APPLICATIONS OF CHROMATOGRAPHY IN THE ANALYSIS OF INORGANIC MATERIALS

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Abstract - The role of separations in inorganic analysis is discussed and the advantages of various chromatographic techniques are stressed. Major separation methods include solvent extraction, column extraction chromatography, gas chromatography of volatile metal chelates, ion-exchange chromatography, and column chromatography employing chelating resins and non-ionic sorptive resins. The use of each of these methods in analysis is illustrated by specific examples.

The state-of-the-art in organic liquid chromatography is contrasted with that in inorganic chromatography. Many organic compounds in a sample can be separated in a few minutes with automatic detection and quantitation from electronically integrated peak areas. Unfortunately, many inorganic separations are still carried out slowly with gravity flow columns and manual analysis of collected fractions. The principles of high-speed inorganic chromatography are outlined and specific examples are given.

Finally, an important role for chelating ion-exchange resins in inorganic separations is predicted. Recent developments in chelating resins are reviewed briefly. Some new resins are discussed, including a non-ionic resin that is selective for uranium and a chelating resin that is highly selective for gold, silver, mercury, and bismuth.

INTRODUCTION

Analysis of inorganic materials by chemical means generally provides results of high accuracy, but complex samples often require preliminary separations before the measurement methods can be applied. Instrumental methods of analysis tend to be faster but somewhat less accurate for major constituents than chemical methods. Separations are often necessary or desirable prior to instrumental analysis because of matrix effects or other interferences that may be encountered.

The objective of this paper is to review some of the major separation methods that can be used in conjunction with inorganic samples, especially those in which determination of various metal ions is desired. Chromatographic separation methods are emphasized because of their ability to achieve clean separations on complicated samples. This review must of necessity be quite selective. The intention is to discuss some of the major separation approaches used together with their advantages and limitations, and to present some recent developments, especially those from the author's own laboratory.

SOLVENT EXTRACTION

This technique is rapid, simple, and can sometimes be used to concentrate low concentrations of substances. A significant disadvantage is that quantitative separation ability is limited by the need for an "all or nothing" situation. This means that one constituent must be completely extracted from one phase to the other while the extraction of another constituent must be nil. Other drawbacks include occasional troublesome emulsion formation and the considerable manipulation that may be involved in making several extractions, each time carefully separating the layers, washing, and finally back-extracting.

Solvent extraction for metal ions includes methods in which an organic chelating reagent is used and those that involve extraction of an ion-association complex. The latter has the advantage that all reagents are generally volatile on heating. Some of the elements that are readily extracted under various conditions as ion-association complexes are listed below.

From HCl: Fe(III), Ga(III), Ge(IV), As(III), Mo(VI), In(III), Sn(IV), Sb(V), Au(III), Hg(II).

From HF: Nb(V), Ta(V).

From HNO$_3$: U(VI), Th(IV), Zr(IV).

From HSCN: Zr(IV), Hf(IV), and many others.

A solvating organic solvent is required for extraction of ion-association complexes. Various acetate esters, ketones (methyl isobutyl ketone), and phosphate esters (tributylphosphate) are some of the widely used solvents. Amides have roughly the same solvating ability as tributylphosphate towards metal halide complexes. The ability of certain amides (1) to extract uranium, thorium and zirconium from aqueous nitrate solutions is remarkable (see Table 1). No strong acid or salting-out reagent is needed, and the specificity, especially for uranium, is outstanding.

TABLE 1. Distribution ratios for metal ions extracted from 1 M nitrate with toluene solutions of N, N-dihexylacetamide (DHA), N, N-dibutylformamide (DBF) and N, N-diethyldodecanamide (DED).

