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ANION EXCHANGE SEPARATIONS OF METAL IONS IN THIOCYANATE MEDIA

by

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INTRODUCTION

Few ideal analytical methods are available in which a limited amount of substance can be determined in diverse matrices. Separation methods, therefore, have proven invaluable to the chemist as a means of isolating a substituent. The two primary reasons for such an isolation step are:

1. To remove the substituent from interferences and vice versa
2. To preconcentrate the substituent prior to analysis

In the area of inorganic analysis, much research has been done on the separation of metal ions. This vast amount of knowledge has been condensed in a book recently published by Korkisch (1) on modern methods of separating metal ions. In this book, the work of over 4,000 authors on separation methods involving more than 50 elements has been included, although the emphasis is on many of the less common elements. However, new separation methods are always needed as more problems present themselves and better separation methods are always welcome if they are faster, easier, and can be accomplished using mild conditions.

The purpose of this research is to investigate systematically the analytical potential of a liquid ion exchanger, Alamine 336, and a weak base macroreticular anion exchange resin, Amberlyst A-21, for the quantitative separation of metal ions in thiocyanate media. Thiocyanate ion was the ligand of choice because it does form complexes with numerous metal ions (2, 3). Furthermore, its analytical potential in weak base anion exchange systems has not been thoroughly investigated.

SURVEY OF LITERATURE

Liquid Ion Exchangers

Actually the first application of a liquid ion exchanger was in 1925 when Girard and Fourneau (4) discovered the extraction of bismuth halides by tetrahexadecylammonium chloride. The investigation of the extraction properties of amines did not begin until 1948 when Smith and Page (5) studied extraction of acids by solutions of high-molecular weight amines in organic diluents. Moore (6, 7, 8, 9) and Coleman and co-workers (10) have demonstrated the selectivity of this class of extractants for the analytical chemistry of a number of elements. They also have compared the extraction behavior of liquid and solid ion exchangers concluding the order of preference of anions for both systems is the same: $\text{ClO}_4^- > \text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{F}^-$. (Fritz and Gillette (11), in their studies on the liquid ion exchanger Alamine 336, have indicated that SCN^- may be placed somewhere between ClO_4^- and Cl^- .)

Kunin and Winger (12) as well as Keder and Wilson (13) have examined the basic technology of liquid ion exchangers, primarily amines and alkyl phosphoric acids, discussing the basic principles of their functioning, the relationship of their structure to selectivity, and details of their use.

Coleman et al. (14, 15) have listed many of the liquid anion and cation exchangers which are available and give some applications to inorganic separations in the Cl^- , NO_3^- , $\text{SO}_4^{=}$ and PO_4^{\equiv} systems. Cerrai (16) and Brinkman et al. (17, 18) have reported separations using paper and inert supports impregnated with liquid ion exchangers. Green (19), in 1964, produced a review of liquid ion exchangers in organic analysis;

since then Brinkman and co-workers (17, 18), Pierce and Henry (20), and Watanabe and Akatsuka (21) have used them for this purpose. Lindenbaum and Boyd (22) have investigated spectrophotometrically the organic phase in the extraction of transition metal halo-complex ions by amine extractants.

Alamine 336 was used by Fritz and Gillette (11) for the column chromatographic separation of sulfate from aromatic sulfonic acids and of individual aromatic sulfonic acids from each other.

Two papers on the theoretical aspects of amine extraction have recently appeared. McDowell and Coleman (23) have examined the interface mechanism for uranium extraction by di-n-decylamine sulfate in benzene. Frolov et al. (24) have systematized the data relating to the influence of various factors on the extraction properties of amines. This comprehensive summary includes some 467 references.

It is of interest to note that the concensus of the above investigators is that liquid ion exchangers have certain advantages over solid resins such as more rapid kinetics, higher selectivity, and a greater capacity. In addition, the liquid-liquid system is easier to operate and the extraction as well as the selectivity is easily controlled by choice of amine structure and diluent, variables which are not easily altered in a solid-liquid system. In general both liquid and solid ion exchangers, of analogous functional group, give a similar order of extraction for identical conditions. The distribution ratios, however, will usually be higher for the liquid ion exchangers.

The use of liquid ion exchangers in the extraction of metal ions from thiocyanate solution has been reported previously. Moore (25)

investigated the extraction of yttrium(III) from 7-8 M ammonium thiocyanate solutions into a xylene solution of methyldioctylamine (MDOA). Sheppard (26) examined the extraction behavior of americium, curium, berkelium, californium and einsteinium between aqueous 5 M ammonium thiocyanate and a xylene solution of tri-n-octylamine (TOA).

Several papers have been concerned with the extraction of cobalt from thiocyanate solution. Wilson and McFarland (27) utilized tri-caprylmethylammonium (Aliquat 336) thiocyanate as a selective extraction agent in the spectrophotometric determination of cobalt(II). The quaternary amine salt was dissolved in benzene and the extraction solution, containing sodium citrate to mask iron(III), was buffered at pH 8.0. One equilibration with a scrub solution containing sodium thiosulfate, sodium citrate, and sodium thiocyanate removes copper(II) and nickel(II) interferences. Selmer-Olsen (28) extracted cobalt thiocyanate with triisooctylamine (TIOA) dissolved in carbon tetrachloride and spectrophotometrically determined cobalt(II) in the green organic phase. A Beer's law plot was obtained for the range 0-10 mg cobalt. Watanabe and Akatsuka (21) used TOA dissolved in various diluents to study the extraction of cobalt(II) from aqueous thiocyanate solutions. They concluded that in all cases the species extracted was bis(tri-n-octylammonium) tetrathiocyanatocobaltate(II), $[(R_3NH)_2Co(SCN)_4]$. They also reported that the smaller the dielectric constant of the diluent, the larger the distribution ratio with the exceptions of nitrobenzene and chloroform.

Brinkman et al. (18) used five different liquid ion exchangers impregnated on paper and thin layer adsorbents to study the behavior of six

metal ions in thiocyanate media. Plots of R_f versus molarity of thiocyanate (0-10 M) are given for copper(II), cadmium(II), lead(II), cobalt(II), manganese(II) and silver(I). The data revealed possible separations of cobalt, manganese and nickel and cadmium and zinc. Huff (29) applied the liquid extraction data of Moore (30) and Gerontopoulos (31) to column partition chromatographic studies of americium, yttrium and the rare earths using Aliquat 336 as the sorbed liquid and aqueous eluents of 0.1 M to 4 M ammonium thiocyanate. Huff obtained linear plots of log distribution ratio versus log ammonium thiocyanate concentration and log distribution ratio versus log percent Aliquat 336 in xylene.

Solid Ion Exchange Resins

A large amount of information has been reported on the anion exchange behavior of metals in a number of media. Probably the most publicized work has been that of Kraus and Nelson (32) who have reported the behavior of most metals in the periodic table over a broad range of hydrochloric acid concentrations. Their work and indeed much of the work reported in the literature involves the use of a strong base anion exchange resin. Somewhere along the way, weak base resins were deemed inferior to strong base resins, probably because the latter can be used over a much wider pH range.

Systematic investigations of the exchange behavior of metals between thiocyanate media and ion exchange resins, both anion and cation, have been reported. Several of these papers have been concerned with the behavior of lanthanide and actinide metals. Hamaguchi et al. (33, 34) used Diaion SK-1, a cation exchange resin very similar to Dowex 50,

to study the sorption of rare earths from eluent mixtures of ammonium thiocyanate (0.1 M - 2.0 M) and hydrochloric acid (0.2 M - 3 M). They also described a separation of scandium(III) from thorium(IV), zirconium(IV), iron(III), titanium(IV), aluminum(III) and calcium(II) using thiocyanate-hydrochloric acid eluents. Hamaguchi et al. (35) described a method for the separation of scandium(III) from rare earths(III) and thorium(IV) using Dowex-1X8 and an eluent of 3 M hydrochloric acid. The column is pretreated with a solution of 2 M ammonium thiocyanate in 0.5 M hydrochloric acid.

Surls and Choppin (36) studied the ion exchange behavior of many tripositive actinides, lanthanides and yttrium with Dowex-1 anion exchange resin and ammonium thiocyanate solutions 0 - 2.5 M. They found stronger complexing of actinides with thiocyanate and offer several explanations for this behavior. Coleman et al. (37) found the same complexing strength using a quaternary amine type anion exchange resin, Bio-Rad 1X10, to determine distribution ratios of trivalent americium, yttrium, lanthanum, europium and ytterbium in 0.5 M - 1.0 M ammonium thiocyanate solutions.

The anion exchange-thiocyanate system has not been restricted to the study of the lanthanide and actinide series. Lure and Filippova (38) used ammonium thiocyanate eluent and a cation exchange resin for the separation of bismuth(III) from copper(II) or antimony. Teicher and Gordon (39) separated iron(III) from aluminum(III) using the strong base anion exchange resin Amberlite IRA-400A and an eluent of 0.3 M ammonium thiocyanate adjusted to pH 1 with hydrochloric acid. Korkisch and Hecht (40) devised a separation of aluminum(III), gallium(III) and iron(III) by

sorbing the thiocyanate complexes of gallium and iron on Amberlite IRA-400. Aluminum passed directly through the column and gallium and iron were desorbed with dilute hydrochloric acid.

Turner et al. (41) used Dowex-1X8 to study the sorption of some 13 metal ions from aqueous potassium thiocyanate solutions. Distribution coefficients were measured as a function of thiocyanate concentration (0 - 8 M) for zinc(II), cobalt(II), cadmium(II), scandium(III) and silver(I). Two separations described are chromium-scandium and nickel-cobalt-iron.

Kawabuchi et al. (42) reported a specific method for the separation of rhenium(VII) from 38 metal ions on Dowex-1 in thiocyanate-chloride media. Rhenium exhibited a rather unique behavior in that the distribution ratio had a minimum value at 0.5 M ammonium thiocyanate and increased at both higher and lower concentrations of ammonium thiocyanate at a fixed concentration of 0.5 M hydrochloric acid (43).

Majumdar and Mitra (44) studied some 20 metal ions. They examined the influence of an increased amount of thiocyanate on the nature of the complexes formed and devised separations on both cation and anion exchange columns. Nine separations of ions from two and three component mixtures were performed using the anion exchange resin IRA-400. Using Amberlite IR-120, a cation exchange resin, separations of ions from two to five component mixtures were achieved.

Most recently Strong (45) has used a strong base anion exchange resin for the sorption of cobalt(II) from aqueous thiocyanate solutions.

The only work reported on the application of weak base anion exchange resins for the selective sorption of metal ions from thiocyanate

media seems to be a series of three papers by Kuroda and co-workers (46, 47, 48). These workers used the weakly basic anion exchanger, diethylaminoethyl (DEAE) cellulose, varying the pH from 1-6 and ammonium thiocyanate concentration from 0.005 M to 1.0 M. A systematic study of the behavior of many metal ions showed that few are sorbed from dilute thiocyanate media onto the cellulose exchanger DEAE. Using this fact several separation methods were developed.

Rhenium(VII), molybdenum(VI) and tungsten(VI) were separated for ratios of molybdenum or tungsten to rhenium as large as 1000:1.

Mercury(II) was highly adsorbed and this allowed a rapid and highly selective separation of mercury from about 40 metal ions.

Platinum(IV) and palladium(II) also are strongly adsorbed under appropriate conditions. It was possible to separate and concentrate these metal ions from a large quantity of base metals such as iron, cobalt, nickel, copper, zinc and lead. As little as 1 mg of platinum(IV) and/or palladium(II) can be quantitatively separated from as much as 20-25 mg of base metals on a small column of DEAE in the thiocyanate form. Furthermore, the noble metal ions adsorbed are easily stripped from DEAE.

THEORY AND BACKGROUND

The following discussions on the theory of solvent extraction, chromatography and ion exchange are not meant to be rigorous. The purpose is to supply sufficient background information necessary for the presentation of the results of the present research. More detailed discussions concerning solvent extraction may be obtained in the general treatments given by Berg (49), Fomin (50), Morrison and Freiser (51) and in the "Treatise on Analytical Chemistry" (52). Chromatographic theory has been thoroughly treated by Giddings (53) and Heftman (54) and the subject has been reviewed by Testa (55). A bibliography of reversed-phase chromatography complete with abstracts has been presented by Eschrich and Drent (56).

More detailed information on the theory and application of ion exchange chromatography may be found in books by Helfferich (57), Samuelson (58) and Marinsky (59).

Liquid-Liquid Solvent Extraction

Solvent extraction enjoys a favored position among the various separation techniques because of its ease, simplicity, speed and wide scope. The method usually involves the distribution of a solute, initially present in an aqueous phase, into an immiscible organic solvent. For all phase distributions, the classical rule of Gibbs is instructive:

$$P + V = C + 2 \quad (1)$$

where P is the number of phases, V is the variance or degrees of freedom and C is the number of components. For the ideal solvent extraction

system $P = 2$, $C = 3$ and thus $V = 3$. If temperature and pressure are held constant, the Nernst distribution law states that a solute will distribute between two essentially immiscible solvents in such a manner that at equilibrium the ratio of concentrations of the solute in the two phases will be a constant. When the experimental data do not conform to the Nernst distribution law the discrepancy may be due to one or more of three distinct effects:

1. The solute species may polymerize, dissociate, or associate with other dissolved species. A complex set of equilibria may result such that the analytically determined ratio of concentrations in the two phases is dependent on total solute concentration.
2. The Nernst distribution law holds only if activity coefficients remain constant in the two phases, independent of solute concentration. Maintaining constant ionic strength in the aqueous phase will usually minimize variations in activity coefficients.
3. A given partition coefficient refers to the partition equilibrium between two particular solvent compositions. Any change in the composition therefore will alter the value of the partition coefficient.

The approximations inherent in the distribution law are best understood in terms of a thermodynamic explanation of the conditions existing in each phase at equilibrium. At equilibrium the chemical potentials, μ_s , of the solute in each phase are equal:

$$\mu_{s(o)} = \mu_s \quad (2)$$

For a standard state of a 1 molal ideal solution,

$$\mu = \mu^0 + RT \ln a$$

where a is the activity, defined as the product of the activity coefficient, γ , and the molal concentration m .

Substitution into equation 2 yields the following expression:

$$\mu_{s(o)}^0 + RT \ln m_{s(o)} + RT \ln \gamma_{s(o)} = \mu_s^0 + RT \ln m_s + RT \ln \gamma_s \quad (3)$$

in which μ_s^0 represents the standard state chemical potential of the solute, m_s is the solute concentration in molality and γ_s is the solute molal activity coefficient. The subscript (o) refers to the organic phases while no subscript implies the aqueous phase. Equation 3 may be rearranged to give

$$\frac{m_{s(o)}}{m_s} = \frac{\gamma_s}{\gamma_{s(o)}} e^{-(\mu_{s(o)}^0 - \mu_s^0)/RT} \quad (4)$$

For most systems the quantity of solute is small enough to allow γ_s and $\gamma_{s(o)}$ to remain constant and if mutual solubilities are not altered significantly the μ_s^0 values are also constant. Thus equation 4 reduces to

$$\frac{m_{s(o)}}{m_s} = \frac{\gamma_s}{\gamma_{s(o)}} K = P \quad (5)$$

where K is a constant for the system at constant temperature and P is the molal distribution coefficient.

The above considerations apply to the distribution of one species between two phases. Of more practical interest to the extraction chemist is the stoichiometric distribution of the component of interest regardless of its composition i.e., the total amount extracted compared to the amount remaining. Thus the volume distribution ratio D_v is defined as

follows:

$$D_v = \frac{\text{total concentration in organic phase}}{\text{total concentration in aqueous phase}} = \frac{[C]_o}{[C]} \quad (6)$$

Another means of expressing the completeness of extraction is the percentage of extraction, % E, which is related to the volume distribution ratio:

$$\% E = \frac{100 D_v}{D_v + V/V_o} \quad (7)$$

where V and V_o are the volumes of the aqueous and organic phases respectively. Figure 1 graphically illustrates the relationship expressed in equation 7. Experimental work is usually simplified by choosing V and V_o to be equal. When multiple extraction is employed using a fresh organic phase, the total percentage of solute extracted after n extractions ($V = V_o$) is given by:

$$\% E = 100 - \frac{100}{(D_v + 1)^n} \quad (8)$$

A term called the separation factor, α , is used to determine the effective separation of two components:

$$\alpha = \frac{D_{v_1}}{D_{v_2}} \quad (9)$$

where D_{v_1} and D_{v_2} are the volume distribution ratios of the two substances to be separated. In practice $D_{v_1} > D_{v_2}$ so that $\alpha > 1$.

In order to obtain a complete separation D_{v_1} must be much larger than D_{v_2} ; the latter should be small enough to be considered as essentially not extracted. Although countercurrent extraction procedures have been successfully employed they are generally to be considered as impractical for analytical separations. These methods tend to be time consuming and usually require a multitude of extraction vessels. Reversed-phase column

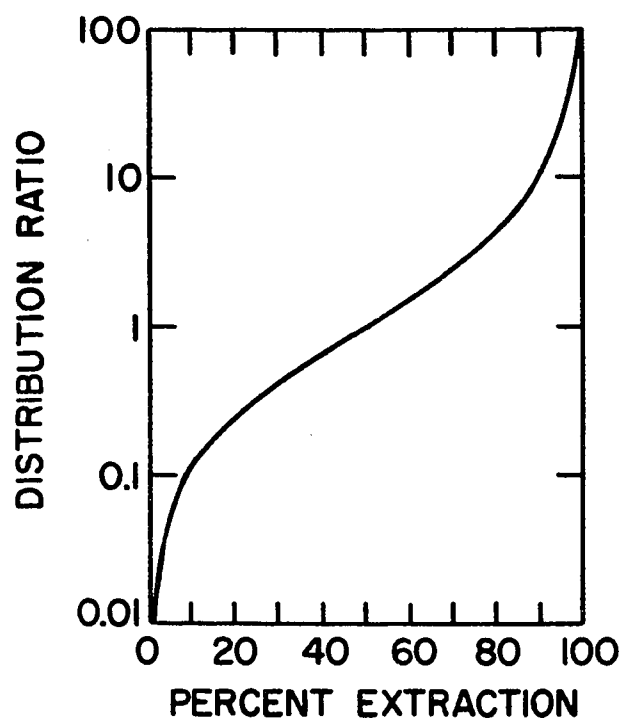


Figure 1. Relation of distribution ratio to percent extraction.
[After Morrison and Freiser (51)]

chromatography seems to be the method of choice for separations that are not simply all or nothing.

Reversed-Phase Column Chromatography

In chromatography, as in solvent extraction, the components to be separated are distributed between two phases. Here one phase is stationary, a bed of large surface area, while the other phase is mobile, a fluid that flows through and along the stationary bed. In liquid-liquid partition chromatography the retention properties of the stationary phase are due to an extractant sorbed onto an inert support. When the sorbed liquid is more polar than the mobile phase the method is called liquid-liquid partition chromatography. In the reverse situation, i.e. sorbing the less polar liquid onto the support and eluting with the more polar solvent, the method is called reversed-phase liquid-liquid partition chromatography. Both situations involve the transference of solute between two phases and the general behavior is referred to as sorption.

The reversed-phase technique used in this work will be referred to simply as reversed-phase column chromatography, thereby indicating the sorption of Alamine 336 onto an inert support packed in a column and eluted with an aqueous solvent.

The principles involved in reversed-phase column chromatography can be thought of as being related to liquid-liquid extraction. In general the various components will move down the column at different rates which are inversely proportional to their volume distribution ratios (assuming kinetics are not a factor). In fact solvent extraction volume distribution ratios may be related to column behavior via the relationship:

$$\bar{V} = V_M + D_V V_S \quad (10)$$

where \bar{V} is the retention volume, the volume necessary to elute a substance to its maximum concentration. V_M is the volume of the mobile phase or interstitial volume and V_S is the volume of the stationary phase. A derivation of equation 10 is presented in the appendix.

In column sorption chromatography non-ideality results because the solute does not form an ideal solution with each of the two immiscible phases. One way to treat this behavior is to use the molal distribution coefficient as defined in equation 5. Then for cases where ideal behavior is met, the molal distribution coefficient will reduce to the simple volume distribution ratio.

Another way of expressing non-ideal behavior is to derive a distribution function which is directly related to the concentrations of solute in the two phases. This is the method most often used when dealing with adsorption phenomena. For chromatographic work done in dilute solution, three types of adsorption isotherms are of interest. These are shown in Figure 2. Type (a) is for the ideal case, i.e. the equilibrium distribution is independent of concentration. Type (b) is the generalized Langmuir isotherm and leads to "tailing" of the elution curve. Type (c) is the inverse of (b) and leads to "fronting" of the elution curve, a phenomena occurring considerably less often than tailing.

