

$$D_W = \frac{\dfrac{\text{milliequivalents of metal on resin}}{\text{grams of dry resin}}}{\dfrac{\text{milliequivalents of metal in solution}}{\text{milliliters of solution}}} \qquad (5)$$

Multiplying D_W by the column bed density (Q_R), grams of dry resin per cm^3 of bed volume, converts this distribution coefficient to D_V as required in Equation 4.

$$D_V = D_W \cdot Q_R \tag{6}$$

Once V_R has been determined, Equation 1 or 3 can be used to calculate the number of theoretical plates (n) for the column and the HETP.

Detailed discussions of the theory of chromatography are given in works by Heftmann (35) and by Giddings (30). Books by Helfferich (36) and by Samuelson (62) deal specifically with ion-exchange chromatography.

EXPERIMENTAL DETAILS

Apparatus

pH meter: A Corning model 12 pH meter with a Sargent combination electrode was used to control the pH in all EDTA titrations.

Spectrophotometer: A Beckman model B spectrophotometer with a modified cell compartment (23) was used for all spectrophotometric titrations.

Scintillation counter: A Nuclear-Chicago scintillation counter model dS5 with a 3"x3" sodium iodide crystal was the detector; a Nuclear-Chicago spectrometer, model 1820, isolated the gamma emission from the tracers used. A decade scaler counted the pulses received from the spectrometer.

Atomic absorption spectrophotometer: A Perkin Elmer model 290 atomic absorption spectrophotometer equipped with Perkin Elmer lamps was used for all atomic absorption analysis.

Chromatographic columns: The chromatographic columns were made by joining two sections of Pyrex brand glass, an upper larger diameter section for an eluent reservoir and a lower smaller diameter section to hold the column support. To the bottom of the column was connected a one millimeter microbore stopcock with a Teflon plug. A small plug of Pyrex or Dynel wool was used to retain the solumn support. Flow rates were regulated by use of the stopcock, or where the flow was too slow, by use of air pressure. A one-hole stopper with a short piece of glass tubing through it was inserted at the top of the column. One end of the glass tubing was then connected to a compressed air line.

A special inert column was used when hydrofluoric acid was present as an eluting solvent. The column was prepared by machining down and drilling out a Kel-F rod of the proper size. By using two bore sizes, a column very similar to the glass columns in shape and dimensions was obtained. A tapered flange was left on the bottom of the column to retain the Dynel wool plug which in turn retained the column support. No stopcock was used with this column.

Reagents

Solvents: The solvent methyl isobutyl ketone (MIBK) was Eastman White Label grade, and was redistilled before use.

The isopropyl ether (IPE) was Eastman White Label and was distilled before use.

The cyclohexane was Eastman White Label grade and was used without further purification.

Chemicals: All metal salts and inorganic acids were reagent grade and were used without further purification.

Trioctylphosphine oxide (TOPO) was Eastman White Label grade and was used without further purification.

Indicator solutions: Xylenol orange (3,3'-bis(N,N'-di-(carboxymethyl)-aminomethyl)-o-cresol sulphonephthalein), obtained from LaMont Laboratories, was used as a 0.5% aqueous solution. Naphthyl Azoxine S (NAS, 8-hydroxy-7-(6-sulfo-2-napthylazo)-5-quinoline-sulfonic acid disodium salt) (13) was obtained from the Eastman Chemical Company and was used as a 0.5% aqueous solution. Arsenazo I (3-(2-arsonophenylazo)-4,5-dihydroxy-2,7-naphtalenedisulfonic acid trisodium salt) was obtained from Eastman Chemical Company and was used as a 0.5% aqueous solution.

A special solution of Arsenazo I containing a specified amount of Martius Yellow and Xylene Cyanole FF, as described in detail in a recent work by Fritz <u>et al</u>. (27), was used as the indicator for some of the EDTA titrations. The added dyes screen the color of the Arsenazo I giving the modified indicator solution (hereafter referred to as Arsenazo I mixed indicator) a color change that is more easily detected visually.

Column supports: Tee-Six, a hard polyfluoroethylene, was obtained as a presieved powder from the Analytical Engineering Laboratories, Hamden, Connecticut. Before using, the powder was washed with 6 <u>M</u> hydrochloric acid and acetone and then air dried.

Amberlyst XAD-2, an inert crosslinked polystyrene polymer, was obtained from Rohm and Haas Company as 20-50 mesh beads. The beads were ground in a Waring blender and sieved to obtain the proper mesh sizes. The sieved product was then washed with 6 M hydrochloric acid and methanol and then air dried.

Plaskon 3200 powder was obtained from Allied Chemical Company. The powder was sieved to obtain uniform mesh sizes and washed with 6 M hydrochloric acid and methanol and then air dried.

Dowex 50W-X8 cation-exchange resin, 100-200 mesh, was used in the hydrogen form. Backwashing of the commercial resin in a large column with distilled water removed the fine particles. The resin was then purified by washing with 10% ammonium citrate and 3 M hydrochloric acid and then washed with distilled water.

Amberlyst A-26 macroreticular anion-exchange resin was obtained from Rohm and Haas Company. It was ground in a Waring blender and sieved to the proper mesh sizes. The anion-exchange resin was then purified by washing with 2 M perchloric acid and 1 M hydrochloric acid and then with water.

Amberlyst 15 macroreticular cation-exchange resin was obtained from Rohm and Haas Company. It was ground in a Waring blender and sieved to the proper mesh sizes. The cation-exchange resin was then purified by washing with 6 M hydrochloric acid and methanol and then air dried.

Eluents: All aqueous eluents were prepared in the proper acid concentration and were stored in glass or polyethylene bottles until needed. When an equilibrated solvent was required, equal volumes of aqueous and organic phases were shaken together for at least one minute in separatory funnels. The phases were then stored in the presence of each other and used as needed.

Analytical Procedures

Preparation of stock solutions

Molybdenum(VI) solutions were prepared by dissolving a sufficient amount of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 8 M hydrochloric acid. Gallium(III) and indium(III) solutions were prepared by dissolving the required weight of 99.99% pure metal in concentrated hydrochloric acid containing a small amount of nitric acid. After dissolution the solutions were diluted to the proper volume with a sufficient amount of water and acid to make a final concentration of 8 M hydrochloric acid. Vanadium(V) solutions were prepared by dissolving ammonium vanadate in 8 M hydrochloric acid. All other metal ion solutions were prepared by dissolving the proper weight of chloride, nitrate or perchlorate salt in 8 M hydrochloric acid.

Column preparation

Columns employing Amberlyst XAD-2 as the inert column support were all prepared using the same procedure. The required amount of support was slurried in methanol and transferred to the column. The stopcock was opened and the methanol was allowed to drain rapidly from the column until the level of the methanol in the column was just above that of the support. The rapid draining of the methanol causes the support to settle quickly, resulting in a fairly uniform distribution of particle size throughout the column. A perforated Teflon disc purchased from Fischer and Porter Company was then placed on top of the support to prevent disturbance of the column bed when other solvents were added to the column.

The extractant (equilibrated IPE, equilibrated MIBK or 0.5 M TOPO-cyclohexane) was then sorbed to the column by adding it to the top of the column and letting it flow down through the bed, displacing the methanol present. Three to five column volumes of extractant were considered sufficient to displace the methanol from the column. The interstitial organic solvent was then removed with equilibrated 8 M hydrochloric acid. Using some pressure and rapid flow rates, up to 20 ml per minute, the organic solvent was sufficiently removed from the interstitial parts of the column that at the slower flow rates used for separations little or no column bleeding was encountered.

The stripping solvent used to remove sorbed metal ions from the IPE and MIBK columns is 0.1 M hydrochloric acid-98% methanol. After the metal ions have been stripped from the column, the support is in essentially the same condition as when the methanol slurry was first added to the column. Therefore by repeating the procedure for conditioning the column, it can rapidly be readied for the next sample.

The metal ions sorbed by the TOPO column are eluted with aqueous solvents so the extractant is not removed. This column can be used a dozen times or more without reconditioning. When reconditioning is necessary it is usually sufficient to pass several milliliters of 0.5 M TOPO-cyclohexane through the column to replace any extractant lost and then displace any extra extractant from the interstitial column volume with an appropriate aqueous solvent, usually 8 M hydrochloric acid.

Amberlyst XAD-2 is somewhat less dense than water, but it is more dense than methanol and the extracting solvents used. Because of its low density, the support may slowly float up when the interstitial phase is an aqueous solvent unless certain simple precautions are taken. If the column is well packed with no channels or air pockets present and the perforated Teflon disc discussed earlier is placed on top of the column to hold the upper particles of column support in place, then the column bed should remain intact.

The ion-exchange columns were prepared by slurrying the appropriate amount of resin in distilled water and transferring to the column. The column was then preconditioned by passing the appropriate solvent through it.

Volumetric procedures

The procedures for the analysis of the metals encountered in this study are given in the order in which they appear in the separation scheme as outlined in Figure 1.

Antimony(V) was determined by reducing it first to antimony(III) and then titrating with standard potassium bromate using α-napthoflavone as a reversible indicator. The method is outlined by Vogel (69). Concentrated hydrochloric acid (10 ml) was added to an antimony(V) sample of total volume 30 to 50 ml. Potassium bromide solution (20 ml of 10% solution) was also added. Then a sufficient amount of 8% sulfurous acid (47) was added for complete reduction of the antimony and the solution was boiled for 10 minutes. If an organic solvent was present, it was removed by boiling the solution before addition of the sulfurous acid. Excess sulfurous acid was removed by bubbling air through the solution for 5 minutes. The solution was then cooled and the antimony(III) was titrated with standard potassium bromate. If the sample contained tartrate ions, 4 ml of sulfuric acid was also added before the reduction step.

Gallium(III) was determined by adding excess EDTA, buffering the solution to pH 6 with pyridine and ammonia, and backtitrating with standard zinc(II) using NAS indicator.

Iron(III) was determined by adding excess EDTA, buffering the solution to pH 2 with ammonia, and backtitrating with standard thorium(IV) using Xylenol Orange indicator.

Tin(IV) was determined by the following procedure. The solution was acidified with hydrochloric acid to pH 1 or below to prevent hydrolysis of the tin(IV). Then 2 g of sodium chloride and a moderate excess of EDTA were added and the solution was boiled for 5 minutes. The solution was then cooled to room temperature and buffered to pH 3.5 with ammonium acetate. Using NAS as the indicator, the solution was titrated just past the endpoint with a standard copper(II) solution and then titrated back to the red endpoint with EDTA. The second endpoint was sharper than the first, thereby justifying the double backtitration.

Copper(II), cobalt(II) and zinc(II) were determined by direct EDTA titration at pH 6 using pyridine buffer and NAS indicator.

Cadmium(II) was determined by adding excess EDTA, buffering the solution to pH 6 with pyridine and backtitrating with standard copper(II) using NAS indicator.

Bismuth(III) was titrated directly with EDTA at pH 2 using ammonia to adjust the acidity and Xylenol Orange as the indicator. Sulfate interferes with the Xylenol Orange endpoint and chloride interferes by causing precipitation of bismuth oxychloride. In the presence of these two anions bismuth was determined by adding excess EDTA at pH 2, boiling the solution for 5 minutes, cooling and backtitrating at pH 6 with standard copper(II) using pyridine buffer and NAS indicator.

Titanium(IV) was determined by adding excess EDTA, adjusting the solution to pH 4.5 with ammonium acetate and ammonia, adding several drops of 30% hydrogen peroxide, boiling the solution for 5 minutes, cooling to room temperature and backtitrating with standard copper(II) using NAS indicator. The solution was titrated to a permanent yellow-green endpoint.

Thorium(IV) was determined by direct EDTA titration at pH 2 using ammonia buffer and Xylenol Orange as indicator.

Zirconium(IV) was determined by adding excess EDTA to an acidic solution of the metal ion, pH 1 or below, and boiling the solution for 10 minutes. The solution was then cooled, carefully adjusted to pH 2 with ammonia and the excess EDTA was titrated with standard thorium(IV) using Xylenol Orange indicator.

Vanadium(IV) was determined by adding excess EDTA and backtitrating with standard zinc(II) at pH 6 using pyridine buffer and NAS indicator. If hydrogen peroxide was present in the sample containing vanadium, it was first removed by boiling. After boiling, a small amount of 8% sulfurous acid or ascorbic acid was added to assure complete reduction to vanadium(IV).

