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The synthesis, characterization, and application of chelating ion-exchange resins

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The synthesis, characterization, and application of chelating ion-exchange resins

by

Elizabeth Marie Moyers

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INTRODUCTION

The genesis of the chelating ion-exchange resin can be traced to Griessbach who in 1939 proposed the synthesis of a series of ion-exchange resins with varying acidic strength which would show selectivity toward particular ions (1-2).

Erlenmeyer and Dahn (3) first demonstrated the usefulness of a chelating resin in their separation of various cationic mixtures on powdered 8-hydroxyquinoline. The method suffered from column bleed, however, and led Mellor (4) to suggest that the complexing group be chemically bonded to the polymer matrix. Anders Skogseid, a Norwegian graduate student, accomplished this in 1946, when he aminated a polystyrene matrix to form a secondary aromatic amine resin (5).

There has been a series of review articles from 1956 to the present day which follow the development of and contribution to chelating ion-exchange. Hale (6) wrote the first such review describing the methods of synthesis and stressing the analytical and industrial importance of such resins. Millar (7) followed a year later with an enlightening historical overview describing the contributions of Griessbach, Skogseid, Mellor, and others to the founding of the method.

The number of chelating resins developed and studied through the 60's and 70's has been voluminous. Only those that directly deal with the research being presented herein or that shed light on theoretical and practical aspects of chelating ion exchange are discussed. A much more extensive look at the development of chelating resins can be attained through review articles. In the mid-60's, Schmuckler (8), Blasius and Brozio (9), Hering (10,11), and Marhol (12) reviewed the preparation, properties, and practical applications of chelating resins through the preceding decade. Work during the late 60's to the present day has been reviewed by Myasoedova et al. (13), Saldadze and Kopylova (14), and Walton (15).

The largest field of application for chelating resins today is in pollution research. The rapidly increasing pollution of our water supplies by heavy metals has created the necessity of measuring ppb and pptril. concentrations of these species. Analysis methods available today cannot adequately measure metal ions at such low levels. High concentrations of sodium chloride and salts of magnesium and calcium also interfere in the determinations. Therefore, a concentration and separation step is required for which chelating resins are ideally suited. Chelating resins bind the heavy metals preferentially to the alkali and alkaline earth metals and are rapid, quantitative concentrating agents (16-20).

Mellor (4) was the first to suggest the superiority of the chelating resin to the ordinary ion-exchange resin for binding heavy metals in the presence of sodium, calcium, and magnesium. He pointed out that an improvement in the efficiency of the resins, containing sulfonic acid, carboxylic acid and phenol functional groups, for trace metals could be effected by devising resins with active groups such as =NOH and =NH that would form more stable metal chelate rings. Holynska (18) gave support to this theory by demonstrating that Chelex 100 could recover 100% of the lead from a solution containing 9000 ppm sodium and 300 ppm calcium while the ion-exchange resin, IR-120, could recover only 40%.

The most commonly used chelating resin for concentrating trace heavy metals is Dowex A-1 (Chelex 100), an iminodiacetic acid resin. It has been used in studies of food extracts (21), brines (22,23), industrial waste water (18, 24), sea water (25-29) and others (30-32). However, this is a gel-type resin which undergoes pronounced shrinking and swelling and has rather slow kinetics. It, therefore, requires long equilibration times for batch procedures and is difficult to use in automated chromatographic techniques (18,26,31,33,34).

A macroporous iminodiacetic acid resin, XE-318, is presently being studied. It does not have the severe shrinking and swelling problem of Chelex 100, allowing XE-318 to be used in automated chromatographic methods. Thus far, XE-318 has been used to concentrate 15 trace metals quantitatively (35).

To meet the growing needs of ecological research in pollution control (17) and elsewhere, new chemically-bonded, chelating resins are continually being developed. Bayer and co-workers (36-38) made the first resins used to concentrate relatively rare metals from sea water. The glyoxal-bis-2-hydroxyanil resin was used to concentrate copper and uranium (36), and gold, silver, and mercury (37). The same resin with thiol groups replacing the hydroxy groups was used for the recovery of gold (38).

Koster and Schmuckler (39) developed an isothiouronium resin, SRXL, that has been used for recovery of gold and platinum metals (32,40,41). Myasoedova, Savvin, and co-workers (42-44) studied a number of resins for the concentration of gold and platinum metals and their separation from other transition metals.

Other resins which have been used for the concentration of trace metals contain hydroxamic acid (45), dithiocarbamate (46-48), aniline sulfur (49), polyamine and imine (50,51), thiol (52), and phenol (53) functional groups.

Theoretical studies of chelating resins have also received much attention. Attempts have been made to describe the mechanism of resin to metal attraction, the effect of physical properties of the matrix on resin behavior, and the selectivity of the resin.

To prove the mechanism of complexation, Schmuckler (54) compared the adsorption curves of Chelex 100 and Dowex 50, a weak-acid ion-exchange resin, for lead (II) and copper (II). In the hydrogen form, Chelex 100 had a much greater affinity for the ions studied than did Dowex 50. Thus, covalent as well as ionic bonding is indicated for the Chelex 100 resin. Eliseeva and Savvin (55) performed similar experiments with a group of "chelating" ion-exchange resins. They concluded that the resins designated as "chelating" did indeed complex metal ions as they retained them at pH values far too acidic for the ion-exchange process to take place.

Myasoedova _et al_. (13) demonstrated that the chelating resin has a higher selectivity for and forms stronger bonds with metal ions than does the ion-exchange resin. They also found that the resin selectivity depended more on the nature of the ligand than on the size, charge, or physical properties of the ion as would be the case with the pure ion-exchange resin.

Turse and Rieman (34) concluded that the kinetics of Chelex 100 are controlled by a second order chemical reaction and are, therefore, slower than the diffusion-controlled ion-exchange process. They further stated that the exchange rate is independent of particle size but is dependent on the concentration of the solution.

Dingman et al. (20) agreed with these findings for high ionic concentrations. However, for trace ions they claim that film diffusion is the controlling process. The rate of exchange for the diffusion process is proportional to the diffusion coefficient and concentration of metal ion in solution and inversely proportional to resin bead radius, film thickness, and concentration of metal ion in the resin.

Today, the majority of chelating resins are made by polycondensation, i.e., by incorporating the functional group into the resin matrix by condensation with a polymerizing agent such as formaldehyde. This method has the advantages of high yield, simplicity of synthesis, and low cost. It also has the disadvantages of mechanical and chemical instability, alteration and steric hindrance of the functional group during synthesis, and rapid deterioration of the resin (9).

The slowness in the development of the alternate synthetic technique, that of chemically bonding the complexing group to the polymer, can be attributed to the poor matrices available. The low cross-linkage of the early styrene-DVB co-polymers made them subject to volume changes on synthesis and use. The rapidity of these changes caused considerable damage to the matrix (12). The volume changes also prevented use of the resins in a closed column where the shrinking and swelling caused great fluctuations in flow rate or stopped the flow entirely.

Macroporous polymers with cross-linkages of 25 to 100% offer matrices of superior chemical and mechanical stability. The polymers maintain essentially constant volumes in all ionic forms. Thus, they are useful in the modern automated chromatographic techniques (56a, 56b)

A number of other supports are available as matrices for chelating resins. The most important of these is silica gel which has been used as the matrix for a number of resins (46-48,50,57). However, it has two disadvantages which limit its usefulness. The siloxy group, which binds the functional group to the matrix, is subject to hydrolysis below pH 1.5 and above pH 10.5 and the free silicic acid groups interfere in many separation procedures. Some effort has been applied to alleviating the second problem by deactivating the silica gel surface with a silanating agent such as methoxy-chlorosilane (50).

The selectivity of resins for metal ions have been determined by percentage sorption (1,26,55,58), distribution coefficient (33,59-63), stability constant (46,64), titration (65-67), and capacity (31,50,56b,57,68-70) studies.

Many workers have concluded that the bond between the resin ligand and the metal ion is stronger than the corresponding bond between the monomeric ligand and the metal ion (9-12,33,47,64,70-72). The ligands used in these studies contained sulfur, phosphorus, arsenic, and iminodiacetic acid groups.

Lewenschuss and Schmuckler (64) concluded that there was a quantitative relationship between the stability constants of the monomer and polymer. They demonstrated mathematically and experimentally, using Chelex 100, how to determine the stability constant of the polymeric complexing group by use of an external ligand whose stability constants are known.

Leyden and Underwood (33) stated that the pH dependence of the distribution coefficients was not predictable from the pK_a values of the ligand using the customary treatment applied to monomeric chelons but that it did follow the same order. Hering (62) believed that K_d, the instability constant of the resin, was a function of the acid dissociation constants of the ligand, $\sum_{i=1}^{N} pk_i$, as well as the pH at which the metal ion dissociated from the resin, DpH. Therefore, K_d could be determined by the equation

$$K_d = \sum_{i=1}^{N} (pk_i - iDpH).$$

Myasoedova *et al.* (73) studied the effect of macroporous, microporous, and polypropylene fiber matrices on the capacity and selectivity of a number of functional groups. They concluded that the selectivity of the chelating resin is affected by the properties of the polymer matrix, and in some cases by the remoteness of the ligand from the matrix.

There have been many studies on the influence of pH, ionic strength and swelling properties on the recovery of metal ions (20,33,74,75).

APPARATUS AND REAGENTS

The liquid chromatograph (Figure 1) has been previously described (76,77). However, modifications have been made on the instrument. A system for monitoring the pH of the eluent after its passage through the resin column and an electronic noise filter which allows readings as low as 0.005 Absorbance units have been added (78). A micro-metering valve is used for fine adjustment of the helium pressure to give faster initial equilibration and diminished drift of the eluent flow rate. The eluent tanks, previously made from cast iron, are now light weight polycarbonate and Plexiglass to eliminate eluent contamination by iron and lead.

A Milton Roy Pump No. 19-60029-003 or helium gas pressure was used to maintain a constant flow rate through the resin column.

A RIDL AEC 320-3 single channel analyzer was used for counting the activity of the radiotracers at a window setting of 1.3 MeV.

The resin matrices, Rohm and Haas' XAD-1, -2, and -4, were air dried, Soxhlet extracted with methanol, ground, and sieved. After washing with 12 M hydrochloric acid, water, and acetone, the 150-200-mesh fraction was used in the syntheses of the AA resins and the 250-325 mesh fraction was used in the syntheses of the HTG and BPDTA resins.