If the volume distribution ratios of two substances are known, a reversed-phase column can be designed to effect their separation. In order that columns of reasonable length and capacity may be used, somewhat arbitrary limits may be imposed upon distribution ratios and separation factors needed in practice. Where possible, the distribution ratio

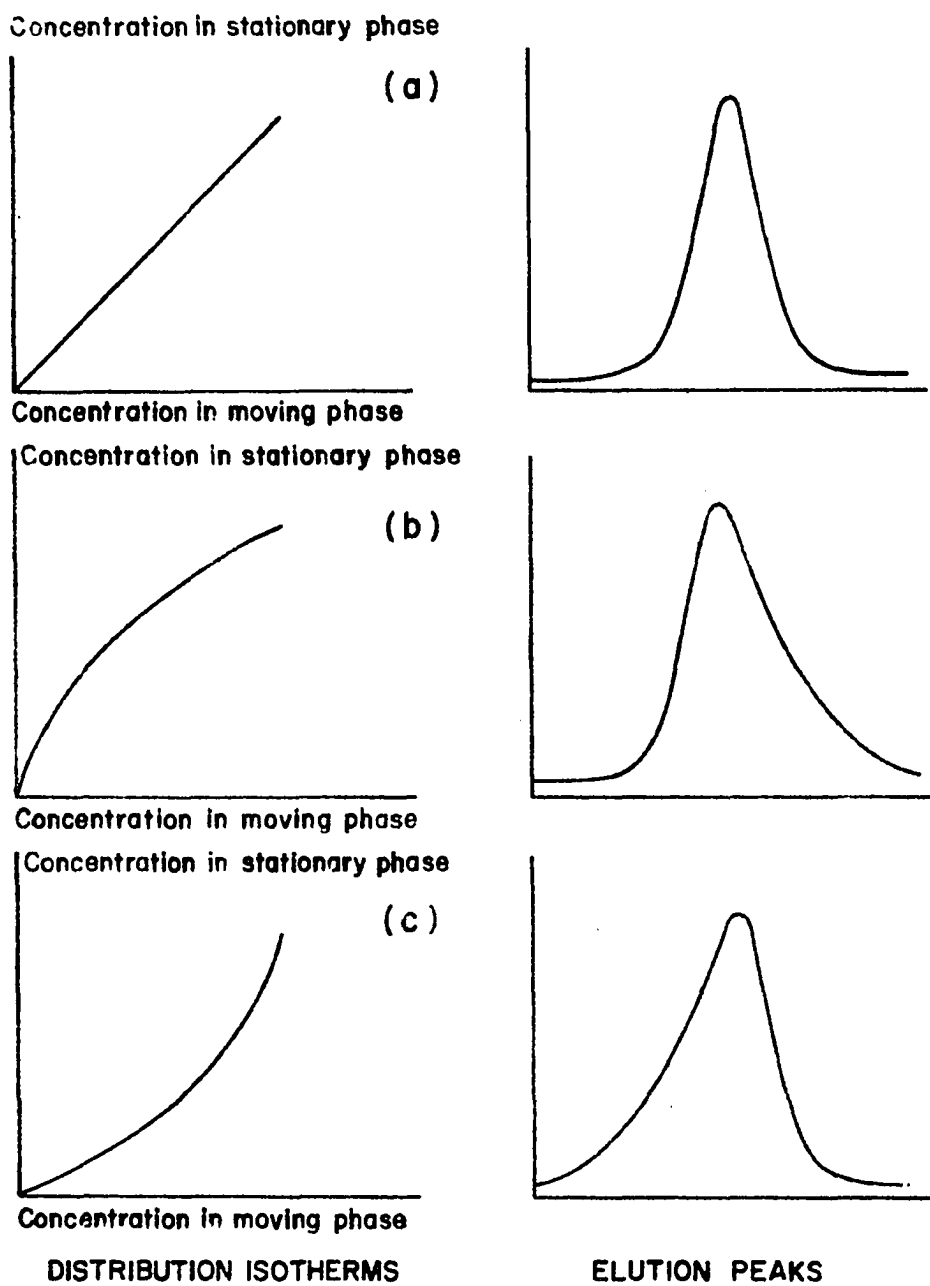


Figure 2. Typical adsorption isotherms and their effects on the shape of the elution curve. [After Irving and Williams (52)]

of the substance being retained on the column should be greater than 10 while that of the substance being eluted should be less than one thereby yielding a separation factor greater than 10.

Ion Exchange

The basic principle of the ion exchange method is simply the exchanging of ions of the same charge, either positive or negative, with the help of an ion exchanger which may be either liquid or a solid resin. The important characteristic difference between sorption and ion exchange chromatography is that the latter is stoichiometric. Every ion removed from the exchanger is replaced by an equivalent amount of another ionic species of the same charge. The process is considered to be reversible and at trace concentrations can be assumed to obey a linear distribution isotherm.

Ion exchange chromatography is of great value in the separation of ions of similar properties. By judicious choice of complex formation and other equilibria in solution, separation factors may be obtained which are not possible in complex free media.

The retention volume, \bar{V} , may also be defined for an ion exchange column analogous to equation 10 for sorption chromatography:

$$\bar{V} = X(D_v + \epsilon) \quad (11)$$

The resin bed volume is X , ϵ is the void fraction of the column and D_v is the volume distribution ratio defined as:

$$D_v = \frac{\frac{\text{millimoles of sorbed solute}}{\text{milliliters of bed volume}}}{\frac{\text{millimoles of solute in solution}}{\text{milliliters of solution}}}$$

In practice it is easier to measure the weight distribution coefficient, D_w , defined as:

$$D_w = \frac{\frac{\text{millimoles of sorbed solute}}{\text{grams of dry resin}}}{\frac{\text{millimoles solute in solution}}{\text{milliliters of solution}}}$$

If the resin bed density, ρ , is defined as

$$\rho = \frac{\text{grams of dry resin}}{\text{milliliters of bed volume}}$$

then D_w and D_v are related as follows:

$$D_w \rho = D_v \quad (12)$$

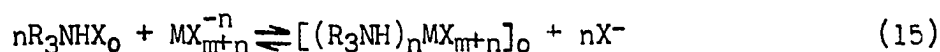
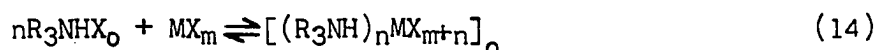
The product $X\rho$ in equation 11 corresponds to the term V_M in equation 10.

The separation factor, α , is again defined as the ratio of the distribution coefficients of the two substances to be separated. In practice the factor should be at least 4 with the higher distribution coefficient being at least 10.

The term liquid ion exchanger refers to those high molecular weight acids and bases which possess low solubility in water and high solubility in water-immiscible solvents. Since the anion attached to the ammonium cation (for bases) is capable of exchanging for other anions and because they resemble the resin exchangers in many of their properties the misnomer "liquid ion exchanger" has come about. The name is a misnomer because the role of the amine is not completely clear and the extraction of acids and metal salts by solutions of amines in organic solvents is an extremely complex problem.

Various spectral results (60, 61) have shown that the complexes most commonly formed in the extraction of metal salts by solutions of high-molecular weight amines are those of the type $(R_4N^+)_n MX_{m+n}^{-n}$ (where X is

an anion and M the central atom of the metal). The first coordination sphere of the metal ion does not contain the alkyl ammonium ion. In the simplest cases then, the extraction of acids and metal salts by amines can be described by the following heterogeneous chemical equilibria:



where the subscript o refers to the organic phase and no subscript implies the aqueous phase. Equation 14 may be described as adduct formation while equation 15 is ion exchange. Although these alternative routes may sound drastically different both equations are thermodynamically equivalent as are the measurable net results. McDowell and Coleman (23) have studied the kinetics of the process and indicate that the two reactions probably occur simultaneously. They determined the kinetics of transfer of $^{35}\text{SO}_4$ between organic (di-n-decylamine sulfate in benzene) and aqueous phases (acid-sodium sulfate) in the extraction of uranium by an amine sulfate. The transfer rates were faster when the aqueous sulfate concentration was $\geq 0.05 \text{ M}$ indicating anion exchange of $\text{UO}_2(\text{SO}_4)_2^{-2}_{(\text{aq.})}$ for $\text{SO}_4^{-2}_{(\text{org.})}$. In contrast the rates were slower when the aqueous sulfate concentration was $< 0.01 \text{ M}$ (essentially no aqueous uranium existing as anion) suggesting neutral transfer.

Thus amines lie between those extractants which have a "purely" anion exchange extraction mechanism and those of the simple and complex ester type. In cases of low equilibrium acidity in the aqueous phase the latter act as ligands and form coordination compounds in the organic

phase. In cases of high acidity they form onium and hydroxonium compounds (24). The actual rates of amine extractions are fast and in general equilibrium is reached in a few minutes. Only in exceptional cases when the process is complicated by hydrolysis, polymerization or other phenomena do the distribution coefficients change slowly with time.

The technique employed in using liquid ion exchangers is identical to that employed in general solvent extraction separations in that there is selective transfer of solute between two immiscible phases, an aqueous phase and an organic phase containing the exchanger. Thus it can be said that liquid ion exchangers combine the advantages of both solvent extraction and ion exchange.

One major difficulty sometimes associated with liquid ion exchangers is the formation of emulsions between the organic and aqueous phases. There are several conditions which may be controlled to minimize the formation of stable emulsions such as temperature, choice of acid, amount of free acid in the aqueous phase, organic diluent for the exchanger, concentration of the exchanger, and relative volumes of organic and aqueous phases.

Another possible problem associated with any reversed-phase column is "bleeding" of the sorbed liquid from the column. This undesirable behavior may be eliminated by not overloading the support with extractant and by using previously equilibrated eluents.

EXPERIMENTAL

Apparatus

pH Meter: A Corning Model 12 pH meter equipped with a Sargent combination electrode was used for pH measurements.

Spectrophotometer: A Bausch and Lomb Spectronic 600 spectrophotometer was used for spectrophotometric measurements. A pair of matched Pyrex cuvettes having a one centimeter path length were used for spectrophotometric determinations.

Radiochemical equipment: A Nuclear Chicago Anti-Walk Single Channel Analyzer Model 27352 spectrometer was used to isolate gamma emissions from the tracers used. The detector used was a 3 x 3 inch NaI(Tl) scintillation crystal obtained from the Harshaw Chemical Company. Pulses received from the spectrometer were counted with a Nuclear Chicago Decade Scaler Model 27104.

Atomic absorption spectrophotometer: A Perkin Elmer Model 290 atomic absorption spectrophotometer equipped with a Perkin Elmer combination Co, Cr, Cu, Mn, Ni hollow cathode lamp was used for the atomic absorption analysis of Co, Cu and Ni.

Grinding mill: A Quaker City Mill Model 4-E was used to grind all resins.

Sieves: A U.S. Standard Sieve Series from LaPine Scientific Company was used to sieve all resins, usually to obtain an 80-100 cut.

Motor drive stirrer: A Bodine Motor from Talborp Instrument Corporation was equipped with a slightly bent Teflon rod to automatically stir both layers in a separatory funnel.

Automatic shaker: A Burrell Wrist Action Shaker was used to shake 125-ml Erlenmyer flasks containing ion exchange resin and aqueous solution of metal ion.

Chromatographic columns: Chromatographic columns of various lengths and diameters were made by joining two sections of Pyrex brand glass. An upper larger diameter section served as an eluent reservoir and a lower smaller diameter section contained the column support, with the aid of a Dynel wool plug. Then a one-millimeter microbore stopcock with a Teflon plug was incorporated into the bottom of the column. Flow rates were regulated simply by adjusting the stopcock.

Laboratory ware: Kimble "Kimax" 125-ml Squibb separatory funnels with Teflon stopcocks were used in extraction studies. Kimble "Kimax" burettes and Corning "Pyrex" pipettes were used throughout. A 2-ml micrometer burette from Cole-Parmer Instrument and Equipment Company was used for some sample additions to columns.

Reagents

Alamine 336: Commercial Alamine 336 (tricapryl tertiary amine) was obtained from General Mills, Inc. and used without further purification. The Company gives a typical analysis as showing:

Tertiary amine content.....	95%
Secondary amine content.....	1%
Primary amine content.....	0.2%
Water.....	0.0%

Alamine 336-S, a reagent grade of Alamine 336, is available as 99-100% tertiary amine.

The Alamine 336 (R_3N) was prepared as a dilute solution in toluene and then converted to the thiocyanate form. Fritz and Gillette (11) have shown via potentiometric titration that a

10% (v/v) solution of R_3N in toluene = 0.2 M

20% (v/v) solution of R_3N in toluene = 0.4 M

30% (v/v) solution of R_3N in toluene = 0.6 M

The amine solution is converted to the thiocyanate form by equilibrating three times with an equal volume of a solution 1.0 M in KSCN and 0.5 M in HCl, followed by an extraction with an equal volume of distilled water.

The original amine solution was yellow while the thiocyanate salt form is orange to red presumably due to traces of iron(III) combining with thiocyanate. A solution of Alamine 336 in toluene converted to the thiocyanate form will subsequently be referred to as the exchanger.

Organic solvents: Purified toluene from the J.T. Baker Chemical Company was used to dilute Alamine 336. Absolute Methyl Alcohol from Mallinckrodt Chemical Works and Acetone from J.T. Baker Chemical Company were used in stripping metal ions from various chromatographic columns.

Indicator solutions: Xylenol Orange (3,3'-bis(N,N'-dicarboxymethyl)-aminomethyl)-o-cresol sulphonephthalein), obtained from Lamont Laboratories, Naphthyl Azoxine S (NAS, 8-hydroxy-7-(6-sulfo-2-naphthylazo)-5-quinoline-sulfonic acid disodium salt) obtained from Eastman Chemical Company were each prepared and used as a 0.5% aqueous solution.

Stock solutions: In almost all cases the reagent grade chloride, nitrate, or oxide of the metal ion was used and diluted to a final acid

concentration of 0.5 M unless hydrolysis was a problem. Gallium and indium solutions were prepared by dissolving the 99.9% pure metal in concentrated hydrochloric acid containing a small amount of nitric acid, and then diluting with distilled water. Titanium(IV) was prepared by dissolving an appropriate aliquot of titanium tetrachloride in concentrated hydrochloric acid and then carefully diluting with distilled water.

NBS Standard Sample 124d was dissolved in concentrated hydrochloric and nitric acid before being diluted to a final acid concentration of approximately 2 M.

EDTA: Solutions of EDTA were standardized against zinc(II) using Naphthyl Azoxine S indicator. For back-titrations, the EDTA solution was standardized relative to a copper(II) or a thorium(IV) solution of approximately equal molarity.

Eluents: The eluents used for column separations were acidic solutions of potassium or ammonium thiocyanate. The acid concentration varied from 0.01 to 0.5 M in hydrochloric acid. Eluents were prepared immediately before use by mixing equal volumes of hydrochloric acid and potassium or ammonium thiocyanate of appropriate molarity.

Column supports: Chromosorb W (non-acid washed, 80-100 mesh) was obtained from Johns-Manville Products Corporation. This diatomaceous earth support was washed with 6 M hydrochloric acid, distilled water, acetone, and oven dried at 110° before use.

Amberlite XAD-2¹, an inert crosslinked polystyrene polymer was obtained from Rohm and Haas Company, as a free sample, in the form of 20-50 mesh hard insoluble beads. This macroreticular adsorbent was ground in a grinding mill and sieved to obtain the proper mesh size. This procedure seems to produce a large percentage of fines so that the fraction collected as 80-100 mesh is small compared to the total amount of resin ground (~20%). The sieved product was washed first with 6 M hydrochloric acid then methanol, and air dried.

Amberlyst A-21 is a macroreticular weak base anion exchange resin in the $-N(CH_3)_2$ form. It was obtained as a free sample from Rohm and Haas Company in the form of 20-50 mesh hard insoluble beads which were ground in a grinding mill and sieved to obtain an 80-100 mesh cut. Again, a great deal of fines were produced. The final product was washed with methanol and air dried.

Techniques

Batch distribution ratios: For solvent extraction work equal volumes of organic and aqueous phases were used whenever possible. The phases were stirred automatically for given time periods with a motor-driven stirrer rotating a bent Teflon rod. Aliquots of the aqueous phase were taken and the metal ion concentration determined using an appropriate analytical method. The amount of metal ion in the organic phase was determined by material balance.

¹Amberlite is a registered trademark of the Rohm and Haas Company, Philadelphia, Pennsylvania. For further information on these macroreticular resins, the reader is referred to the Rohm and Haas booklet, "Amberlite XAD Macroreticular Adsorbents".

For ion exchange work, 2.0 g of dry equilibrated resin were added to 125-ml Erlenmeyer flasks containing either 28 or 30 ml of metal ion solution of the appropriate thiocyanate concentration. The flasks were automatically shaken for 30 minutes and aliquots of the aqueous phase taken and analyzed. The amount of metal ion retained by the resin was determined by material balance.

Sample preparation: Synthetic sample mixtures for column separation studies were prepared by mixing given volumes of standardized metal ion solutions and eluent. Concentration ranges were adjusted so that the sample volume added to the column was either one or at most two milliliters.

Standardizations and standard curves: The practice of treating standard and sample solutions in like manner was maintained throughout this work. Thus each sample determined was compared to a control run insuring that the results indeed were representative. For example, the atomic absorption calibration curves for copper, cobalt and nickel were obtained by taking standard solutions of these metal ions and simulating the separation process before determining their absorbance.

Column preparation: For reversed-phase column chromatographic work, three methods of preparing the column support were used. For work with Chromosorb W as the support, the method of preparation involved dissolving X ml of Alamine 336 in ether and then continuously slurring this solution with Y g of support till no ether fumes were present. For increased capacity it was possible to sorb 40 ml of Alamine 336 onto 35 g of support, but any further increase resulted in the amine bleeding off the column when eluting. The dry coated support was slurried in a

solution 1.0 M in potassium thiocyanate and 0.5 M in hydrochloric acid, then poured into a column and allowed to settle via gravity flow. Some tamping with a glass rod was also performed to insure a firmly packed column. A Dynel wool plug was snugly fitted at the top of the bed to prevent disturbance when adding sample or eluent.

For the XAD-2 support two methods of preparation were tried, both giving the same net results:

1. X g of XAD-2 were allowed to sit in Y ml of exchanger solution overnight before slurrying and packing into a column. A Dynel wool plug was placed on top of the bed and the interstitial volume, V_M , was displaced with the appropriate equilibrated eluent.
2. X g of XAD-2 were slurried in toluene and packed into a column placing a Dynel wool plug on top of the bed. The interstitial toluene was displaced with distilled water and then Y ml of exchanger solution was passed through the column. The interstitial exchanger solution, V_M , was displaced with the appropriate equilibrated eluent.

By collecting the column effluent and noting the volumes Y and V_M , values for the volume of exchanger solution sorbed to the support, V_S , were obtained. Then the retention volume, \bar{V} , for a metal ion of known volume distribution ratio, D_V , could be calculated using equation 10.

$$\bar{V} = V_M + D_V V_S \quad (10)$$

The A-21 resin was slurried with water, poured into a column, and allowed to settle via gravity flow. A Dynel wool plug was placed on top of the bed. The column was converted to the thiocyanate form by washing

with a solution 1.0 M in potassium thiocyanate and 0.5 M in hydrochloric acid. Prior to addition of a sample, the column was washed with the first eluent to be used for the sample. The void fraction, ϵ , of the column was measured by displacing the interstitial aqueous solution with cyclohexane. The bed volume, X , was calculated from column dimensions and the retention volume, \bar{V} , of a metal ion of known volume distribution ratio could be calculated from equation 11.

$$\bar{V} = X(D_v + \epsilon) \quad (11)$$

Analytical Determinations

Titration methods: Further details of any of the following methods involving Naphthyl Azoxine S (NAS) indicator may be found in a paper by Fritz et al. (62). In some cases back-titration procedures were used where direct titrations were applicable. Although the direct method was applicable to standard solutions it was not always as trouble-free for the metal ion after extraction or separation. Since a distinct color change always occurred in the back-titration, the end point was determined with consistency throughout.

Aluminum(III), bismuth(III), cadmium(II), cobalt(II), gallium(III), mercury(II), indium(III), nickel(II), lead(II) and zinc(II) were determined by adding excess EDTA, buffering the solution to pH 5-6 with pyridine and ammonia, and back-titrating with standard copper(II) using NAS indicator.

Magnesium(II), calcium(II), strontium(II) and barium(II) were determined using the method of Fritz et al. (63). The procedure involves a direct titration with EDTA using a mixed Arsenazo I indicator. The

solution was buffered at pH 10 using a THAM-ammonia buffer. (THAM is 2-amino-2(hydroxymethyl)-1,3-propanediol.)

Copper(II) was titrated directly with EDTA at pH 5 using pyridine and ammonia to adjust the acidity. The indicator used was NAS.

Rare earths(III) were determined by direct EDTA titration at pH 6 using a pyridine buffer and Arsenazo I indicator.

Iron(III) was determined in two ways:

1. Excess EDTA was added, the solution buffered to pH 2 with ammonia and back-titration carried out with standard thorium(IV) using Xylenol Orange indicator.
2. Excess EDTA was added, the solution buffered to pH 5.5 with pyridine and ammonia and back-titration carried out with standard copper(II) using NAS indicator.

Method 2 was most frequently used but it was checked with method 1 to insure there was no hydrolysis of iron(III) occurring.

Hafnium(IV) and zirconium(IV) were determined by back-titrating excess EDTA with standard thorium(IV) at pH 2.0 using Xylenol Orange indicator.

Manganese(II) was titrated directly with EDTA at pH 8.5, adjusted with ammonia-ammonium chloride buffer, using NAS indicator. Ascorbic acid was added before each titration to insure complete reduction to manganese(II).

Scandium(III) was determined by back-titration of excess EDTA with standard copper(II) at pH 4, acetate buffer, using NAS indicator.

Tin(IV) was determined by the following procedure. The solution was acidified to pH 1 or below and 2 g of sodium chloride added. After

addition of excess EDTA the solution was boiled for five minutes, cooled to room temperature and the pH adjusted to 6 with pyridine and ammonia. The titration was completed with standard copper(II) using NAS indicator.

Thorium(IV) was determined by back-titration of excess EDTA with copper(II) at pH 3, adjusted with ammonia, using NAS indicator.

Titanium(IV) was determined by adding excess EDTA, adjusting to pH 4.5 with ammonium acetate and ammonia, adding several drops of 3% hydrogen peroxide and back-titrating with standard copper(II) using NAS indicator.

Vanadium(IV) was determined by back-titration of excess EDTA with standard copper(II) at pH 6, acetate buffer, using NAS indicator. Some ascorbic acid was added before the titration to insure all the vanadium present was in the plus four state.

Spectrophotometric methods: Uranium(VI) was determined as the Arsenazo I complex at pH 7.5 according to the method of Fritz and Richard (64).

Palladium(II) was determined by measuring the absorption of its chloro-complex, $\lambda_{\max} = 225 \text{ nm}$, in 0.1 M hydrochloric acid.

Spot tests: The elution behavior of metal ions on chromatographic columns was qualitatively established by performing a colorimetric spot test on the effluent. This procedure works well for determining the beginning and end of an elution curve and in some cases a semi-quantitative elution profile curve could be constructed due to the varying intensities of the spots. Table 1 lists the reagents used and the affirmative tests obtained for several metal ions. In addition several

Table 1. Colorimetric spot tests used to determine the presence or absence of metal ions

Metal ion	Reagent used	Positive test
Alkaline earths(II)	Arsenazo I, ammonia	Violet spot
Aluminum(III)	Alizarin sodium sulfonate, ammonia	Red spot
Cadmium(II)	NAS, pyridine	Yellow spot
Gallium(III)	Arsenazo I, pyridine	Violet spot
Hafnium(IV)	Arsenazo I, pyridine	Violet spot
Iron(II)	1,10 phenanthroline	Red spot
Manganese(II)	Diethyldithiocarbamate	Gray precipitate
Nickel(II)	Dimethylglyoxime, ammonia	Red precipitate
Rare earths(III)	Arsenazo I, pyridine	Violet spot
Scandium(III)	Arsenazo I, pyridine	Violet spot
Thorium(IV)	Arsenazo I	Violet spot
Titanium(IV)	Arsenazo I, pyridine	Violet spot
Vanadium(IV)	Arsenazo I, pyridine	Violet spot
Zinc(II)	NAS, pyridine	Yellow spot
Zirconium(IV)	Arsenazo I, pyridine	Violet spot

metal ions had colored complexes when extracted into the organic phase or sorbed onto a column thus allowing their elution behavior to be watched directly. These colored complexes are listed in Table 2.

Gravimetric methods: Palladium(II) was determined by precipitating with dimethylglyoxime (DMG) (65).