Lead(II) was determined by adding excess EDTA, adjusting the solution to pH 6 with pyridine and backtitrating with standard copper(II) using NAS indicator.

Manganese(II) was determined by direct titration with DCTA (1,2 diaminocyclohexanetetraacetic acid) at pH 9 using ammonia and ammonium chloride as the buffer system and Arsenazo I as the indicator. Several drops of 8% sulfurous acid were added to assure complete reduction to manganese(II). Although the endpoint can be detected visually, more accurate results are obtained by doing a spectrophotometric titration at 565 nm.

Aluminum(III) was determined by adding excess DCTA, adjusting the solution to pH 6 with pyridine and ammonia, boiling for five minutes, cooling and backtitrating with standard copper(II). NAS indicator was used and the backtitration was continued to a permanent yellow-green endpoint.

Hydrofluoric acid, if present, was first removed by adding several milliliters of sulfuric acid to the sample and then evaporating down to heavy fumes of sulfur trioxide. Some aluminum sulfate may precipitate but it can be readily redissolved by diluting the cooled sample with water and heating.

Nickel(II) was determined by adding excess EDTA and backtitrating with standard zinc(II) at pH 6 using pyridine buffer and NAS indicator.

Magnesium(II) was titrated directly with EDTA at pH 10 using ammonia and ammonium chloride as the buffer system. The indicator used was Arsenazo I. The endpoint can be detected visually but better accuracy can be obtained using a spectrophotometric endpoint at 565 nm. The visual endpoint can be improved by using the Arsenazo I mixed indicator solution.

Nickel(II) and magnesium(II) were both determined in a mixture by the following procedure. The solution was first adjusted to pH 6 with pyridine and ammonium hydroxide. Excess EDTA was added and the excess was backtitrated with standard zinc(II) using a minimum amount of NAS indicator. The difference between the amount of EDTA added and the excess backtitrated was equivalent to the amount of nickel(II) present. The solution was then adjusted to pH 10 with ammonia and the magnesium present was titrated directly with EDTA using the Arsenazo I mixed indicator. Fair results were obtained visually using the Arsenazo I mixed indicator, but more accurate results were obtained using a spectrophotometric endpoint at 565 nm.

Rare earth elements were determined by direct EDTA titration at pH 6 using pyridine buffer and Arsenazo I as the indicator (22).

Calcium(II), strontium(II) and barium(II) were determined by direct titration with EDTA at pH 10 using ammonia and ammonium chloride as the buffer system. The Arsenazo I mixed indicator was used for visual endpoint detection. In certain instances a spectrophotometric endpoint at 565 nm was used.

Total rare earths and also total calcium(II), strontium (II) and barium(II) were determined in the same solution by the following procedure. Total rare earth content was determined by direct EDTA titration at pH 6 using pyridine buffer and Arsenazo I mixed indicator. Then the solution was adjusted to pH 10 with ammonia and the alkaline earths present were titrated directly with EDTA using the indicator already present in the solution. A spectrophotometric endpoint detection could be used if so desired.

Chromium(III) was determined by oxidizing it to chromium (VI) with ammonium persulfate, adding a known excess of standard iron (II) solution and then titrating the excess iron(II) with standard cerium(IV) using ferroin indicator. The method is outlined in Vogel (69).

When citrate ion was present, it was first removed by the following procedure. Sulfuric acid (5 ml) was added to the sample and it was fumed down until sulfur trioxide fumes evolved and the organic residue was charred. The sample was then cooled, 10 ml of nitric acid added and the solution again evaporated down to fumes of sulfur trioxide. After cooling, the walls of the beaker were washed down with water and the sample was again evaporated to fumes of sulfur trioxide. This washing step was repeated to assure complete removal of nitric acid from the sample. The chromium(III) was then oxidized with ammonium persulfate and determined by the procedure described earlier.

Microvolumetric procedures

Relatively small sample sizes were used to decrease the time required for dissolution and chromatographic separation. Therefore, minor constituents of the sample were present in the separated fractions in rather small amounts. Two general methods were used to analyze these fractions, direct titration and atomic absorption spectrophotometry. Where a good complexometric titration method was available, it was simply scaled down by using smaller volumes and more dilute reagents, 0.001 M EDTA for instance. Because the titrant was of known concentration, the absolute amount of metal determined was also known, eliminating the need of a series of standard samples and calibration curves.

Atomic absorption methods

Atomic absorption methods were used to analyze for metals where a good microtitration method was not available or where more than one component was to be analyzed for in a fraction without further separation. A Perkin Elmer model 290 atomic absorption unit was used and the procedures followed for determining the elements of interest were those recommended by the manufacturer. In general, standard solutions were prepared in the same solvent used to elute the metal of interest from the chromatographic column.

Elution curves

Several procedures were used for the construction of elution curves. When the exact shape of the elution curve was of interest, or when a good spot test was not available, aliquot fractions were collected and analyzed for solute by appropriate means. In several instances radioactive tracers were used to determine elution curves and to check for incomplete separations.

In most instances only the beginning and the end of the elution curve were of interest, in which case spot tests were sufficient. The spot tests used have been compiled in Table 1.

Table 1. Spot tests used to determine elution curves

Metal ion	Reagent used	Confirmation
Gallium(III)	Arsenazo I, pyridine	Violet spot
Iron(III)	KSCN	Red spot
Antimony(V)	Thioacetamide, heat, dil. NaOH	Orange precipitate
Tin(IV)	Thioacetamide, heat, dil. NaOH	Yellow precipitate
Molybdenum(VI)	KSCN, $SnCl_2$	Red spot
Bismuth(III)	NAS, pyridine	Yellow spot
Cadmium(II)	NAS, pyridine	Yellow spot
Zinc(II)	NAS, pyridine	Yellow spot
Copper(II)	Diethyldithiocarbamate	Red spot
Uranium(VI)	Arsenazo I, pyridine	Violet spot
Cobalt(II)	NAS, pyridine	Yellow spot
Titanium(IV)	Benzohydroxamic acid	Yellow spot
Scandium(III)	Arsenazo I, pyridine	Violet spot
Thorium(IV)	Arsenazo I	Violet spot
Zirconium(IV)	Arsenazo I, pyridine	Violet spot
Rare earths(III)	Arsenazo I, pyridine	Violet spot
Alkaline earths(II)	Arsenazo I, pyridine	Violet spot
Alkaline earths(II)	Arsenazo I, ammonia	Violet spot
Nickel(II)	Dimethylglyoxime, ammonia	Red precipitate
Aluminum(III)	Alizarin sodium sulfonate, ammonia	Red spot
Manganese(II)	Diethyldithiocarbamate	Gray precipitate
Lead(II)	NAS, pyridine	Yellow spot
Vanadium(IV)	Pyrocatechol violet, pyridine	Green precipitate
Chromium(III)	$K_2S_2O_8$, $AgNO_3$, H_2SO_4, Diphenylcarbazide	Red spot

SEPARATION SCHEME

Selection of Systems

Solvent media

A major consideration in an undertaking of this type is the selection of a suitable solvent. The solvent must be able to dissolve the samples to be encountered either by itself or with the aid of small amounts of oxidizing or complexing agents. The solvent system must also lend itself to separation procedures so that sequential separations may be performed without the frequent need of solvent modifications. Another important consideration is that the solvent should be readily removable, should the need arise.

Hydrochloric acid was selected because it meets the requirements well. The complexing ability of this solvent allows it to dissolve a large number of metals. Because of the low boiling point of hydrochloric acid, it can be removed by volatilization when necessary. Also, a number of chloride complexes are easily extracted by oxygenated solvents and sorbed by anion-exchange resins, thereby permitting several useful group separations. The acid concentration required to obtain the best separation is not the same for all the extractive systems and metal ions considered. A compromise was made and 8 M hydrochloric acid was selected as the solvent to be used because this acid concentration permitted all the necessary separations to be performed. Hydrochloric acid concentrations as low as 6 M or as high as 10 M would be somewhat better for certain separations, but would not work for all metal ion combinations considered.

Column supports

A number of separations in this scheme are performed by reversed-phase chromatography. The column support used is an important consideration in any partition chromatographic separation. Several important properties of a good chromatographic support include the following: 1) It should have a porous structure with a large surface area giving it ability to sorb the organic solvent. 2) It should be made of a relatively hard material that can withstand packing without breaking, or compressing into a nonporous mass. 3) The support must be inert to corrosive or organic solvents and not decompose or release contaminating materials. 4) The support must also be inert with respect to the substances sorbed onto the column via the extracting agent present. The strength of the sorption onto the column and the ease with which constituents are desorbed should be a function of the distribution ratio only.

C. E. Hedrick (34) reviewed the use of a number of column supports for reversed-phase chromotography and found that Tee-Six, a hard polyfluoroethylene polymer, had the properties desired. In a previous study (21) the present author also obtained good results using the Tee-Six support.

The present study involves the use of several columns arranged "piggyback" so that flow is directly from one column to the next. This means that the sample volume passing through the second column is larger than the original sample by the amount of eluting solvent required to remove nonextracted components from the first column. It is important that this sample volume be kept reasonably small for two reasons; first to decrease the time involved in allowing the elution to take place, and second the distribution ratios for several of the metal ions considered are sufficiently low that the sample band should be as tight as possible to assure complete removal of the nonextracted ions before the extracted metals appear in the eluate. The amount of eluting solvent required to remove the nonextracted components from the column is obviously proportional to the size of the column. Therefore, the smaller the column used the smaller will be the sample size for the next column.

The column size required is dependent on its capacity to extract and retain the metal ions sorbed by that column. The capacity is related to the amount of extractant that can be retained by the column support. The greater the capacity for extractant, the smaller the column required to accomplish the separation.

Therefore, a study was conducted to try to find a column support with as large a solvent capacity as possible. Rohm and Haas Company has developed a new type of macroreticular resin that has larger pore sizes than microreticular resins of the past. This resin has a much higher capacity for organic solvents because the pores do not disappear in the absence of water as a swelling solvent. By careful regulation of the conditions used in making the resin, the pore size and the surface area can be controlled within certain limits. One resin of this type prepared by Rohm and Haas is Amberlyst XAD-2. It is a crosslinked polystyrene polymer that contains no functional groups itself.

Pietrzyk (55) has studied the solvent uptake properties of several synthetic resins including Amberlyst XAD-2 by a centrifugation method. He has shown that the solvent uptake for methyl isobutyl ketone and cyclohexane on Amberlyst XAD-2 are 0.82 and 0.73 grams per gram of dry resin, respectively.

The present author used the following method to get an indication of the relative extractive capacities of several materials presently used as reversed-phase chromatographic supports. Enough ferric chloride was dissolved in pre-equilibrated MIBK to give a final concentration of approximately 0.025 M in iron(III). The exact concentration was determined by EDTA titration. 50 ml of this solution was then transferred to a stoppered flask. To this flask was also added enough dry 60-100 mesh support to make a soaked bed volume of 5 ml. The amount of resin required was determined by first preparing 5 ml of soaked resin bed, washing the organic solvent from this bed with methanol and drying the resin at 100 degrees Centigrade. This resin was then weighed to determine the weight of resin required. The flask was then shaken for 1 hour to allow the resin to absorb as much solvent as possible.

The contents of the flask were poured into a course glass filtering crucible, allowing most of the MIBK to drain off. Then the support was washed with 20 ml of pre-equilibrated 8 M hydrochloric acid to remove any interstitial ketone.

The resin was washed with methanol to remove the ketone and the iron(III) contained in it. This iron(III) was collected in a beaker and determined by EDTA titration as described earlier in the section on analytical procedures. The amount of ketone on the resin can then be calculated if it is assumed that the iron(III) is homogeneously distributed throughout the sorbed solvent.

Three supports were studied with Amberlyst XAD-2 and Tee-Six being of primary interest. Also included was Plaskon 3200 powder from Allied Chemical Company (53). The results of the study are given in Table 2.

Table 2. Solvent capacities of several column supports

Type of support	MIBK sorbed to support per 1 ml of column bed volume
Tee-Six	0.23 ml
Amberlyst XAD-2	0.48 ml
Plaskon 3200	0.56 ml

Another study was also conducted as a check on the reliability of the first study. 60-100 mesh fractions of Tee-Six, Amberlyst XAD-2 and Plaskon 3200 were boiled in MIBK to saturate the support with solvent. Then each support was used to pack a chromatographic column. A solution of 8 M hydrochloric acid approximately 0.05 M in iron(III) was passed through each column until the capacity was exceeded and iron(III) was detected in the eluate. The column was then washed with equilibrated 8 M hydrochloric acid until no iron(III) could be detected in the wash. The MIBK and extracted iron(III) were washed from the column with methanol and the iron(III) determined by EDTA titration. The results obtained are given in Table 3.