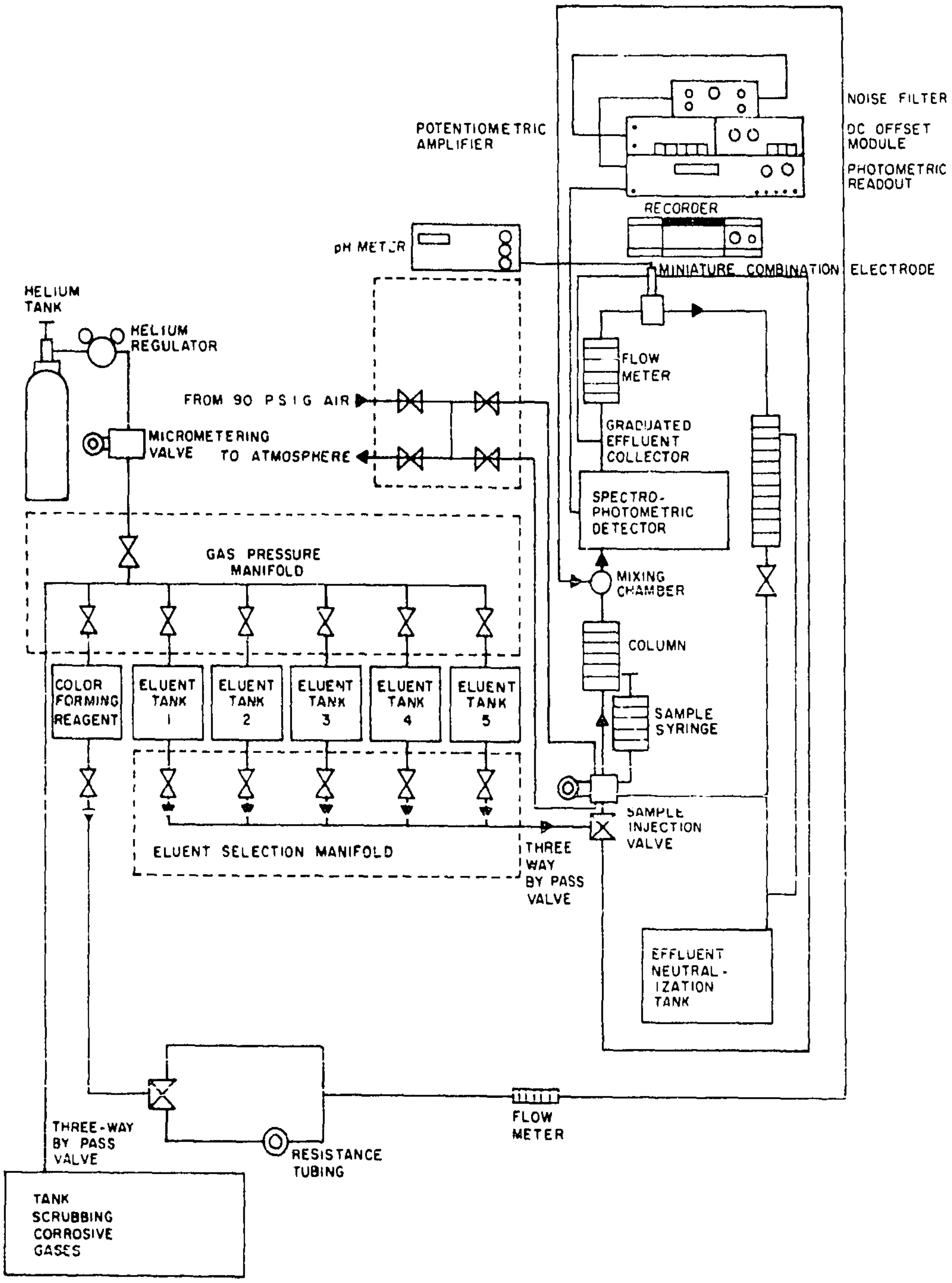


Figure 1. Schematic diagram of the liquid chromatograph

All chemicals used were of reagent grade or better. Manganese-54, zinc-65, iron-59, and chromium-51 gamma-emitters with 99% radiometric purity were obtained from New England Nuclear Co.

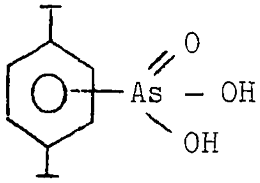
THE CONCENTRATION AND SEPARATION OF TRACE METALS ON ARSONIC ACID RESIN

The first phenyl arsonic acid resins were made by polycondensation of hydroxyphenyl arsonic acid (74,79-81) or aminophenyl arsonic acid (69) with formaldehyde. Davies _et al_. (81) used one such hydroxylphenyl arsonic acid resin to extract uranium from sea water.

Eliseeva, Myasoedova, Savvin and co-workers (55,73, 82-84) prepared a number of Arsenazo I resins by attaching chromotropic acid-phenyl arsonic acid groups to a polystyrene or polypropylene matrix through an azo-linkage. These resins complexed copper (II), zirconium (IV), lanthanum (III), and uranium (VI) from hydrochloric acid media (84) and had a high affinity for thorium (IV) (73). Kim and Kim (85) reacted Arsenazo I with Amberlite IRA-50 and used this resin for the separation of uranium (VI) and thorium (IV).

Hirsch _et al_. (56a) synthesized and characterized an arsonic acid resin using XAD-1, a macroporous polystyrene-DVB matrix, which had a selectivity order of Cu(II) >> Zn(II) > Ni(II) > Co(II) > Mn(II) > Ca(II) > Mg(II).

A series of resins were prepared on XAD-1, -2, and -4 following the procedure of Hirsch _et al_. (56a). The structure of this resin is



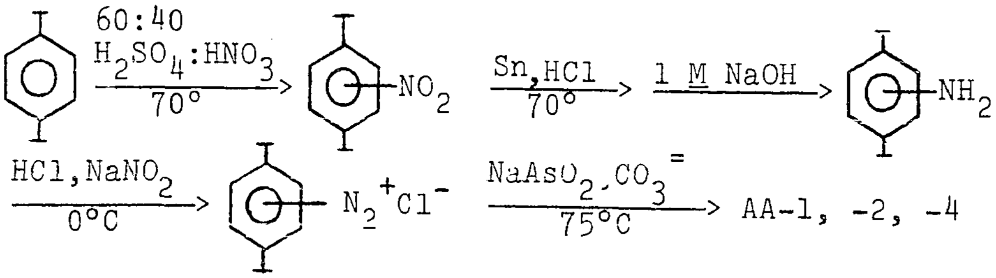
AA-1, -2, and -4

where  represents the polystyrene-divinylbenzene matrix.

The effect of varying pore diameter and surface area on the properties of the resin was studied. AA-4 was used for the concentration of trace metal ions from deionized water, tap water, and salt water. The effect of pH and complexing agents on the recovery of the ions was studied. A comparison was made of the batch and column methods of concentration. AA-4 was also used to separate thorium (IV) from other metal ions in a 0.1 M nitric acid medium and to separate uranium (VI) from other metal ions in a pH 5.0, 0.01 M EDTA medium.

Experimental

Synthesis



To 5.0 g of XAD-1, -2, and -4 was added 100 ml of a 60:40 mixture of sulfuric and nitric acids at 0°C. After addition, the mixture was reacted for 12 hours at 70°C. Product I, which was reddish-brown, was collected by suction filtration and washed with water and acetone.

I was reduced to the amine by stirring for 12 hours in mossy tin and concentrated hydrochloric acid at 75°C. Product II, which was dull brown, was slurried with 1.0 M sodium hydroxide to remove tin salts. It was then collected by suction filtration and washed with concentrated hydrochloric acid, water, and acetone.

II was chilled to 0°C in concentrated hydrochloric acid and diazotized by slow addition of 50 ml of 1.0 M sodium nitrite. Product III, which was bright red, was collected by suction filtration and washed with ice water and ice-cold, saturated sodium carbonate.

III was chilled to 0°C in aqueous solution. Sodium arsenite, 10 g, was added to the solution with stirring. After 1 hour, the mixture was heated to 75°C and reacted for 12 hours. The final product was collected by suction filtration and washed with water, concentrated hydrochloric acid, water, and acetone. It was brick red in color.

IR spectra for the resins, AA-1, -2, and -4 (Figures 2-4), show 2.9 micron arsonic acid O-H stretches and matching bands in the region of 11.0-13.0 microns for the resins and

Figure 2. Infrared spectrum of AA-1

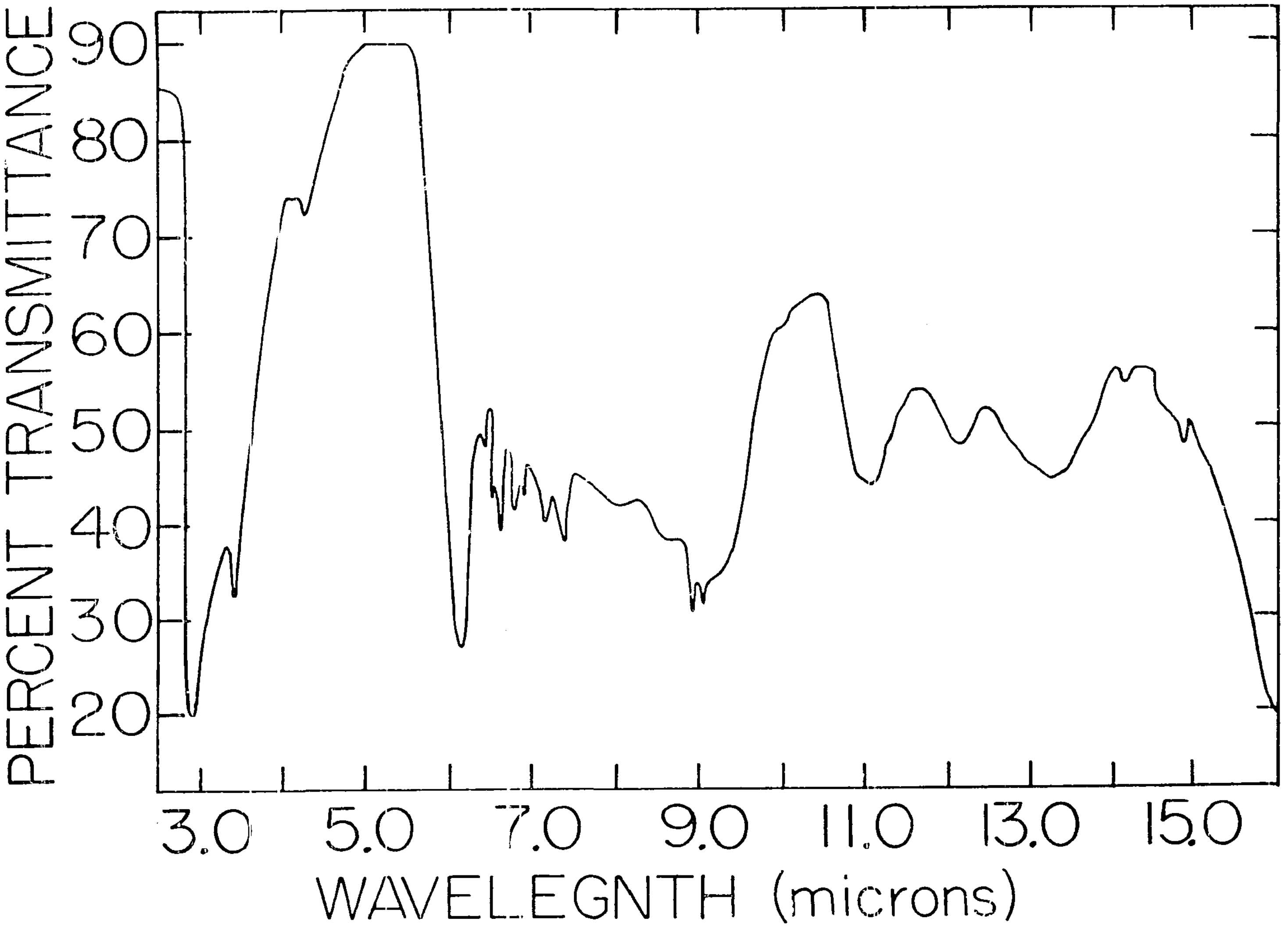

PERCENT TRANSMITTANCE
90
80
70
60
50
40
30
20
3.0
5.0
7.0
9.0
11.0
13.0
15.0
WAVELEGNTH (microns)