Molybdenum(VI) was determined by precipitating with

Table 2. Colored thiocyanate complexes of metal ions

Metal ion	Color of metal thiocyanate complex after extraction into organic phase or sorption onto a column
Bismuth(III)	yellow
Copper(II)	purple-brown
Cobalt(II)	blue
Iron(III)	blood red
Palladium(II)	red
Ruthenium(III)	red
Vanadium(IV)	light green

8-hydroxyquinoline (65).

Atomic absorption methods: Copper(II), cobalt(II) and nickel(II) were determined by atomic absorption using the procedures recommended by the Perkin-Elmer Company (66).

Radiochemical tracers: Iron 59 and cobalt 60 tracers were used to determine the elution behavior of these metal ions. Both the effluent and the column support were counted to determine the extent of column extraction.

RESULTS AND DISCUSSION

Alamine 336

Distribution data for the extraction of some 32 metal ions into $R_3NH^+SCN^-$ in toluene are given in Table 3. The extractions were performed for initial aqueous thiocyanate concentrations of 0.0 M and 0.063 M. Twenty percent (v/v) solutions of Alamine 336 in toluene were used for most of the solvent extraction procedures. Toluene was always used as the diluent for the amine. Preliminary work performed with 10%, 20% and 30% solutions indicated that the 20% solution (0.4 M) was of sufficient concentration to quantitatively extract a number of metal ions. This solution was not very viscous and phase separations were generally fast and clean.

Five minutes was chosen as the stirring time mainly for convenience because the rates of amine extraction systems are generally considered to be fast. To check this general qualitative statement and also to substantiate the five-minute stirring time, a series of gallium(III) extractions were performed for different stirring times. Figure 3 shows a plot of $D/D_{\text{equilibrium}}$ versus stirring time for the extraction of 0.3 mmoles gallium(III) from 0.5 M hydrochloric acid into 6.0 mmoles of $R_3NH^+SCN^-$. These extractions were performed for different initial aqueous thiocyanate concentrations. The results indicate that a five-minute equilibration period is more than adequate to insure that equilibrium is attained.

A few ions gave intensely colored complexes when extracted and the phase separations were hindered by emulsion formation.

Table 3. Distribution data for extraction of ~ 0.3 mmoles metal ion into 6.0 mmoles of 20% (v/v) $R_3NH^+SCN^-$ in toluene from 0.5 M HNO_3

Metal ion	Extraction data			
	Aq $[SCN^-] = 0.00$		Aq $[SCN^-] = 0.063$	
	D	% E	D	% E
1. Al(III)	0.077	7.17	0.11	9.11
2. Ba(II)	0.019	1.70	0.019	1.70
3. Bi(III)	---	100.0	---	100.0
4. Ca(II)	0.00	0.00	0.0015	0.14
5. Cd(II)	29.2	96.7	48.2	97.8
6. Co(II)	---	100.0	---	100.0
7. Cu(II)	---	100.0	---	100.0
8. Eu(III)	0.012	1.20	0.013	1.28
9. Fe(III)	---	100.0	---	100.0
10. Ga(III)	2.23	69.0	3.36	75.9
11. Hf(IV)	1.60	61.5	3.32	75.7
12. Hg(II)	---	100.0	---	100.0
13. In(III)	37.6	97.4	174.1	90.4
14. La(III)	0.0092	0.91	0.0098	0.91
15. Lu(III)	0.012	1.22	0.013	1.21
16. Mg(II)	0.00	0.00	0.0052	0.48
17. Mn(II)	0.20	16.7	---	---
18. Mo(VI)	---	100.0	---	100.0
19. Ni(II)	0.0044	0.44	---	---
20. Pb(II)	0.03	2.90	0.074	6.92
21. Pd(II)	1185	99.9	---	99.9
22. Ru(III)	Aqueous layer remained red with very poor phase separation			
23. Sc(III)	0.059	5.53	0.11	9.65
24. Sn(IV)	---	100.0	---	100.0
25. Sr(II)	0.036	3.52	0.039	3.52
26. Th(IV)	0.00	0.00	---	---
27. Ti(IV)	0.46	31.5	1.28	54.5
28. U(VI)	113.7	99.1	151.4	99.4
29. V(IV)	21.5	95.6	37.4	97.2
30. Y(III)	0.016	1.16	0.025	2.28
31. Zn(II)	---	100.0	---	100.0
32. Zr(IV)	0.23	22.8	0.66	38.2

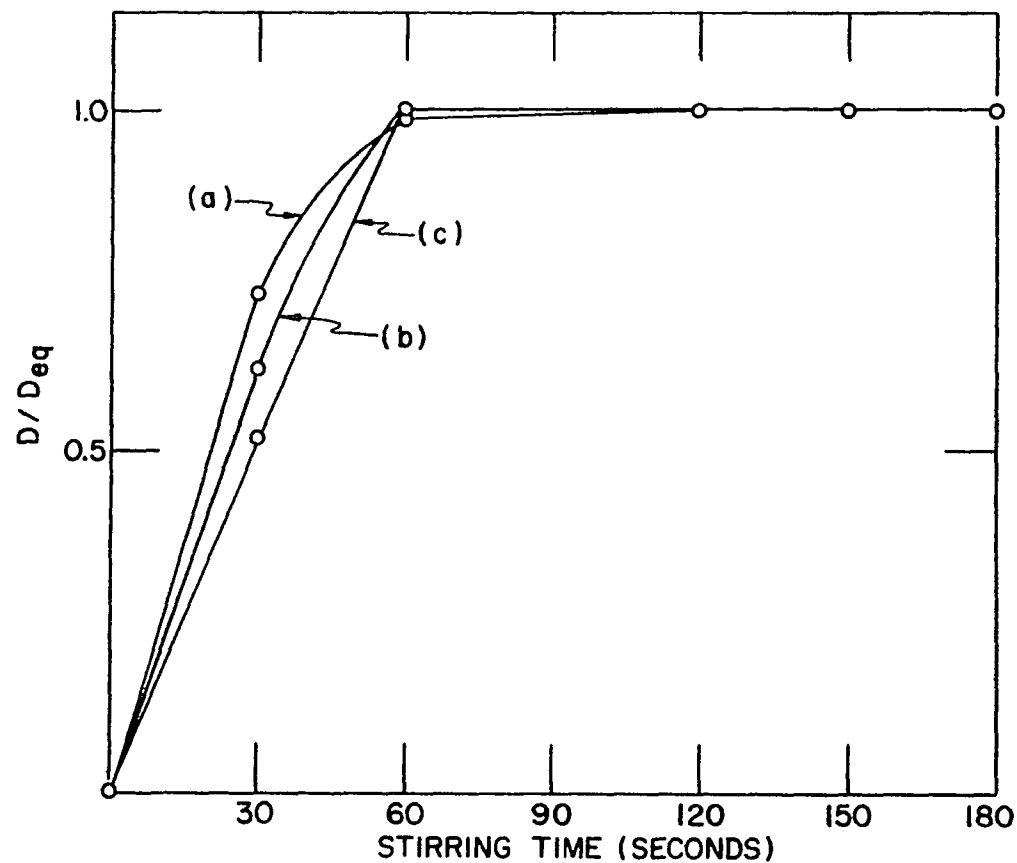


Figure 3. Rate of extraction of Ga(III) into a 20% (v/v) solution of $R_3NH^+SCN^-$ in toluene for various aqueous thiocyanate concentrations. Solution (a) is 0.0 M KSCN-0.5 M HCl, (b) is 0.30 M KSCN-0.5 M HCl and (c) is 0.70 M KSCN-0.5 M HCl.

1. Cu(II) - purple-brown complex with no phase separation
2. Fe(III) - blood red complex with poor phase separation
3. Ru(III) - red complex with no phase separation
4. V(IV) - green complex with poor phase separation

It should be noted however that palladium(II) gave a clear red organic phase with a perfect phase separation, as did cobalt(II) with its deep blue organic phase.

It is obvious from the distribution data in Table 3 that for the most part, complete separations of metal ions cannot be accomplished in a single solvent extraction procedure. A few notable exceptions might be the following:

1. 0.0% extracted; Ca(II), Mg(II), Th(IV)
2. 100.0% extracted; Bi(III), Co(II), Fe(III), Cu(II), Hg(II), Pd(II), Sn(IV), Zn(II) and possibly U(VI) (99.1%)

The extraction data for the metal ions studied may be divided into three distinct groups.

Group 1 - Low percentage extraction, i.e. % E < 5%. Ions included are Ba(II), Ca(II), Eu(III), La(III), Lu(III), Mg(II), Ni(II), Pb(II), Sr(II), Th(IV), Y(III)

Group 2 - High percentage extraction, i.e. % E > 95%. Ions included are Bi(III), Cd(II), Co(II), Fe(III), Hg(II), In(III), Pd(II), Sn(IV), U(VI), Zn(II), Mo(VI)

Group 3 - Intermediate percentage extraction, i.e. 5% < E < 95%. Ions included are Al(III), Ga(III), Hf(IV), Mn(II), Sc(III), Ti(IV), Zr(IV)

Figure 4 shows these three groups with respect to their position in the periodic table, making some generalizations apparent. It appears as though all the first row transition metal ions (chromium was not studied) except nickel(II) are extracted to some degree. Notice, however, that in the second row transition metals palladium(II) is highly extracted. The alkaline earths and rare earths are not extracted to any extent while uranium(VI) is highly extracted. Also, the percentage extraction increases in going down the group of aluminum(III), gallium(III) and indium(III).

Further study of the intermediate extraction group was concerned with the effect of increasing aqueous thiocyanate concentration on the distribution ratio. Equal volumes of aqueous and organic phases were used and the equilibration time was five minutes as before. Two ions from the low percentage extraction group, thorium(IV) and nickel(II), were included in this study of increasing thiocyanate concentration. Their behavior is quite different from the intermediate extraction group ions, with the exception of manganese(II), in that their percentage extraction does not increase significantly over the entire thiocyanate concentration range studied. This behavior is important because it indicates that metal ions in the intermediate extraction group may be separated from both the low and high percentage extraction groups by simply controlling the eluent thiocyanate concentration in a reversed-phase column procedure. The results of the study of increasing thiocyanate concentration are listed in Table 4.

The distribution ratios of the intermediate extraction group can also be enhanced by increasing the exchanger concentration. Several

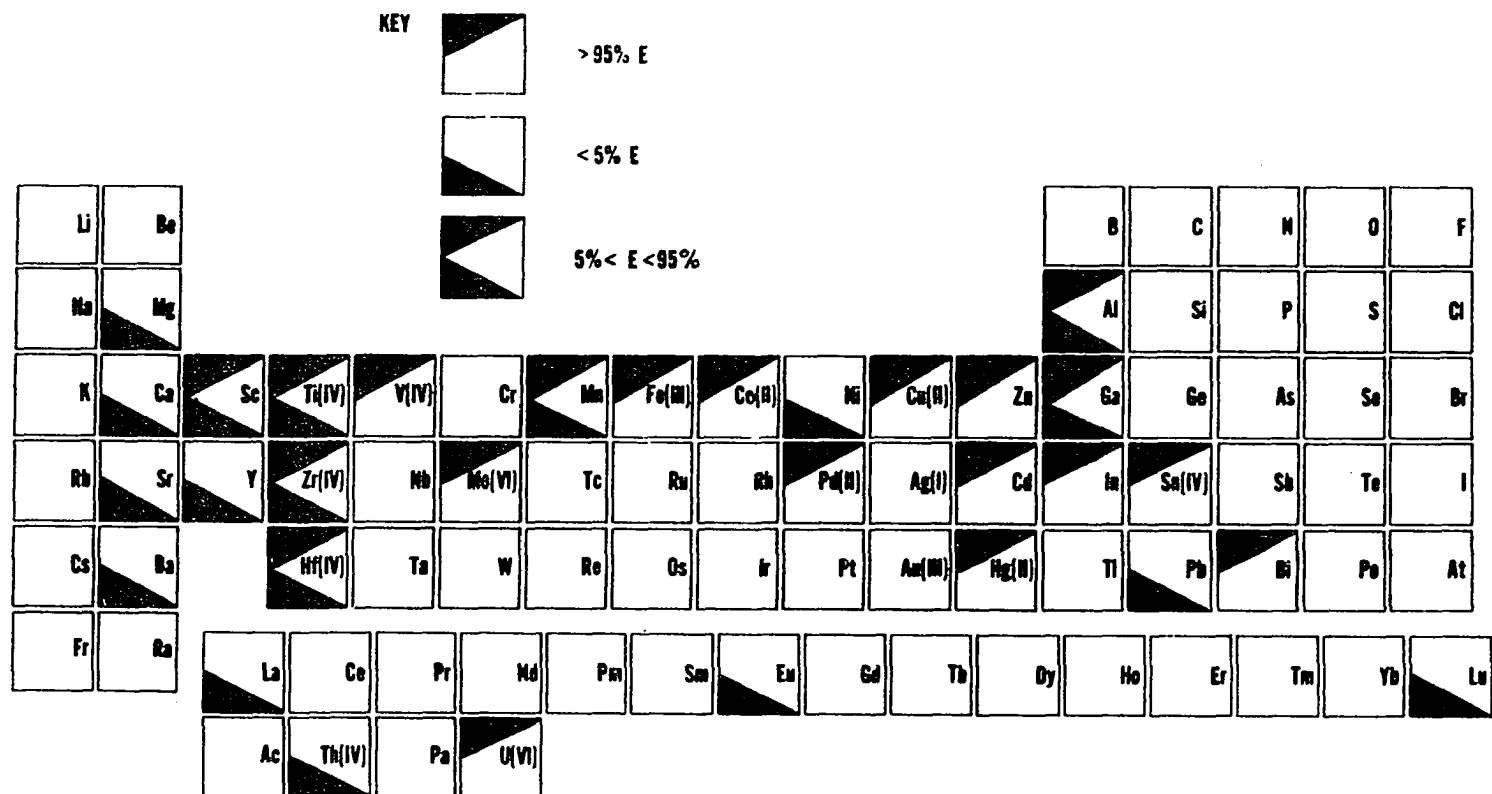


Figure 4. Distribution data for the extraction of 0.3 mmoles metal ion into 6.0 mmoles of 20% (v/v) $R_3NH^+SCN^-$ in toluene. The aqueous phase was 0.5 M in HCl and ≤ 0.06 M in KSCN

Table 4. Summary of distribution ratios and percentage extraction for intermediate extraction group ions at increasing aqueous thiocyanate concentrations

Aqueous [SCN ⁻]	Th		Ni		Sc		Ga		Ti		Mn	
	D	% E	D	% E	D	% E	D	% E	D	% E	D	% E
0.00	0.00	0.00	0.0044	0.44	0.054	5.14	2.33	69.9	0.50	34.0	0.20	16.7
0.25	0.0017	0.17	0.013	1.31	0.35	25.7	12.5	92.6	3.33	76.8	0.43	30.1
0.50	0.0034	0.34	0.028	2.73	0.75	42.8	40.3	97.6	6.96	87.4	0.51	33.8
0.75	0.0034	0.34	0.028	2.73	1.05	51.2	81.5	98.8	11.2	91.8	0.53	34.6
1.00	0.0017	0.17	0.028	2.73	1.41	58.5	136.5	99.3	14.4	93.5	0.54	35.1
1.50	---	---	---	---	---	---	---	---	16.2	94.2	---	---
2.00	---	---	---	---	3.09	75.5	---	100.0	19.2	95.0	0.54	35.1

metal ions were extracted with a 30% exchanger solution for zero mmoles of thiocyanate ion in the aqueous phase. The distribution ratios and percentage extractions are compared for the 20% and 30% exchanger solution in Table 5.

Table 5. Comparison of distribution ratio and percentage extraction for two different concentrations of $R_3NH^+SCN^-$ in toluene

Exchanger concentration metal ion	20%		30%	
	D	% E	D	% E
Ga(III)	2.23	69.0	5.89	85.5
Hf(IV)	1.60	61.5	2.44	70.9
Mn(II)	0.41	29.0	0.94	48.5
Ti(IV)	0.46	31.5	1.82	64.5
Zr(IV)	0.23	22.8	0.44	30.6

The magnitude of the distribution data suggests that it should be possible to extract any combination of ions in Group 2 from any combination of ions in Group 1, provided of course that the exchanger capacity is not exceeded. A practical application of this possibility was in the determination of water hardness (calcium plus magnesium) by the method of Fritz *et al.* (63).

Traces of iron, copper and certain other metal ions dissolved in water constitute interferences in the determination of water hardness. Their presence may either seriously reduce the sharpness of the end point or prevent it completely by blocking the indicator. Masking agents such as cyanide have been used but their effectiveness for iron is still somewhat limited. Furthermore, the use of dangerous chemicals such as cyanide is to be avoided whenever possible. The indicator used by

Fritz et al. is a mixed indicator containing Arsenazo I and a buffer containing THAM. The end point is blocked if the amount of iron(III) present > 20 ppm and cobalt(II) present > 3 ppm. Copper(II) will titrate as hardness.

The procedure involved extraction of 200 ml of hard water, containing 50 ppm each of Fe(III), Co(II) and Cu(II) as CaCO_3 , with 200 ml of 20% exchanger. The flask was shaken moderately for 45 seconds and the phases separated within 90 seconds. The clear but reddish aqueous layer was drawn off into another separatory funnel containing 20 ml of a 20% (v/v) solution of Alamine 336 in toluene. The funnel was shaken moderately for 30 seconds and the phases separated within 20 seconds. The cloudy aqueous layer was passed through a glass wool plug and aliquots were titrated for water hardness.

Total initial hardness = 110.3 ppm

Total hardness found = 111.7 ppm

This separation problem was also attempted using a column procedure, with the idea that the whole process should be as fast as possible. One problem is that with no thiocyanate in the aqueous eluting agent, the blue cobalt band starts to bleed down the column because of replacement of thiocyanate in the exchanger. The following three separations are considered to have been successful:

1. Sample - 20 ppm Cu(II), 20 ppm Fe(III), and 10 ppm Co(II) as CaCO_3

Column - 1.0 cm X 6.0 cm

Support - mixture of 10 ml Alamine 336/17.5 g Chromosorb W converted to $\text{R}_3\text{NH}^+\text{SCN}^-$

Flow rate - 80 ml at 4 ml/min

150 ml at 12 ml/min

Results

total initial hardness = 93.0 ppm

total hardness found = 93.0 ppm

2. Sample - same as 1

Column - same as 1

Support - 20 ml Alamine 336/17.5 g Chromosorb W converted to $R_3NH^+SCN^-$

Flow rate - 100 ml at 9 ml/min

Results

total initial hardness = 93.0 ppm

total hardness found = 91.8 ppm

3. Sample - 20 ppm Fe(III), 20 ppm Cu(II), and 2 ppm Co(II) as $CaCO_3$

Column - same as 1 and 2

Support - same as 2

Flow rate - 400 ml at 9 ml/min

Results

total initial hardness = 110.3 ppm

total hardness found

1st 150-180 ml = 109.9 ppm

2nd 150-180 ml = 109.9 ppm

3rd 100 ml = 109.9 ppm

For all of the above separations, the indicator change at the equivalence point was considered excellent, indicating that the iron, cobalt and copper had been removed. A comparison of total initial hardness and total hardness found indicates within experimental error no

calcium or magnesium was lost during extraction. An important aspect of these separations is that they are fast and the conditions used are mild. The water sample is not pretreated in any manner except to adjust the acidity to below pH 1 for the solvent extraction procedure. The column procedure could actually be used as part of an "in the field" analysis method because the procedure is simple and the column is small and can be prepared in advance.

The possibility of developing a large scale solvent extraction cobalt-nickel separation was investigated. Such a process would be of value in a salt purification scheme i.e. the removal of cobalt from nickel salts. An important factor in any large scale solvent extraction procedure is the total capacity of material that can be handled. A loading study was performed by extracting increasing concentrations of cobalt(II) and nickel(II). Both for 15.0 ml of 10% exchanger and 15.0 ml of 30% exchanger the concentration of cobalt or nickel ranged from 0.01 M - 0.40 M. It should be noted that these extractions were performed with no thiocyanate initially present in the aqueous phase. The data obtained are shown in graphical form in Figures 5-9.