Table 3. Extractive capacities for several chromatographic columns

Type of support	Millimoles iron(III) extracted per ml of column bed
Tee-Six	0.06
Amberlyst XAD-2	0.11
Plaskon 3200	0.13

The Amberlyst XAD-2 appears to have approximately twice the solvent capacity of the Tee-Six. Also the Amberlyst XAD-2, although having slightly less solvent capacity than the Plaskon 3200, is harder and does not compress under pressure or deform when packed into a column. The unaided flow rate for Amberlyst XAD-2 is faster than for either Tee-Six or

Plaskon 3200 of the same mesh size. A major disadvantage of Plaskon 3200 powder is the difficulty in obtaining it. The manufacturer is not overly cooperative about supplying this compound in the small quantities generally required for analytical chromatography.

Amberlyst XAD-2 has not been found to have any extractive properties of its own for any of the metal ions studied except iron(III). After iron(III) has been extracted from 8 M hydrochloric acid by the IPE column, it should be possible to strip it rapidly from the column again with dilute acid, 0.1 M hydrochloric acid for example. Greater than 98% of the iron (III) is rapidly eluted but a small amount remains strongly sorbed to the support and comes off very slowly. This problem has been completely eliminated by stripping the iron(III) from the column with 0.1 M hydrochloric acid-98% methanol, in which case all the iron(III) is rapidly desorbed from the column.

The anion-exchange resin used in this study was Amberlyst A-26 macroreticular resin manufactured by Rohm and Haas Company. This resin is very similar to the Amberlyst XAD-2 inert support used except that it contains active basic sites suitable for anion exchange. Because Amberlyst A-26 is of the macroreticular type, the resin beads are permeated with large pores, several hundred angstroms in size, which do not shrink or swell as solvent properties are changed, permitting the free flow of nonaqueous solvents through the structure. This allows for faster flow rates and smaller elution volumes when nonaqueous eluting solvents are used. Gel type resins have smaller pore sizes which hinder the flow of organic solvents through the bead. This restriction is compounded by the fact that the resin beads shrink when treated with nonaqueous solvents. It has been shown (18) that the equilibration rates for metal ions between Amberlyst A-26 and organic solvents is faster than for conventional gel type resins.

Dowex 50W-X8 was selected as the cation-exchange resin for this study. It was found to be better suited for the use intended than the corresponding macroreticular Amberlyst 15. The separation scheme employs several nonaqueous eluting solvents to remove metal ions from the cation-exchange column and here the macroreticular resin would probably have an advantage over the gel type. It was found, however, that the alkaline earths, particularly barium(II), are much more difficult to elute with 4 $\underline{M}$ nitric acid from the Amberlyst 15 resin than from Dowex 50W-X8. The use of radioactive Ba^{133} as a tracer to follow the elution behavior of barium(II) on Amberlyst 15 showed that even after three times the volume of eluting solvent required to quantitatively remove barium(II) from a comparable Dowex 50W-X8 column had been used, some barium(II) remained sorbed to the top of the Amberlyst 15 column.

General Discussion

Sorption steps, group separations

The separation scheme presented here employs five different chromatographic columns to divide the sample under consideration into five major groups. The following elements have been included in the scheme:

Group I	Sb(V), Ga(III), Fe(III)
Group II	Sn(IV), Mo(VI)
Group III	Bi(III), Cd(II), Zn(II), Cu(II), U(VI), Co(II)
Group IV	Zr(IV), Hf(IV), Th(IV), Ti(IV), Sc(III)
Group V	V(V), Pb(II), Mn(II), Al(III), Mg(II), Ni(II), Ca(II), Sr(II), Ba(II), R.E.(III), Cr(III).

A flow chart for the overall separation scheme is given in Figure 1. The sample is dissolved in 8 M hydrochloric acid and passed through a column of Amberlyst XAD-2 which has been treated with isopropyl ether (IPE). The IPE will extract the chloride complexes of antimony(V), gallium(III) and iron(III). The nonextracted metals are eluted from the columns with 8 M hydrochloric acid (Note 1).

The eluate is passed directly onto a column of Amberlyst XAD-2 which has been treated with methyl isobutyl ketone (MIBK). The MIBK will extract the chloride complexes of tin (IV) and molybdenum(VI). The nonextracted metals are eluted from the column with pre-equilibrated 8 M hydrochloric acid.

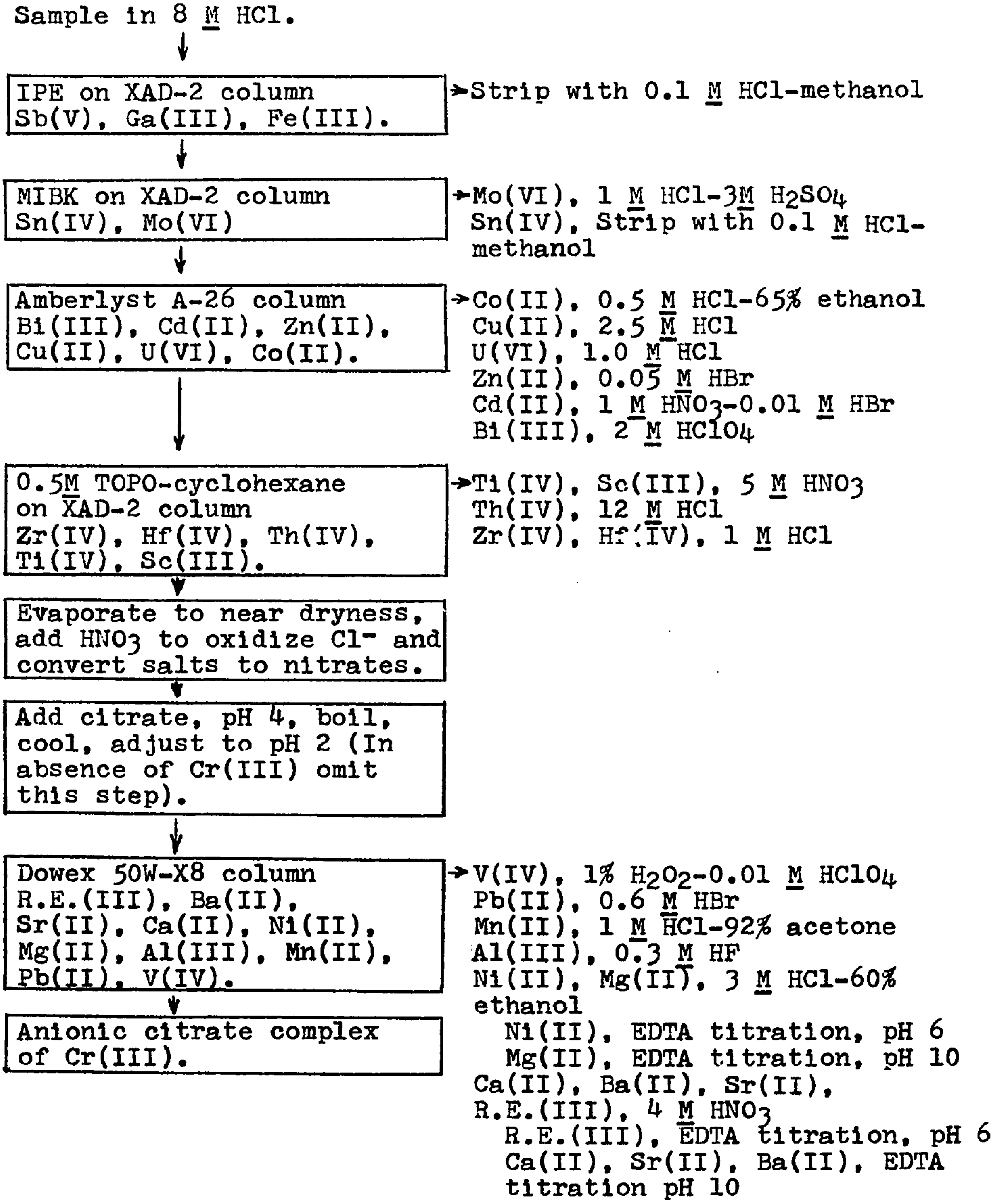

Figure 1. Flow chart for overall separation scheme

The eluate from the MIBK column is then passed directly onto a column of Amberlyst A-26 anion-exchange resin that has been preconditioned with 8 M hydrochloric acid. The anionic chloride complexes of cobalt(II), uranium(VI), copper(II), zinc (II), cadmium(II) and bismuth(III) are sorbed to the support while the weakly or nonextracted metals are eluted with 8 M hydrochloric acid (Notes 2 and 3). The eluate from this column can then be passed directly onto a column of Amberlyst XAD-2 resin that has been treated with 0.5 M TOPO-cyclohexane and preconditioned with 8 M hydrochloric acid (Note 4). This column will extract zirconium(IV), hafnium(IV), thorium(IV), titanium(IV) and scandium(III) from 8 M hydrochloric acid. The nonextracted metals are eluted with 8 M hydrochloric acid.

The eluate from the TOPO column is collected in a beaker and evaporated to near dryness. If lead(II) is present, nitric acid is added to oxidize the chloride ion and convert all the salts to nitrates. The residue is then taken up in water or 0.1 M nitric acid and diluted to approximately 20 ml. Enough ammonium citrate is added to complex all the metal ions present plus 100% excess. The solution is then adjusted to pH 4 with ammonium hydroxide and boiled for 20 minutes to assure complete complexation of the chromium(III). After cooling, the sample is adjusted to approximately pH 2 with dilute nitric acid and transferred to a column of hydrogen form Dowex 50W-X8 cation-exchange resin preconditioned with 0.1 M nitric acid. Because of the inertness of chromium(III), its anionic citrate complex passes directly through the cation-exchange column while under the slightly acid conditions used, the other metal ions considered are released from their citrate complexes and remain tightly sorbed onto the resin (Notes 5 and 6).

Notes:

1) The eluting solvent found to work best here is a 1:1 mixture of equilibrated 8 M hydrochloric acid and nonequilibrated acid. Apparently when the eluting solvent is first added to the column some of the dissolved ether is salted out of solution and can cause streaking of the sorbed metal bands and bleeding of extracting agent from the column. This situation is completely avoided if the 8 M hydrochloric acid is not saturated with organic solvent.
2) Manganese(II) and lead(II) are weakly extracted by the resin. The elution volume required for these two metals is greater than for the other metals considered. An elution volume equivalent to 8 column volumes is sufficient to elute these metals from the column.
3) Copper(II), although retained by the resin, has a sufficiently low distribution coefficient so that it slowly moves down the column. Therefore, when large amounts of copper(II) are present in the sample, care must be taken

to assure a column of sufficient size to perform the desired separations.

4) IPE and MIBK are both somewhat soluble in 8 M hydrochloric acid. Therefore, if the composition of the sample being considered is such that rather large IPE or MIBK columns are required, there may be sufficient organic solvent in the sample being received by the TOPO-cyclohexane column to dissolve part of the extractant and cause it to bleed off the column. This situation can be corrected by collecting the eluate from the anion-exchange column in a beaker, heating the contents to boiling for several minutes to evaporate off the organic solvent, cooling, and then transferring to the TOPO-cyclohexane column.

5) In the absence of chromium(III), the addition of the citrate ion is not necessary. The sample, after having been diluted with water or 0.1 M nitric acid, is transferred directly to the cation-exchange column. If the citrate ion is not added, difficulty may be encountered in dissolving any vanadium(IV) residue formed when the sample is evaporated down with nitric acid. The vanadium can be easily taken into solution by adding several drops of hydrogen peroxide.

6) A similar but faster method can be used for separation of small amounts of chromium(III) (less than 1% of sample) if the sample is such that sulfate will not interfere. After

removing the hydrochloric acid, the sample is fumed down with a small amount of sulfuric acid. In this case chromium(III) forms the anionic sulfate complex instead of the citrate complex. The sample is cooled, diluted with water until the sulfuric acid concentration is 0.2 to 0.5 N and then transferred to a cation-exchange column conditioned with 0.2 N sulfuric acid. The anionic complex of chromium (III) is then eluted from the column with 0.2 N sulfuric acid while the other cations present in the sample are retained. This method will recover approximately 99% of the chromium(III) present in the sample.