Element	Distribution Ratio			
	DHA 1 M	DHA 3.5 M	DBF 5 M	DED 3 M
U	25.3	249	177	27.1
Th	0.33	26.5	41.2	0.66
Zr	0.02	0.09	38.8	0.08
Hg	0.03	1.12	4.85	0.25
Fe	0.00	0.22	1.13	0.00
Pb	0.00	0.00	0.19	0.00
Al, Ca, Cd, Co, Mg, Ni, Zn	0.00	0.00	0.00	0.00

Solvent extraction using chelating reagents or liquid ion-exchangers provides many additional separation possibilities, but in the author's opinion these are more useful when employed in the column extraction mode to be described next.

COLUMN EXTRACTION CHROMATOGRAPHY

In this technique a column is packed with a solid support that holds an organic stationary phase. In the sorption step an aqueous sample is added to the column and the various solutes are distributed between the organic and aqueous phases. Then the column is eluted with an aqueous solution (or series of solutions) so that the inorganic solutes move down the column at different rates and are separated. Sometimes the phases are reversed so that the aqueous phase is stationary and elution is performed with an organic phase.

Extraction chromatography is a multistage separation method and permits much more subtle separations than are possible with simple solvent extraction. Manipulation is minimal and the scope of possible separations is quite large. One disadvantage of this technique is that there is often some bleeding or dissolving of the organic phase from the solid support. Presaturation of the eluent with the organic solvent helps to prevent this.

An excellent bibliography of inorganic applications of extraction chromatography through 1971 has been published (2). Separations of individual rare earths (3-5) illustrate the tremendous separating power of extraction chromatography (Fig. 1). Ion-association complexes can also be used in column chromatography, such as the chloride and fluoride complexes used in the separation of niobium, tantalum, molybdenum and tungsten from each other (6). In this work radio tracers were used to demonstrate that separations of the above elements could be achieved in ratios as great as 10^6 to 1.

GAS CHROMATOGRAPHY OF METAL CHELATES

Here a sample containing a mixture of metal ions is reacted with an organic chelating reagent and metal chelates are then isolated by solvent extraction. An aliquot of the extract is injected into a gas chromatograph and the volatile metal chelates are separated from each other. Polyfluorinated 1, 3-diketones have been extensively used. It is usually
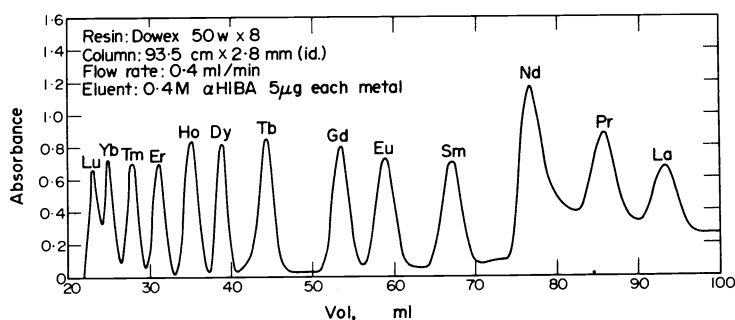
Fig. 1. Chromatographic separation of rare earths.

necessary to add a secondary ligand such as dibutylsulfoxide or tributylphosphate to satisfy completely the metal ion coordination sphere. If this is not done residual water of hydration may partially decompose the complex during the separation.

Advantages of this method are that it is rather fast and is tremendously sensitive because of the great sensitivity of the gas chromatographic detectors (electron-capture or the flame-ionization detector). Thus far satisfactory methods have been worked out for only a limited number of elements. Frequently there is some difficulty with partial decomposition of chelates in the gas chromatograph. Loss of metal chelate by irreversible adsorption on the GC column is another disadvantage; this may be partially compensated by several injections to saturate the so called "active sites" on the column.

ION-EXCHANGE CHROMATOGRAPHY

This is one of the most powerful separation techniques available for metal ion mixtures. There is some difference in affinity of ion-exchange resins for various metal ions, but many separations are based on selective complexing. Chloride, fluoride and hydrogen peroxide complexes are particularly useful for separations using either anion- or cation exchange resins. Use of the lower alcohols, acetone and other organic solvents increases the separation possibilities. The scope of the method is perhaps best illustrated by some specific examples.