Figure 6 indicates that for conditions under which cobalt is 100% extracted a small amount of nickel is also extracted. This is not a major problem if a backwashing step is included. Essentially all of the nickel is back-extracted with two washings of water or very dilute acid solution (to help obtain a better phase separation), while essentially all of the cobalt remains in the organic phase. The cobalt may be back-extracted from the organic phase with two washings of 1-1 sulfuric acid. In a continuous procedure the exchanger may be kept in

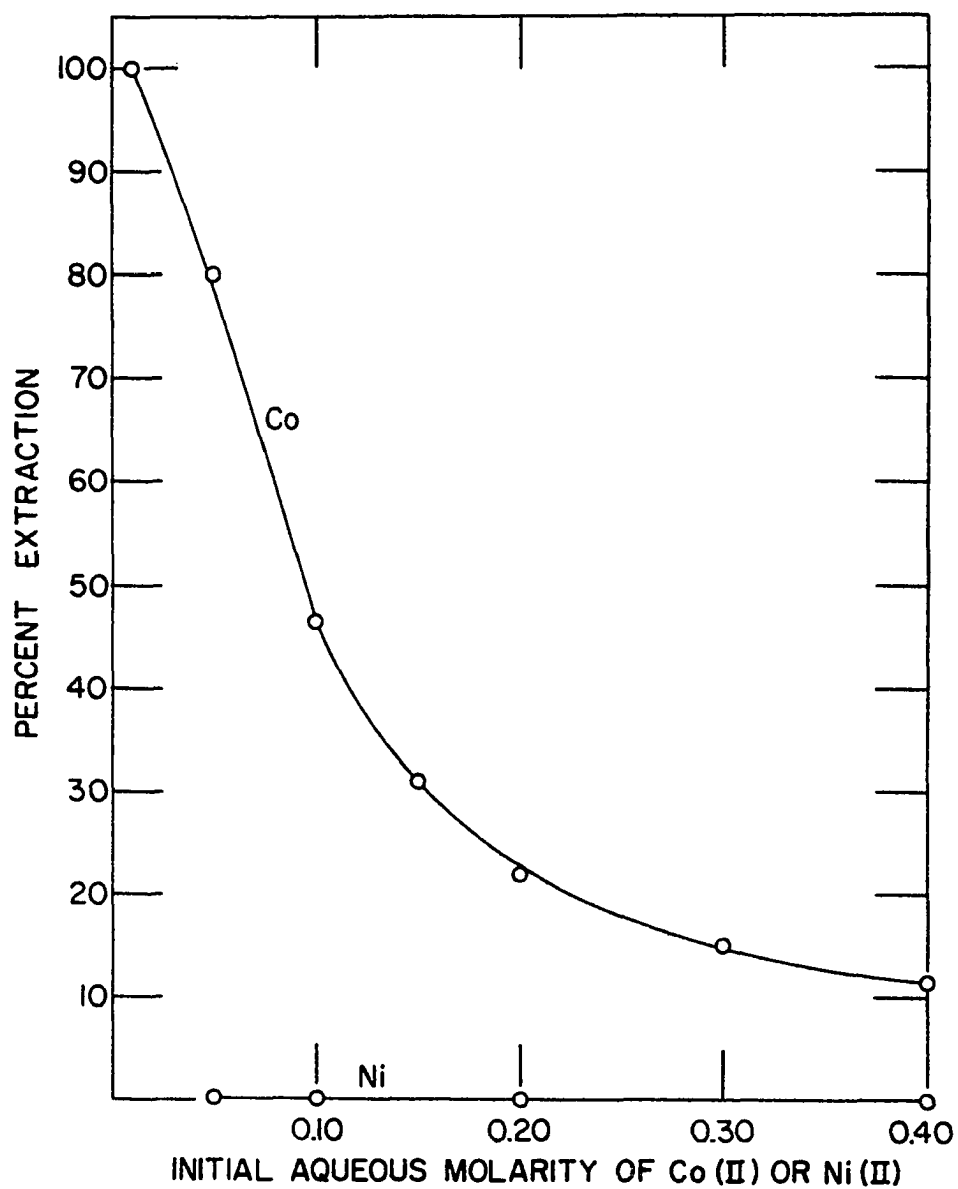


Figure 5. Percent extraction of Co(II) or Ni(II) from 0.1 M HNO_3 into an equal volume of 0.2 M $R_3NH^+SCN^-$ in toluene

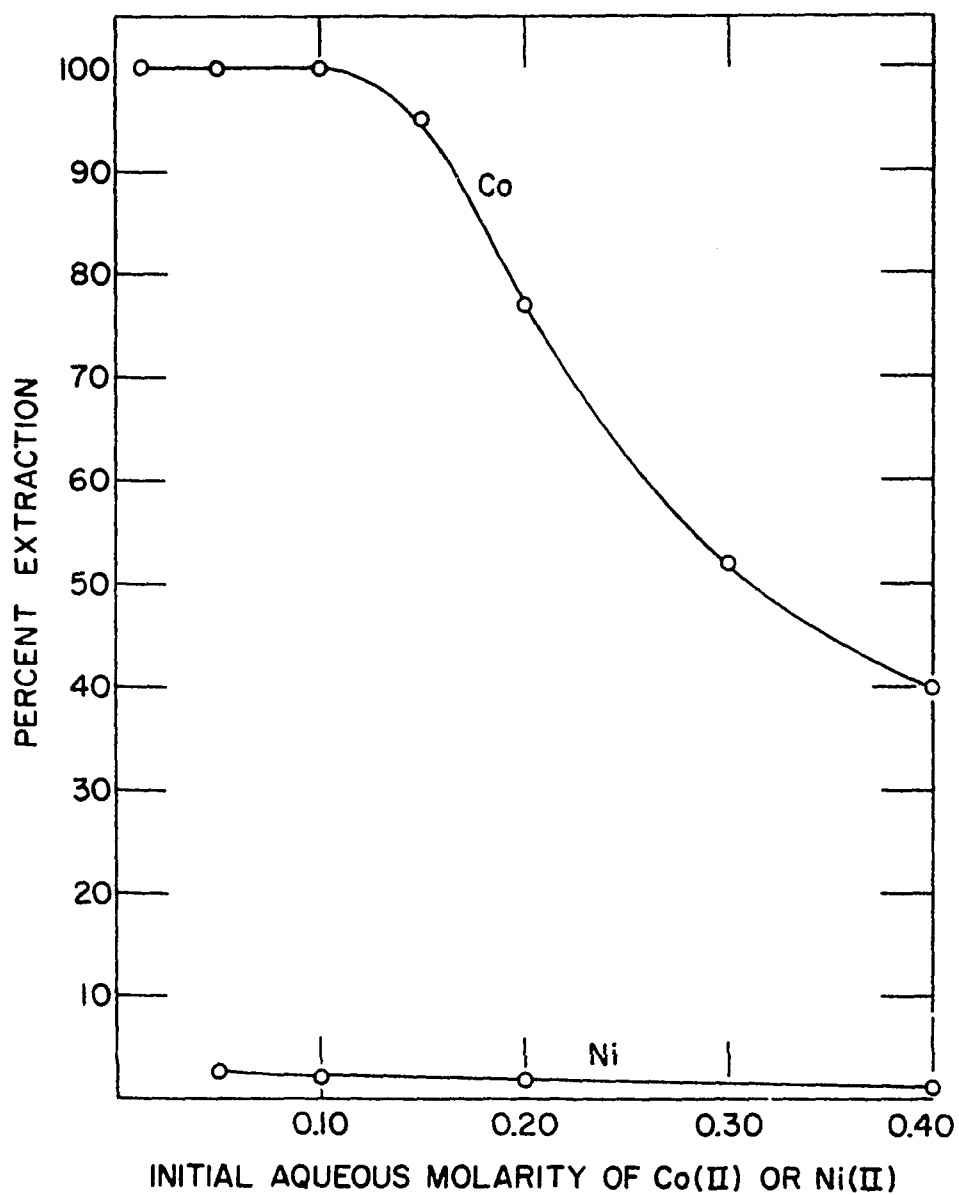


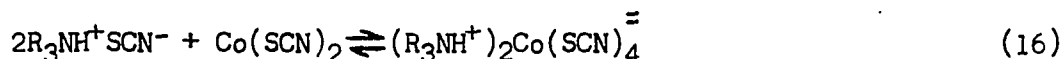
Figure 6. Percent extraction of Co(II) or Ni(II) from 0.1 M HNO_3 into an equal volume of 0.6 M $\text{R}_3\text{NH}^+\text{SCN}^-$ in toluene

its extracting form simply by adding thiocyanate to the aqueous feed solution.

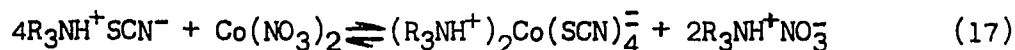
Figures 7 and 8 show the exchanger capacity for cobalt and nickel individually. Figure 9 is a limiting loading curve for cobalt and from it the cobalt to amine ratio for the extraction may be determined by the limiting loading method (67).

For the 30% solution the initial mmoles of $R_3NH^+SCN^-$ is $15.0(0.6) = 9.0$ mmoles. The amount of cobalt in the organic phase levels off at 2.34 mmoles. The limiting cobalt/amine ratio is $\frac{2.34}{9.0} = \frac{1}{3.85}$. For the 10% solution the limiting cobalt/amine ratio is $\frac{0.70}{3.0} = \frac{1}{4.28}$. These results indicate a cobalt/amine ratio of 1/4. Watanabe (21) extracted cobalt into a TOA/xylene solution and determined the limiting cobalt/amine ratio to be 1/2.

The discrepancy is resolved when one considers that Watanabe used 0.24 M thiocyanic acid in the aqueous phase for the extraction of cobalt in the concentration range $(1-6) \times 10^{-2}$ M. Therefore, the equation for extraction may be written as:



For the situation where no thiocyanate is present in the aqueous phase, the full capacity of the exchanger cannot be used. In fact only one half the exchanger capacity is utilized. Therefore, the equation for extraction may be written as:



The presence of initial thiocyanate in the aqueous phase should therefore increase the capacity of the exchanger for cobalt, but possibly also for nickel.

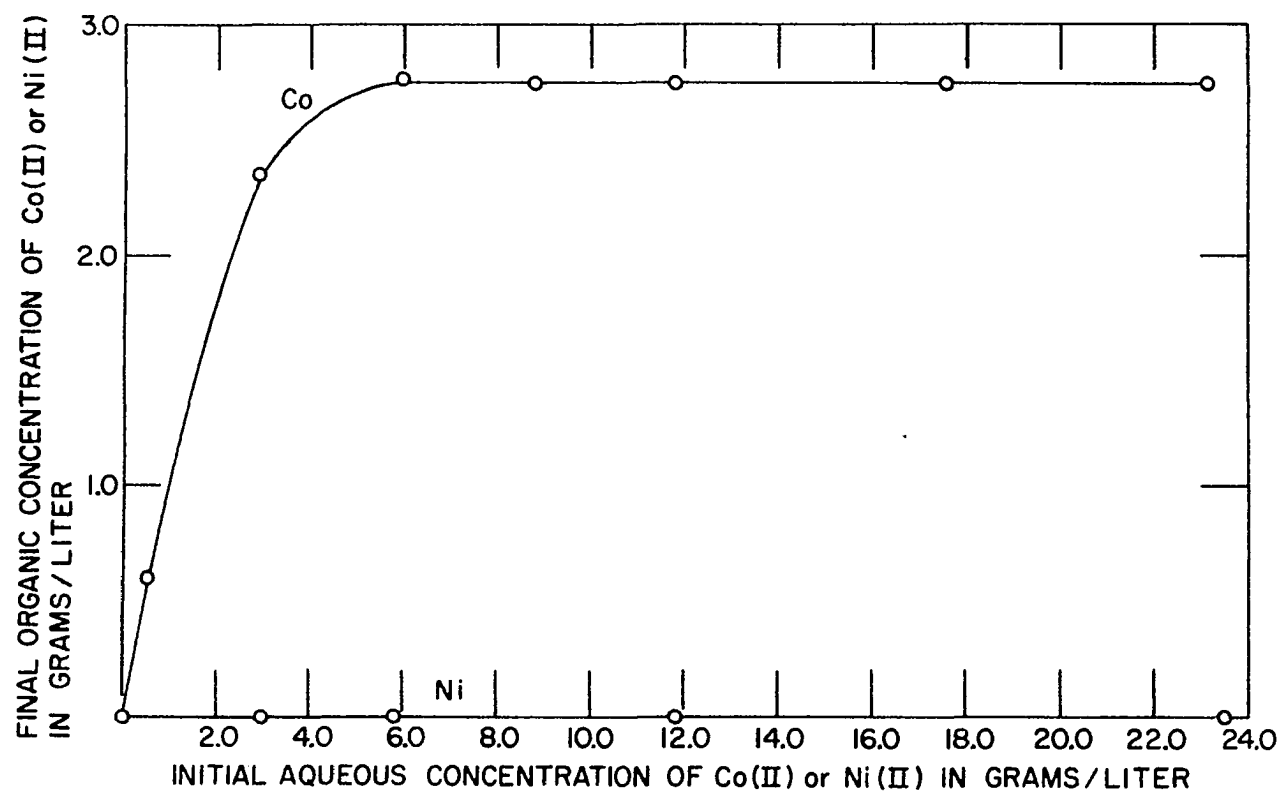


Figure 7. Capacity study for the extraction of Co(II) or Ni(II) from 0.1 M HNO₃ into an equal volume of 0.2 M R₃NH⁺SCN⁻ in toluene

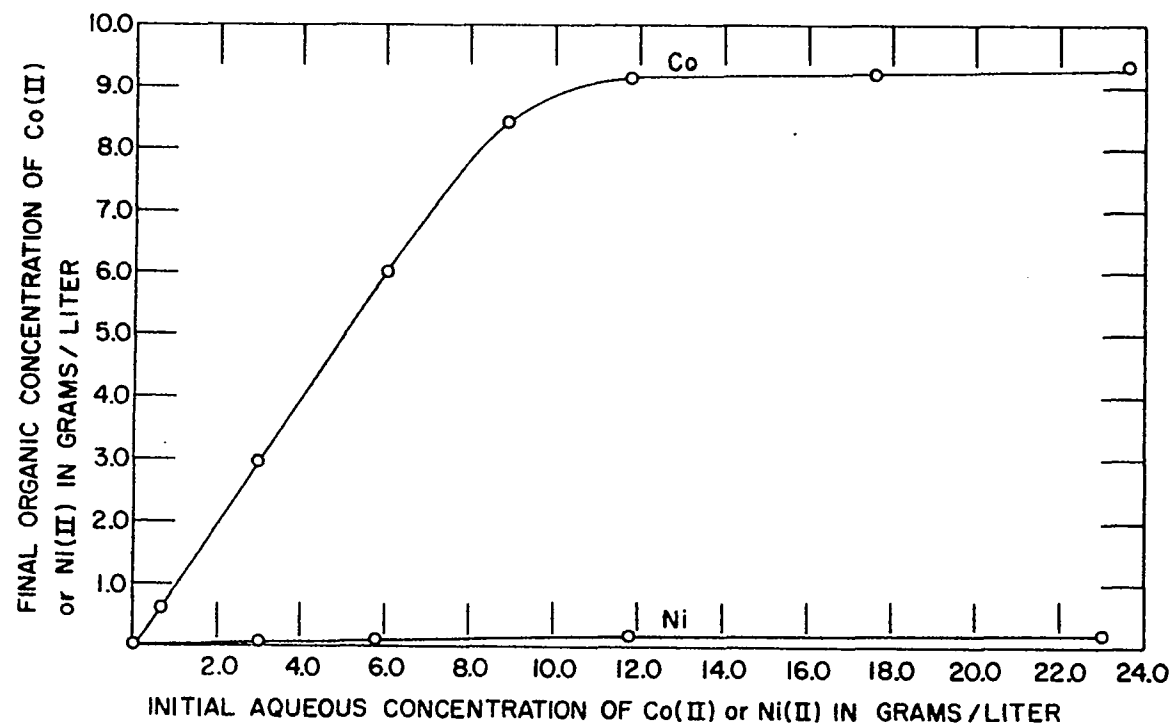


Figure 8. Capacity study for the extraction of $Co(II)$ or $Ni(II)$ from 0.1 M HNO_3 into an equal volume of 0.6 M $R_3NH^+SCN^-$ in toluene

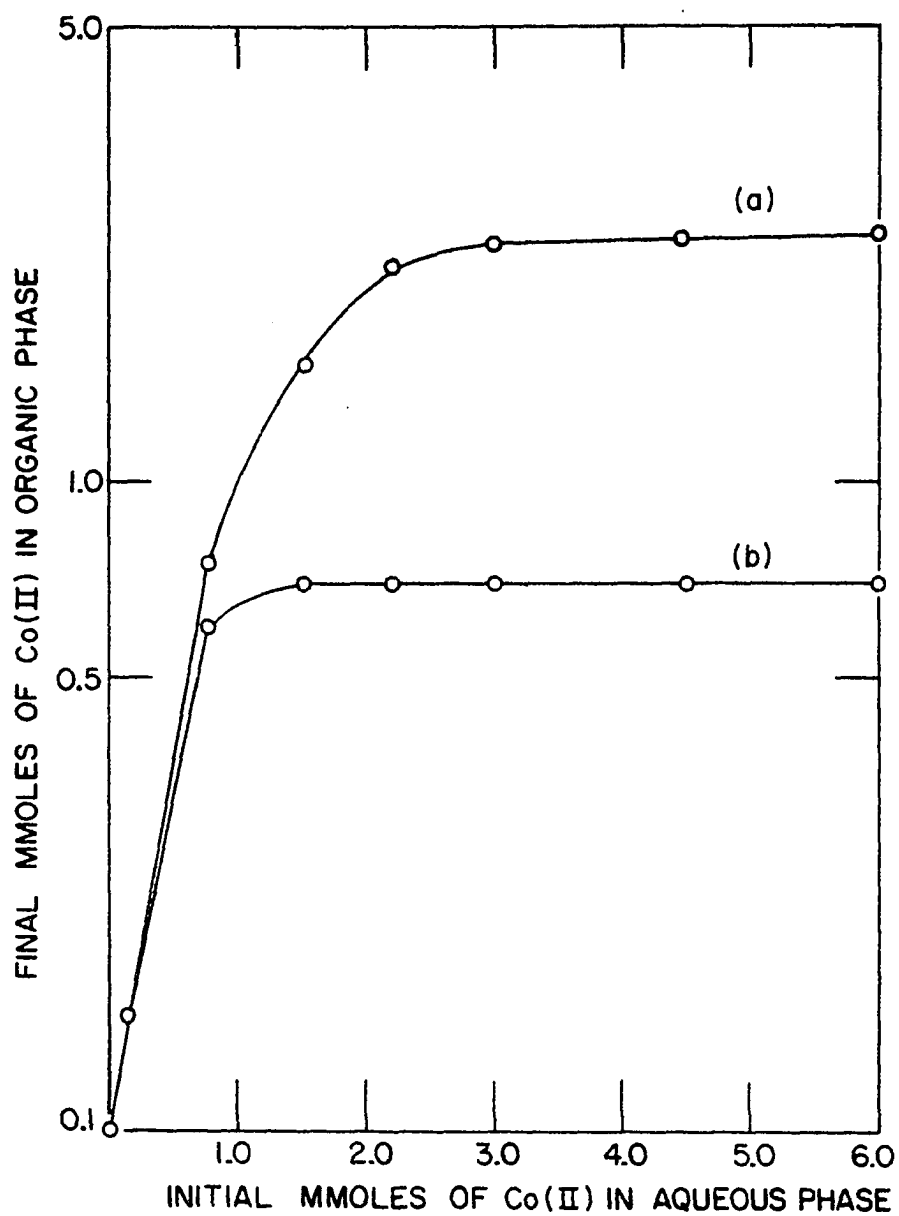


Figure 9. Limiting loading curve for the extraction of Co(II) from 0.1 M nitric acid into (a), 9.0 mmol of 30% (v/v) solution of $R_3NH^+SCN^-$ in toluene and (b), 3.0 mmol of 10% (v/v) solution of $R_3NH^+SCN^-$ in toluene

The concentration of both components in both phases at equilibrium should be determined when evaluating the applicability of any extractant. In other words, one should not assume that the ratio of distribution coefficients for the pure components is the same as when both are present in the same system.

Two extractions of cobalt and nickel with 30% exchanger solution were performed. The ratios of nickel to cobalt in these experiments were made 5/1 and 10/1, respectively, on the assumption that if the distribution ratios were to deviate they would do so in the case where the less extracted component was in excess. The aqueous nickel solution was determined by EDTA titration and the organic cobalt solution was determined by atomic absorption after an appropriate solvent extraction calibration curve had been obtained (Figure 10). The results are given in Table 6. They indicate that the lesser extracted component (nickel) is extracted less while the cobalt extraction is still complete.

Table 6. Extraction of cobalt and nickel with 30% exchanger solution

Experiment #	Initial concentration		Percentage extraction	
	mmoles Ni	mmoles Co	Ni	Co
1	4.05	0.40	0.74	100
2	4.05	0.80	0.37	100

A reversed-phase column procedure seemed advantageous for obtaining quantitative separations of metal ions in the three extraction groups. One such application, in the determination of water hardness, has already been described (p. 41). Further reversed-phase column work was concerned

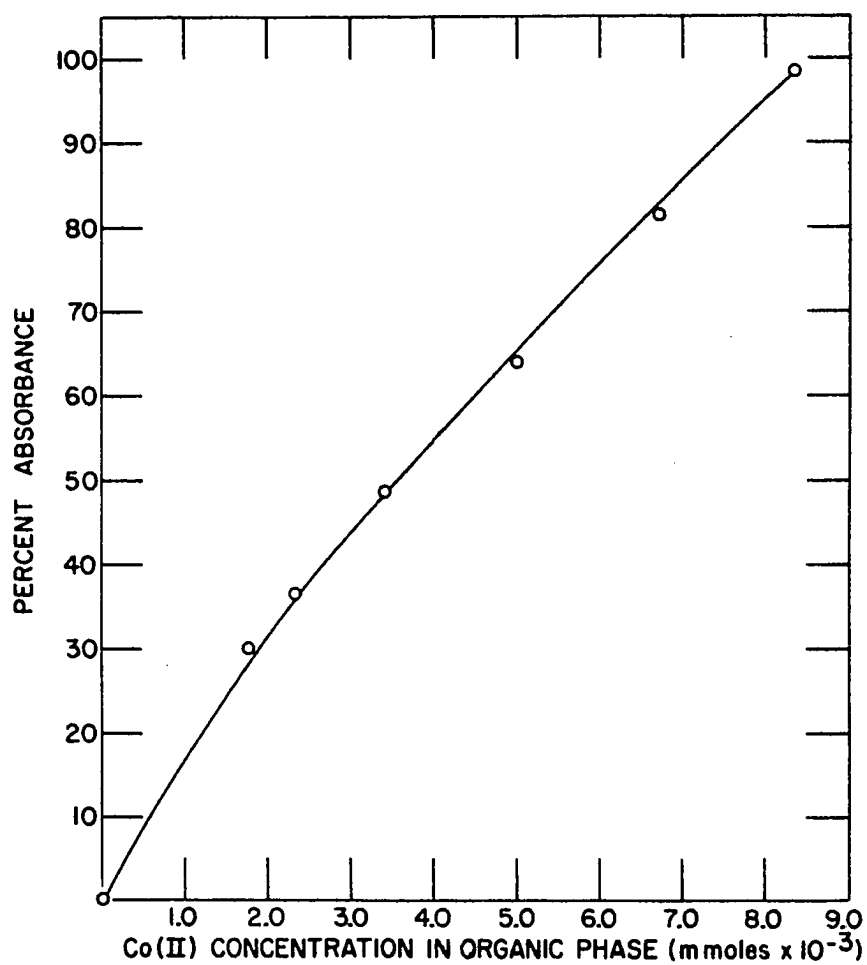


Figure 10. Atomic absorption calibration curve for Co(II) after extraction into a 30% (v/v) solution of $R_3NH^+SCN^-$ in toluene

with the separation of nickel(II) from copper(II) or cobalt(II). These rather simple separations were performed to demonstrate the relative ease and speed with which a metal ion from the low percentage extraction group can be quantitatively separated from a metal ion or ions in the high percentage extraction group. Furthermore, direct determination of a metal ion in the presence of $R_3NH^+SCN^-$ was performed. This demonstrated that the presence of the liquid ion exchanger, if properly accounted for, can be tolerated in the direct determination of metal ions.

The column used for separations was 1.0 cm X 9.0 cm. This volume contained 2.50 g of impregnated Chromosorb W and only 1.70 g of dry Chromosorb W. Thus there were $0.80 \text{ g} / 392 \text{ g/mole} = 2.07 \text{ mmoles}$ Alamine 336 on the column. The procedure consisted of washing nickel through the column with 15-25 ml of 0.1 M HNO_3 and then stripping the copper or cobalt with 25 ml of methanol and diluting to the mark in a 50-ml volumetric flask with methanol. Macro amounts of nickel were determined by EDTA titration, while smaller amounts of nickel and nonaqueous cobalt or copper were determined by atomic absorption using an air-acetylene flame.

Before determining the calibration curves for the nonaqueous copper and cobalt samples, the influence of several variables on the metal ion absorbance was investigated.