Desorption steps, additional separations

The metal ions extracted by the IPE column are recovered as a group by stripping them from the column with IPE or 0.1 M hydrochloric acid-98% methanol (Note 1). The tin(IV) and molybdenum(VI) extracted by the MIBK column can be separated by eluting the molybdenum(VI) from the column with 1 M hydrochloric acid-3 M sulfuric acid while leaving the tin(IV) on the column. The tin(IV) is then stripped from the column with MIBK, 0.1 M hydrochloric acid-98% methanol or dilute hydrochloric acid. This stripping technique will also remove molybdenum(VI) if the separation from tin(IV) is not required.

The metals sorbed by the Amberlyst A-26 anion-exchange column can be separated further by proper selection of eluting solvents. Cobalt(II) can be separated from the other sorbed ions including copper(II) by eluting with 0.5 M hydrochloric acid-65% ethanol (Note 2). Next, copper(II) and uranium(VI) are eluted with 1 M hydrochloric acid (Note 3). Zinc(II) can then be eluted from the column with 0.05 M hydrobromic acid. Cadmium(II) is eluted next from the column with 1 M nitric acid-0.01 M hydrobromic acid. Finally bismuth(III) can be eluted with 2 M perchloric acid.

Additional separations of the group sorbed to the TOPO column are also possible by proper choice of eluting solvents. Titanium(IV) and scandium(III) can be eluted from the column with 5 M nitric acid while leaving the other metal ions present sorbed to the column. Thorium(IV) can then be eluted with 12 M hydrochloric acid followed by elution of zirconium (IV) and hafnium(IV) with 1 M hydrochloric acid (Note 4).

A combination of proper choice of eluting solvent and differentiating EDTA titration allows for a considerable number of separations of the metal ions sorbed onto the cation-exchange column. Vanadium can easily be eluted with 0.01 M perchloric acid-1% hydrogen peroxide as the eluting solvent. Lead (II) can then be eluted with 0.6 M hydrobromic acid (Note 5). Manganese(II) is then eluted with a solution of 1 M hydrochloric acid-92% acetone. Aluminum(III) can be eluted from the column with 0.3 M hydrofluoric acid (Note 6). Nickel (II) and magnesium(II) are eluted as a group using 3 M hydrochloric acid-60% ethanol as the eluting solvent (Note 7).

Finally calcium(II), strontium(II), barium(II) and the rare earths are eluted with 4 M nitric acid (Note 8).

Notes:

1) No reliable method was found for separating antimony(V), iron(III) and gallium(III) on the IPE column. Antimony(V) can be separated from iron(III) and gallium(III) by taking advantage of the fact that in a weakly acid solution, the tartrate complex of antimony(V) passed through a column of cation-exchange resin while under the same conditions iron (III) and gallium(III) are sorbed onto the column.

   Iron and gallium can be separated from each other on an anion-exchange column using 0.45 M hydrobromic acid-90% methanol as the eluting solvent if some ascorbic acid is also added to reduce the iron to iron(II). Under these conditions the anionic bromide complex of gallium(III) remains on the column while iron(II) is eluted.

2) When copper(II) and cobalt(II) are both present in the sample, the cobalt(II), having the higher distribution coefficient from 8 M hydrochloric acid, will be sorbed onto the column above the copper(II) band. When the eluting solvent is changed to 0.5 M hydrochloric acid-65% ethanol the order of elution is reversed and cobalt(II) is eluted from the column ahead of copper(II). This means that the cobalt(II) band must pass through the copper(II) band and off the column before any of the copper(II) is eluted.

Because copper(II) is also slowly eluted by this solvent, extra care must be taken to assure a column of sufficient size to allow for a clean separation of these two metals.

3) Where approximately equimolar amounts of copper(II) and uranium(VI) are present, it is possible to elute the copper(II) with 2.5 M hydrochloric acid while leaving the uranium(VI) on the column. This separation is marginal, however.

4) Several good methods for separating zirconium(IV) and hafnium(IV) are available in the literature (16,41), should it be desirable to separate these two metals.

5) When 0.6 M hydrobromic acid is added to the column, $PbBr_2$ initially precipitated at the top of the column. If the amount of lead(II) present in the sample is small, this precipitate readily redissolves with continued elution. When larger amounts of lead(II) are present, the dissolving of the precipitate can be hastened by eluting with hot 0.6 M hydrobromic acid or better by using a hot water jacketed exchange column.

6) When the composition of the sample is such that the aluminum(III) is eluted with 0.3 M hydrofluoric acid, a column of Kel-F is used to prevent possible contamination from etching of the glass. A description of this column is given in an earlier section on apparatus.

7) Both nickel(II) and magnesium(II) can be determined in the

mixture by EDTA titration of the nickel(II) at pH 6 and the magnesium(II) at pH 10. A detailed description of the method is given in the section on analytical procedures.

8) The total of calcium(II), strontium(II) and barium(II) and total rare earths can be determined in the mixture by EDTA titration of the rare earths at pH 6 and the alkaline earths at pH 10. A detailed description of the method is given in the section on analytical procedures.

Special considerations

Although the separation scheme developed can be applied to a great variety of samples without special consideration of the particular combination of metal ions present, there are some exceptions. It is important that the metal ions in the sample be present in the proper oxidation state. To be extracted by the column containing IPE, for example, antimony(V) and iron(III) must be present because antimony(III) and iron (II) are not extracted. Tin and molybdenum must be in their 4 and 6 oxidation states, respectively, to be extracted by the MIBK column. It is important, however, that vanadium and chromium be present as vanadium(IV) and chromium(III) if these metals are to behave as predicted by the separation scheme.

Vanadium(V) is extracted by the MIBK column, but in the presence of the organic solvent, it is partially reduced to vanadium(IV) which is not extracted. Vanadium(V) is also extracted by the TOPO column. Chromium(VI) is extracted by both the MIBK and the TOPO columns.

In the absence of iron(III) or antimony(V), vanadium(V) can easily be reduced to vanadium(IV) with ascorbic acid. In the presence of iron(III) or antimony(V), however, a weaker reducing agent must be used. Vanadium(V) in 8 M hydrochloric acid can be reduced to vanadium(IV) by boiling with formaldahyde while iron(III) and antimony(V) remain in their higher oxidation states.

A common procedure for dissolving mineral samples is first to perform a fusion, often with sodium carbonate, to render the silicates soluble. The amount of sodium chloride formed when the melt from this type of fusion is treated with 8 M hydrochloric acid is too large to be conveniently taken into solution, however, because sodium chloride is not as soluble in 8 M hydrochloric acid as in solutions having a lower chloride ion concentration. For mineral samples the separation scheme is limited to those that can be dissolved without fusion or those where only a small amount of sodium carbonate is required to convert the sample to a soluble form.

Additional elements considered

Tungsten, niobium and tantalum have not been included in the present scheme. Fritz and Dahmer (14) have reported a cation-exchange procedure which will separate these three metals plus molybdenum as a group from a large number of other cations. In many instances, if any members of the tungsten, niobium, tantalum, molybdenum group are present in the sample, it should be possible to remove them by this method before dealing with the remaining components of the sample according to the separation scheme. Fritz and Dahmer (15) have also described a scheme for the separation of tungsten, niobium, tantalum and molybdenum from each other by reversed-phase partition chromatography.

It is well known that gold(III) will extract into oxygenated solvents from hydrochloric acid media. If present in the sample being considered, gold(III) will be retained by the IPE column.

Indium(III) should behave similarily to tin(IV) and molybdenum(VI) and be retained by the MIBK column. Goto (33) has reported a distribution ratio of approximately 20 for the extraction of indium into MIBK from 8 M hydrochloric acid. This author has also studied the extraction of indium(III) into MIBK and obtained results very similar to those reported by Goto.

It would seem possible to extract indium(III) onto a column conditioned with MIBK. Repeated attempts to do this have been only partially successful, however. At certain times indium(III) is strongly retained by the MIBK column, while at other times part of the indium(III) is extracted and part passes on through the column to contaminate the rest of the sample. Studies of loading, flow rate and sample purity did not uncover the cause of this problem. Indium(III) was therefore removed from the separation scheme.

Mercury(II) is not retained by the IPE column from 8 M hydrochloric acid, but is weakly retained by the MIBK column. It can be easily removed from this column by continued elution with 8 M hydrochloric acid, however. Mercury(II) will be strongly extracted by the anion-exchange column under these conditions. With the exception of 2 M perchloric acid, none of the eluting solvents used for the sequential removal of metals from the anion-exchange column will elute mercury(II). If present in the sample, mercury(II) will therefore be found in the fraction containing bismuth(III).

Silver is somewhat soluble in 8 M hydrochloric acid because of the formation of an anionic chloride complex. It will dissolve to the extent of approximately 0.018 moles per liter at 23°C. Moderate amounts of silver can therefore be present in the sample and will remain in solution in 8 M hydrochloric acid. Silver(I) present in the sample will pass quantitatively through the IPE, MIBK and TOPO columns.

After passing through the TOPO column, the separation scheme calls for the evaporation of the eluate to near dryness. If silver(I) is present, the eluate should be evaporated to a final volume of only 2 to 5 ml. Dilution with water will cause complete precipitation of silver(I) as the chloride, which can easily be removed by filtration. Interferences such as bismuth, antimony and tin would be removed previously and could not contaminate the precipitate. Interference from lead(II) can be avoided by washing the precipitated silver chloride repeatedly with hot nitric acid (44).

For trace amounts of silver(I), the sample is treated as in the absence of silver. After evaporation of the sample to near dryness, nitric acid is added to oxidize the chloride ion present and convert the salts to nitrates. The sample is then diluted with 0.1 M nitric acid and the silver(I) extracted with isooctyl thioglycolate (19). Under these conditions none of the other metal ions remaining in the sample are extracted.

The alkali metals will quantitatively pass through the first four chromatographic columns and can therefore be separated from any of the metals retained by these columns. The cation-exchange column, however, will retain the alkali metals along with the other metal ions remaining in the sample. Most of the eluting solvents used to selectively remove metals from the cation-exchange column are sufficiently acidic to partially or completely elute the alkali metals as well. In most cases, it would not be possible to quantitatively separate the alkali metals from other metals retained by the cation-exchange column.

Schmitt and Fritz (63) have shown that a chromatographic column of cellulose phosphate can be used to separate a number of divalent and trivalent metal ions from the alkali metals. Where there is a need to separate the alkali metals from any of the metals in the scheme that are taken up by the cation-exchange column, it should be possible to do so by substituting a cellulose phosphate column for the column of Dowex 50W-X8.

Arsenic(III) and germanium(IV) are selectively extracted into benzene from 10 to 12 M hydrochloric acid (4). Fritz and Sickafoose (26) have used this fact to separate arsenic(III) and germanium(IV) from many other metal ions by reversed-phase partition chromatography. The aqueous phase used in this case was 10 M hydrochloric acid and the stationary phase was equilibrated benzene. It should be possible to add this separation step to the overall separation scheme and remove arsenic(III) and germanium(IV) from the sample before proceeding to the IPE column. Dilution with water would easily adjust the concentration of the eluate from 10 M hydrochloric acid to 8 M hydrochloric acid.

Development of conditions for separation

This separation scheme is a composite of many individual separation procedures, most of which already have been reported in the literature. The purpose of this section is to recognize the source of the various conditions used to accomplish the numerous separations in the scheme. Only the procedures that are incorporated into the scheme are documented.

Because the scheme was essentially constructed by piecing together information from a number of sources, many separation procedures had to be evaluated before the final form of the scheme could be established. Systems were most often evaluated by actually trying them under the conditions likely to be used in the scheme. The effectiveness of a separation technique was determined by applying it to synthetic sample, first qualitatively using spot tests or other means to check for overlap of elution curves and then quantitatively to determine if recovery of metal ions was complete.

Several attempts were made to adapt extractive agents to reversed-phase partition chromatographic techniques. Some of the reagents considered were N-benzoylphenylhydroxylamine, di(2-ethylhexyl)phosphoric acid, dioctyl dithiophosphate, isooctylthioglycolate and trioctylphosphine oxide oxide. In many instances the reversibility of the extracting system presented difficulties. Often reagents would retain the metal ions, but unless very light loading of reagent on the column and small amounts of metal ions were used, back-extraction became very difficult. Frequently the elution curves indicated considerable tailing when attempts were made to remove metal ions from the column and/or the recoveries of metals from the column were not quantitative.