Figure 3. Infrared spectrum of AA-2

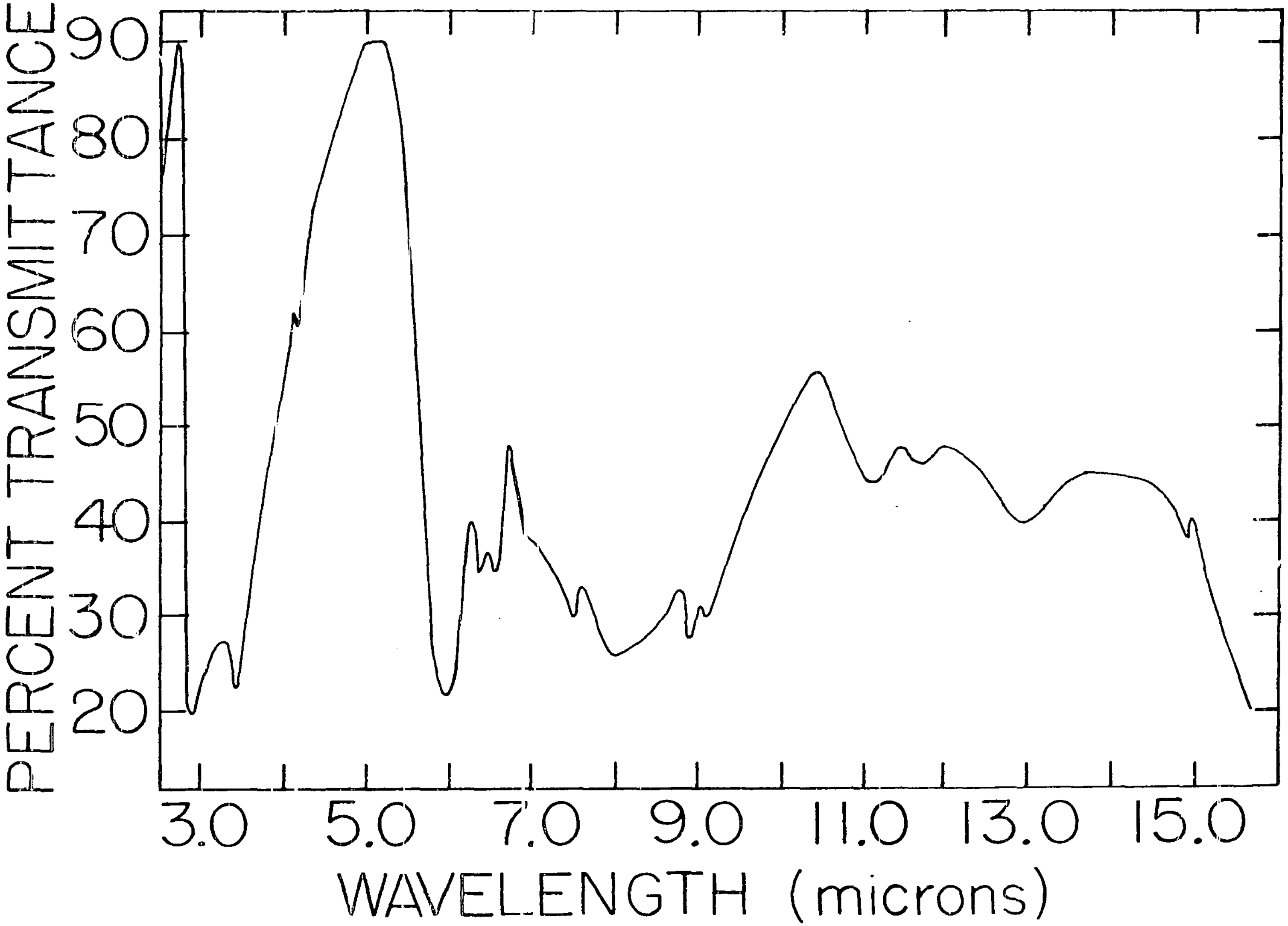
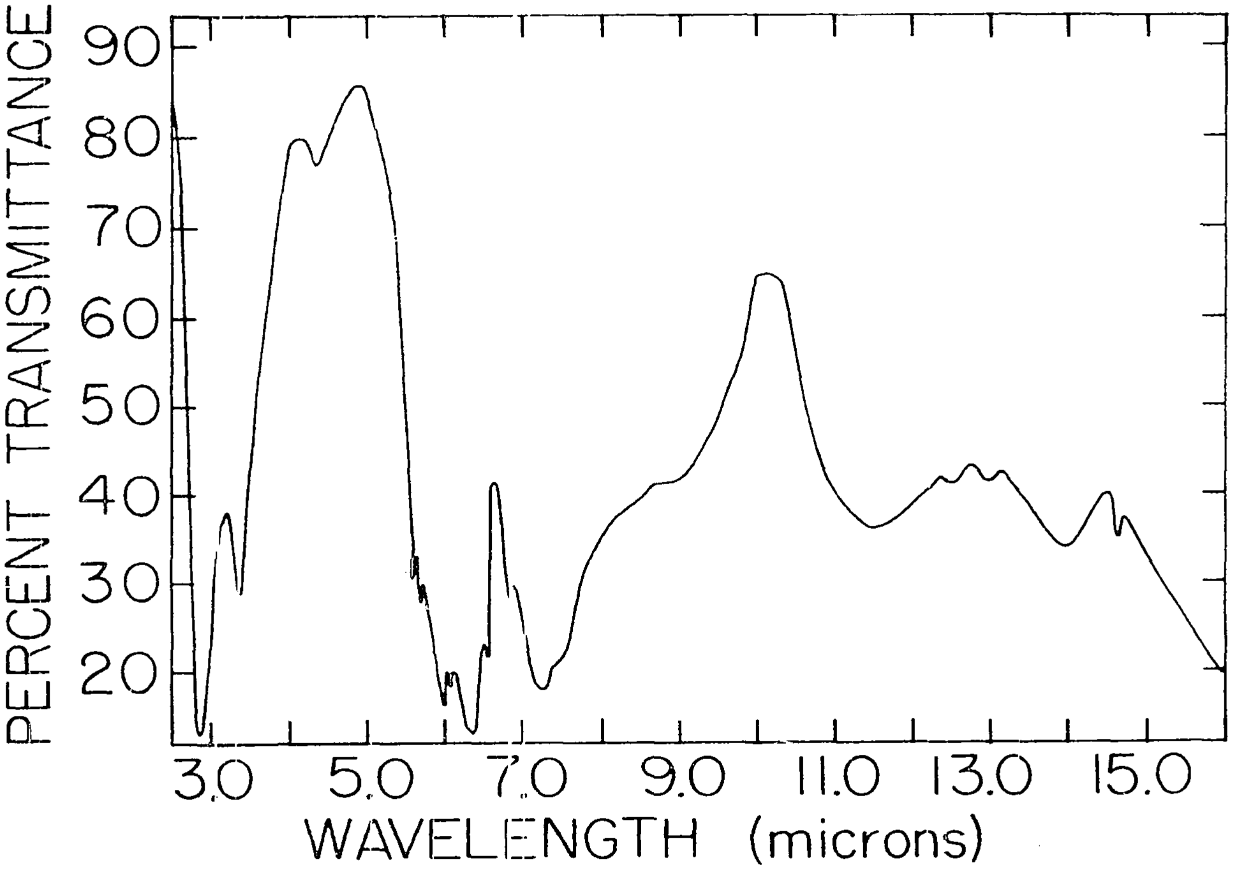

PERCENT TRANSMITTANCE
90
80
70
60
50
40
30
20
3.0
5.0
7.0
9.0
11.0
13.0
15.0
WAVELENGTH (microns)

Figure 4. Infrared spectrum of AA-4


PERCENT TRANSMITTANCE
90
80
70
60
50
40
30
20
3.0
5.0
7.0
9.0
11.0
13.0
15.0
WAVELENGTH (microns)

the monomer, phenyl arsonic acid, which can be ascribed to the arsonic acid group.

Arsenic, hydrogen analyses

Total arsenic content of the resins was determined by the molybdenum blue method (86) after digestion of 10.0 mg of the resin with sulfuric acid and hydrogen peroxide.

Total acidic hydrogen content was determined by back titration. A 100.0-mg sample of the resin in the acidic form was added to 10.0 ml of 0.1000 N sodium hydroxide. It was equilibrated for 2.0 hours at room temperature with stirring. The effluent was collected by suction filtration and the excess base determined.

Concentration of trace metals

For all column studies a 2.8 x 0.6 cm column of AA-4 resin was used. It was washed with 25 ml of a pH 6.0 phosphate buffer followed by 100 ml of the eluent to be used in the study. The pH of the column effluent was checked and if necessary, it was adjusted. The one-liter sample was passed through the resin column at a flow rate of 7 ml/min. After collection, the column was washed with 100 ml of the eluent. The complexed metals were stripped from the column with 25 ml of 4.0 M perchloric acid. They were determined by plasma emission, by atomic absorption, by gamma emission, or colorimetrically with Arsenazo I.

For the pH study, the sample was deionized water containing 0.5 ppm of each ion and was buffered to the desired pH with phosphoric acid, perchloric acid, and ammonium hydroxide.

For the recovery of trace metals, the sample was deionized water, tap water, or synthetic sea water (87) containing 0.5 ppm of each ion and buffered to pH 5.0. Similarly, the recovery of trace metals below the ppb level was determined by substituting 5 ml of 2 μCi/ml tracer solution for the 0.5 ppm of heavy metals.

The effect of ligands on the recovery of the ions used a 250-ml sample of deionized water. To this was added 10 ppb of each metal ion including the radiotracer for detection, 10 ppm of ligand, and 5-6 drops of orthophosphoric acid. The phosphoric acid was added as a buffer and was necessary for 100% recovery of iron (III). The procedure was identical to that given above.

Batch abstraction

AA-4, 0.5 g, was added to 250 ml of pH 5.0 solution containing 2.0 ppm of the heavy metals. The solutions were stirred for 2, 6, and 24 hours before collection of the resin. The complexed metals were stripped from the resin with 25 ml of 4.0 M perchloric acid and determined by plasma emission.

Separation procedures

A 1-liter sample containing 0.5 ppm of thorium (IV) and 50 ppm of other heavy metals and 0.1 M in perchloric acid was passed through the resin at 7 ml/min. The resin column was washed with 100 ml of 0.1 M perchloric acid and stripped with 25 ml of concentrated perchloric acid. The thorium and other heavy metals were determined by plasma emission.