1. Influence of amine concentration. Undiluted Alamine 336 was converted to $R_3NH^+SCN^-$, various amounts were added to a 20 ppm copper or 20 ppm cobalt sample and the absorbance was determined. A plot of percent absorbance versus concentration of $R_3NH^+SCN^-$

is shown in Figure 11. The absorbance value for both metal ions seems to be approaching a constant value for amine concentrations above 1.0 mmoles/ml. Since there are 2.07 mmoles of Alamine 336 on the columns used, it is assumed the effect caused by the amine is constant.

The fact that the amine decreases the absorbance of metal ions is noteworthy because it is usually considered that organic solvents enhance the absorbance of metal ions. The amine effect has been reported by Hartlage (68) for iron, copper, cobalt and nickel in the presence of methylamine, diethylamine and trimethylamine. This interference appears to be caused by the formation of metal-amine complexes which do not dissociate at the temperature of the air-acetylene flame. Hartlage has shown that the interference can be overcome by using a nitrous oxide-acetylene flame, but there is also a decrease in sensitivity.

2. Influence of methanol - no amine present owing to the problem of solubility. The absorbance of an aqueous 10 ppm copper solution and a 20 ppm cobalt solution was determined while increasing the percentage of methanol present. A plot of percent absorbance versus percent methanol is shown in Figure 12. The methanol definitely enhances the absorbance of both copper and cobalt.
3. When the copper or cobalt is stripped from the column with methanol it is collected in a 50-ml volumetric flask, shaken and allowed to sit. It appears that some amine salt eventually

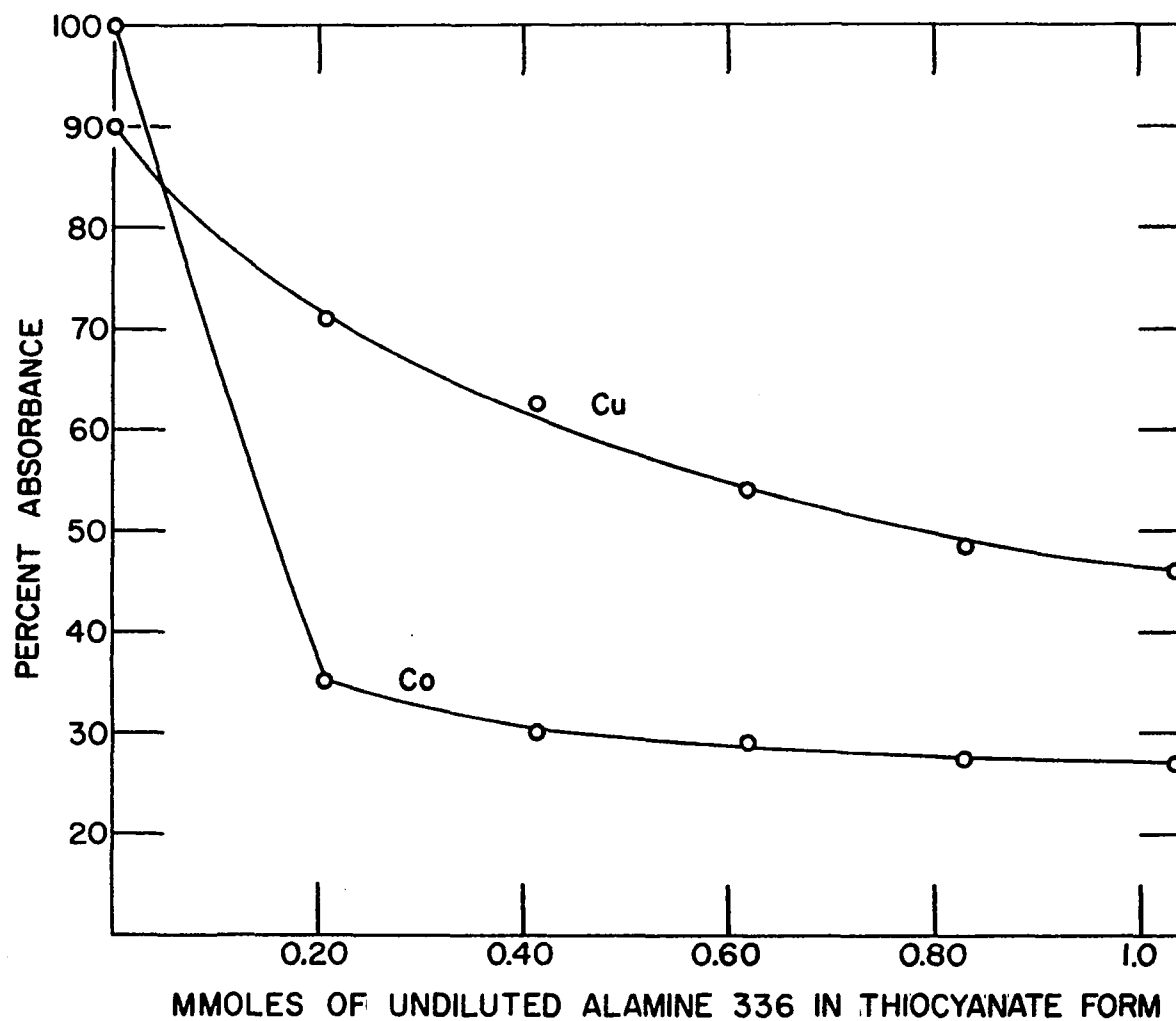


Figure 11. Effect of $R_3NH^+SCN^-$ concentration on the atomic absorption determination of a methanolic 20 ppm Co(II) solution or 20 ppm Cu(II) solution. An air-acetylene flame was used

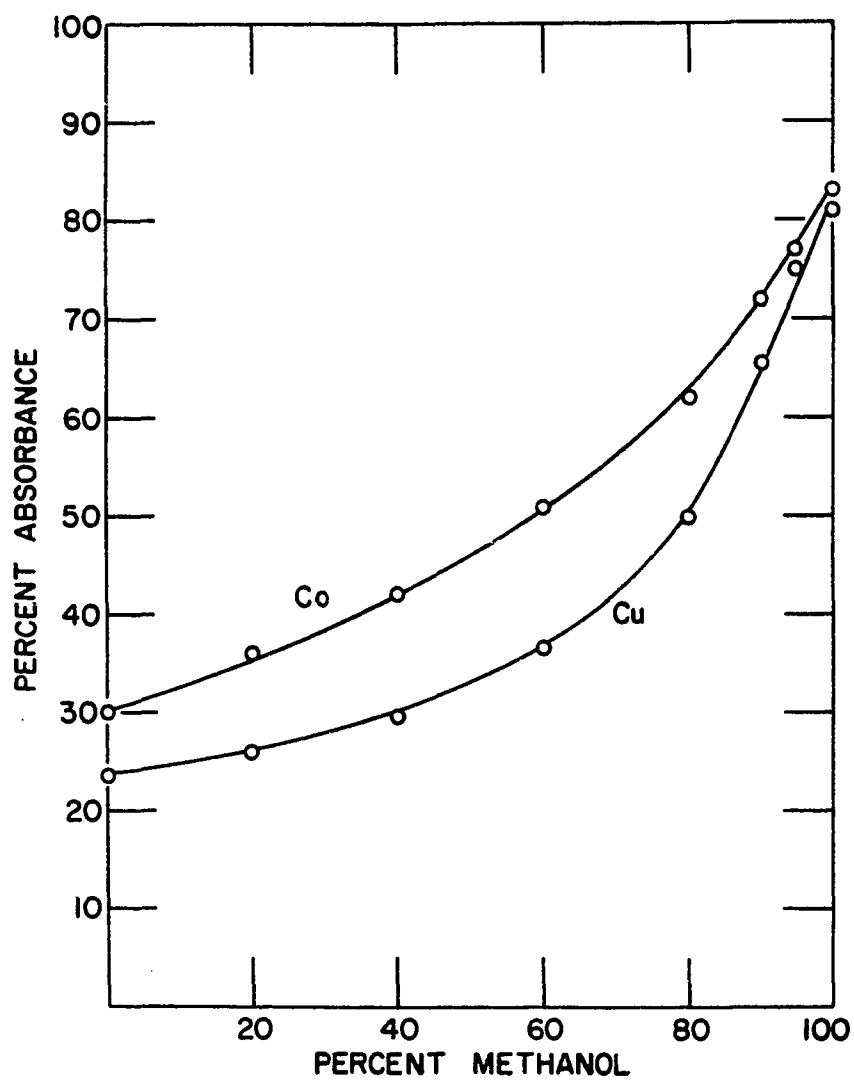


Figure 12. Effect of methanol on the atomic absorption determination of an aqueous 20 ppm Co(II) solution or a 10 ppm Cu(II) solution

settles out. The flask is usually shaken before reading, but an experiment was tried where the absorbance was determined before and after shaking some cobalt samples obtained from actual separations.

<u>Conc. Co (ppm)</u>	<u>Meter reading</u>	
	<u>No shaking</u>	<u>Shaking</u>
4.0	16.5	17.0
16.0	53.0	53.0
24.0	76.5	76.0
34.0	93.0	93.5

Standard calibration curves of percent absorbance versus concentration were made for copper, cobalt and nickel by taking an appropriate amount of each metal ion and simulating the column separation procedure. Then the unknown sample was taken through the same column procedure, its absorbance read and its concentration determined directly from the appropriate calibration curve (Figures 13 and 14).

The procedure for measuring the unknown involves setting the zero reading on the absorbance scale with a blank solution which contains everything the sample solution does except the metal ion. The 100% reading is then set with the most concentrated solution used in determining the calibration curve. For copper, this solution must be prepared at the same time the unknown is obtained.

The curvature of the cobalt curve is in agreement with a series of cobalt curves obtained using different absorption lines, in a paper by Harrison (69). For the case of the 2407.2 Å line, which was used in this work, Harrison claims the deviation from linearity is caused by the presence of an adjacent interfering line which is too close to allow resolution with the monochromator.

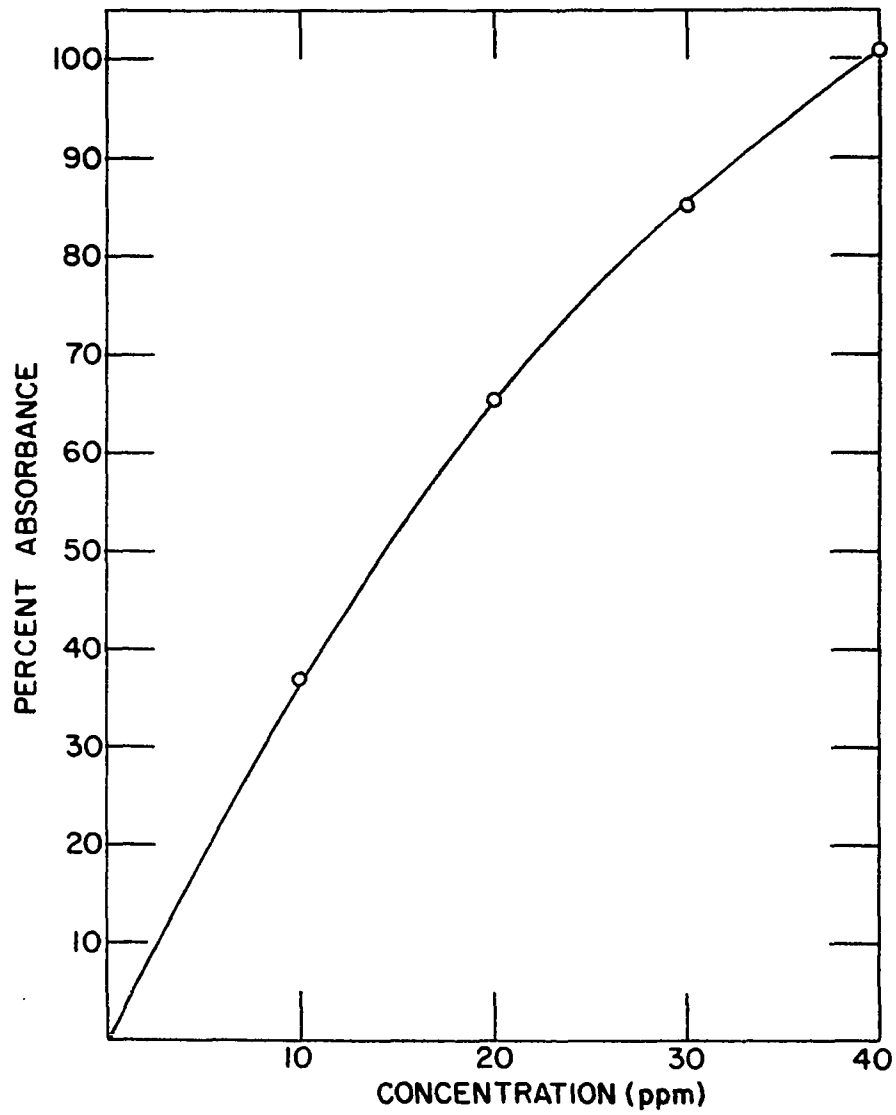


Figure 13. Atomic absorption calibration curve for Co(II)

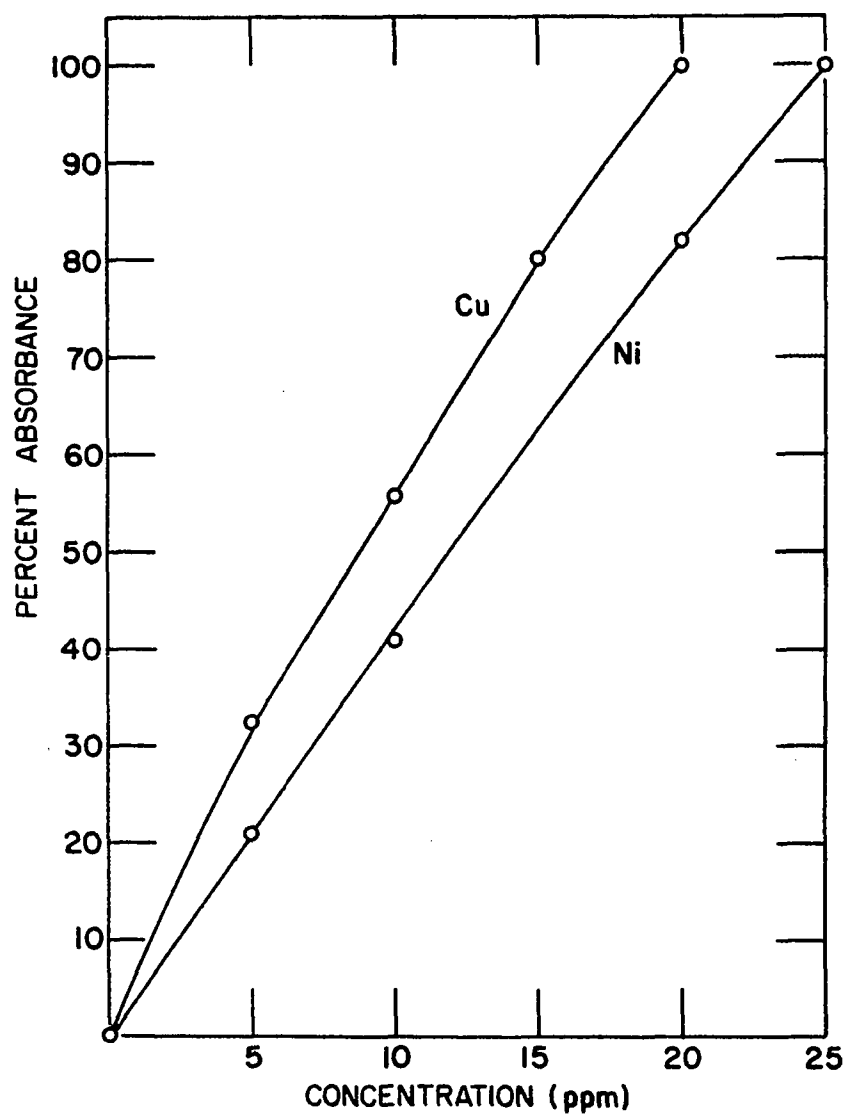


Figure 14. Atomic absorption calibration curves for Cu(II) and Ni(II)

The results of a series of cobalt-nickel and copper-nickel separations performed for different concentration ratios are given in Table 7. In these separations large amounts of copper and cobalt were not determined. The colored cobalt or copper band at the top of the column made it apparent that a separation was achieved.

In addition to using synthetic sample mixtures, the separation procedure was applied to an NBS standard sample, 124d, for isolation of nickel prior to its determination by atomic absorption. This sample consists of the following elements and percentage composition:

Cu - 83.60%	Ni - 0.99%	P - 0.02%
Pb - 5.20%	Fe - 0.18%	As - 0.02%
Zn - 5.06%	Sb - 0.17%	S - 0.093%
Sn - 4.56%	Ag - 0.02%	

A larger column was used for this separation because the high percentage of copper necessitates a larger capacity. The column height was still 9.0 cm but the i.d. of the column was 2.0 cm instead of 1.0 cm. This effectively increases the volume fourfold and four times as much impregnated support was used.

A 2.0 ml sample was added and the nickel was eluted with 50 ml of 0.1 M nitric acid into a 50-ml volumetric flask. The column was then stripped with 200 ml of methanol. The results of two separate determinations are given in Table 8.

One might question the need for the separation of nickel from copper, zinc and tin in the NBS standard sample prior to its determination by atomic absorption. After all, one of the proposed advantages of atomic absorption is that it is free from spectral interferences if properly designed (70). However, there are two other types of interferences that

Table 7. Column separations of nickel from cobalt or copper

Separation	Concentration (ppm)		Concentration ratio	Ni ^a	Recovery, %	
	Initial	- for final analysis			Cu ^b	Co ^c
Cu/Ni	5,000/500	/20.0	10/1	96.0	---	---
	5,000/50	/2.0	100/1	100.0	---	---
	400/400	8.0/8.0	1/1	---	101.2	---
				99.4	98.8	---
				96.2	95.0	---
				96.2	98.8	---
	600/600	12.0/12.0	1/1	98.8	95.8	---
				97.6	101.7	---
				---	100.8	---
				98.2	100.0	---
	800/800	16.0/16.0	1/1	98.8	100.0	---
				97.2	101.9	---
				98.2	101.9	---
				98.2	100.0	---
Co/Ni	5,000/500	/20.0	10/1	101.0	---	---
	5,000/50	/2.0	100/1	100.0	---	---
	800/600	16.0/12.0	4/3	99.3	---	95.7
	1,200/800	24.0/16.0	3/2	95.7	---	102.0
	1,700/300	34.0/6.0	17/3	103.0	---	100.0
	400/800	8.0/16.0	1/2	99.4	---	103.8
Ni/Cu	5,000/500	0.085 mmoles/10.0	10/1	99.4	103.1	---
	5,000/50	0.085 mmoles/1.0	100/1	99.8	100.1	---
	5,000/5	0.085 mmoles/0.1	1000/1	100.0	---	---
Ni/Co	5,000/500	0.085 mmoles/10.0	10/1	99.8	---	100.9
	5,000/50	0.085 mmoles/1.0	100/1	100.1	---	102.8
	5,000/5	0.085 mmoles/0.1	1000/1	100.3	---	---

^aAverage recovery for 6 Ni determinations by EDTA titration is $99.9 \pm 0.33\%$. Average recovery for 18 Ni determinations by atomic absorption method is $98.5 \pm 2.44\%$.

^bAverage recovery for 14 Cu determinations by atomic absorption method is $99.9 \pm 2.28\%$.

^cAverage recovery for 6 Co determinations by atomic absorption method is $100.9 \pm 3.02\%$.

Table 8. Results of nickel determination in NBS standard 124d

Trial	mg Ni initial	mg Ni found by AA	Recovery, %
1	0.5003	0.4998	99.9
2	0.5003	0.5098	101.9

are operative in this situation. Chemical interferences result from incomplete dissociation of compounds of the element being determined. These differences in completeness of dissociation mean that the analytical result for a given metal may very well be dependent on the other elements present in the solution. Interferences of this type may be eliminated by using a flame of higher temperature or adding a substance which preferentially binds the interferences, leaving the desired element unbound.

The second type of interference that also may be operative is called a bulk or matrix interference. Different concentrations of dissolved solids alter the nature and viscosity of the sample solution. The more concentrated solution flows through the burner at a slower rate, thereby decreasing the absorption.

Two milliliters of the dissolved NBS standard 124d were diluted to 50.0 ml and the nickel determined by atomic absorption using an air-acetylene flame. The absorbance reading indicated the concentration of nickel was 9.1 ppm. The actual concentration was 10.0 ppm; therefore, the atomic absorption method used without prior isolation of nickel gave a recovery of only 91.0%.

In order to explain the low result, the effect of increasing amounts of copper(II) and zinc(II) on the absorbance of an aqueous 20 ppm nickel(II) solution was studied. The results, shown in Figure 15, indicate the absorbance of the nickel solution is decreased for ratios of Cu/Ni above 1/1. The absorbance of the nickel solution is increased for ratios of Zn/Ni above 1/10. The sample analyzed for nickel consisted of a Cu/Ni ratio of 84/1 and a Zn/Ni ratio of only 5/1. From the appearance of the curve for the effect of copper on nickel absorbance it would be expected that the determination of nickel in NBS standard sample 124d would be even lower than 91.0%. Apparently the presence of other metal ions that increase the absorbance of nickel, e.g. zinc, helps somewhat to compensate for the effect of the copper matrix. Thus the most satisfactory way to eliminate spectral, chemical and matrix interferences is to isolate the substituent via separation methods prior to its analysis.

The elution behavior of several metal ions from an amine impregnated Chromosorb W column was determined by taking spot tests on effluents at 2 ml intervals. The metal ions studied, their breakthrough volumes and band widths are recorded in Table 9.

The data indicated some possible separations, which were performed quantitatively. The column used was 1.0 cm x 18.0 cm. It was prepared and regenerated by washing with 1 M potassium thiocyanate-1 M hydrochloric acid. The eluent was 0.1 M nitric acid and the flow rate was controlled at 1 ml/min. The separations and their results are listed in Table 10.