A number of problems were also encountered using literature data from ion-exchange work. Numerous workers reported extensive lists of distribution coefficients, many of which indicated useful separations. In many instances the actual separations were not tried by the original authors, however. Often separation systems derived from tables of distribution coefficients did not work as well as expected, particularly when the systems were partially nonaqueous. One possible reason for the failure of the methods to work as well as indicated is that the exchange rates are slower in nonaqueous media. This factor is often neglected when determining distribution coefficients, but is important when separations are actually performed. Another possibility for difficulty is in reproducing or reporting the exact composition of the solvent media employed. When partially nonaqueous systems are used, the concentration of complexing agent and organic diluent are often critical. For these reasons and others, a surprisingly large number of what seemed to be useful separations had to be discarded.

It should be clearly understood that in no way are the proceeding remarks intended to degrade the work of other researchers or to imply that some extractive reagents are of little value. The comments are intended only as an indication of some of the problems encountered in modifying the work of others to apply it to this project.

The effect of eluting solvent changes on chromatographic separations is usually determined by batch distribution studies. In this case, however, enough information to indicate general trends about the effect of solvent changes on distribution ratios usually already was available. Therefore, whenever systems were modified in a search for better eluting solvents, more distribution studies as such were not performed. Instead, elution curves were constructed and compared to determine which eluting solvent modification actually gave the best separation or fastest elution of the metal ions of interest. The elution curves were constructed as plots of concentration in arbitrary units versus volume of eluate in milliliters, with primary emphasis being placed on the beginning and the end of the curve. The actual shape of the elution curve was not of importance here except when considerable tailing was present.

Morrison and Freiser (50) have tabulated the extractabilities of a number of chloride complexes of metal ions into various organic solvents. Careful examination of the data given reveals that few metals are strongly extracted from 8 M hydrochloric acid into IPE. Of those metals considered in this scheme only iron(III), antimony(V) and gallium(III) are strongly extracted while several others are partially extracted. This constitutes the basis for the first group separation. No method of further separating this group by selective elution from the IPE column was found. These three metal ions are removed from the column as a group by stripping with 0.1 M hydrochloric acid-98% methanol.

Khorasani and Khundkar (43) reported a method for the separation of antimony(V) from a large number of other metal ions including iron(III) and gallium(III). They found that by forming the tartrate complex of antimony(V) in the presence of excess tartaric acid, antimony(V) was not retained by a cation-exchange column while the other metal ions present were. This method was used here to separate antimony(V) from iron(III) and gallium(III). Recovery of antimony was always low by 0.5-0.7%, however.

Korkisch and Hazan (45) have reported a method for separating iron and gallium by anion-exchange. Using 0.45 M hydrobromic acid-90% methanol containing ascorbic acid as the solvent, gallium(III) is retained by the resin while iron, as iron(II), is eluted from the column. Using Amberlyst A-26 resin this method gives a quantitative separation of these two metals.

Several authors (32,21) have reported distribution data for extraction of numerous metal ions from 8 M hydrochloric acid into MIBK. The metal ions extracted by IPE are also extracted by MIBK. In addition, tin(IV) and molybdenum(VI) are sufficiently extracted under these conditions so that they can be separated by reversed-phase chromatography from all the other metal ions considered in this separation scheme.

Further separation of this group is possible by eluting the molybdenum(IV) with 1 M hydrochloric acid-3 M sulfuric acid while the tin(IV) remains on the column (21). Tin(IV) can then be removed from the column with 1 M hydrochloric acid or 0.1 M hydrochloric acid-98% methanol.

Kraus and Nelson (46) reported a systematic study of the uptake of a large number of metal ions from hydrochloric acid by an anion-exchange resin. The information presented in their work was used as the basis for the third major group separation. Of the metal ions remaining in the scheme, only cobalt(II), copper(II), uranium(VI), zinc(II), cadmium(II) and bismuth(III) form sufficiently strong anionic chloride complexes in 8 M hydrochloric acid to be retained by the resin. Other metal ions considered are eluted from the column with 8 M hydrochloric acid.

The six metal ions of this group can be further separated by selective elution using the proper solvents. Fritz and Pietrzyk (24) studied the effect of nonaqueous solvents in anion-exchange separations and reported a separation of cobalt (III) from copper(II) and zinc(II) by eluting the cobalt(II) with 0.3 M hydrochloric acid-72% ethanol. The present author, after further studying this small segment of their work, varied both the acid concentration and the percentage of ethanol present and found that a better separation could be obtained using 0.5 M hydrochloric acid-65% ethanol.

Copper(II) can next be separated from the elements remaining on the column, the most difficult separation being that of copper(II) and uranium(VI). Referring to the work cited earlier by Kraus and Nelson (46), it should be possible to separate these two metals by eluting the copper with 2.5-3.0 M hydrochloric acid. This separation is marginal, but can be performed quantitatively if care is taken to select a column of sufficient size for the sample considered. The same work by Kraus and Nelson also suggests that uranium(VI) can now be eluted selectively from the anion-exchange column with 1 M hydrochloric acid.

Strelow and Toerien (66) studied the absorptivity of a number of elements from 0.1 M hydrobromic acid onto an anion-exchange column. They found that from this acid concentration zinc(II) was quantitatively eluted while cadmium(II) and bismuth(III) were retained. Further study of this system indicated to the present author that zinc(II) could be eluted more rapidly by reducing the acid concentration to 0.05 M hydrobromic acid, cadmium(II) and bismuth(III) still remaining tightly sorbed to the column.

In the same publication Strelow and Toerien describe a study of the effect of various mixtures of nitric and hydrobromic acid on the absorptivity of cadmium(II) on an anion-exchange column. A more detailed investigation of this work revealed that 1 M nitric acid-0.01 M hydrobromic acid would be a good solvent mixture for eluting cadmium(II) from an anion-exchange column while leaving bismuth(III) sorbed to the support.

Bismuth(III) is difficult to remove from an anion-exchange column. Strelow and Bothma (65) have reported distribution coefficients for many metal ions between sulfuric acid and a strongly basic anion-exchange resin. They report a distribution coefficient of less than 0.5 for bismuth(III) from 3 N sulfuric acid. Considering only the distribution coefficient, it would then seem possible to elute bismuth(III) rapidly from an anion-exchange column with 3 N sulfuric acid. The authors also pointed out, however, that exchange rates for strongly absorbed species are considerably slower for sulfuric acid than for hydrochloric acid.

The present author tried eluting bismuth(III) from a column of Amberlyst A-26 anion-exchange resin with 3 N sulfuric acid and found that it was eluted slowly and with considerable tailing. An attempt was made to obtain a more useful solvent for eluting bismuth(III) from a column of Amberlyst A-26. The solvent 2 M perchloric acid was finally chosen as the eluting agent. This solvent will quantitatively elute bismuth(III), but here too a fairly large elution volume is required.

The next major group separation is achieved by extracting titanium(IV), scandium(III), thorium(IV), zirconium(IV) and hafnium(IV) from 8 M hydrochloric acid onto a column containing TOPO as the extracting agent. Here again the technique of reversed-phase partition chromatography allows quantitative separation of the strongly extracted metal ions from those which are weakly extracted.

The use of TOPO as an extractant for metal ions from aqueous solution has been extensively investigated by White and Ross (70). TOPO has also been studied as the stationary phase for paper and column reversed-phase partition chromatography (5,6,7,52). A major consideration in the use of TOPO as the stationary phase for reversed-phase partition chromatography is the concentration of TOPO on the column. The exchange rates are usually faster when lower concentrations of extractant are used. Thus clean separations are possible with a minimum of tailing of the elution curves when sorbed ions are desorbed. The capacity of a column of this type is quite low, however, requiring the use of small samples or larger columns. At high concentrations of extractant the capacity of the column is increased, but it is often difficult to get quantitative desorption of extracted metal ions. Amberlyst XAD-2 columns conditioned with cyclohexane containing various concentrations of TOPO ranging from 0.1 M to 1.25 M were studied. An extractive solvent of 0.5 M TOPO in cyclohexane was found to be a useful compromise between capacity and reversibility.

The group extracted from 8 M hydrochloric acid by the TOPO column can be further separated by eluting titanium(IV) and scandium(III) with 5 M nitric acid while the other extracted metal ions remain on the column. This eluting solvent was selected after studying R_f values reported in the literature by Cerrai and Testa (7). They used reversed-phase paper chromatographic techniques to study the extractive properties of TOPO as a function of nitric acid molarity. The solvent 12 M hydrochloric acid was then selected to elute thorium(IV) from the column while zirconium(IV) was retained. Ross and White (56) indicated that the extractability of thorium(IV) by TOPO in cyclohexane reaches a maximum at about 6 M hydrochloric acid. They also showed (71) that the extraction of zirconium (IV) is low at 1 M hydrochloric acid but increases continuously as the acid concentration increases. The highest acid concentration studied was 10 M hydrochloric acid. By extrapolating the trends indicated in these two papers and then experimentally investigating the extractability of both thorium(IV) and zirconium(IV) by TOPO from 10-12 M hydrochloric acid, it was found that a quantitative separation of these ions could be obtained. Zirconium was then eluted from the TOPO column with 1 M hydrochloric acid. This procedure seems to be a direct contradiction to work reported by Cerrai and Testa (5) who separated thorium(IV) from zirconium(IV) by first eluting the thorium(IV) with 1 M hydrochloric acid while the zirconium(IV) remained sorbed to the column. It should be noted, however, that Cerrai and Testa were using a different column support, a different concentration of TOPO in cyclohexane and were separating smaller amounts of metal ions.

Up to this point separations have been accomplished by using various means of retaining solvated chloride complexes of the metal ions on chromatographic columns. The metal ions yet to be considered do not easily form extractable chloride complexes. A new approach for performing the rest of the separations was therefore required. Cation-exchange chromatography can successfully separate the remaining metals in the scheme provided the hydrochloric acid is first removed so the metal ions will be taken up by the resin.

Blaedel et al. (2) took advantage of the low rate of complexation of chromium(III) with the citrate ion to separate radioactive chromium(III) from a number of other metallic radioelements by cation-exchange chromatography. The anionic citrate complex of chromium(III), once formed by heating, will quantitatively pass through a cation-exchange column because the inert complex breaks up again very slowly at room temperature. The method was found to work well for larger amounts of chromium(III) also and was used in this scheme to separate chromium(III) from the other metals remaining with it. The citrate complexes of all the other metals present at this stage in the scheme are broken up by the cation-exchange resin and the metal ions are taken up by the column.

A similar, but somewhat faster method has been reported by de Gelis (10). He separated chromium(III) from a number of other metal ions by forming the anionic sulfate complex and passing it through a cation-exchange column. The inert anionic complex will pass through the column while from dilute sulfuric acid the other metal ions present are retained. This method has been found to be satisfactory for small amounts of chromium(III), but for larger amounts recoveries are approximately 1% low.

The metals sorbed onto the column can be further separated by proper choice of eluting solvents. Vanadium is rapidly and quantitatively eluted from the cation-exchange column with 0.01 M perchloric acid-1% hydrogen peroxide (12). Lead(II) can then be separated from the other sorbed metal ions by elution with 0.6 M hydrobromic acid (20). Work by Fritz and Rettig (25) indicates that manganese(II) can be quantitatively eluted with 1 M hydrochloric acid-92% acetone. Aluminum(III) is then eluted with 0.3 M hydrofluoric acid (17).

A recent publication by Strelow and Van Zyl (67) suggested the next separation step. Magnesium(II) and nickel(II) can be eluted with 3 M hydrochloric acid-60% ethanol while the other sorbed metals remain on the column. The remaining alkaline earth and rare earth metals are then eluted with 4 M nitric acid. This solvent has been shown to be particularily useful for eluting barium(II) from a cation-exchange column (42).

Specific Methods

Analysis of synthetic samples

The samples discussed here were prepared by pipetting aliquots of standard stock solutions of the elements of interest into a container and then performing the separations and analyses on this mixture. Flow rates used for the elution of metals from the columns were 1 ml per minute when the elution volume was less than 20 ml and 2 ml per minute when larger elution volumes were required. All analyses were performed by complexometric titrations as described in the section on analytical procedures.