A 1-liter sample containing 0.5 ppm of uranium (VI) and 50 ppm of other heavy metals and 0.01 M in EDTA was buffered to pH 5.0 with orthophosphoric acid and ammonium hydroxide and passed through the resin column at 7 ml/min. The column was then washed with 100 ml of 0.01 M EDTA at pH 5.0 and 100 ml of pH 5.0 wash solution. Both solutions were buffered with phosphoric acid and ammonia. The column was then stripped with 25 ml of 4.0 M perchloric acid. The uranium was determined colorimetrically and the other heavy metals were determined by plasma emission.

Results and Discussion

Evaluation of the resins

Emergence of macroporous resins such as the XAD series which show little of the shrinking and swelling seen in gel matrices, kindled interest in determining the effect of structural changes on the physical properties of resins. Various chelating groups have been incorporated in matrices by chemical bond. The effects have been studied of percentage cross-linkage, group distribution, i.e., the spacing of the groups, and affinity for metal ions of the resin matrix on kinetics, swelling behavior, and stability of the resin and its chelates (13,20,58-60,88-91).

To study the effect of pore size and surface area on the yield, kinetics and swelling behavior of resins, arsonic acid resins are prepared from XAD-1, -2, and -4, macroporous polystyrene-DVB co-polymers. A comparison of the physical properties of the resins are summarized in Table 1.

The synthetic yield appears to be dependent on both pore size and surface area. The yield for XAD-4 is twice that of the XAD-2 as expected since the available surface area of the XAD-4 is approximately twice that of the XAD-2. The yield for XAD-1, however, is much higher than expected. It appears that the large pore size of the XAD-1 makes the internal as well as external surface area available for bonding leading to a high synthetic yield. It is also very likely that some of the arsenic-containing groups are merely trapped within the matrix making the yield less than the given value.

The ratios of arsonic acid per benzene ring and acidic hydrogen per benzene ring were calculated from the arsenic and hydrogen analyses. The molecular weight of the matrix was determined by assuming the matrix to be 50% styrene

Table 1. Properties of the XAD-arsonic acid resins

	Surface area m^2/g	Pore diam Å	As/benzene ring	H/benzene ring	%C	%H	%N	Kinetics
AsO_3H_2-XAD I	100	205	2.4	5.2	52.80	5.25	3.31	Slow
AsO_3H_2-XAD II	300	90	0.3	0.8	58.10	5.42	5.00	Rapid
AsO_3H_2-XAD-IV	784	50	0.75	1.8	51.30	5.21	3.17	Rapid

and 50% DVB. The equation used for arsenic is

$$\mathrm{As}/⌬ = \frac{\dfrac{(\text{mg AsO}_3\text{H}_2/\text{g resin})}{\text{MW AsO}_3\text{H}_2}}{\dfrac{1000\text{ mg resin/g resin} - (\text{mg AsO}_3\text{H}_2/\text{g resin})}{\text{MW matrix} = 116}}$$

The acidic hydrogen content is more than the 2:1 ratio of H:As expected for an arsonic acid group and probably represents titratable carboxylic acid and protonated amine. Although exact values may be somewhat in question the trend seems clear; conversion into the arsonic acid is highest for XAD-1 and lowest for XAD-2.

Column experiments with various cations demonstrated that kinetics of AA-2 and -4 are excellent while that of AA-1 is somewhat slow as evidenced by tailing of the elution peaks. AA-1 also gives two peaks for a single metal ion in some cases, further indicating that multiple arsenic-containing species are present that have different retention values for the cation. Because of this and the higher capacity of AA-4 compared to AA-2, AA-4 was chosen for all subsequent experiments.

To characterize AA-4 further, a repeat of the resin synthesis was performed in which the yield of each synthesis step was estimated by analysis for the appropriate functional group. Nitration gave approximately 1.2 nitro groups per ring. Reduction to the amine gave approximately 0.8 amine groups per benzene ring for a 67% yield. Conversion to the arsonic acid then gave approximately 0.6 arsonic acid groups per benzene ring for an overall yield of about 50%. Thus, the resin is estimated to contain 0.4 nitro groups, 0.2 amine and carboxylic acid groups, and 0.6 arsonic acid groups.

The selectivity order of the resin is Th (IV) >> U (VI) >> RE (III) > Cu (II) > Pb (II) > Al (III), Fe (III) > Zn (II) > Ni (II), Co (II) > Cd (II), Mn (II) > Mg (II) as determined by a plot of percentage recovery of the ions versus pH. This is in agreement with the order reported by Hirsh et al. (1) of Cu (II) >> Zn (II) > Ni (II) > Co (II) > Mn (II) > Ca (II) > Mg (II). The percentage recovery of 9 representative trace metals as a function of pH are given in Figures 5-7. All ions tested except magnesium (II) and calcium (II) were quantitatively recovered at pH 5.0 and some were recovered quantitatively at much lower pH. For instance, uranium (VI) was quantitatively recovered at pH 2.0 and thorium (IV) at pH 1.0.

Trace metal studies

For the recovery of trace elements, Chelex 100 is the resin used most often. However, this resin has slow kinetics, imposing a maximum flow rate of 4 ml/min for quantitative recovery. It exhibits pronounced shrinking

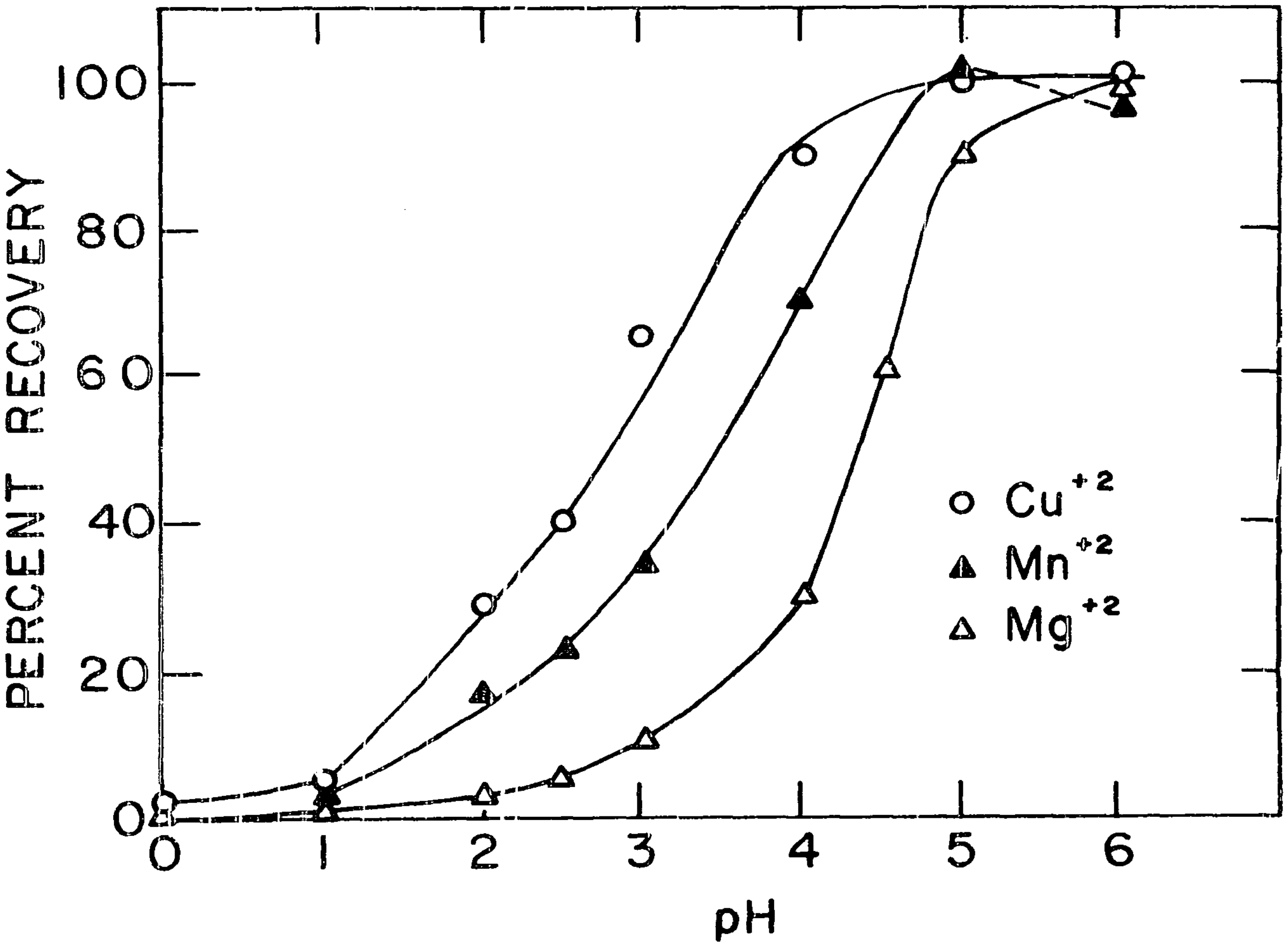


Figure 5. Effect of pH on recovery of Cu(II), Mn(II) and Mg(II)