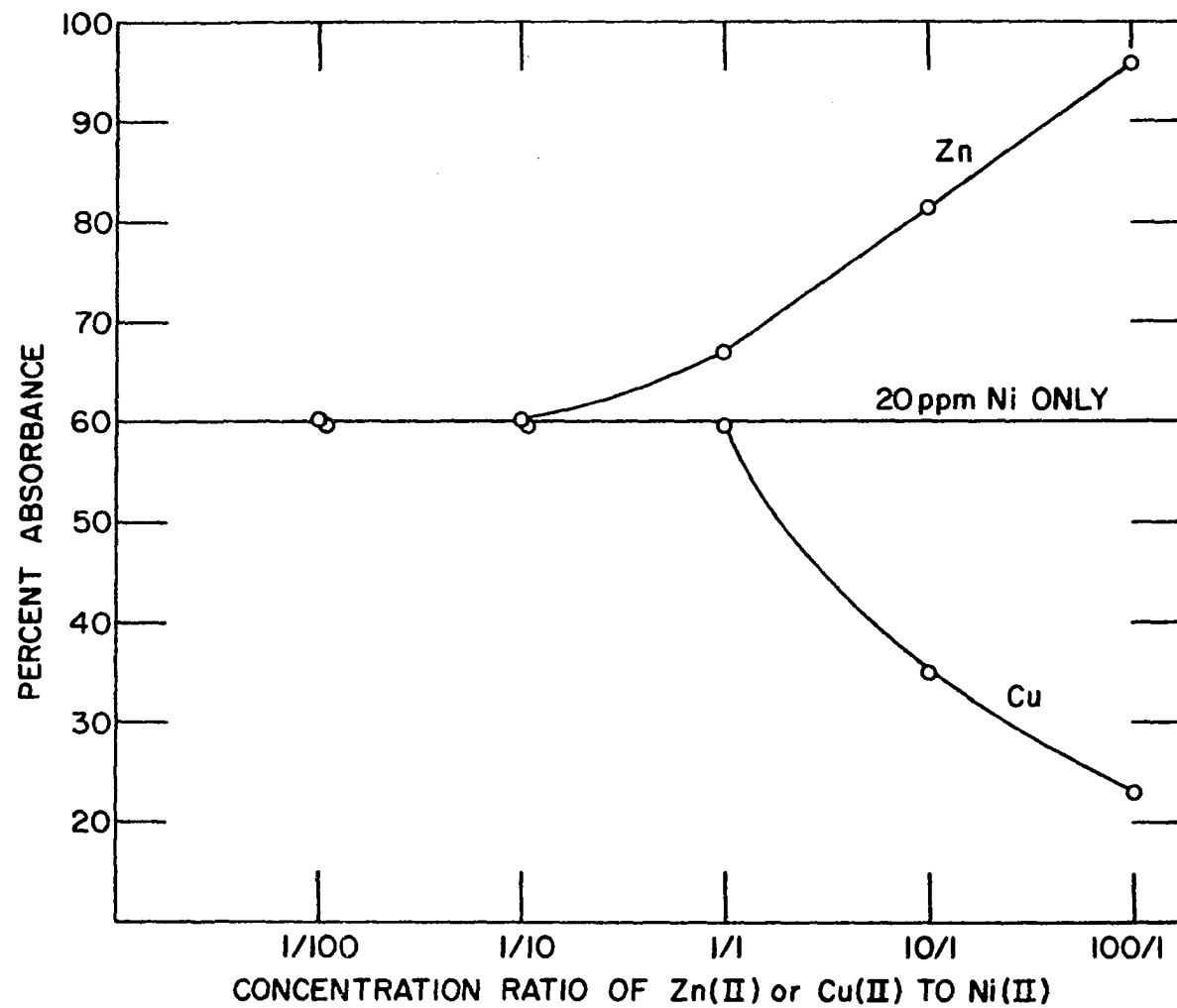


Figure 15. Effect of Zn(II) or Cu(II) on the atomic absorption determination of an aqueous 20 ppm Ni(II) solution. An air-acetylene flame was used

Table 9. Elution volumes of metal ions on an Alamine 336 impregnated Chromosorb W column using 0.1 M nitric acid as eluent

Metal ion	Mmoles added	Breakthrough volume (ml)	Band width (ml)
Ga	0.01	43-60	17
		36-60	19
Ga	0.05	46-120	74
		48-125	77
Ni	0.02	All off within 20 ml	
Al	0.02	All off within 20 ml	
Mn	0.05	34-100	66
Ti	0.05	31-140	109
Fe	0.02	Still remained on column after 255 ml	

Table 10. Separations on Alamine 336 impregnated Chromosorb W columns

Sample - mmoles	Fraction collected	Recovery, %
1. Ni 0.017	0-30	98.9
Ga 0.019	30-115	99.5
Ni 0.017	0-30	98.1
Ga 0.019	30-115	99.0
2. Al 0.02	0-35	99.1
Ga 0.02	35-185	99.3
Al 0.02	0-35	99.1
Ga 0.02	35-210	99.9
Fe 0.01	210-260 (MeOH)	99.4 ^a

^aFe was determined radiometrically.

The reversed-phase column chromatographic work was continued using an Alamine 336 in toluene solution and a new inert support, Amberlite XAD-2. In order to predict column elution behavior from batch distribution data via equation 10, several experimental restrictions were imposed.

1. The sample solution and the eluent were of the same composition used for determining the batch D.
2. The column was prepared very carefully to insure uniform packing.
3. The sample volume was small, 1.0 ml.
4. Flow rates were adjusted between 0.5 - 1.0 ml/min.

An elution profile of 0.015 mmoles of gallium(III) from a 1.0 cm x 12.0 cm column is shown in Figure 16. Three milliliter fractions were collected and determined spectrophotometrically as the gallium-Arsenazo I complex at λ_{\max} of 580 nm. For this column, $V_S = 3.0$ ml, $V_M = 5.1$ ml and therefore $\bar{V} = 20(3.0) + 5.1 = 65.1$ ml. The experimental \bar{V} is approximately 40 ml. This discrepancy is too large to be accounted for by small errors in determining V_S and V_M . Referring back to page 33, Figure 3, it was noted that increasing thiocyanate concentration did not affect the rate at which equilibrium was obtained in the extraction of gallium(III) by a 20% exchanger solution. This implies that in the amine system, the rates of exchange are fast. In a reversed-phase column procedure, however, the continuous flow of solute and solvent past exchange sites does not permit equilibrium to be completely attained. Thus it seems possible that a competition for resin sites exists between free thiocyanate ion and the exchangeable gallium thiocyanate complex.

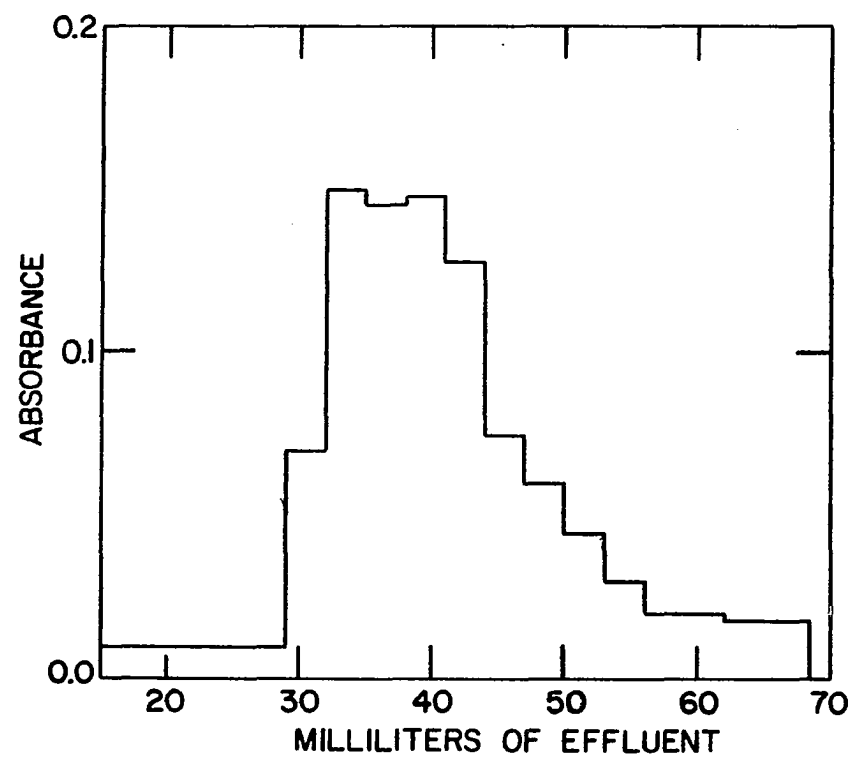


Figure 16. Elution profile of 0.015 mmoles of Ga(III) at a flow rate of 0.5 ml/min on a column 1.0 cm x 12.0 cm. The eluent was 0.33 M KSCN-0.5 M HCl

In order to test this behavior, a series of gallium elutions were performed for various eluent thiocyanate concentrations. The results, listed in Table 11, indicate that at low thiocyanate concentrations ($< 0.25 \text{ M}$) the agreement between the experimental and calculated retention volumes is fair. For larger thiocyanate concentrations ($\geq 0.33 \text{ M}$), the agreement is very poor. The experimental retention volume was used to calculate a new distribution ratio via equation 10. A comparison of column distribution ratios and the batch distribution ratios is shown in Figure 17. The column distribution ratio levels off to a constant value for thiocyanate concentrations above 1.0 M .

Table 11. Column elution experiments for 0.015 mmoles of gallium(III)

ht	Column parameters			Eluent		Batch data		Column data	
	i.d. cm	V_S ml	V_M ml	$x \text{ M KSCN}$ - 0.5 M HCl	D	calc. \bar{V} ml	\bar{V} ml	calc. D	Band ml
12.6	1.3	2.9	6.1	0.0	2.33	11.6	15.0	3.07	9-21
12.0	1.3	5.0	7.2	0.19	8.0	47.2	34.5	5.5	16-53
12.0	1.3	3.6	7.4	0.25	12.5	52.4	41.5	9.5	25-58
12.9	1.3	3.2	6.8	0.25	12.5	46.8	39.5	10.2	23-56
12.6	1.3	2.9	6.1	0.33	20.0	64.1	45.7	13.7	28.5-63.0
17.0	1.0	5.0	7.2	0.33	20.0	84.0	58.0	13.5	31.0-85.0
12.9	1.3	3.2	6.8	0.50	40.3	129.0	61.0	16.9	36.0-86.0

A three component separation was performed, based on batch distribution data for a 30% exchanger solution. The column used was 1.0 cm x 18.0 cm and $V_S = 3.0 \text{ ml}$. Using an eluent of 1 M potassium thiocyanate- 1.0 M nitric acid, nickel(II) passes directly through the column while gallium(III) and cobalt(II) are sorbed. Gallium is eluted from the column with 0.2 M nitric acid while cobalt is stripped with 12 M hydrochloric

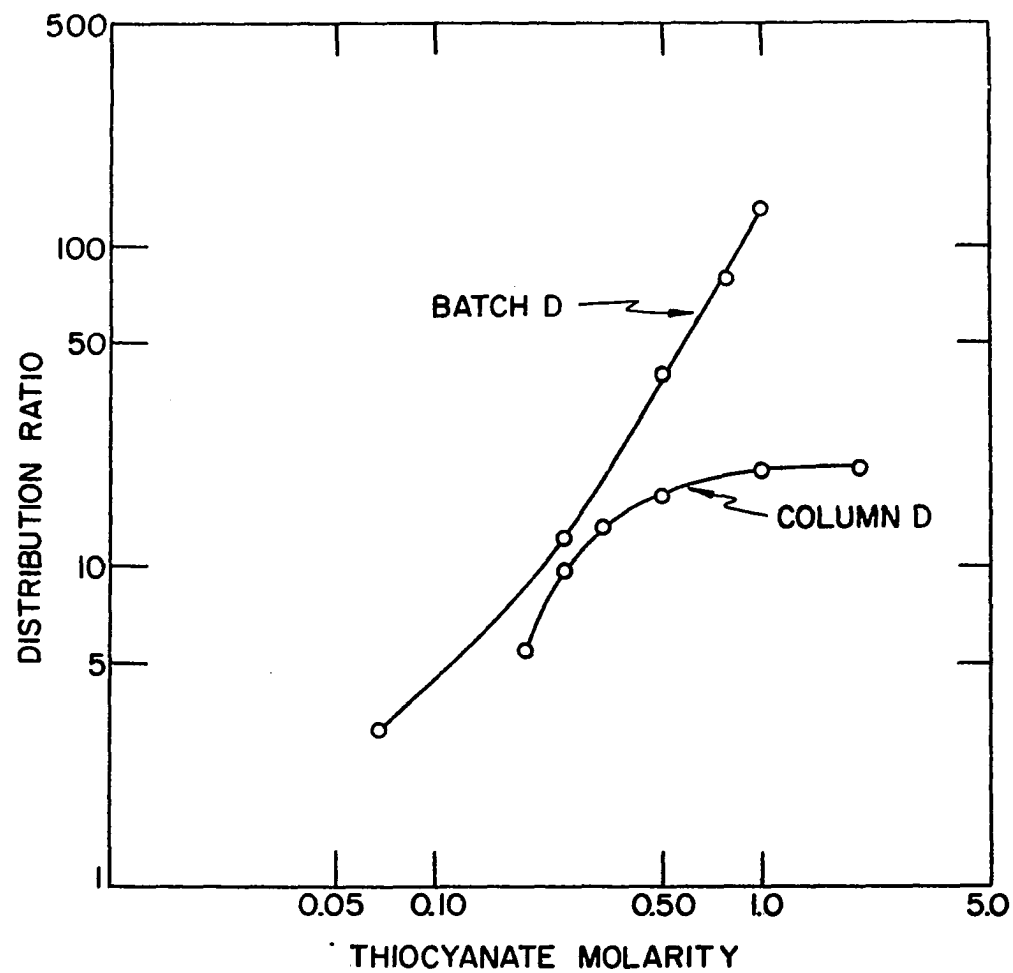


Figure 17. Comparison of batch distribution ratio and column distribution ratio for Ga(III)

Table 12. Separation of nickel(II), gallium(III) and cobalt(II) on an XAD-2 column impregnated with 30% exchanger

Metal ion, mmoles	Milliliters eluent used	Recovery, %
Ni-0.06	25 ml 1.0 M KSCN-0.1 M HNO ₃	99.7, 100.0
Ga-0.05	50 ml 0.2 M HNO ₃ 30 ml 0.2 M HClO ₄ ^a	99.8, ---
Co-0.05	35 ml 12 M HCl	100.0, 100.0

^a0.2 M HClO₄ starts eluting the blue cobalt band down the column.

acid. The results of two attempts of this separation are listed in Table 12.

Amberlyst A-21

The capacity of the A-21 weak base resin was determined by the following procedure.

The resin was packed into two large columns and washed successively with 1.0 M potassium thiocyanate-0.5 M hydrochloric acid, 2.0 M potassium thiocyanate, and distilled water. Using a Büchner funnel the resin was filtered and washed three times with 1.0 M potassium thiocyanate-0.5 M hydrochloric acid and twice with distilled water before being oven dried at 110° C. One-gram samples were washed with 0.1 M sodium hydroxide and distilled water. The stripped thiocyanate was determined by the Volhard method¹.

¹Excess silver nitrate was added and back-titrated with standard potassium thiocyanate using a saturated solution of ferric ammonium sulfate as the indicator (65).

Two determinations were made on each of three batches of resin prepared by the above method. The average for the three batches was 3.24, 3.27 and 3.24 milliequivalents, giving an overall average capacity of 3.25 meq/g.

Batch distribution ratios were determined for a large number of metal ions at thiocyanate concentrations varying from 0.03 M - 1.0 M. Metal ion concentrations were in the range of 0.10 - 0.20 mmoles. Since 2.0 g resin were used, the highest loading percentage was $(0.20/6.50)100 = 3.1\%$. The distribution data are listed in Table 13. Plots of $\log D$

Table 13. Batch distribution ratios (D_W) for metal ions from aqueous thiocyanate solutions into Amberlyst A-21 resin

Metal ion	D_w at given aqueous [thiocyanate]					
	0.03	0.10	0.20	0.30	0.50	1.0
1. Al(III)	2.87	2.87	---	---	7.16	19.4
2. Ca(II)	0.0	---	---	---	---	---
3. Dy(III)	0.92	---	---	---	---	---
4. Ga(III)	1.9	9.54	---	---	---	---
5. Hf(IV)	0.17	6.41	42.6	167	273	1500
6. La(III)	0.89	0.92	---	---	0.89	1.68
7. Lu(III)	0.94	---	---	---	---	---
8. Mg(II)	0.0	---	---	---	---	---
9. Mn(II)	0.08	1.0	3.08	---	13.6	25.1
10. Ni(II)	1.44	6.86	---	---	47.3	86.0
11. Sc(III)	0.0	0.70	3.61	---	45.2	158
12. Th(IV)	0.0	0.0	0.11	---	2.48	9.76
13. Ti(IV)	0.84	6.53	22.8	63.0	129	300
14. Zr(IV)	0.67	10.3	48.5	157	320	1000

15-25. The following metal ions were quantitatively ($D_w > 1000$) taken up from 0.03 M thiocyanate solution: Bi(III), Co(II), Cd(II), Cu(II), Fe(III), Mg(II), In(III), Mo(VI), U(VI), V(IV), and Zn(II).

versus $\log[\text{thiocyanate}]$ for several metal ions are shown in Figures 18 and 19.

A study of D_w versus shaking time was performed for the uptake of scandium(III) from two different thiocyanate concentrations. A plot of $D/D_{\text{equilibrium}}$ shown in Figure 20 indicates that the 30-minute equilibration period is more than adequate. The rate of attainment of equilibrium is slower when higher concentrations of thiocyanate ion are present. Thus experimental retention volumes would be expected to be less than calculated retention volumes for eluents of higher thiocyanate concentration. This effect is most likely explained in terms of an increased competition for the resin site between thiocyanate ion and the anionic metal thiocyanate complex.

A series of elution curves were determined by eluting ~ 0.03 mmoles of metal and testing the effluent at 3-ml intervals. The spot tests were qualitatively rated according to intensity so that elution profile curves could be constructed. The results of these elution curves and the pertinent column data are listed in Table 14.

The tailing of elution curves is generally due to poor sorption-desorption kinetics. In other words, for a solute band to remain compact as it traverses down the column the ions must become attached to and then be detached from the resin site at comparable rates. A study of the rate of desorption of scandium(III) from A-21 resin was performed in the following manner. Scandium(III) was extracted from 1.0 M potassium thiocyanate-0.5 M hydrochloric acid into five 2.0 g samples of resin. The amount of metal ion sorbed was determined by difference after

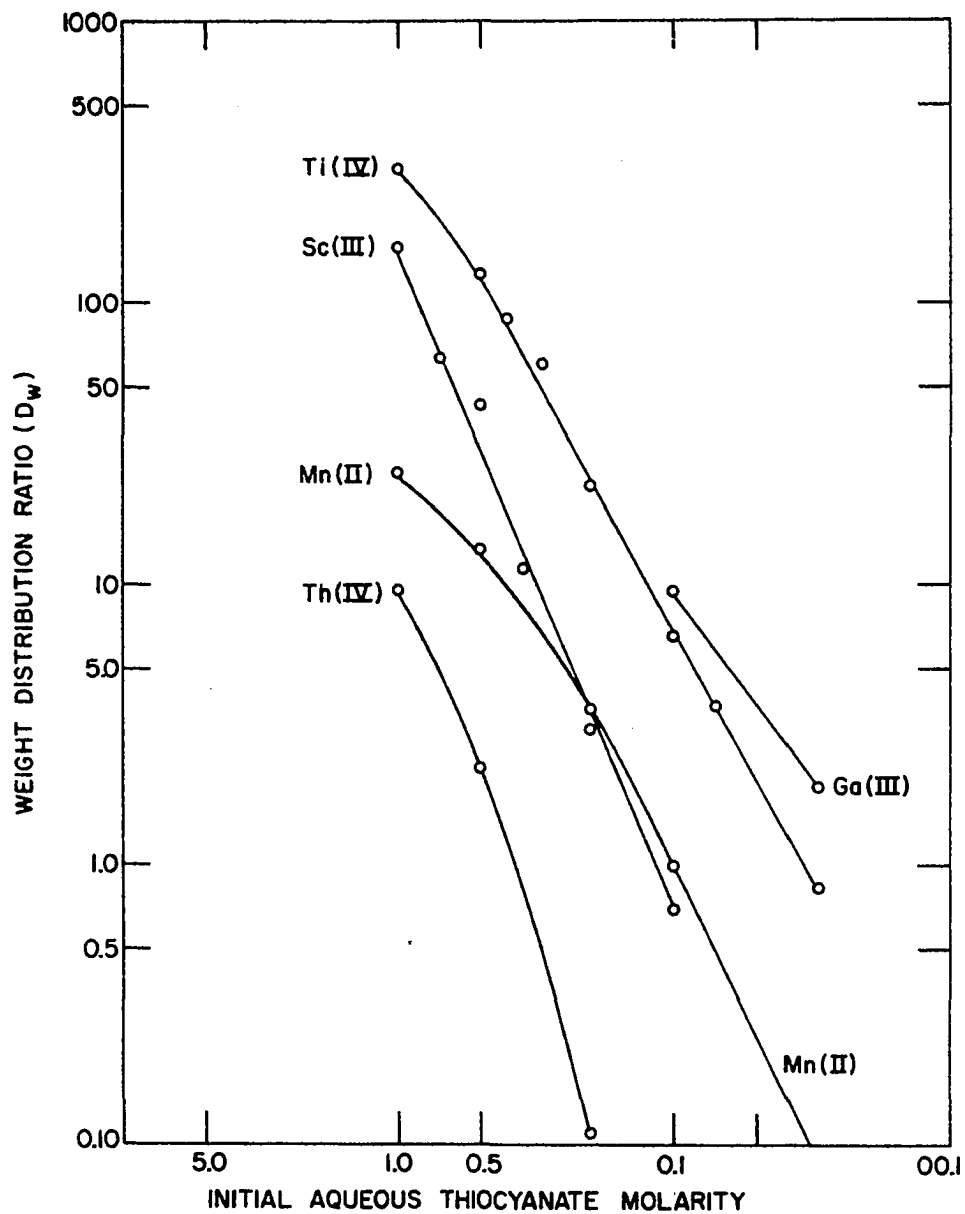


Figure 18. Distribution data for the sorption of metal ions from aqueous thiocyanate-0.5 M HCl solution into Amberlyst A-21 resin