(1) K. A. Kraus (7) showed that metal ions can be separated on an anion-exchange column after conversion to complex anions with hydrochloric acid (up to 12 M). Metals are eluted with varying concentrations of hydrochloric acid (see Table 2).

TABLE 2. Approximate concentration of hydrochloric acid for elution of metal ions from Dowex 1

Metal	HCl conc., M
Alkali metals, alk. earths, rare earths, Al(III), Ni(II)	10-12
Titanium(IV)	9.5
Lead(II), zirconium(IV)	8.0
Cobalt(II)	4.5
Copper(II)	3.0
Iron(III), molybdenum(VI), uranium(VI)	1.0
Zinc(II)	0.02
Cadmium(II)	0.001

(2) F. W. E. Strelow and his coworkers have published a large number of excellent methods for analytical ion-exchange separations. For example, ten major and minor elements in silicate rocks have been separated on a single cation-exchange column using a variety of selective eluents (see Fig. 2).
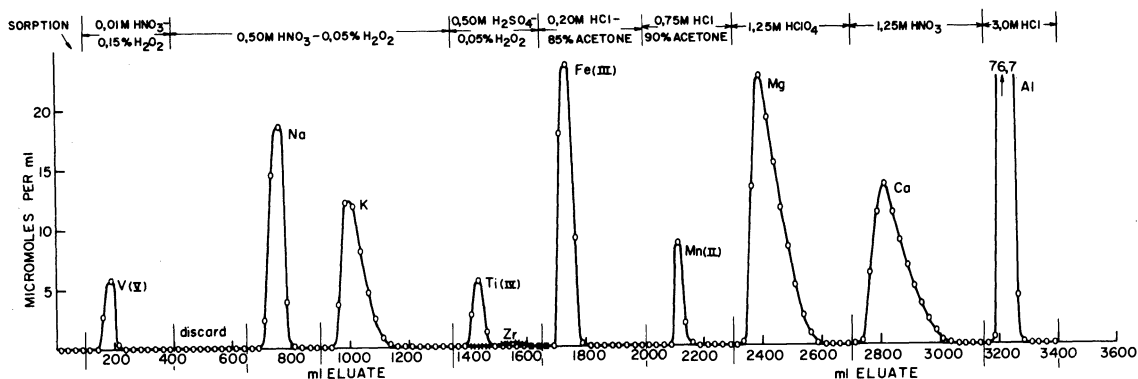
Fig. 2. Elution curve for V, Na, K, Ti, Zr, Fe(III), Mn, Mg, Ca, Al.
F. W. E. Strelow, C. J. Liebenberg, and A. H. Victor, <u>Anal. Chem.</u>, <u>46</u>,
1409 (1974).

(3) J. Korkisch is another leader in developing useful ion-exchange separations. Thus a study of anion exchange behavior in 90 to 95% methanol, 0.6 M in hydrochloric acid showed that virtually all of the elements studied fall into two groups (8). One group is strongly retained by the resin and includes iron(III), uranium(VI), cobalt(II), maganese(II) and other metals that form chloride complexes in the methanol media. The other group is not retained at all and includes alkaline earths, aluminum(III), nickel(II), among others. Thus, a very simple and rapid group separation of metal ions is possible.

Ion-exchange chromatography is attractive because it is possible to separate almost any inorganic mixture by a judicious choice of methods. Separations are complete and very good accuracy can be obtained. As commonly performed, a disadvantage of ion-exchange chromatography is that separations are often slow, especially if we include the time required for analysis of the various fractions of effluent that are collected. It would also be convenient to have resins that are more selective for various metals in solution so that recourse to selective complexation in solution would not always be necessary. The remainder of this paper will deal with answers to these two problems.