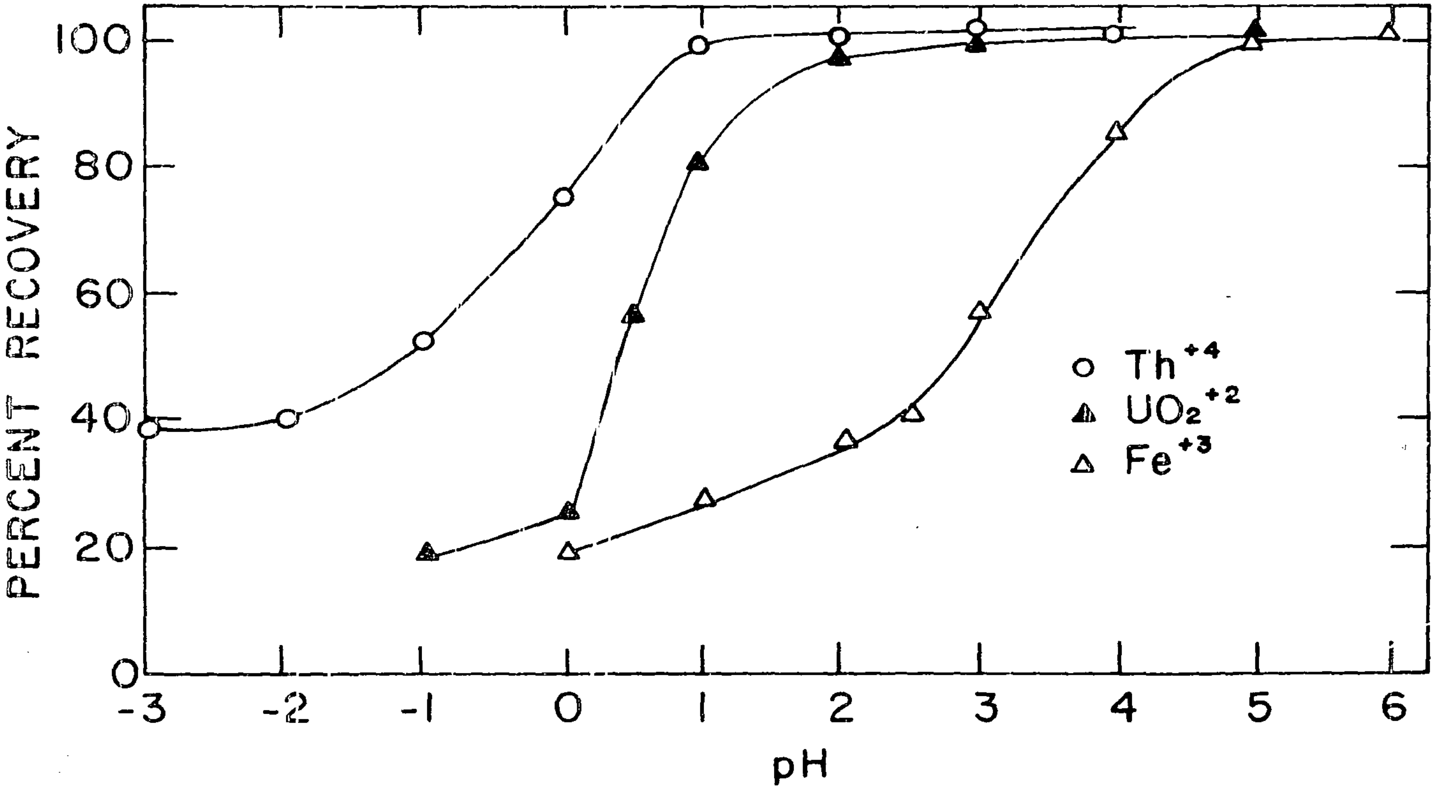


Figure 6. Effect of pH on recovery of Th(IV), U(VI) and Fe(III)

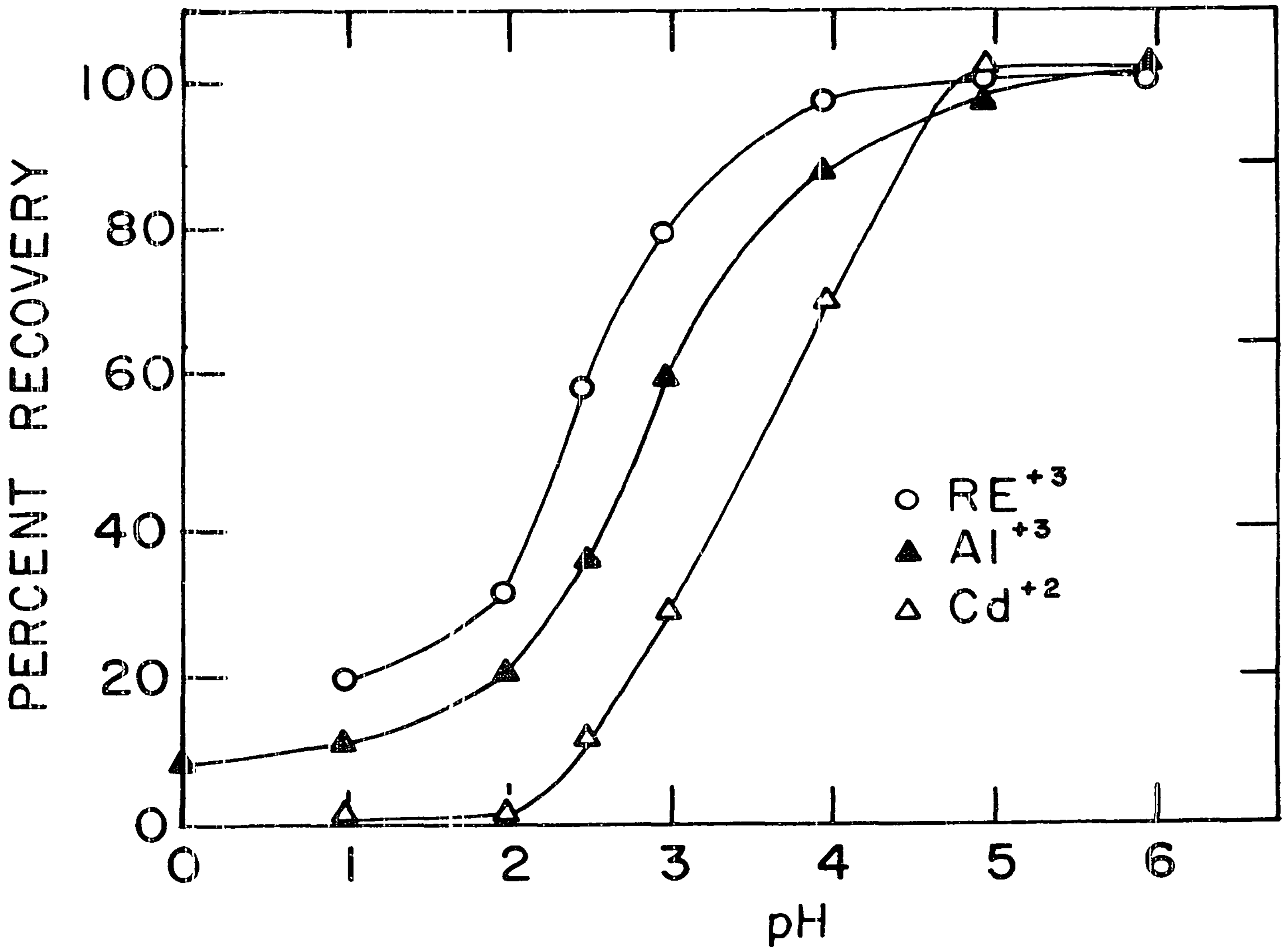


Figure 7. Effect of pH on recovery of Re(III), Al(III) and Cd(II)

and swelling which interfere with closed column, automated methods. And, it has a relatively high affinity for calcium (II) and magnesium (II), that of calcium (II) being equal to that of zinc (II) (20,26,32,92).

AA-4 was chosen as a resin that could overcome these difficulties and still strongly complex the heavy metals. Its rapid kinetics were demonstrated in the percentage recovery versus pH study in which a flow rate of 7 ml/min was used with no loss in efficiency. This study also showed that the resin's affinity for calcium (II) and magnesium (II) is less than that of Chelex 100. Previous workers (56a,56b, 70) demonstrated that the matrix has little tendency to shrink or swell.

To demonstrate the usefulness of AA-4 for concentrating heavy metals, the recovery of eight trace metals for deionized water, tap water, and salt water at 0.5 ppm was tested. The results are given in Table 2 and show excellent recovery for all except chromium (III) which has a very slow reaction rate with ligands. Using radiotracers, the experiment was repeated for three metal ions at the low pptril. (10^{-12}) concentration level. As shown in Table 3, the recovery is still quantitative within experimental error, even in the presence of a large concentration of sodium, calcium, and magnesium salts. The data in Table 4 demonstrates the reproducibility of the method when applied to tap water.

Table 2. Recovery of trace metals in aqueous media using resin IV (concentration of each element - 0.5 ppm)

Metal	Recovery[a] d d water, %	Recovery[b] Tap water, %	Recovery[b] Syn sea water, %
Cd^{+2}	102	98.7	100.5
Co^{+2}	100	102.3	104.0
Cr^{+3}	74.5	57.3	---
Cu^{+2}	103	96.8	101.0
Fe^{+3}	101.5	101.2	102.0
Mn^{+2}	97	97.2	22
Ni^{+2}	101	100.5	105
Pb^{+2}	98	100.3	100.3
Zn^{+2}	98	96.0	100.8

[a] Plasma emission.

[b] Atomic absorption.

Table 3. Recovery of ultra-trace metals in aqueous media using resin IV

Metal	Conc pptril	Recovery d d water, %	Recovery Tap water, %	Recovery Syn sea water, %
Fe^{+3}	38	105.6	101.2	106.3
Mn^{+2}	5	96.2	97.2	94.6
Zn^{+2}	32	97.2	94.9	100.8

Table 4. Recovery of trace metals in ISU tap water using resin IV

All values listed ppb as found in ISU tap water

	Ni	Zn	Fe	Pb	Mn	Cu
No. 1	41.2	66.2	123.7	11.2	91.3	900
No. 2	40.0	68.8	123.7	11.2	56.3	1160
No. 3	36.2	65.0	127.5	16.2	105.0	1160

In the tap water and salt water studies, some of the calcium (II) and magnesium (II) was retained by the AA-4 column at pH 5.0. If desired about 95% of these species can be removed by washing the resin with pH 4.0 buffer prior to stripping the trace metals from the resin.

The effect of complexing agents on the recovery of zinc (II), manganese (II), and iron (III) at 10 ppb concentrations was studied by adding a thousand-fold excess of various ligands. As shown in Table 5, the recovery of manganese (II) and zinc (II) was unaffected by any of the complexers except EDTA. The recovery of iron was low in the presence of substances that form complexes having a stability constant greater than 10^8.

There are two generally accepted methods for concentrating trace metals. One is the column method which was demonstrated in this work. The other is the batch method in which the resin extracts the ions while being slurried directly in the sample solution.

A comparison of the two methods was made using AA-4. Using the batch method, 90% of the copper (II) and lead (II), 70% of the iron (III), 40% of the nickel (II), and 15% of the cadmium (II) were recovered after 24 hours. All of these ions were 100% recovered (see Table 2) by column method in 3.5 hours which included the time for column preparation, collection, and elution.

Table 5. Present recovery of trace metals in presence of various ligands

Ligand	Fe-59	Mn-54	Zn-65
Acetic acid	105.8	100.3	99.4
Dihydrogen phosphate	105.6	---	---
UREA	23.0	99.6	98.2
Chloride	106.4	94.6	100.8
Glycine	21.3	93.0	96.2
Citrate	54.0	99.6	102.6
Anthranilic acid	13.4	95.7	101.3
Salicylic acid	48.2	94.0	93.5

Other researchers (31,45,47) have similarly found that the batch method has long equilibration times and incomplete recovery. For instance, Blasius and Moeschter (45) demonstrated the reduction of iron (III) from 10^{-6} to 10^{-8} M could be accomplished in 3 hours by a column method but took 24 hours by batch extraction. Dingman et al. (47) obtained better recovery of heavy metals with a column of dithiocarbamate resin than they did by batch method.

Resin separations

The affinity of AA-4 for thorium in acidic media made possible a separation of thorium from aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, tin, and zinc. Recovery of 0.5 ppm thorium in the presence of 50 ppm of the other ions at pH 1.0 was 102.5% based on spectrophotometric determination, with none of the other metal ions being retained more than 1.0%.

A separation was also attained for 0.5 ppm uranium from 50 ppm of the 11 metals listed above and from 50 ppm thorium by adding EDTA as a masking agent. Spectrophotometric analysis showed 98.3% recovery of uranium at pH 5.0 in the presence of 0.01 M EDTA. Chromium was the only interference with 11% recovery.

THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A HEXYLTHIOGLYCOLATE RESIN

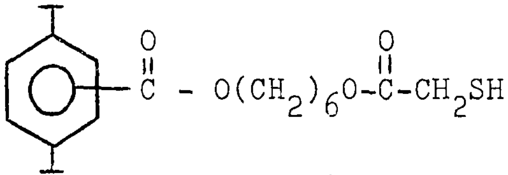
Studies have shown that sulfur-containing ligands are more selective toward the noble and heavy metals than their oxygen and nitrogen analogues (93-97). Chelating resins employing these ligands have been used for concentrating and separating mercury (II), silver (I), and gold (III) from each other (38) and as a group from the base metals (37,57). Other sulfur chelating resins have been of valuable assistance in toxicity studies of mercury (49,98) and in recovering trace quantities of gold (42,44,99) and of mercury and silver (46,47,99).

Rhodamine resins are typically selective for gold, silver, mercury, copper, and the platinum metals (44,99,100). Thiourea resins are selective for mercury (65,68,101) and for gold and silver (44,65,68). Dithiocarbamate resins quantitatively complex silver and mercury among others (46-48).

Koster and Schmuckler developed a benzyl-isothiouronium resin (39), commercially marketed as SRXL, which has received the most attention for its recovery of gold (32,40,41). It has also been used for studies of mercury (98) and the platinum metals (41,98,102). There are a number of other sulfur resins that have shown selectivity for these metals (68,103-105).

In addition, there have been a few non-sulfur resins with selectivity for these ions. Blasius and Laser (106) condensed maleic hydrazide with formaldehyde and resorcinol to form a resin selective for mercury (II) and $(\text{mercury})_2$ (II) in weak acid. Melby (107) also showed the aromatic amine resin to selectively remove silver from acidic aqueous media. Fritz and Millen (59) used an ester resin, XAD-7, to separate gold from 23 metals. Egawa and Saeki (108) used a polyamine-polystyrene resin to complex gold, mercury, and copper selectively. Chelex 100 was used by Hering to recover bismuth (39).

The behavior of iso-octylthioglycolate (IOTG), another sulfur-containing ligand, which can extract quantitatively from aqueous media silver (I), mercury (II), gold (III), bismith (III), and copper (II) (109) suggested the synthesis of an analogous chelating resin. This resin, HTG-4, has an n-hexylthioglycolate group attached to an XAD-4 polymer matrix through an ester-linkage. The structure of this resin is

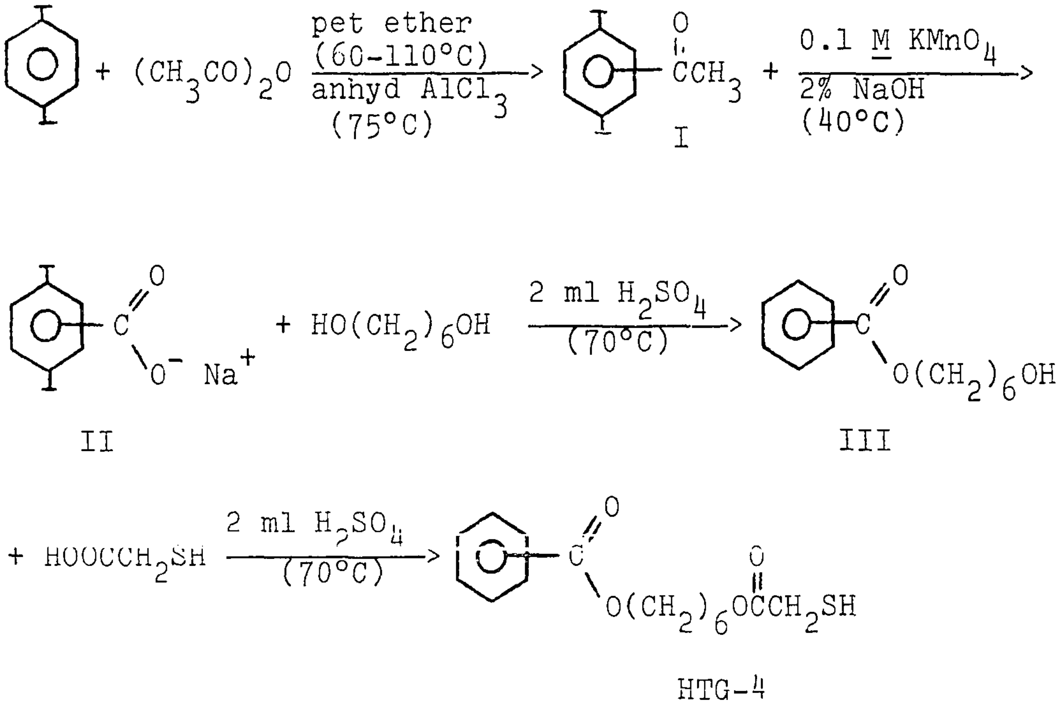


HTG-4

HTG-4 retains the first four of the aforementioned metal ions from acidic solution. Separation of these metal ions from each other and from other metal ions is achieved by liquid chromatography using a short column of HTG-4 resin.

Experimental

Synthesis



To 5 g of XAD-4 resin was added 35 g of anhydrous aluminum trichloride and 20 ml of petroleum either (60-110°). Then 20 ml of 50:50 petroleum ether/acetic anhydride was added over a period of 30 minutes through a water cooled condenser, and the resulting mixture was refluxed at 75° for 3.5 hours. Product I was cooled to room temperature and hydrolyzed in 12 M hydrochloric acid and ice. It was then collected by suction filtration and washed with 15 M ammonium hydroxide, 12 M hydrochloric acid, water, and acetone. This procedure was repeated to obtain a higher yield, I was light green when dry, dark green in acid, and brown in base.

I was oxidized to the carboxylic acid by stirring for 1.0 hour at 40°C in 0.1 M potassium permanganate which was 2% in sodium hydroxide. II, which was light yellow, was collected and washed in a like manner to I.

II was mixed with 30 g of melted 1,6 hexanediol (mp 41°) containing 2 ml of 18 M sulfuric acid as catalyst. The mixture was reacted at 70° for 0.5 day. III was collected by a hot suction filtration using boiling methanol as the wash solution.

III was added to 40 ml of thioglycolic acid containing 2 ml of 18 M sulfuric acid. The mixture was reacted at 70° for 0.5 day. The final product was collected by suction filtration and washed with 12 M hydrochloric acid, water, and acetone. The HTG-4 was tan in color and darkened somewhat with use.

Characterization

To determine the hydrogen capacity, 0.2 g of the resin in the acidic form was weighed into 20 ml of deionized water. A 10-ml aliquot of 0.1 N sodium hydroxide was added and the mixture was equilibrated with stirring for 2.0 hours. The excess base was collected by filtration and titrated to a methyl red endpoint with 0.1 N hydrochloric acid.

For the potentiometric titration, 0.2 g of resin was slurried in 50 ml of deionized water and 0.1 N sodium hydroxide was added in 0.05 to 0.20 ml increments. Between each increment, the mixture was equilibrated with stirring for 0.5 hour and the pH of the solution was read. Nitrogen gas was bubbled through the solution during the titration.

Batch capacities of the resin were determined by weighing 0.3 g of resin (batch 1) to 25 ml of 0.1 M perchloric acid - 0.0002 M sodium hydrogen tartrate to which 10 ml of 0.1 M silver (I), mercury (II), or gold (III) were added. After a 2.0 hour equilibration, the mixture was filtered and the resin washed with four 10-ml portions of perchloric acid-tartrate. The eluent from the filtration and the wash procedure was analyzed for metal content.

Column capacities were determined for gold (III) in 0.0 to 8.0 M hydrochloric acid media using 0.18 g of the resin in a gravity flow column. The resin was conditioned by passing 30 ml of the acid through the column at 2.0 ml/min. Similarly, 0.1 M gold (III) in the acid solution was passed through the resin until saturation was reached. The column was then washed with 50 ml of acid to remove excess metal. The bound metal was eluted with 25 ml of pH 3.0, 10^{-3} M thiourea. All solutions used in this study contained 2 drops of 0.01% bromine water per 100 ml to prevent gold reduction on the resin.

Bismuth (III) and mercury (II) were determined by titration with 0.025 M EDTA to a Xylenol Orange endpoint, silver (I) by potentiometric titration with 0.1 M sodium chloride using a silver wire electrode, and gold (III) by spectrophotometry as the thiourea complex.

An IR spectrum of the HTG-4 resin shows bands for ester carbonyl and hydroxyl groups (Figure 8).

Gold-thiourea spectrophotometric determination

The absorbance of 1.2×10^{-4} M gold (III) in 10^{-3} M thiourea against a 10^{-3} M thiourea blank was measured on a Cary Model 14. Bromine and hydrochloric acid were omitted to show that the absorbance was indeed due to the gold-thiourea complex.

Separation procedure

Samples were made by weighing 10 to 400 mg of each of the metals, the metal salt, or the metal oxide into a digestion flask and wet ashing with aqua regia-hydrogen peroxide or with nitric acid alone when silver was present. The species used were reagent grade antimony, bismuth, copper, iron, silver, and tin metals, gold chloride, and mercuric oxide.