Ga(III), Pb(II), Zn(II) A synthetic mixture of gallium(III), lead(II) and zinc(II) was prepared and separated to test the reliability of the extraction of gallium(III) by the IPE column. Approximately 0.1 mmole of each of the metals in a total sample size of 6 ml of 8 *M* hydrochloric acid was transferred to a 6 x 1.2 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with IPE. The nonextracted metals were eluted with 10 ml of 8 *M* hydrochloric, the eluate being passed directly onto a 6 x 1.0 cm column of 80 to 120 mesh Amberlyst A-26 anion-exchange resin conditioned with 8 *M* hydrochloric acid. The lead(II) was then eluted from the anion-exchange column with 15 ml of 8 *M* hydrochloric acid and collected in a beaker for analysis. Gallium(III) was removed from the IPE column with 20 ml of 0.1 *M* hydrochloric acid-98% methanol while zinc(II) was eluted from the anion-exchange column with 25 ml of water. The recoveries are given in Table 4.

Ni(II), Co(II), Cu(II), Zn(II), Cd(II), Bi(III) A sample containing approximately 0.1 mmole each of nickel(II), cobalt(II), copper(II), zinc(II), cadmium(II) and bismuth(III) was prepared to check the reliability of the part of the scheme using the Amberlyst A-26 anion-exchange column. The sample in 12 ml of 8 M hydrochloric acid was transferred to a 14 x 1.0 cm column of 80 to 120 mesh Amberlyst resin. The nonextracted nickel(II) was eluted with 25 ml of 8 M hydrochloric acid. Cobalt(II) was then eluted with 30 ml of 0.5 M hydrochloric acid-65% ethanol. Elution of copper(II) then followed using 20 ml of 1 M hydrochloric acid. Zinc(II) was next eluted with 100 ml of 0.05 M hydrobromic acid. Cadmium (II) was eluted with 100 ml of 1 M nitric acid-0.01 M hydrobromic acid. Finally bismuth(III) was removed from the column with 100 ml of 2 M perchloric acid. The recoveries are given in Table 4.

Ti(IV), V(IV), Al(III) Titanium, vanadium and aluminum frequently occur together in alloys, so a mixture containing these three metals was studied. Approximately 0.1 mmole of each element in 6 ml of 8 M hydrochloric acid was transferred to an 11 x 1.4 cm column of Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and 8 M hydrochloric acid. The aluminum(III) and vanadium(IV) were eluted with 30 ml of 8 M hydrochloric acid. The eluate was collected in a beaker, evaporated down to near dryness, cooled, diluted to 15 ml with water and transferred to a 6 x 1.2 cm column of 100 to 200 mesh Dowex 50W-X8 cation-exchange resin. The vanadium was then eluted from the column with 20 ml of 0.01 M perchloric acid-1% hydrogen peroxide. Aluminum was removed from the column with 25 ml of 3 M hydrochloric acid. Titanium(IV) was eluted from the TOPO column with 30 ml of 0.5 M hydrochloric acid. The recoveries are given in Table 4.

Th(IV), Ti(IV), Ni(II) Several synthetic samples were prepared to evaluate the separations requiring the use of the TOPO column. A sample containing 0.1 mmole each of thorium (IV), titanium(IV) and nickel(II) in 6 ml of 8 M hydrochloric acid was transferred to a 10 x 1.3 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and 8 M hydrochloric acid. Nickel(II) was eluted from this column with 20 ml of 8 M hydrochloric acid. Next titanium(IV) was eluted with 50 ml of 5 M nitric acid and the thorium(IV) was removed with 100 ml of 0.2 M hydrochloric acid. The results of the separation are given in Table 4.

Ti(IV), Th(IV), Zr(IV), La(III) A sample containing 0.1 mmole each of titanium(IV), thorium(IV), zirconium(IV) and lanthanum(III) in 8 ml of 8 M hydrochloric acid was transferred to a 13 x 1.2 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and 8 M hydrochloric acid. Titanium(IV) was then removed from the column with 40 ml of 5 M nitric acid. Thorium(IV) was then eluted with 50 ml of 12 M hydrochloric acid followed by the elution of zirconium(IV) with 125 ml of 1 M hydrochloric acid.

The recoveries are given in Table 4.

Th(IV), Ti(IV), La(III), Ca(II) A sample containing 0.1 mmole each of thorium(IV), titanium(IV), calcium(II) and lanthanum(III) in 8 ml of 8 M hydrochloric acid was also separated by a similar procedure. The sample was transferred to a 13 x 1.2 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and 8 M hydrochloric acid. Calcium(II) and lanthanum(III) were eluted from the column with 15 ml of 8 M hydrochloric acid and were both determined separately by EDTA titration in the same solution as described earlier in the section on analytical procedures. Then titanium(IV) was eluted with 40 ml of 5 M nitric acid. Thorium(IV) was eluted from the column with 75 ml of 0.2 M hydrochloric acid. The recoveries are given in Table 4.

Ni(II), Mg(II), Ca(II) A sample containing 0.1 mmole each of nickel(II), magnesium(II) and calcium(II) was prepared to test the reliability of several parts of the separation scheme. The sample in 6 ml of 0.1 M nitric acid was transferred to a 7 x 1.2 cm column of 100 to 200 mesh Dowex 50W-X8 cation-exchange resin. Nickel(II) and magnesium(II) were eluted from the column with 100 ml of 3 M hydrochloric acid-60% ethanol. These metals were then both determined separately in the eluate by EDTA titrations as described in the section on analytical procedures. Calcium(II) was eluted from the cation-exchange column with 40 ml of 4 M nitric acid. The recoveries are reported in Table 4.

Table 4. Analysis of synthetic metal ion mixtures[a]

Metal ion mixture	Present, mmole	Found, mmole	Percent recovery
Gallium(III)	0.1694	0.1699	100.3
Zinc(II)	0.1022	0.1020	99.8
Lead(II)	0.1129	0.1132	100.3
Nickel(II)	0.1107	0.1111	100.4
Cobalt(II)	0.1010	0.1014	100.4
Copper(II)	0.1032	0.1030	99.8
Zinc(II)	0.0926	0.0926	100.0
Cadmium(II)	0.0916	0.0920	100.4
Titanium(IV)	0.1088	0.1087	99.9
Vanadium(IV)	0.0974	0.0970	99.6
Aluminum(III)	0.1008	0.1007	99.9
Titanium(IV)	0.1016	0.1010	99.4
Nickel(II)	0.1174	0.1174	100.0
Thorium(IV)	0.0990	0.0986	99.6
Lanthanum(III)	0.0889	0.0891	100.2
Titanium(IV)	0.0971	0.0971	100.0
Thorium(IV)	0.0969	0.0969	100.0
Zirconium(IV)	0.1013	0.1017	100.4
Thorium(IV)	0.0969	0.0973	100.4
Titanium(IV)	0.0971	0.0971	100.0
Lanthanum(III)	0.0889	0.0891	100.2
Calcium(II)	0.1065	0.1071	100.6
Nickel(II)	0.1169	0.1167	99.8
Magnesium(II)	0.0939	0.0941	100.2
Calcium(II)	0.1090	0.1092	100.2

[a] Detailed discussions of the conditions and procedures used for the separations are given earlier in this section.

Analysis of National Bureau of Standards samples

The separation scheme was applied to the analysis of a number of National Bureau of Standards samples to check the dependability of the method on some independently analyzed samples. Small sample sizes were used to see how well the separation scheme would work under these conditions. Flow rates used for the chromatographic elutions (except where specifically stated otherwise) were 1 ml per minute for total elution volumes of less than 20 ml and 2 ml per minute for total elution volumes of greater than 20 ml per minute. Unless otherwise stated, all analyses were performed by complexometric titration methods using 0.02 M or 0.002 M reagent as outlined in the section on analytical procedures.

NBS 54d This is a tin-base alloy containing sizable amounts of antimony, lead, and copper. The sample was dissolved by treating approximately 250 mg of the alloy with the solvent mixture; 10 ml 8 M hydrochloric acid, 0.5 ml nitric acid, 1 ml 30% hydrogen peroxide. After the sample was dissolved, it was transferred to a 25 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. Aliquots containing approximately 40 mg of sample were then used for analysis.

Antimony(V) was extracted by a 6 x 1.0 cm chromatographic column of 80 to 100 mesh Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The nonextracted metals were eluted from the column with 7 ml of 8 M hydrochloric acid, and the eluate was passed directly onto a 12 x 1.4 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with MIBK and 8 M hydrochloric acid. This column extracted the tin(IV) while the nonextracted metal ions were eluted with 9 ml of 8 M hydrochloric acid.

The eluate from the MIBK column was passed directly onto a 5 x 1.0 cm column of 80 to 120 mesh Amberlyst A-26 resin which retained the copper(II). Lead(II) passed through this column, being completely eluted with 10 ml of 8 M hydrochloric acid.

Antimony(V) was removed from the IPE column with 20 ml of IPE that was pre-equilibrated with 8 M hydrochloric acid. Tin (IV) was eluted from the MIBK column with 30 ml of MIBK that had been pre-equilibrated with 8 M hydrochloric acid. Copper (II) was eluted from the anion-exchange column with 20 ml of water. The results obtained for the analysis of this sample are given in Table 5.

NBS 124d This is a copper-base alloy. It was analyzed for iron, tin, copper, zinc, lead and nickel. The sample was dissolved by treating approximately 250 mg of the alloy with 10 ml of 8 M hydrochloric acid and 1 ml of 30% hydrogen peroxide. After the sample was dissolved, it was transferred to a 25 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. A 4 ml aliquot (containing approximately 40 mg of sample) was then used for analysis.

Iron(III) was retained by a 5 x 1.0 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The nonextracted metals were eluted from the column with 6 ml of 8 M hydrochloric acid. The eluate from this column was passed directly onto a 15 x 1.0 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with MIBK and 8 M hydrochloric acid. Tin(IV) was extracted here. The nonextracted metals were eluted from this column with 10 ml of 8 M hydrochloric acid, and the eluate was passed directly onto a 13 x 1.2 cm column of Amberlyst A-26 anion-exchange resin that had been preconditioned with 8 M hydrochloric acid. Copper(II) and zinc(II) were sorbed by this column. The lead (II) and nickel(II) were eluted from the column with 50 ml of 8 M hydrochloric acid.

The eluate containing the lead(II) and nickel(II) was then evaporated down to near dryness, diluted with 10 ml of water and transferred to a 3 x 1.0 cm column of 100 to 200 mesh Dowex 50W-X8 cation-exchange resin. Both the nickel(II) and the lead(II) were sorbed by this column.

Iron(III) was stripped from the IPE column with 15 ml of 0.1 M hydrochloric acid-98% methanol. Tin(IV) was stripped from the MIBK column with 30 ml of 0.1 M hydrochloric acid-98% methanol. Copper(II) was eluted from the anion-exchange column with 30 ml of 1 M hydrochloric acid, and zinc(II) was removed from the same column with 50 ml of water. Lead(II) was eluted from the cation-exchange column with 30 ml of 0.6 M hydrobromic acid, and nickel(II) was removed from the same column with 15 ml of 3 M hydrochloric acid. The results obtained for the analysis of this sample are given in Table 5.

NBS 173a This titanium-base alloy was analyzed for iron, vanadium, and aluminum. The sample was dissolved by treating approximately 50 mg of the alloy with 5 ml of 8 M hydrochloric acid and heating to 90° for 2 hr. When the sample was dissolved, 0.25 ml of 30% hydrogen peroxide was added to oxidize the titanium(III) to titanium(IV). Next, the sample was boiled to remove most of the excess hydrogen peroxide. Then 0.5 ml of 6% sulfurous acid was added to destroy any remaining hydrogen peroxide and reduce vanadium(V) to vanadium(IV). The sample, in 5 ml 8 M hydrochloric acid, was transferred to a 7 x 1.0 cm column of Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The iron(III) was extracted here and the nonextracted metals were eluted with 10 ml of 8 M hydrochloric acid. The eluate from the IPE column was passed directly onto a 30 x 1.4 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and then 8 M hydrochloric acid. The column retained the titanium(IV) matrix as a yellow band on the column while aluminum(III) and vanadium(IV) were eluted from the column with 30 ml of 8 M hydrochloric acid.