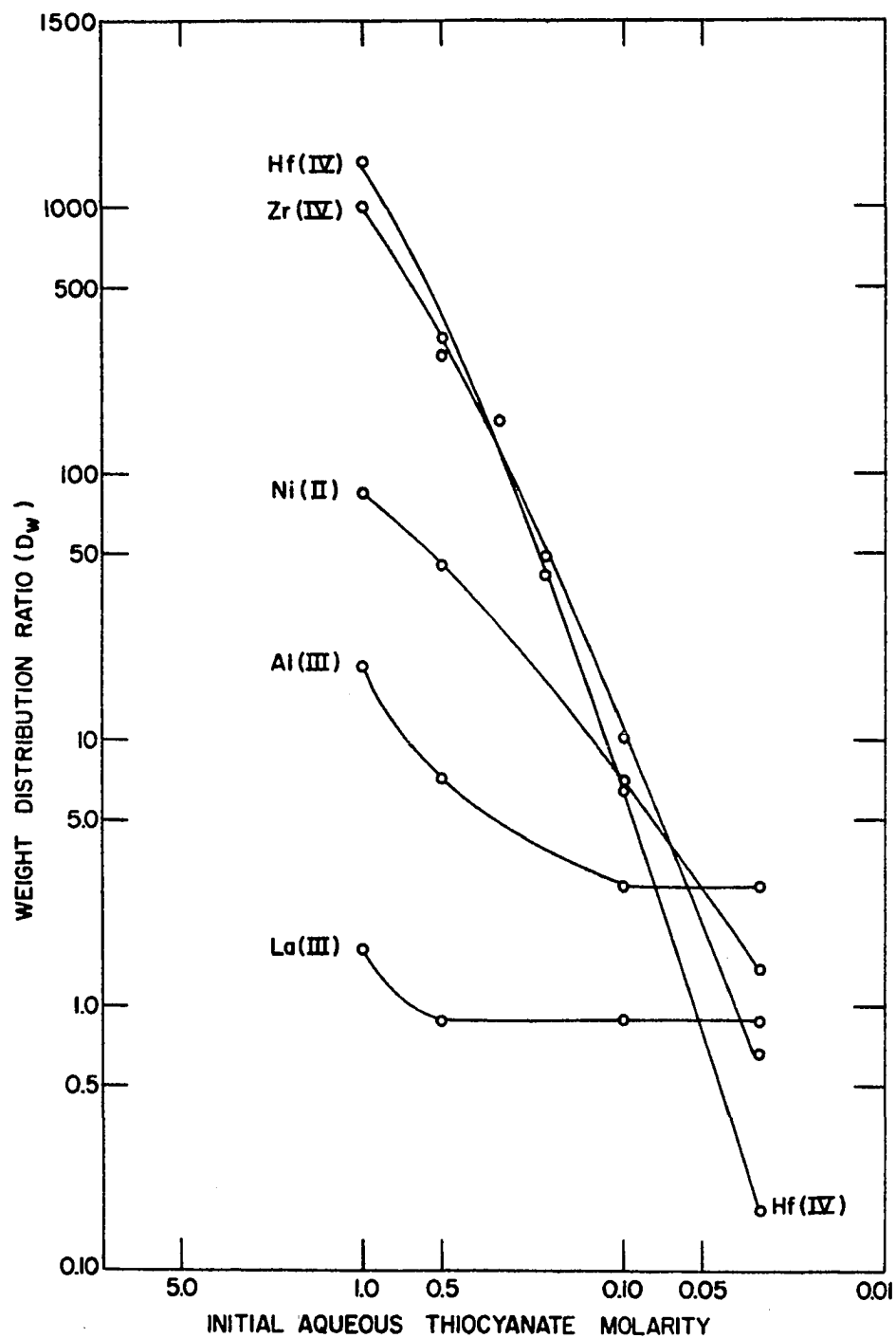


Figure 19. Distribution data for the sorption of metal ions from aqueous thiocyanate-0.5 M HCl solution into Amberlyst A-21 resin

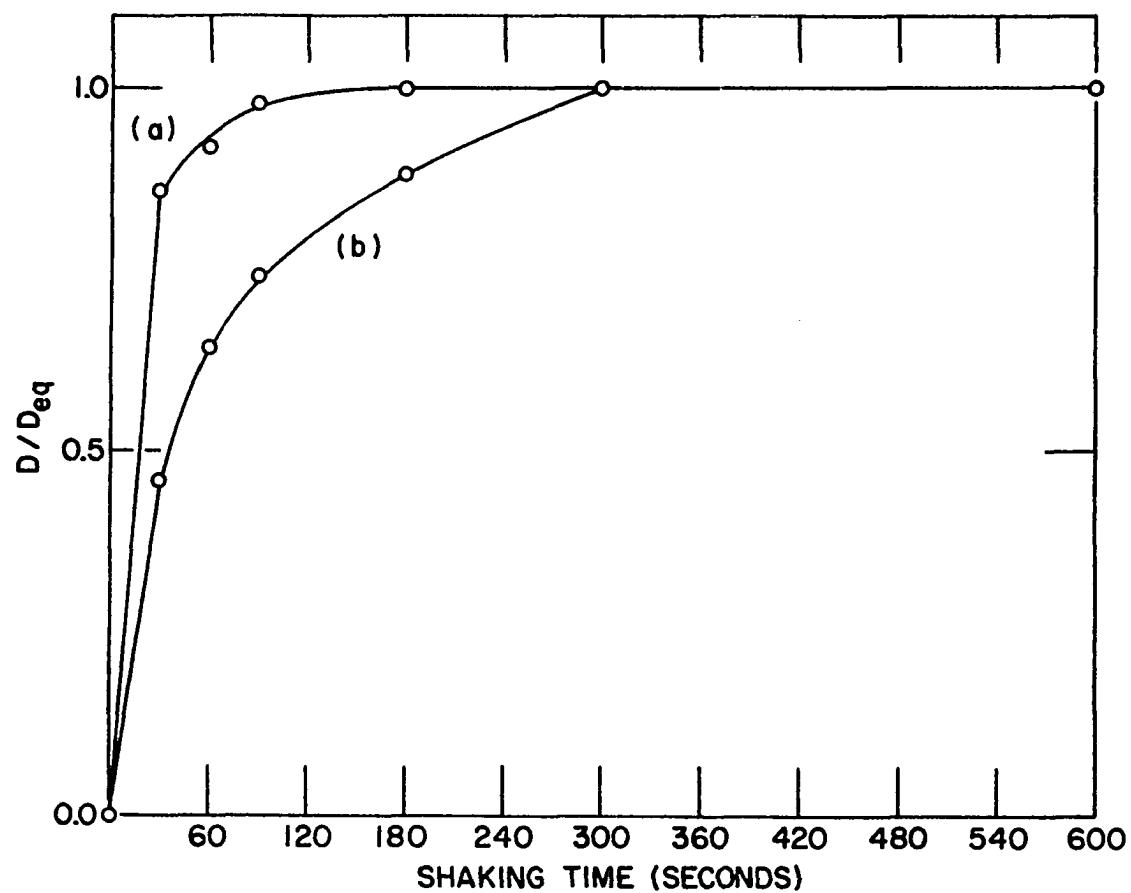


Figure 20. Rate of sorption of Sc(III) from aqueous thiocyanate solution into Amberlyst A-21 resin. Solution (a) is 0.35 M KSCN-0.5 M HCl and (b) is 0.70 M KSCN-0.5 M HCl

Table 14. Elution behavior of metal ions on Amberlyst A-21

Metal ion	Column parameters ^a				Eluent	Band ^b			
	ht. (cm)	i.d. (cm)	X (ml)	D _v		width (ml)	Calc. \bar{V} (ml)	Expt. \bar{V} (ml)	
1. Sc(III)	3.7	1.0	2.90	11.4	0.5 M KSCN- 0.5 M HCl	15-88	36.3	33-39	
	3.7	1.0	2.90	24.8	0.7 M KSCN- 0.5 M HCl	34-130	75.1	53-59	
2. Mn(II)	4.0	1.0	3.14	7.99	1.0 M KSCN- 0.5 M HCl	14-55	28.9	24-28	
	9.2	1.0	7.21	6.95	1.0 M KSCN- 0.5 M HCl	35-90	70.4	52-58	
3. Th(IV)	16.1	1.0	12.6	2.71	1.0 M KSCN- 0.5 M HCl	20-95	95.6	38-44	

^aFlow rates were controlled at 0.5 ml/min.

^bSome tailing exists for all elutions giving rise to wide bands.

titrating an aliquot of the aqueous phase. Then the scandium(III) was back-extracted from the resin samples at various shaking times. The eluent used for back-extraction was 0.02 M potassium thiocyanate-0.5 M hydrochloric acid. D_w for scandium(III) is zero for this eluent. A plot of percent back-extracted versus time is shown in Figure 21.

Although a constant value of scandium back-extracted is reached fairly rapidly (90 seconds), all of the metal ion has not been removed from the resin. In a column elution sequence, fresh eluent is continually moving down the column so that all of the metal ion is eventually desorbed. However, the small amount of metal ion which remains on the resin site longer than the bulk concentration is spread out as it is eluted and gives a "tail" to the elution curve.

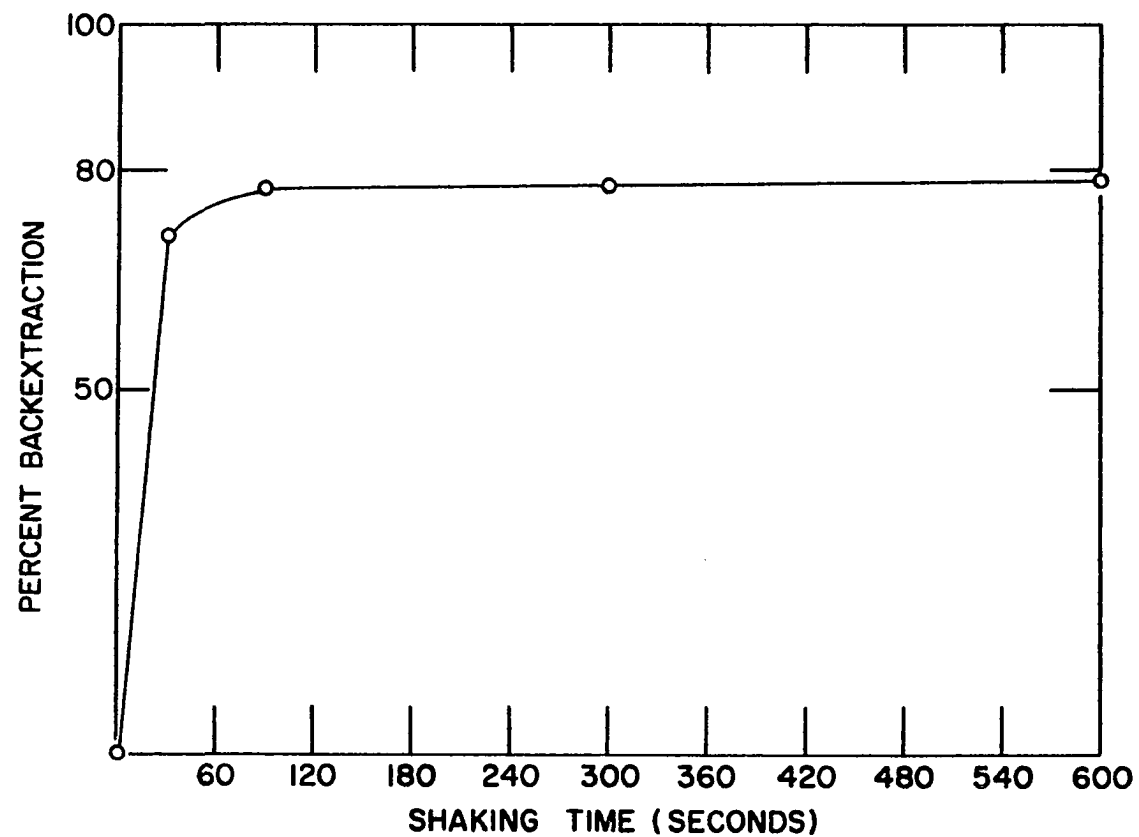


Figure 21. Rate of desorption of Sc(III) from Amberlyst A-21 resin into an aqueous 0.03 M KSCN-0.5 M HCl solution

It is always advantageous if strongly sorbed metal ions can be removed from the resin with little difficulty. A study to find possible stripping agents for strongly sorbed metal ions was performed in the following manner. The metal ion, 0.03 - 0.05 mmoles, was sorbed to a 1.0 cm x 9.0 cm column using an eluent of 1.0 M potassium thiocyanate-0.5 M hydrochloric acid. The column was then eluted with a given solution and the effluent quantitatively analyzed for the metal ion. The results of these stripping experiments are listed in Table 15. The success of perchlorate solutions was expected because the resin does have a greater affinity for perchlorate ion than for thiocyanate ion.

The A-21 resin was used to remove iron(III) and copper(II) from hard water samples (see p. 41). The procedure involved first washing a 2.0 cm x 9.0 cm column of resin with approximately 50 ml 1 M potassium thiocyanate-0.5 M hydrochloric acid. The sample used was one liter of Ames, Iowa water and was pretreated as follows:

1. made 0.01 M in hydrochloric acid
2. made 0.01 M in ammonium thiocyanate
3. 20 ppm iron(III) added
4. 10 ppm copper(II) added

This one-liter sample was continuously passed through the column and various fractions collected and titrated for hardness. The effluent was clear and all end points were excellent. The colored iron and copper bands were visible on the top 4 cm of the column. The titration results are listed in Table 16. The flow rates were very fast and the results indicate that no magnesium or calcium is being retained by the column.

Table 15. Stripping experiments of highly sorbed elements from Amberlyst A-21

Metal ion	Eluent - ml	Recovery, %
1. Co(II)	0.5 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 35	100.3
	0.5 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 35	99.7
	Acetone:H ₂ O:HCl(25:2:2) - 10	100.8
	0.5 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 10	
2. Fe(III)	Acetone:H ₂ O:HCl(25:2:2) - 30	103.4 ^a
	Acetone:H ₂ O:HCl(25:2:2) - 30	104.1 ^a
3. Cd(II)	1.0 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 35	100.4, 100.0
4. Zn(II)	1.0 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 35	100.4, 100.3
5. Bi(III)	1.0 <u>M</u> HClO ₄ - 35	99.2, 100.0
6. In(III)	1.0 <u>M</u> HClO ₄ - 40	100.0
7. V(IV)	1.0 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 30	99.6, 100.8
8. U(VI)	1.0 <u>M</u> NaClO ₄ - 0.01 <u>M</u> NH ₄ SCN - 40	qualitative
	Acetone:H ₂ O:HCl(25:2:2) - 30	qualitative

^aFe(III) was determined radiometrically. After stripping, the resin was removed from the column and counted in sections. None of the sections gave counts significantly above background.

Table 16. Removal of added iron(III) and copper(II) from Ames city water

Fraction effluent collected	Flow rate ml/min	ml titrated	Ca + Mg Recovery, %
50-100	10.9	50	100.0
150-200	11.1	50	100.2
250-350	---	100	100.2
450-500	---	50	100.0
600-700	9.5	100	100.4
850-900	---	50	100.2

The magnitude of the distribution data suggests many possible separations so some representative and interesting examples were chosen to illustrate the utility of the system. One such separation possibility was that of scandium(III) from thorium(IV) and rare earths(III). Preliminary studies involving spot tests on individual metal ions indicated that the separation could be accomplished on a column 1.0 cm x 9.0 cm. The elution curve for the separation of 0.01 mmoles of lanthanum(III), and 0.02 mmoles of thorium(IV) from 0.02 mmoles of scandium(III) is shown in Figure 22. For two such separations the recovery of scandium(III) was 100.5% and 100.0% respectively. This separation was qualitatively confirmed using dysprosium(III) or lutecium(III) in place of lanthanum(III). Thus the method presented here is a simple, rapid and convenient way to separate scandium using a rather short column. In fact, this particular separation shows a marked advantage over a similar separation using the strong base anion exchange resin Dowex 1X8. Hamaguchi et al. (35) converted the resin to the thiocyanate form, sorbed the sample and then eluted with 3 M hydrochloric acid. Their column was 1.1 cm x 18 cm and they used a flow rate of only 0.17 ml/min because an equilibrium study by a batch method indicated that scandium(III) required 20 hours to attain exchange equilibrium in the anion exchanger-thiocyanic acid system at room temperature. Their system required approximately 55 ml to elute europium, terbium or lutecium while scandium was eluted in a 95-180 ml band. The thorium-scandium separation was not even complete because thorium required 100 ml for elution. The authors suggested using a longer column to accomplish a complete separation.

Other separations accomplished using a 1.0 cm x 9.0 cm column are

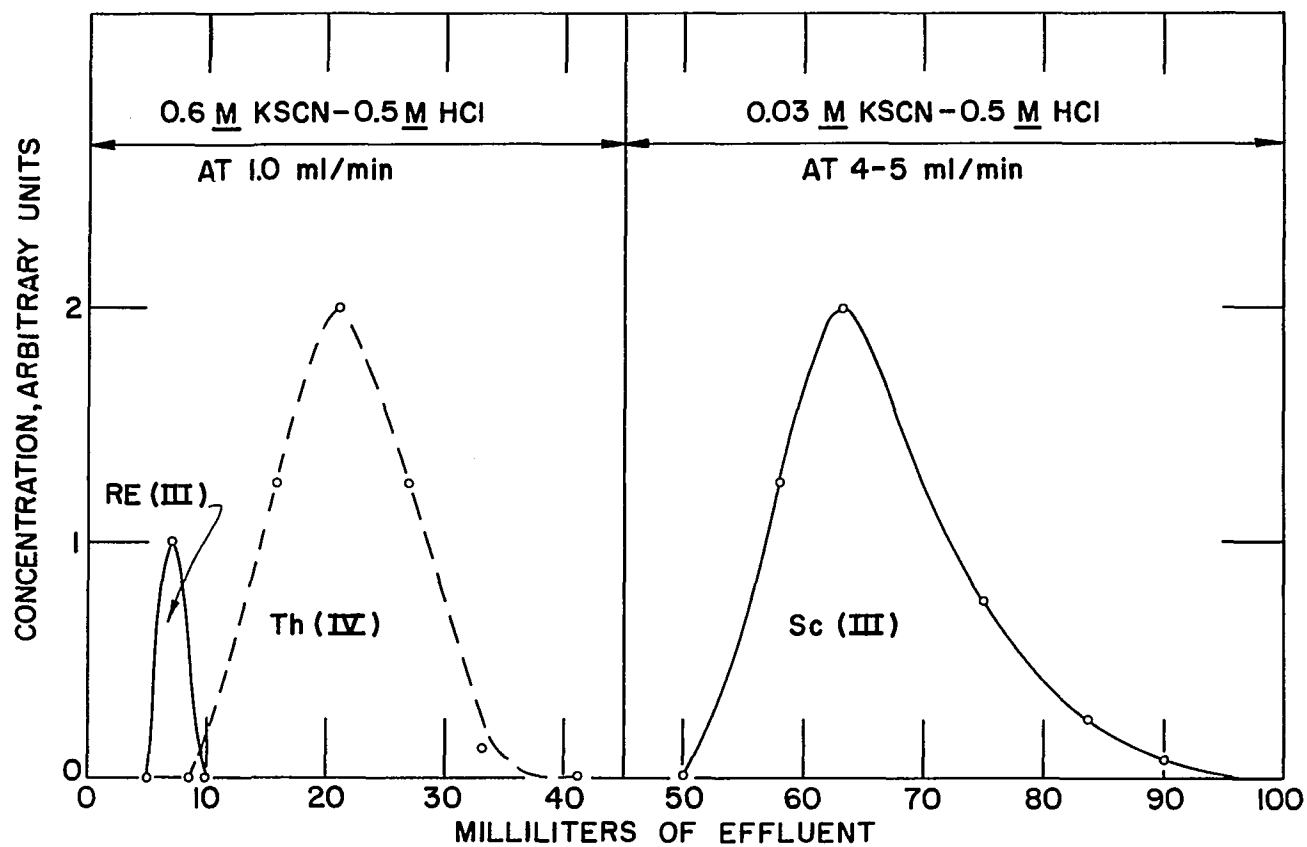


Figure 22. Elution curve for the separation of 0.01 mmoles of rare earths(III) and 0.02 mmoles of thorium(IV) from 0.02 mmoles of scandium(III)

listed in Table 17. Elution curves for the nickel(II)-vanadium(IV) and the thorium(IV)-titanium(IV) separations are shown in Figures 23 and 24. The flow rates used for these separations were controlled at 1.0 ml/min.

A shorter column and faster flow rate should be applicable for separations involving metal ions with very low distribution ratios (such as nickel or rare earths) and ions with distribution ratios above 1000 [such as vanadium(IV), iron(III) and uranium(VI)]. The separation of rare earth (dysprosium) from iron and uranium was performed on a 1.0 cm x 5.0 cm column. Dysprosium was eluted with 15 ml of 0.5 M potassium thiocyanate-0.5 M hydrochloric acid and iron and uranium were stripped with 13 ml of acetone:H₂O:HCl(25:2:2). The total time elapsed beginning with the addition of the 1.0 ml sample and ending with the complete stripping of iron and uranium was five minutes. This gives an average flow rate of $29 \text{ ml}/5 \text{ min} = 5.8 \text{ ml/min}$. The iron and uranium bands were still located at the top 1-2 cm of the column until they were stripped. The recovery of dysprosium was 100.0% while the recovery of iron was 99.5%.