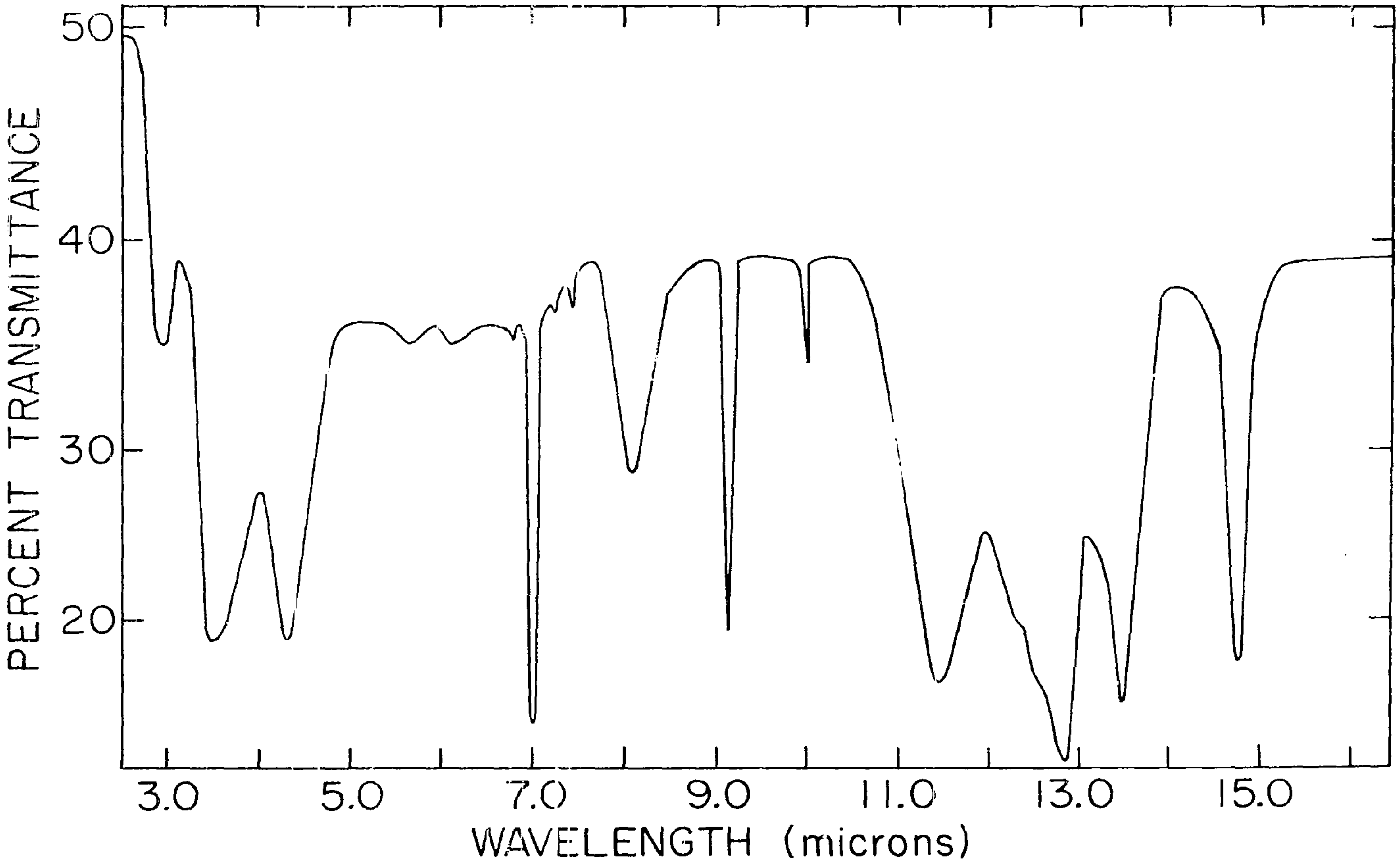


Figure 8. Infrared spectrum of HTG-4

The samples were diluted to 100 ml with distilled, deionized water and two 5 to 10-ml aliquots were taken. These were further eiluted to 100 ml so that the samples injected were 1.0 to 20.0 ppm in analyte. All samples in which hydrochloric acid was used contained 0.3 to 0.4 g of copper, and gold samples contained 2 drops of 0.01% bromine water per 100 ml solution.

The resin was conditioned with 20 ml of 0.1 M perchloric acid - 0.0002 M tartrate at 2.0 ml/min and 51.4 μl of the sample was injected onto a 3.3 x 0.6 cm column of HTG-4 resin. After injection the resin was further washed with perchloric acid-tartrate for 5 to 10 minutes. Bismuth (III), silver (I), and mercury (II) were sequentially eluted with 0.5, 2.0, and 6.0 M hydrochloric acid using a stepwise gradient, mixed on line 1:1 with 12 M hydrochloric acid and determined as the chloride complexes at 225 nm (110). Gold (III), which was retained by the resin during this process, was eluted by 25 ml of 10^{-3} M thiourea-pH 3.0 in hydrochloric acid, and diluted by half with deionized water. After a 15 minute wait, the gold (III) was determined spectrophotometrically at 256 nm as the thiourea complex.

Results and Discussion

Evaluation of the resin

Of the various synthetic procedures tried, those described in this paper gave the maximum yield with least degradation of the polymer matrix.

Petroleum ether (60-100°) was used as solvent for the Friedel-Crafts acetylation since it is inert, has a convenient boiling range, and unlike nitrobenzene or dioxane, does not produce a tarry product. The yield of the acetylation was increased by recycling I and by use of acetic anhydride rather than acetyl chloride.

Oxidation of I to II was first tried with 5% sodium hypochlorate at 65°C. However, the yield from this method was low so that the much stronger oxidant, potassium permanganate, had to be used. Conditions were kept mild to prevent degradation of the polymer matrix.

The final two reactions are esterifications. These are equilibrium-controlled reactions and therefore must be driven toward completion. Thus, the melted diol and liquid thiol were used as solvent and excess reagent in their respective reactions to produce maximum yield. A small amount of sulfuric acid was also added as catalyst. A six carbon diol was chosen over a two or four carbon diol as linking agent between the resin matrix and the thiol functional group to avoid any steric hindrance from the matrix. Thus, the ligand was free to assume a geometric configuration around the metal ion similar to the monomer's.

Being a mercapto compound, the resin is not stable to oxidizing agents or excessive heat, but is stable to concentrated, non-oxidizing acids and bases. It is immediately destroyed by concentrated nitric acid and more slowly oxidized by higher concentrations of sulfuric and perchloric acids.

The sulfur contents for the two batches of HTG-4 are 1.96 and 2.43 mmole/g, respectively. The total acidic hydrogen capacity of batch 1 is 2.61 mmole/g, which is shown to be 1.84 mmole/g mercaptan and 0.54 mmole/g carboxylic acid by potentiometric titration (Figure 9). The two titratable hydrogens with pK values of 4.40 and 7.90 are assigned to the remaining carboxylic acid and the mercaptan, respectively. These assignments seem valid because the pK of benzoic acid is 4.20 and that of ethyl mercaptoacetate is 7.95.

The selectivity order of the resin for metal ions is Bi (III) < Ag (I) < Hg (II) << Au (III). This is based on back extraction of the ions from the resin with hydrochloric acid. This order is in agreement with the selectivity order of the monomer, IOTG (109). However, the extraction of the ions from the resin can be accomplished at lower hydrochloric acid concentrations than required in the solvent extraction of IOTG.

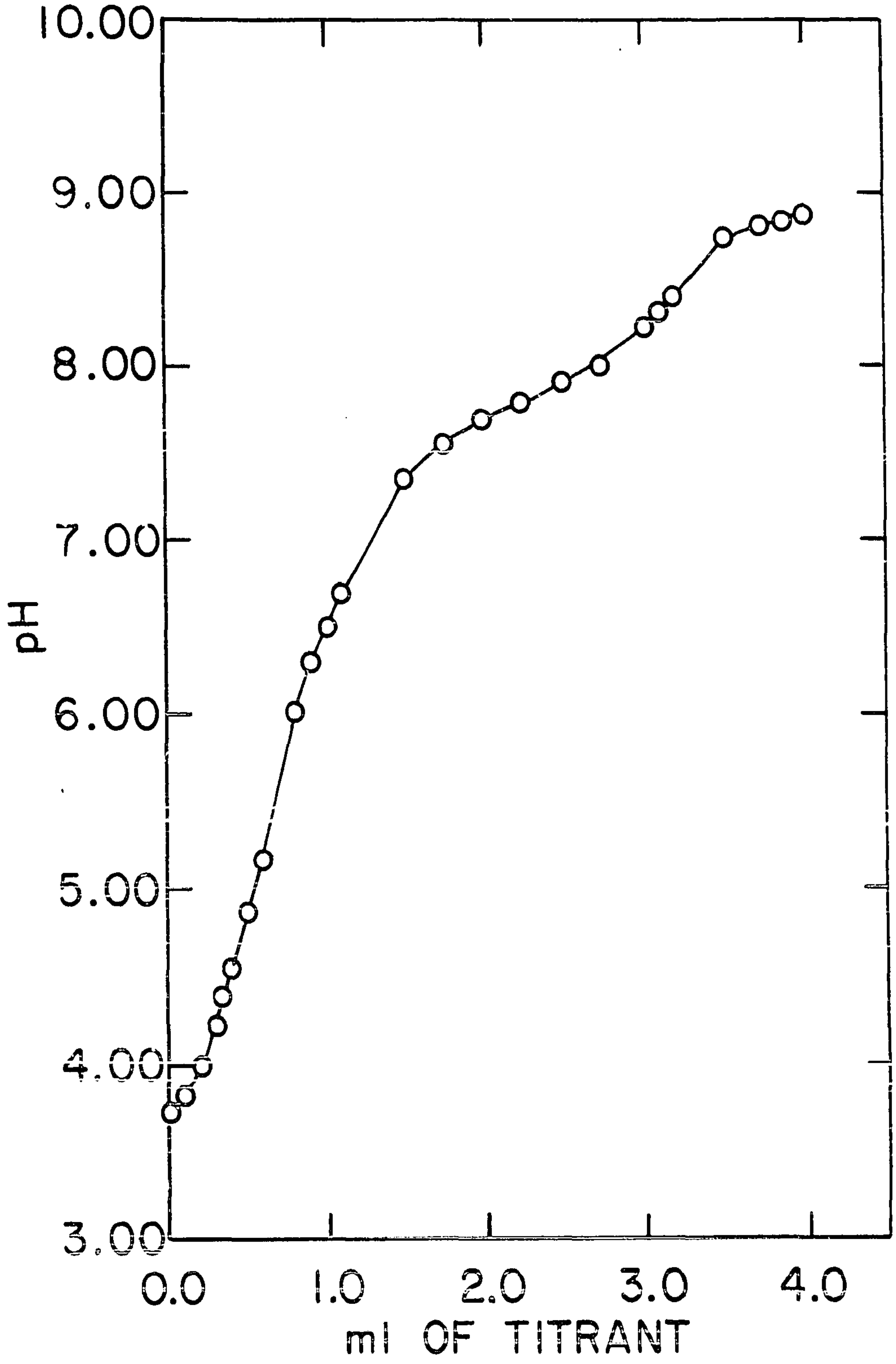


Figure 9. Titration of HTG-4 with 0.1 N sodium hydroxide

The HTG-4 resin readily retains silver (I), mercury (II), gold (III), and bismuth (III) from either 0.1 M perchloric acid or 0.1 M hydrochloric acid. A small amount of dilute bromine solution is added to the sample to prevent loss of gold (III) by reduction. As expected from the extraction studies on iso-octyl thioglycolate (109), the HTG-4 resin shows no affinity for alkaline earths (II), cadmium (II), cobalt (II), iron (III), lead (II), manganese (II), molybdenum (VI), nickel (II), or zinc (II) in 10^{-1} M perchloric acid. Unlike IOTG, it does not retain copper (II) or ruthenium (III). If the solution also contains 0.0002 M sodium hydrogen tartrate, tin (IV) and antimony (V) are likewise not retained. Care must be taken in the eluent preparation since bismuth (III) is partially eluted by 10^{-3} M tartrate. Platinum (II), palladium (II), and rhodium (III) are partially retained by the resin from either tartrate-perchloric acid or hydrochloric acid medium.

The capacity of the HTG-4 resin for certain metal ions was determined by batch and column methods. The batch capacity is 1.93 mmole/g for silver (I), 0.99 mmole/g for mercury (II), and 0.76 mmole/g for gold (III). Since the sulfur content of this batch of resin is 1.96 mmole/g, 1:1, 2:1, and 3:1 complexes of the resin functional group with silver, mercury, and gold, respectively, are indicated. These capacity measurements were carried out at pH 1.0, which is sufficiently acidic to avoid any interaction of the metal ions with unreacted carboxyl groups in the HTG-4 resin. A number of researchers have similarly studied chelating resins which bound metal ions at 2:1 and 3:1, R:M, ratios (39,46,64,81,102,111).

The column capacity of HTG-4 for gold (III) in 0.1 to 8.0 M hydrochloric acid is given in Table 6. The capacity reaches a maximum at 5.0 M hydrochloric acid, indicating that there is a competition between the chloride ions in the eluent and the sulfur groups of the resin for the coordination sites of the gold.