The eluate containing the aluminum(III) and vanadium(IV) was then evaporated to near dryness, taken up in 15 ml of water and transferred to a 6 x 1.2 cm column of 100 to 200 mesh Dowex 50W-X8 cation-exchange resin. Both aluminum(III) and vanadium(IV) were sorbed by this column.

The iron(III) was stripped from the IPE column with 20 ml of 0.1 M hydrochloric acid-98% methanol. The vanadium(IV) was eluted from the cation-exchange column with 15 ml of 0.01 M perchloric acid-1% hydrogen peroxide. The aluminum(III) was then eluted with 20 ml of 3 M hydrochloric acid. The titanium (IV) on the TOPO column was eluted with 50 ml of 0.5 M hydrochloric acid. The TOPO column was then washed with 25 ml of 8 M hydrochloric acid after which time it was ready to receive another sample. The results obtained for the analysis of this sample are given in Table 5.

NBS 343 This is a steel alloy having a high chromium content. It was included to evaluate the part of the scheme involving the separation of chromium(III) from other metal ions using a citrate system. Chromium was the only metal determined in this sample. The alloy was dissolved by treating approximately 500 mg of sample with 2 ml hydrochloric acid, 1 ml nitric acid and 5 ml water and then evaporating down to approximately 3 ml. Then the sample was transferred to a 25 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. A 4 ml aliquot containing approximately 80 mg of sample was then transferred to a 9 x 1.2 cm column of Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The iron(III) from the steel matrix was extracted by this column. The non-extracted metals were eluted with 15 ml of 8 M hydrochloric acid, the eluate being collected in a beaker and evaporated down to dryness over low heat. The residue was then dissolved in 20 ml of 0.05 M citric acid. Then several drops of ammonium hydroxide were added to adjust the acidity to pH 5. The sample was boiled slowly for 20 minutes, cooled, adjusted to pH 2 with dilute nitric acid and transferred to a 5 x 1.2 cm column of 100 to 200 mesh Dowex 50W-X8 cation-exchange resin. The sample was passed through the column using a flow rate of 3 ml per minute. The column was then washed with 20 ml of water also at a flow rate of 3 ml per minute. The eluate was analyzed for chromium(III) by the method given in the section on analytical procedures. The results obtained for the analysis of chromium (III) are given in Table 5.

NBS 20f This is a steel sample containing small amounts of a number of metals. It was analyzed for copper, chromium, manganese and nickel. The alloy was dissolved by treating a 1 g sample with 10 ml hydrochloric acid-1 ml nitric acid and evaporating down to almost dryness. The residue was transferred to a 100 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. A 10 ml aliquot of this solution, containing approximately 100 mg of sample, was then transferred to a 10 x 1.3 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The iron(III) from the matrix was sorbed to this column while the nonextracted metal ions were eluted with 15 ml of 8 M hydrochloric acid. The eluate was passed directly onto an 8 x 1.0 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with MIBK and 8 M hydrochloric acid. A small amount of molybdenum (VI) present in the sample was extracted here, the nonextracted metals being eluted with 10 ml of 8 M hydrochloric acid. The eluate from this column was passed directly onto a 5 x 1.0 cm column of 80 to 120 mesh Amberlyst A-26 anion-exchange resin which retained the copper(II) while the weakly retained metal ions were eluted with 30 ml of 8 M hydrochloric acid.

The eluate was collected in a beaker and evaporated down to near dryness. Then 2 ml nitric acid and 0.5 ml sulfuric acid were added and the solution was evaporated down to fumes of sulfur trioxide. This solution was cooled, diluted to 20 ml with water, several drops of 6% sulfurous acid were added to assure complete reduction of manganese to the plus (II) oxidation state, and transferred to a 5 x 1.0 cm column of Dowex 50W-X8 conditioned with 0.2 N sulfuric acid. The anionic sulfate complex of chromium(III) passed through this column while nickel(II) and manganese(II) were retained.

Chromium in the eluate was determined by atomic absorption spectrophotometry. The fraction was evaporated down to 0.5 ml volume. The solvent remaining at this point was fuming sulfuric acid. It was then transferred to a 10 ml volumetric flask and diluted to volume with water. Standard chromium samples were prepared such that the solvent used contained 0.5 ml of sulfuric acid per 10 ml of solvent.

Copper(II) was eluted from the anion-exchange column with 30 ml of water. Manganese(II) was eluted from the cation-exchange column with 30 ml of 1 M hydrochloric acid-92% acetone. Nickel(II) was then eluted from the cation-exchange column with 50 ml of 3 M hydrochloric acid-60% ethanol. The results obtained for the analysis of this alloy are given in Table 5.

NBS 101e This is a steel alloy. It was analyzed for molybdenum, cobalt, copper, manganese, nickel and chromium. The sample was dissolved by treating 500 mg of sample with 10 ml hydrochloric acid-1 ml nitric acid and slowly evaporating down to near dryness. The sample was then transferred to a 100 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. A 5 ml aliquot of this sample, containing approximately 25 mg of alloy, was used for analysis.

The iron(III) matrix was extracted by a 10 x 1.0 cm column of 80 to 100 mesh Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The nonextracted metal ions were eluted with 20 ml of 8 M hydrochloric acid. The eluate was passed directly onto an 8 x 1.0 cm column of the same support conditioned with MIBK and 8 M hydrochloric acid. Molybdenum (VI) was sorbed by this column. The nonextracted metal ions were eluted from this column with 5 ml of 8 M hydrochloric acid, the eluate being passed directly onto a 5 x 1.0 cm column of 80 to 120 mesh Amberlyst A-26 anion-exchange resin conditioned with 8 M hydrochloric acid. Cobalt(II) and copper(II) were retained by this column while chromium(III), nickel(II) and manganese(II) were eluted with 30 ml of 8 M hydrochloric acid.

The eluate was evaporated down to dryness over low heat. The residue was then dissolved in 20 ml of 0.05 M citric acid. Then several drops of ammonium hydroxide were added to adjust the acidity to pH 5. The sample was boiled slowly for 20 minutes, cooled and adjusted to pH 2 with dilute nitric acid. Several drops of 6% sulfurous acid were added to assure complete reduction of manganese to manganese(II). The sample was then transferred to the top of a 7 x 1.0 cm column of 100 to 200 mesh Dowex 50W-X8 conditioned with 0.1 M nitric acid and passed through the column using a flow rate of 3 ml per minute. The column was then washed with 20 ml of water also using a flow rate of 3 ml per minute. The eluate was analyzed for chromium(III) by the method given in the section on analytical procedures.

Molybdenum(VI) was removed from the MIBK column with 0.1

M hydrochloric acid-98% methanol. The eluate was then removed by evaporation and the residue taken up in 10 ml of 1.5 M hydrochloric acid-50% methanol. Molybdenum was determined in this solution by atomic absorption spectrophotometry. Copper (II) and cobalt(II) were eluted together from the anion-exchange column with 20 ml of 0.001 M hydrochloric acid; both metals were determined in this eluate by atomic absorption spectrophotometry. Manganese(II) was eluted from the cation-exchange column with 50 ml of 1 M hydrochloric acid-92% acetone. Nickel(II) was eluted from the same column with 25 ml of 3 M hydrochloric acid. The results obtained for the analysis of this alloy are given in Table 5.

NBS 1a This sample is an argillaceous limestone. It was analyzed for iron, titanium, aluminum, magnesium and calcium. Before the limestone was dissolved, approximately 500 mg samples were transferred to platinum crucibles and ignited for 30 minutes at 1000°C in a muffle furnace. After cooling, the residue was treated with 5 ml water, 4 ml perchloric acid and 5 ml hydrofluoric acid. The sample was then slowly heated and evaporated down to fumes of perchloric acid and a final volume of 2 ml. The acid solution was then transferred to a 25 ml volumetric flask and diluted to volume with 8 M hydrochloric acid. A 5 ml aliquot of this sample, containing approximately 100 mg of limestone, was then used for analysis.

The iron(III) was extracted onto a 6 x 1.0 cm column of

80 to 100 mesh Amberlyst XAD-2 conditioned with IPE and 8 M hydrochloric acid. The nonextracted ions were eluted with 10 ml of 8 M hydrochloric acid, the eluate being passed directly onto an 8 x 1.0 cm column of Amberlyst XAD-2 conditioned with 0.5 M TOPO in cyclohexane and 8 M hydrochloric acid. The titanium(IV) was sorbed to this column while the nonextracted ions were eluted with 15 ml of 8 M hydrochloric acid.

The eluate from the TOPO column was evaporated down to near dryness to remove most of the hydrochloric acid. The residue was taken up in 15 ml of water and transferred to a 12 x 1.0 cm column of 100 to 200 mesh Dowex 50W-X8. The column itself was made of Kel-F. Iron(III) was eluted from the IPE column with 20 ml of 0.1 M hydrochloric acid-98% methanol. Titanium(IV) was removed from the TOPO column with 20 ml of 0.5 M hydrochloric acid. Aluminum(III) was eluted from the cation-exchange column with 60 ml of 0.3 M hydrofluoric acid. The column was then washed with 20 ml of water to remove any excess hydrofluoric acid. Magnesium was then eluted from the cation-exchange column with 100 ml of 3 M hydrochloric acid-60% ethanol, followed by calcium (plus strontium) with 40 ml of 4 M nitric acid. The results obtained for the analysis of this limestone are given in Table 5.

Evaluation of analytical data

The list of relative standard deviations given in Table 6 reveals that when the separation scheme is applied to the

Table 5. Analysis of National Bureau of Standards samples[a]

Sample number	Metals determined	Percent reported	Percent[b] found
NBS 54d	Antimony	7.04	7.06
	Tin	88.57	88.41
	Copper	3.62	3.61
	Lead	0.62	0.61
NBS 124d	Iron	0.18	0.19
	Tin	4.56	4.51
	Copper	83.60	83.60
	Zinc	5.06	5.05
	Lead	5.20	5.22
	Nickel	0.99	1.00
NBS 173a	Iron	0.15	0.15
	Vanadium	4.06	4.04
	Aluminum	6.47	6.49
NBS 343	Chromium	15.76	15.74
NBS 20f	Copper	0.239	0.238
	Chromium	0.097	0.097
	Manganese	0.754	0.764
	Nickel	0.243	0.258
NBS 101e	Molybdenum	0.43	0.40
	Cobalt	0.18	0.19
	Copper	0.36	0.36
	Manganese	1.77	1.74
	Nickel	9.48	9.44
	Chromium	17.98	17.89
NBS 1a	Iron as Fe_2O_3	1.63	1.60
	Titanium as TiO_2	0.16	0.17
	Aluminum as Al_2O_3	4.16	4.12
	Magnesium as MgO	2.19	2.27
	Calcium plus strontium as CaO	41.44[c]	41.26

[a] Detailed discussions of the conditions and procedures used for the separations are given earlier in this section.

[b] Values reported are the average of two or three determinations.

[c] Sample reported to contain 41.32% CaO and 0.23% SrO.

the analysis of major components in a sample, good precision can be expected. The relative standard deviation obtained for minor constituents in NBS samples is not as good, but it must be remembered that emphasis was placed on using small samples, which does not favor the determination of minor constituents. Also, the analytical techniques used for determining minor constituents are not as precise.

Table 6. Summary of analytical data

Type of samples	Number of samples	Average % recovery	Relative standard deviation (%)
Synthetic samples	25	100.1	0.3
NBS samples, components greater than 2% of sample	14	99.7	0.4
NBS samples, components less than 2% of sample	14	101.0	3.5

The average recovery for the synthetic samples is slightly high. This trend can be attributed to the way the analyses were performed. In most cases 1 aliquot of the metal ion of interest was used to prepare the sample and another was placed in a beaker to be analyzed directly and used as a control. The only acid present in the control sample was that from the original aliquot, while in many cases the sample off the column contained a considerable amount of acid because of the conditions used to elute it. The samples were analyzed by

EDTA titration after first neutralizing most of the acid present and buffering the solutions to the proper pH. The endpoint transitions are not as sharp in solutions of high ionic strength and often appear somewhat late. This situation could account for the high results.

The average recovery for the major constituents in the NBS samples is somewhat low. This is probably best explained as loss on the chromatographic columns and sample transfer. Most of the procedures for the NBS samples required the use of several chromatographic columns and several transfers of sample from beakers to columns. The average recovery for the minor constituents of the NBS samples is acceptable, especially when the circumstances are realized.