Table 17. Separations on a 1.0 cm x 9.0 cm column of A-21 resin

Sample mixture	Eluent - volume (ml)	Recovery, %
Ni(II) - 0.04 mmoles	0.045 <u>M</u> NH_4SCN - 0.5 <u>M</u> HCl - 30	100.0, 100.7, 100.7, 100.0
V(IV) - 0.025 mmoles	1.0 <u>M</u> NaClO_4 - 0.01 <u>M</u> NH_4SCN - 25	--- --- 99.6, 100.8
La(III), Er(III), Lu(III) - 0.01 mmoles	0.5 <u>M</u> NH_4SCN - 0.5 <u>M</u> HCl - 20	100.0, 101.0, 100.0
Fe(III) - 0.01 mmoles	Acetone: H_2O : HCl (25:2:2) - 25	99.5, 99.5, 99.9
U(VI) - 0.013 mmoles		qualitative
Th(IV) - 0.02 mmoles	0.3 <u>M</u> KSCN - 0.5 <u>M</u> HCl - 35	99.1, 99.6
Ti(IV) - 0.02 mmoles	0.02 <u>M</u> KSCN - 0.5 <u>M</u> HCl - 40	qualitative

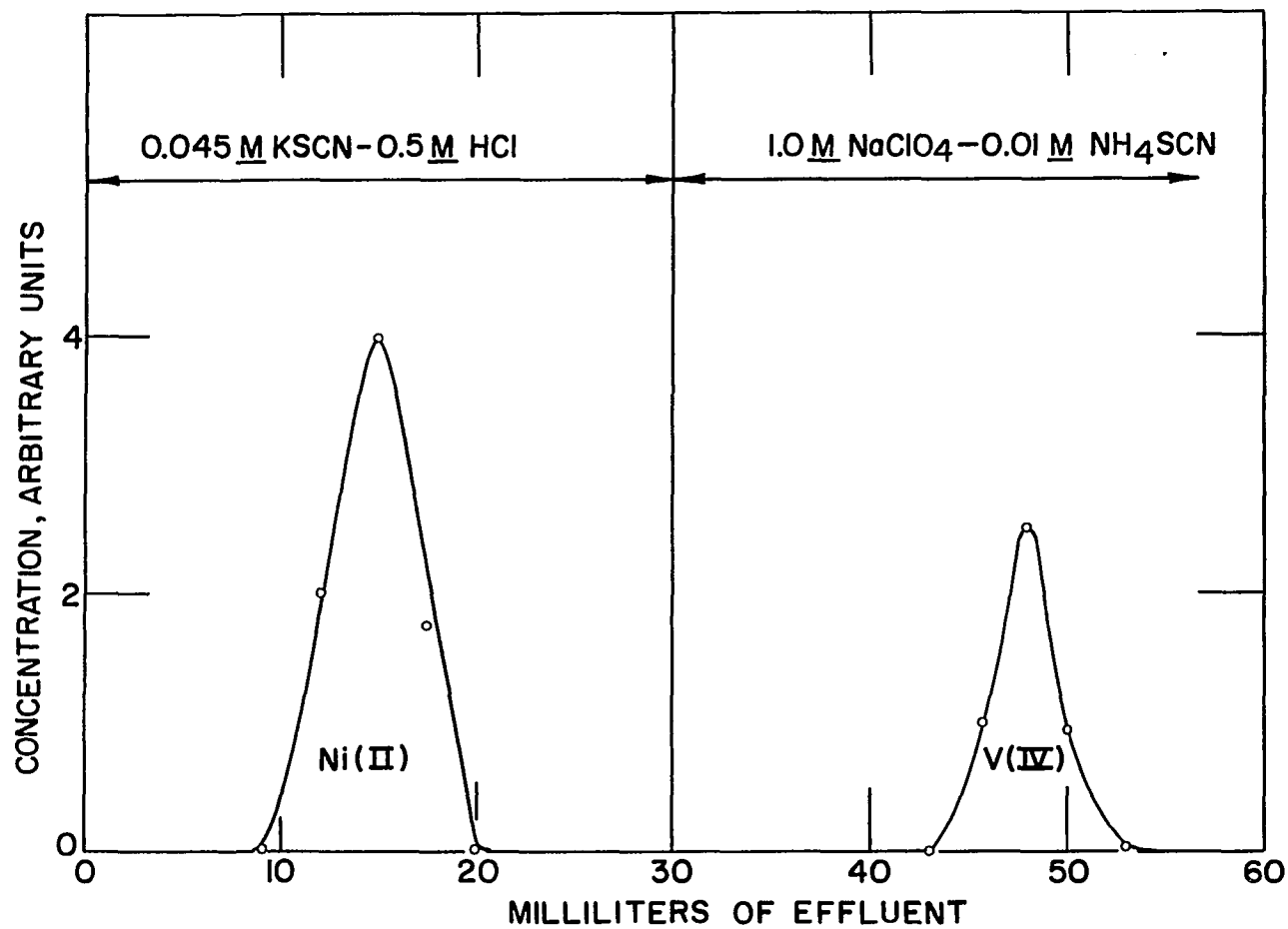


Figure 23. Elution curve for the separation of 0.04 mmoles of nickel(II) and 0.025 mmoles of vanadium(IV)

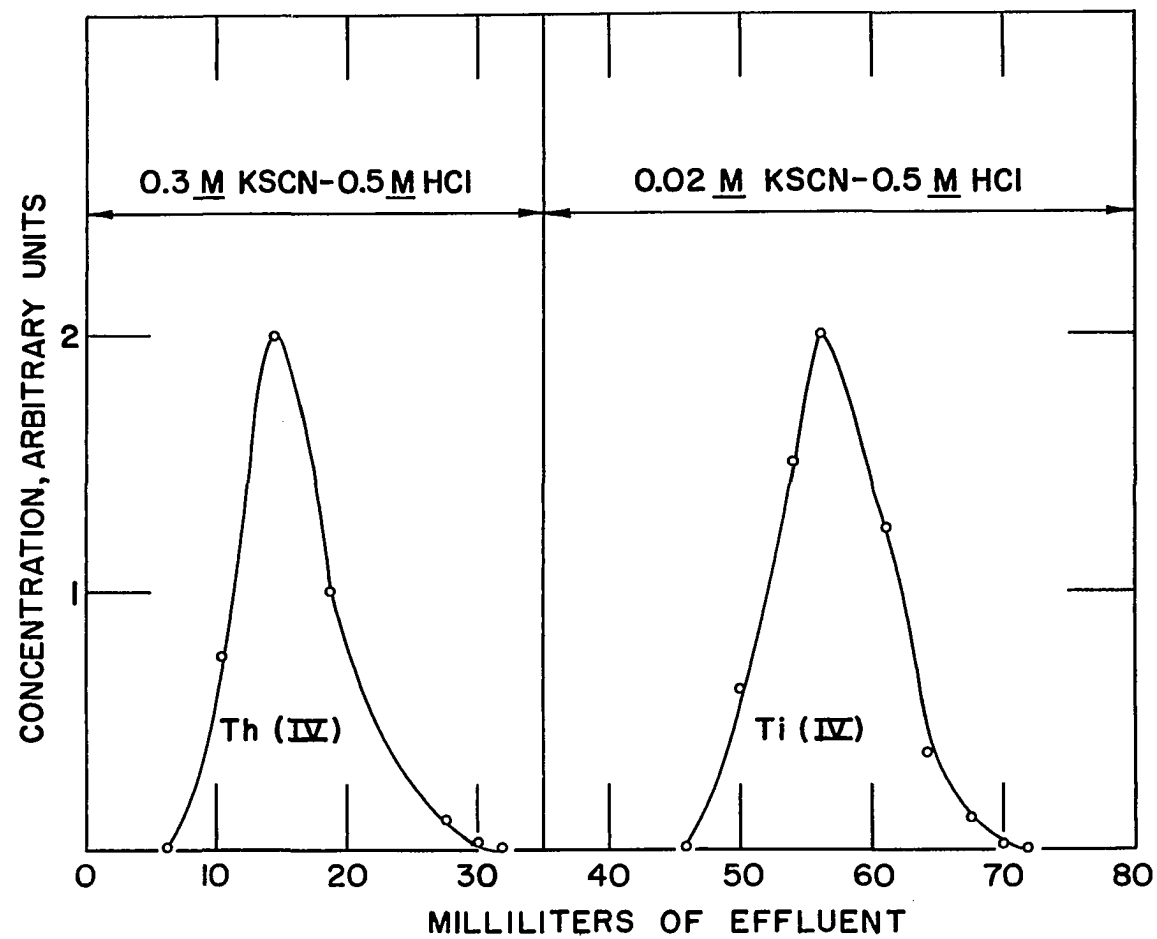


Figure 24. Elution curve for the separation of 0.02 mmoles of thorium(IV) and 0.02 mmoles of titanium(IV)

CONCLUSIONS

The liquid ion exchanger investigated, Alamine 336, may be used to effect numerous separations of metal ions in thiocyanate media. Some of these separations have been quantitatively demonstrated while others are suggested by the analogous behavior of metal ions in their particular extraction group.

Any combination of metal ions in Group 1 (low percentage extraction) may be rapidly and quantitatively separated from any combination of metal ions in Group 2 (high percentage extraction) by a simple reversed-phase column chromatographic technique. However, one solvent extraction procedure was successful in completely removing interfering ions while the ions of interest were not extracted. Thus the quantitative removal of iron(III), copper(II) and cobalt(II) from hard water samples substantiated the solvent extraction distribution data which indicated 100% extraction of these metal ions and 0% extraction of calcium(II) and magnesium(II).

Some intermediate extracted metal ions, Group 3, were studied further and the analogous behavior of gallium(III), manganese(II) and titanium(IV), which would allow them to be separated from Groups 1 and 2, has been noted and quantitatively demonstrated (Tables 9 and 10, p. 64). The Chromosorb W-Alamine 336 column and the XAD-2 $R_3NH^+SCN^-$ /toluene column may be used interchangeably for work involving Groups 1 and 2 metal ions. However, their "unique" behavior under conditions used to study the intermediate extracted group has been mentioned and led to the analytically important iron(III)-gallium(III) separation (p. 64).

The correlation of batch distribution data to the experimental

elution behavior of gallium(III) via equation 10 was fair for low thiocyanate concentrations ($< 0.33 \text{ M}$) but poor for higher thiocyanate concentrations. Of course, only a very general correlation is to be expected when sorbing the pure Alamine 336 to the Chromosorb W column. The exact behavior of the metal ion may be determined by eluting it on a column of known parameters. Although this procedure may be time consuming for highly extracted metal ions, it may be advisable initially to determine distribution ratios in this manner. That is, experimentally determine retention volumes and then calculate D via equation 10. This procedure has been used by Huff (29) with a slight modification. He defined the distribution coefficient, K_d , in the following manner:

$$K_d = \frac{\text{ml of effluent at elution maximum}}{\text{g of extractant mixture}}$$

The extractant mixture was 50% Aliquat 336 in xylene.

In the separations described in this work, the metal ions retained on the column have been stripped, along with the liquid ion exchanger, with methanol. The metal ion was then determined by atomic absorption spectrophotometry using an air-acetylene flame. The results have shown that for both the solvent extraction and reversed-phase column work, the metal ion can be determined directly in the presence of the organic phase. However, matrix and interelement effects should never be underestimated and always investigated. The analysis is fast and simple once the appropriate calibration curves are obtained by simulating the separation procedure with standard solutions. The complete procedure should readily lend itself to automation.

Under the mild conditions used in this study, i.e. room temperature and pressure, 10-30% (v/v) solution of exchanger in toluene, and aqueous acid concentrations of 0.05 - 1.0 M, the physical handling of the amine was no problem. Phase separations were quick and clean for the solvent extraction work. In the reversed phase column work, there was no problem of extractant bleeding from the support.

The author realizes many other avenues of investigation could have been undertaken in the study of a liquid ion exchanger. Different solvents could have been researched as well as different structures of amines. An interesting study would be to look at the variation of distribution ratios in the presence of diverse anions. Such a system might very well break down the "grouping" of metal ions which has occurred here. However, it is felt that the results presented here are sufficient to characterize the utility of the system. The distribution data have been determined with respect to certain variables and the validity of these data has been quantitatively demonstrated.

A study of Amberlyst A-21 in a thiocyanate system was included for two reasons:

1. A-21 is a weak base resin and furthermore, it is a macroreticular ion exchange resin.
2. A comparison of a liquid ion exchanger and a resinous ion exchanger of analogous functional group seemed logical.

The study of the rate of sorption of metal ion from thiocyanate media (p. 71) indicates that the macroreticular resin with its higher porosity and surface area exchanges anionic species at a faster rate than conventional weak base gel type resins (58, 59). However, the

exchange rates are somewhat slower compared to the liquid anion exchanger but the difference does not appear to be significant, for the following reason. The elution behavior of a metal ion on both the Alamine 336 column and the A-21 column is about the same in that the elution curves exhibit a minor degree of "tailing". If there were a significant difference in exchange rates, the Alamine 336 should give more symmetrical elution curves than the A-21 column. Bear in mind that these results are based on flow rates adjusted to 0.5 - 1.0 ml/min at room temperature. Reducing the flow rate and increasing the temperature might have revealed a difference. However, as indicated throughout this work, the interest here was in developing fast and simple separations.

The extent of extraction for the two exchangers is comparable for those highly extracted metal ions, namely copper(II), cobalt(II), iron(III), cadmium(II), bismuth(III), indium(III), mercury(II), zinc(II), uranium(VI) and molybdenum(VI). The distribution ratios of the lower extraction group elements in the liquid ion exchange system do not vary as widely with aqueous thiocyanate concentration as in the A-21 system. This variation could be of value in effecting separations into more than just two groups. For instance, in the separation of thorium and rare earths from scandium (p. 79), uranium(VI) would have remained on the column while the scandium(III) was being eluted with a dilute thiocyanate solution. The uranium(VI) would then have been isolated from scandium and from thorium and rare earths.

The one real advantage that the A-21 system seems to have is in the stripping of highly sorbed metal ions from the column in such a manner

that regeneration of the column is simple. For the Alamine columns, methanol removed the metal ion and the amine from the column making regeneration impossible for the Chromosorb W columns and tedious for the XAD-2 column.

Hamaguchi et al. (35) studied the sorption of some metal ions from thiocyanate - 0.5 M hydrochloric acid solution onto the strong base anion exchange resin Dowex 1-X8. Thus a comparison between strong base data and weak base data is possible. Their data is reproduced in Table 18 (35).

As might be expected, there is agreement for the highly extracted metal ions. The behavior of rare earths¹ and calcium is also comparable. Two discrepancies which do exist are thorium and scandium. In their work the distribution coefficients for these elements are higher and show a substantial increase as the thiocyanate concentration increases. Obviously this behavior is the reason why the separation of rare earths and thorium from scandium was accomplished faster and more completely on the weak base resin than the **strong** base resin (see p. 79).

Another example of the inferior elution behavior of a strong base resin in a thiocyanate system as compared to the weak base system investigated here is the work of Majumdar and Mitra (44). They used the resin Amberlite IRA-400 in columns 1.3 cm x 16 cm. Their distribution data suggest similar separation possibilities but the elution curves obtained for the separation of simple two and three component mixtures

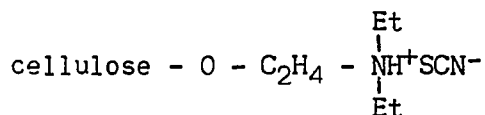
¹In the survey of literature section several papers dealt with the sorption of rare earths and actinides from aqueous thiocyanate solution onto strong base resins. In general sorption did not occur until the thiocyanate concentration was above 1 M, e.g. in the range 2 M - 10 M.

Table 18. Distribution coefficients of some elements in $\text{NH}_4\text{SCN-HCl}$ medium on Dowex-1X8 (35)

Element	Concentration of NH_4SCN in 0.5 M HCl , M					2.0
	0.2	0.4	0.6	0.8	1.0	
Sc	56	250	905	5040	2818	$>10^4$
La	<1	<1	<1	<1	<1	
Sm	<1	<1	<1	<1	<1	
Lu	<1	<1	<1	<1	<1	
Th	3.3	19	43	74	106	
Ca	0.0	0.0	0.0	0.0	0.0	
Al	0.0	0.0	0.7	0.7	0.9	
Cu	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	
Zn	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	
Cd	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	
In	579	646	734	580	706	
Hg	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	

required large volumes of eluent. The average band widths for their separations were 150-200 milliliters. However, they were using flow rates between 2-3 ml/min.

Another weak base system used to sorb metal ions from aqueous thiocyanate solution is described by Kuroda *et al.* (46, 47, 48). They used the cellulose ion exchanger, diethylaminoethyl (DEAE) cellulose. The structure of this exchanger may be depicted as follows:



Their distribution data indicate that only 6 metal ions are strongly sorbed to the resin, i.e. rhenium(VII), molybdenum(VI), tungsten(VI), mercury(II), platinum(IV) and palladium(II). Thus the other metal ions strongly sorbed in the Alamine 336 and A-21 systems, e.g. iron(III), cobalt(II), copper(II), cadmium(II) etc., are easily eluted from the

column.

Another difference which the work of Kuroda et al. presents with the work here is that for increasing aqueous thiocyanate concentrations, 0.005 M - 1.0 M, the distribution ratios of rhenium, molybdenum and tungsten decreased throughout the pH range of 1.0 - 6.0.

Two reasons for these differences in distribution behavior are:

1. The DEAE system involved less acidic aqueous phases.
2. The capacity of the DEAE cellulose resin was only 0.51 meq/g.

Both these factors indicate that there is a severe limitation on the resin sites available for exchange. This limitation is apparently the cause for selective sorption of a few metal ions.

In summary then, either the Alamine 336 or Amberlyst A-21 thiocyanate system described in this work has analytical potential for the "group" separation of metal ions. However, if a sample has a fortuitous combination of metal ions, conditions may be adjusted so that one element may be completely isolated. The separations are fast and simple. Phase separations were no problem for solvent extraction work and column flow rates were generally controlled at 1.0 ml/min although flow rates as high as 5-10 ml/min were used and are applicable in some instances. The column most often used was only 1.0 cm x 9.0 cm.

The conditions used to effect the separations are mild. Much of the anion exchange work reported in the literature involves strong hydrochloric acid. Separations involving nickel(II), cobalt(II), iron(III), copper(II) and other common elements derived from the work of Kraus and Nelson (32) use 7-12 M hydrochloric acid as eluents. In this study the thiocyanate concentration ranged from 0.0 M to 1.0 M

while the acidity was usually 0.5 M or less. These mild conditions lead to one very real advantage. There is no need to boil down solutions or treat them with large amounts of base prior to the determination of the metal ion. The resultant analyses are performed directly in either phase for solvent extraction work or on column effluents for chromatographic work.

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APPENDIX

The fundamental equation used to describe retention in liquid-liquid column chromatography is

$$\bar{V} = V_M + D_V V_S \quad (10)$$

In order to derive this equation according to plate theory, several assumptions should be outlined (71):

1. D_V reflects true liquid-liquid partition as the only retention mechanism. This condition is necessary for relating solute retention to fundamental thermodynamic properties of bulk liquid solutions.
2. D_V is a constant throughout the column.
3. The partition equilibrium is established rapidly in relation to the rate of solute migration down the column.
4. Eddy diffusion is negligible.
5. Axial diffusion is negligible.
6. The sample is introduced as a thin plug.

The plate theory of chromatography adopts the view that even though a partition chromatographic column is a continuous system it is equivalent to a series of units in each of which equilibrium is achieved. The column may be considered as consisting of layers of thickness such that the solution leaving each layer is in equilibrium with the average concentration of solute in the stationary phase throughout the layer. Each of these layers is called a plate and the thickness of each layer is called the height equivalent to a theoretical plate, HETP. Obviously the separating power of a column is directly related to the number of

theoretical plates which in turn is determined by the length of the column and the HETP.

Ideally the solute band migrating down the column occupies the plates according to the binomial distribution. An ideal elution curve may be depicted as in Figure 25. The symbols used in Figure 25 are defined as follows:

$T_{r,n}$ = fraction of solute in the r^{th} plate after n mobile phase volumes have passed into the column

n = number of mobile phase volumes required to elute the zone maximum

r = number of theoretical plates (0, 1, 2..., r)

\bar{V} = retention volume, the volume necessary to elute a solute to its maximum concentration

According to statistical theory, the maximum or mean in the elution curve is given by r/p . Therefore, at point G in the curve $r/p = n$.

The retention volume (\bar{V}) is determined by column characteristics and the distribution coefficients of the compounds. Let:

p = fraction of solute per plate in mobile phase at equilibrium.

i.e. $p = \frac{\text{amount of solute per plate in mobile phase}}{\text{total amount of solute}}$

C_m = concentration of solute per plate in mobile phase

C_s = concentration of solute per plate in stationary phase

V_m = volume of mobile phase per plate

V_s = volume of stationary phase per plate

$D_v = \frac{C_s}{C_m}$ = distribution ratio

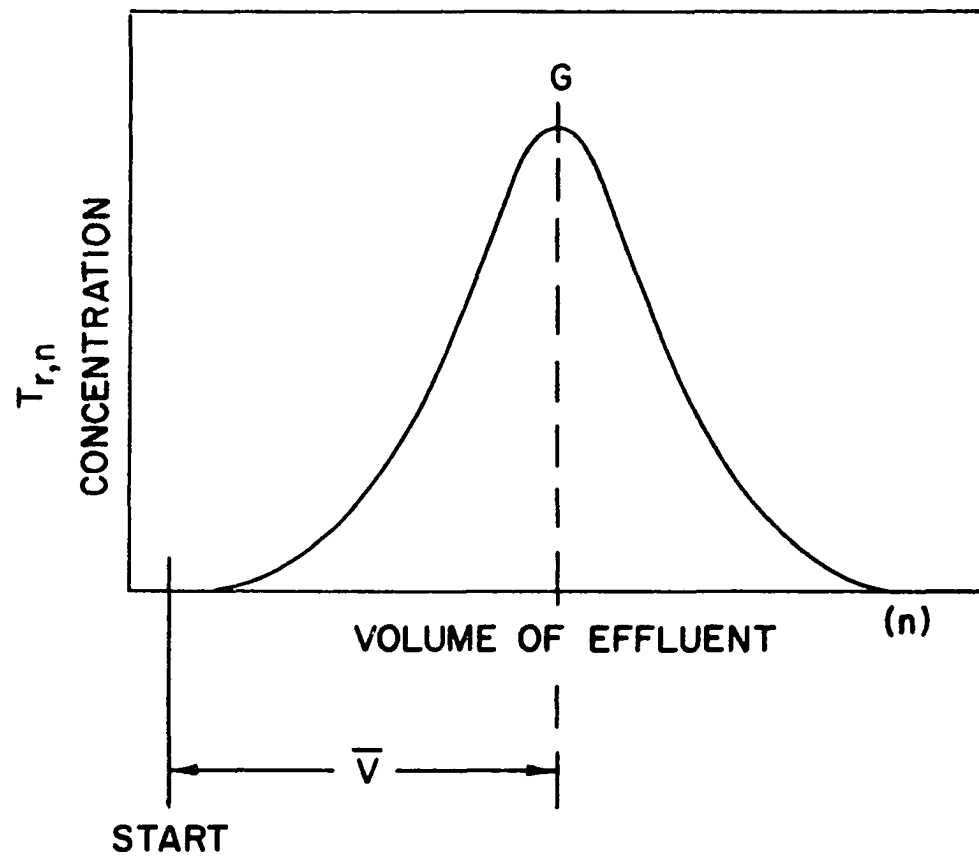


Figure 25. An ideal chromatographic elution curve

$$Q = \frac{V_m}{V_s}$$

P can be further defined as:

$$P = \frac{C_m V_m}{C_m V_m + C_s V_s} = \frac{\frac{Q}{D_v}}{\frac{Q}{D_v} + 1}$$

Substituting $r = np$ and rearranging yields:

$$r = \frac{nQ}{Q + D_v} \cdot \frac{\frac{V_m}{V_s}}{\frac{V_m}{V_s} + D_v} = \frac{nV_m}{V_m + D_v V_s}$$

Then

$$rV_m + rD_v V_s = nV_m$$

Since V_m and V_s are volumes per theoretical plate and n is the number of mobile phase volumes to elute the zone maximum

$$rV_m = \text{total mobile phase volume} = V_M$$

$$rV_s = \text{total stationary phase volume} = V_S$$

$$nV_m = \bar{V}, \text{ the retention volume}$$

Finally,

$$\bar{V} = V_M + D_v V_S$$

Further details concerning this derivation may be found in Connors (72) and Eriksen (73).