RAPID ION EXCHANGE SEPARATIONS

With modern liquid chromatographs separation of <u>organic</u> compounds can often be accomplished in only a few minutes, even for samples containing a fairly large number of constituents. The state-of-the-art for separation of metal ions and inorganic anions is generally not so favorable. Most laboratories that do inorganic ion-exchange separations still tend to use rather slow gravity flow, collect fractions, and analyze the various fractions individually. Inorganic chromatography needs (1) faster separations with better resolution, and (2) automatic detection of separated substances.

The first of these goals necessitates the use of smaller samples than are now generally used so that the chromatographic peaks will be more narrow. Faster eluent flow rates must also be used; this requires a pump or pressure system for the eluent and small resin particle size, packed efficiently in a column.

A liquid chromatograph designed with these points in mind is shown in Fig. 3. All of the tubing and valves are constructed of plastic or glass so that concentrated acids and other corrosive chemicals can be used if desired. Surge-free pressure to force the eluent through the column is provided by a helium tank. Typical conditions used for ion-exchange separations are as follows: resin is 150-200 mesh, sample volume is 50 µl, column is 2 to 10 cm X 0.6 cm i. d., eluent flow rate is 1 to 3 ml/min.

There are several possibilities for automatic detectors. In the author's laboratory spectrophotometric detection is employed with a flow-through cell of low dead volume but with a light path of 1 cm. In aqueous hydrochloric acid medium approximately 35 elements can be detected by the ultraviolet absorbance of their chloride complexes.   For metal ions that cannot be detected in this manner, a solution containing pH buffer and color-forming reagent can be mixed with the effluent stream and the absorbance of the resulting metal complex measured in the flow-through cell. This constitutes almost a universal detection system for metal ions because of the wide variety of color-forming reagents available. One problem is that radical changes in eluent composition causes a temporary optical disturbance that may result in spurious peaks.
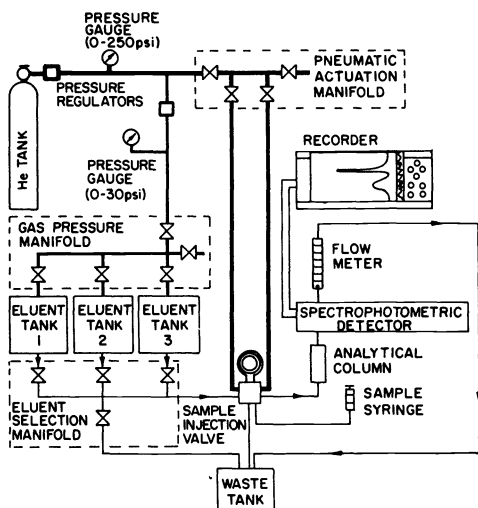
Fig. 3. Schematic diagram of liquid chromatograph. Heavy lines, high pressure gas; medium lines, low pressure gas; light lines, liquid. M. D. Seymour, J. P. Sickafoose, and J. S. Fritz, Anal. Chem., 43, 1734 (1971).

Electrochemical detectors have been used successfully for some systems (9). A system that uses a conductivity detector works very well for ion-exchange separation of anions and for separation of a few metal cations (10). What makes this detector viable is that the ionic substances in the eluent are removed by a second ion-exchange column that follows the column in which separation occurs. For example, alkali metal ions are separated on a small cation-exchange column of low capacity using 0.01 $\underline{M}$ hydrochloric acid. Then the chloride is converted to hydroxide in a second resin of higher capacity.

$$HCl + LiCl, NaCl + Anex-OH^- \rightarrow H_2O + LiOH, NaOH$$
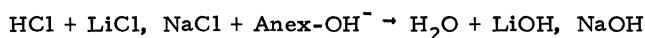
Examples of rapid separations with automatic detection are shown in Figs. 4 and 5. The separations are complete and require only a few minutes per element separated. Quantitation is achieved by means of a calibration plot of peak height vs. micrograms of the element in standards. Still faster separations should be possible using resin of smaller and more homogenious particle size.