ANALYSIS OF LEAD-INDIUM ALLOYS

A need arose to determine the composition of several lead-indium alloys. As stated earlier in the thesis (page 50), the behavior of indium in the separation scheme is not predictable. Therefore, it was decided to try to separate lead(II) and indium(III) by using a hydrobromic acid system instead of hydrochloric acid.

A number of metal bromide complexes are easily extracted into oxygenated organic solvents from hydrobromic acid. The system is analogous to the extraction of chloride complexes into oxygenated solvents from hydrochloric acid. Several researchers have studied the extractability of metal bromide complexes into organic solvents.

Bock and coworkers (3) studied the extractability of many metal bromides into ethyl ether. Hudgens and Nelson (38) studied the extractability of indium(III) into ethyl ether and isopropyl ether from hydrobromic acid media. Denaro and Occleshaw (11) studied the extractability of a number of metal bromide complexes into methyl ethyl ketone and methyl isobutyl ketone. Owens (54) performed a similar study using 2-pentanone as the organic extractant. Irving and Rossotti (39) extensively studied the extractability of indium(III) into methyl isobutyl ketone and other oxygenated organic solvents from aqueous bromide solutions. Their primary interest was to determine the species extracted. Therefore, most of their work was done using mixed systems of acid and bromide salts to maintain a nearly constant ionic strength. When acid was the only source of bromide ion in the aqueous phase, 1 M hydrobromic acid was the maximum concentration studied. Henning and Specker (37) also studied the type of species formed when indium(III) was extracted into methyl isobutyl ketone from bromide media.

A number of useful inorganic separations have been performed by solvent extraction techniques using hydrobromic acid as the aqueous phase and a ketone or ether as the organic phase. The technique of reversed-phase partition chromatography can be applied to perform cleanly and rapidly many more separations than are possible by batch extraction because the values of the distribution ratios are not so critical. Except for the work by Irving and Rossotti using dilute acid, the extent of extractability of indium(III) into methyl isobutyl ketone (MIBK) from hydrobromic acid has not been reported in the literature. Distribution ratios for the extraction of indium(III) into ethyl ether, isopropyl ether and 2-pentanone indicate that indium(III) should be strongly extracted into MIBK from fairly concentrated solutions of hydrobromic acid. On determining the distribution ratio for indium(III) from 4.4 M hydrobromic acid into MIBK a value of 200 was obtained. A check of the extent of extraction of lead(II) under the same conditions produced a value of 0.06 for a distribution ratio.

These values indicated than an excellent separation of lead(II) and indium(III) should be possible by reversed-phase partition chromatography.

Before trying the separation method on an alloy sample, the method was tested using a synthetic sample of 0.1 mmole each of lead(II) and indium(III) in 4 ml of 4.4 M hydrobromic acid. A 9 x 1.2 cm column of 60 to 80 mesh Amberlyst XAD-2 conditioned with MIBK and 4.4 M hydrobromic acid was used. Sulfide spot tests were used to follow the elution of lead(II) from the column with 4.4 M hydrobromic acid, a total elution volume of 15 ml being required. Indium(III) was then eluted from the column with 15 ml of 0.1 M hydrochloric acid. Titration of 5 ml fractions of the eluate with EDTA determined when the indium(III) was completely eluted.

The method was then applied to the analysis of lead-indium alloys (5-20 mole % indium). The samples (600-800 mg) were dissolved in 15 ml hydrobromic acid. Moderate heat was used to speed the dissolving of the sample and to evaporate off most of the acid after dissolution. The residue was taken up in 4.4 M hydrobromic acid, transferred to a 25 ml volumetric flask and diluted to volume with the same solvent. Aliquots (5 ml) were then transferred to the previously described column for separation. Lead(II) was eluted from the column with 15 ml of equilibrated 4.4 M hydrobromic acid using a flow rate of 2 ml per minute. The indium(III) was then stripped from the column with 20 ml of 0.1 M hydrochloric acid, also at a flow rate of 2 ml per minute. The two fractions were then analyzed for metal ion content by EDTA titration. Lead(II) was determined as described in section on analytical procedures. Indium(III) was determined by the same procedure except the titration was performed at pH 5.3.

The compositions of the alloys were only approximately known. Because they were not analyzed by other methods, the values obtained could not be compared with accepted values. Also, the samples were not homogeneous, so the composition of different parts of the alloys varied considerably.

The values given in Table 7 are for an alloy containing approximately 10 mole % indium. Three different sections of the sample were analyzed, two identical aliquots for each section. The precision for each of the sets of two aliquots is very good. The difference in the mole % indium found for the various sections is an example of nonhomogeneity in the alloy. The material balance was slightly high in each case, although here too the precision was very good. The high results are undoubtedly a result of an error in the accepted concentration of the EDTA used as titrant. If these values are accepted as indicating the reliability of the method, it appears that this is a dependable method for analyzing lead-indium alloys. More experimentation in this area would certainly reveal other useful separations.

Table 7. Analytical data for lead-indium alloys

Sample number	Mmole In(III) present	Mmole Pb(II) present	Mole % indium	Material balance, % of total recovered
I, aliquot a	0.0731	0.6279	10.43	100.22
I, aliquot b	0.0729	0.6279	10.40	
II, aliquot a	0.0862	0.7244	10.64	100.20
II, aliquot b	0.0860	0.7229	10.63	
III, aliquot a	0.0941	0.7474	11.18	100.36
III, aliquot b	0.0945	0.7479	11.22	

DISCUSSION

In an undertaking of this type, there are always a number of other routes that could have been followed, each having certain distinct advantages, but also disadvantages. The systematic procedures worked out for this scheme resulted from a number of compromises in order to develop a scheme that could accommodate all possible combinations of metal ions considered. In actual practice, however, samples will usually contain only a fraction of the total number of metals included in the scheme. Then too, it is not always necessary to analyze for each component in a sample, but only a select few. Also, analytical techniques such as atomic absorption spectrophotometry often permit the analysis of more than one element in the same sample without further separation, once matrix effects or other interferences have been removed. For these reasons specific separations can often be achieved more simply if some changes in the proposed procedures are made.

There are probably as many useful modifications for the overall scheme as there are different combinations of metal ions possible from the elements considered. To discuss all these modifications would be time consuming and probably not very meaningful. Awareness of the extraction behavior of the metals considered under conditions different from those proposed for the scheme often enables the analyst to improve upon the procedures for the separations being considered. Several examples taken from the list of samples discussed in the section headed "Specific Methods" may help to illustrate this point.

Work by Kraus and Nelson (46) reveals that in most cases metals retained by an anion-exchange resin from strong hydrochloric acid are not retained when the chloride ion concentration is lowered. Copper(II), cobalt(II) and zinc(II) can easily be removed from an anion-exchange column with 0.001 M hydrochloric acid or even water.

The tin-base alloy NBS 54d contains only copper as a component retained by the anion-exchange column in the separation scheme. The scheme requires that copper(II) be removed from this column with 2.5 M hydrochloric acid. In this case copper(II) was actually removed with water, saving time and simplifying the subsequent analysis step. From the copper-base alloy NBS 124d both copper and zinc are retained by the anion-exchange column. Here copper(II) was eluted from the column with 1 M hydrochloric acid instead of the recommended 2.5 M hydrochloric acid. Zinc(II) was then eluted from the column with water instead of 0.05 M hydrobromic acid. Both changes shortened the required elution times and lowered the acidity of the eluate fraction, again simplifying the subsequent analysis step.

The steel sample NBS 101e contains small amounts of both copper and cobalt. In the specific method reported for this alloy, only these metals are sorbed by the anion-exchange column used. The separation scheme requires that cobalt(II) be eluted with 0.5 M hydrochloric acid-65% ethanol followed by copper(II) with 2.5 M hydrochloric acid. Both metals were easily eluted together with 0.001 M hydrochloric acid. Copper(II) and cobalt(II) were then analyzed for in the mixture by atomic absorption spectrophotometry. In this same procedure nickel(II) was eluted from the cation-exchange column with 3 M hydrochloric acid instead of 3 M hydrochloric acid-60% ethanol as required by the scheme because no other interfering metal ions were on the column. The elution of nickel(II) is faster using the aqueous solvent.

The separation scheme requires that aluminum(III) be separated from the rare earth and alkaline earth elements by elution from a cation-exchange column with 0.3 M hydrofluoric acid. The fluoride ion interferes with the analysis of aluminum(III) by CDTA titration, requiring that it first be removed by distillation from a sulfuric acid solution. The use of 0.3 M hydrofluoric acid as an eluting solvent also requires the use of an inert column such as one prepared from Kel-F. When the separation of aluminum(III) from alkaline earths or rare earths is not required, aluminum(III) can be eluted from a cation-exchange column with 3 M hydrochloric acid (64), thus simplifying the analysis step. The separation procedure for the analysis of NBS 173a titanium base alloy illustrates this modification of the separation scheme.

When thorium(IV) and zirconium(IV) are to be separated by the proposed scheme, thorium(IV) is eluted from a TOPO column with 12 M hydrochloric acid. The acid concentration in the eluate is so high that before the thorium(IV) content can be determined by EDTA titration, most of the acid must be removed by volatilization. In the absence of zirconium(IV), or hafnium(IV), thorium(IV) can be eluted from the same column with 0.2 M hydrochloric acid (56). The acid concentration of the eluate is now sufficiently low to permit the direct determination of thorium(IV) by EDTA titration with little further sample preparation. The separation procedures reported for two synthetic samples illustrate this point.

The chemical literature contains many reports of systematic studies of extraction of metal ions by various solvent extraction and ion-exchange techniques. The information contained in these reports is of great value when devising specific modifications of the separation scheme. A list of useful reports is given in the appendix.

CONCLUSION

A separation scheme was developed to aid in the analysis of complex samples. Ion exchange and partition column chromatographic techniques were utilized to separate sample components into groups that could more easily be determined by conventional analytical methods. A great variety in sample composition and concentration range gives the scheme potential for wide analytical application as well as a systematic approach to the analysis of many new or nonroutine samples. Therefore, even new and difficult samples often can be handled by unskilled personal without the frequent need of first developing an original analytical procedure.

Use of the separation scheme should shorten the time required to complete the analysis of a new sample. Because a systematic approach for analysis is already available, little time is lost in planning an analytical procedure. Accurate results can be obtained on small amounts of sample (20 to 100 mg) so the time required for dissolving the sample and actual separation times are reduced. The final analysis step is often faster because interferences have been removed. Another advantage of using the separation scheme is that excellent accuracy can be obtained for the determination of major constituents in a sample even when only a small amount is available or when intentionally the analysis is performed on only a small part of a larger sample, as in checking for nonhomogeneity.

The equipment required to perform the separations can be very inexpensive, thereby giving a reliable analytical method to laboratories where the cost of equipment such as x-ray fluorescence is prohibitive. On the other hand, where many analyses are required and more expensive equipment can be used to advantage, the scheme may also find application. Automation has played an important part in recent analytical developments and the proposed scheme should lend itself to automated techniques, at least in part if not in its entirety. In many cases the procedures followed to pass a sample through the first four chromatographic columns and the sequential elution of sorbed metals from the columns could be performed automatically. A major difficulty from the standpoint of automation would be the evaporation step required before proceeding on to column five. Once this step was performed manually and the sample was readied for the cation-exchange column, however, the actual sample transfer and subsequent elution steps could be controlled automatically again.

It should be possible to have the automated scheme controlled by a computer so that the whole separation process could be simplified even further. Once the computer was supplied with the proper qualitative information about the sample composition, it could automatically select the proper sequence of chromatographic columns and eluting solvents needed to complete the desired separation. Then by proper control of valves, pumps, timers, and other hardware, the sample would be processed and the metal ion fraction collected in appropriate containers. All the analyst would have to do is supply the machinery with the approximate composition of the sample of interest and wait for the components to be separated or even determined automatically.

The author is aware of some limitations of the proposed separation scheme and realizes that certain improvements that would enhance the usefulness of the scheme have probably been overlooked. It is hoped that the development of this separation scheme is sufficiently important to make interested persons aware that an approach of this type is possible and has potential as an aid in analytical chemistry. If this separation scheme stimulates the thoughts of others to devise additional systematic approaches to analytical problems, then a major purpose has been fulfilled.

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APPENDIX: SELECTED BIBLIOGRAPHY OF DISTRIBUTION STUDIES

Solvent Extraction:

Isopropyl ether

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Methyl isobutyl ketone

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