NON-IONIC RESINS

An alternative to using a liquid organic solvent (as in solvent extraction or in column extraction chromatography) is to employ a porous resin that has a functional group similar to that of the liquid solvent. When packed in a column such a resin will sorb selectively metal ion association complexes and thus permit some very useful separations. For example, a polyacrylate resin will extract gold(III) almost specifically from dilute aqueous chloride solution (11). The probable mechanism is one of solvation of the $AuCl_4^-$ or $H_3O^+ AuCl_4^-$ ion pair by the ester group of the resin. This is analogous to what occurs in the extraction of gold(III) by a liquid ester.

A few examples of non-ionic resins in inorganic chromatography may be noted. Tin(IV) can be analyzed by liquid column chromatography with sorption from 1 $\underline{M}$ hydrochloric acid onto Rohm and Haas XAD-11 resin (12). The tin is eluted by 0.1 $\underline{M}$ hydrochloric acid and is detected automatically through absorbance of its chloride complex in the ultraviolet spectral region.
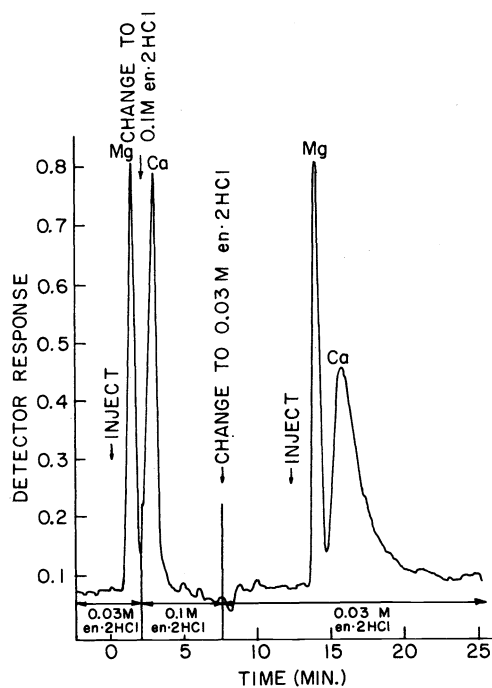
Fig. 4. Comparison of stepwise elution and single-stage elution of calcium and magnesium from a low-capacity cation exchange resin. J. S. Fritz and M. D. Arguello unpublished data, 1976.
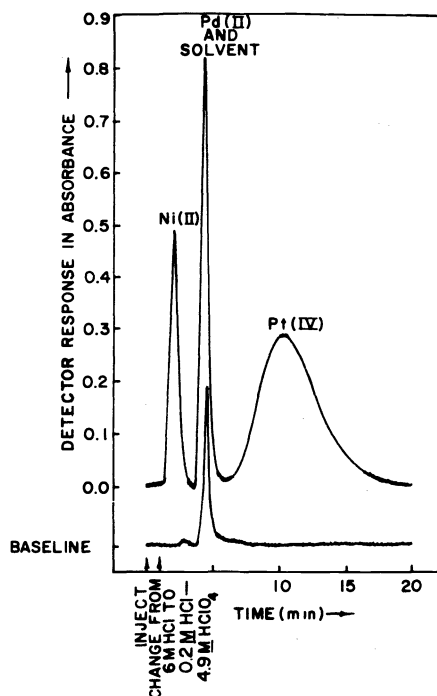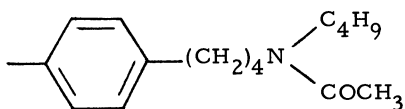

Fig. 5. Anion-exchange separation of nickel(II), palladium(II) and platinum(IV). M. D. Seymour and J. S. Fritz, Anal. Chem., 45, 1394 (1973).

A new amide resin has been developed in the author's laboratory that sorbs only uranium (VI) from aqueous nitrate solution (13). The resin has the following formula:

$$-\langle\text{benzene ring}\rangle-(CH_2)_4N\begin{smallmatrix}C_4H_9\\COCH_3\end{smallmatrix}$$

CHELATING ION-EXCHANGE RESINS

Resins containing a chelating functional group are attractive for analytical separations providing that the requisite selectivity for the desired metal ions can be attained. Chelating resins may prove useful for large-scale separations in the mining industry. Although the initial cost of such resins would be rather high, regeneration by low-cost acids is usually possible and the resins could be used over and over. Unlike solvent extraction which entails some solvent loss during processing, chelating resins are non-polluting.

Two resins for selective removal of gold from natural waters and other solutions have been described. One contains a benzylthiuronium functional group (14), while the other (15) has the following function:

$$-CH=N-\langle\text{benzene ring, SH top, SH bottom}\rangle-N=CH-$$
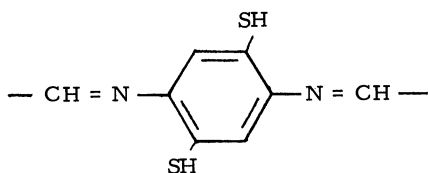
An efficient chelating resin must be porous and have enough cross-linking so that the resin does not undergo extensive swelling and shrinking in various solution media. Rohm and Haas XAD-2 or XAD-4 is an excellent starting material for synthesis of chelating resins. Conventional organic reactions can be carried out to introduce the desired functional groups.

One successful resin synthesized from XAD-4 has a thioglycolate functional group (16)

$$-\langle\text{benzene ring}\rangle-CO_2(CH_2)_6OCOCH_2SH$$
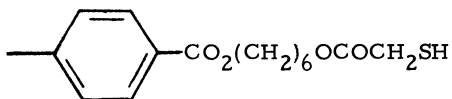
From 0.1 $\underline{M}$ acid this resin retains only silver(I), gold(III), mercury(II) and bismuth(III). These elements may be then separated from each other by sequential elution; bismuth with 0.5 $\underline{M}$ hydrochloric acid, silver with 2.0 $\underline{M}$ hydrochloric acid, and mercury with 6.0 $\underline{M}$ hydrochloric acid. Gold remains and can be eluted with an aqueous thiourea solution.

Another chelating resin made from XAD-4 has the 1,3-diaminopropanetetraacetic acid functional group (17). Most divalent metal ions are retained by this resin at pH 3 or above. The best selectivity appears to be in more acidic solutions. Uranium(VI), thorium(IV) and zirconium(IV) are strongly taken up from 0.01 $\underline{M}$ hydrochloric acid; most other metal ions are washed through the column by acid of this strength. Then uranium is eluted with 0.1 $\underline{M}$ hydrochloric acid, thorium with 4.0 $\underline{M}$ hydrochloric acid and zirconium with 1.0 $\underline{M}$ sulfuric acid. A separation of these metal ions using this resin with a liquid chromatograph is shown in Fig. 6. Thorium has been successfully determined in monazite and uranium has been determined in low-grade ores using this separation procedure.
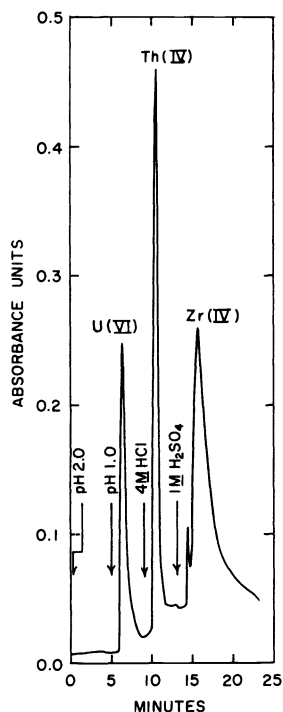
Fig. 6. Separation of metal ions on a column of XAD-4-diaminopropane-tetraacetic acid resin (17).

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