Table 6. Capacity of resin for gold(III)

M HCl	μmole Au(III)g resin	M HCl	μmole Au(III)/g resin
0.0	29.4	4.0	160
0.5	94.4	5.0	170
1.0	111	6.0	160
2.0	117	7.0	153
3.0	133	8.0	133

Data obtained on batch II of HTG-4.

Resin separations

Of the metal ions retained by the resin in 0.1 M perchloric acid, bismuth (III) is eluted by 0.5 M hydrochloric acid, silver (I) by 2 M hydrochloric acid, and mercury (II) by 6 M hydrochloric acid using a stepwise gradient. A typical separation is shown in Figure 10. Gold (III) is quantitatively retained by the resin during this process but is eluted by 0.001 M thiourea in pH 3.0 hydrochloric acid and determined as the gold-thiourea complex. Figure 11 shows the spectrum of the complex *versus* a 0.001 M thiourea blank. The absorbance maximum is at 256 nm with a molar absorptivity of 7.2×10^3 l. mole^{-1} cm^{-1}. It does obey Beer's law.

Table 7 gives the results obtained in the separation of bismuth (III), silver (I), and mercury (II) from 5 interfering metals and of gold (III) from 12 interfering metals at a 1:1 molar ratio. These ions were chosen as the most likely interfering ions on the basis of their metal to sulfur complexes. It was found that tin (IV) and antimony (V) do not interfere with the determination even though they did interfere with the IOTG solvent extraction. Copper (II), which was quantitatively extracted by IOTG, has no affinity for the resin in 0.1 M perchloric acid, and therefore, does not interfere even when present at > 100:1, Cu:Bi, molar ratio (see Table 8). A typical calibration curve for each of the ions determined is given in Figure 12.

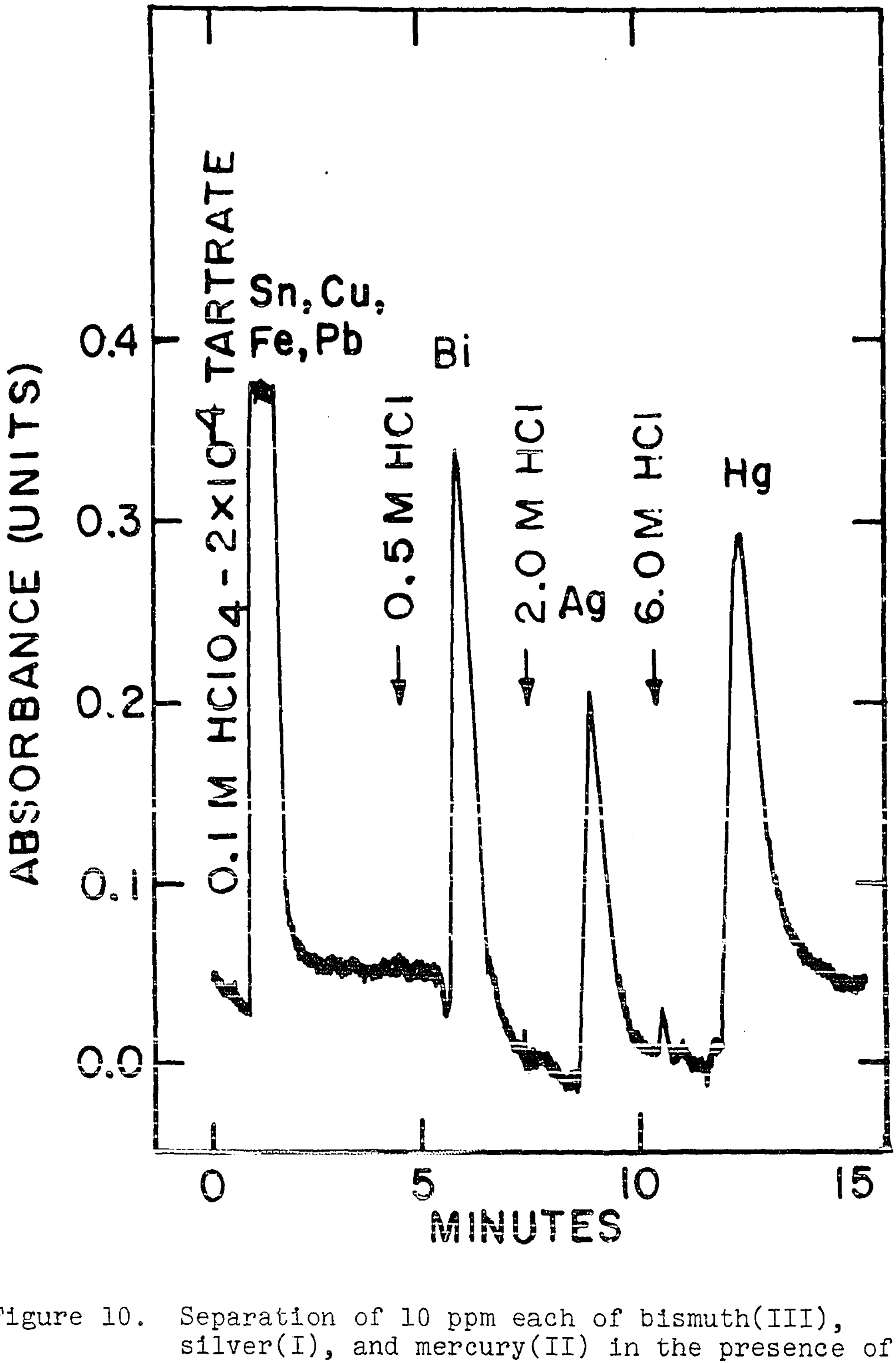


Figure 10. Separation of 10 ppm each of bismuth(III), silver(I), and mercury(II) in the presence of 100 ppm each of tin(IV), copper(II), iron(III), and lead(II)

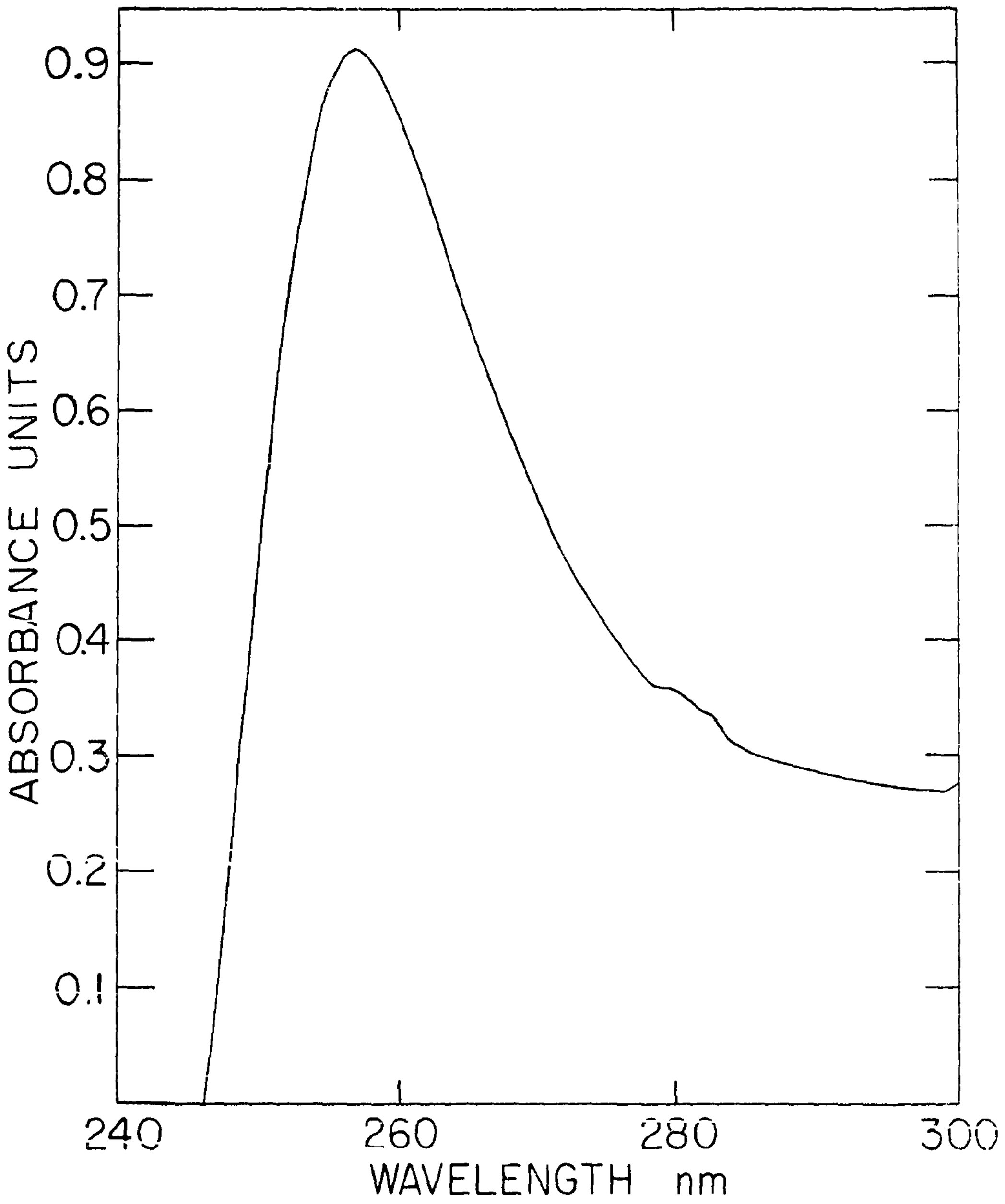


Figure 11. Absorption spectrum of 5 x 10^{-3} <u>M</u> gold-thiourea <u>versus</u> 5 x 10^{-3} <u>M</u> thiourea reference

Table 7. Silver, gold, bismuth and mercury recovery in the presence of other metals

Metal det'd	Amount taken (μg)	Amount found (μg)	% Recovery	Rel dev (pph)	Molar Ratio Cu/M	Molar Ratio Fe/M	Molar Ratio Pb/M	Molar Ratio Sn/M	Molar Ratio Sb/M
Ag	0.861	0.856	99.4	0.6	18	3	1	---	---
Au[a]	0.409	0.409	100.0	0.1	44	3	2	2	2
Bi	0.412	0.412	100.0	0.5	73	12	1	5	2
Hg	1.092	1.093	100.0	0.3	15	2	1	1	2

Quadruplicate analyses using least-squares plot

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[a] X1 bismuth and X2 mercury also present.

Table 8. Bismuth recovery in the presence of other metals

Bismuth taken (μg)	Bismuth found (μg)	% Recovery	Rel dev (pph)	Interf. ion	Molar ratio inter/Bi	Molar ratio Cu/Bi
0.292	0.283	97.0	3.2	Fe(III)	10	134
0.394	0.387	98.4	3.1	Sb(V)	10	87
0.306	0.310	101.4	1.4	Pb(II)	10	---
0.403	0.404	100.2	0.7	Sn(IV)	10	66

Quadruplicate analyses using least-squares plot

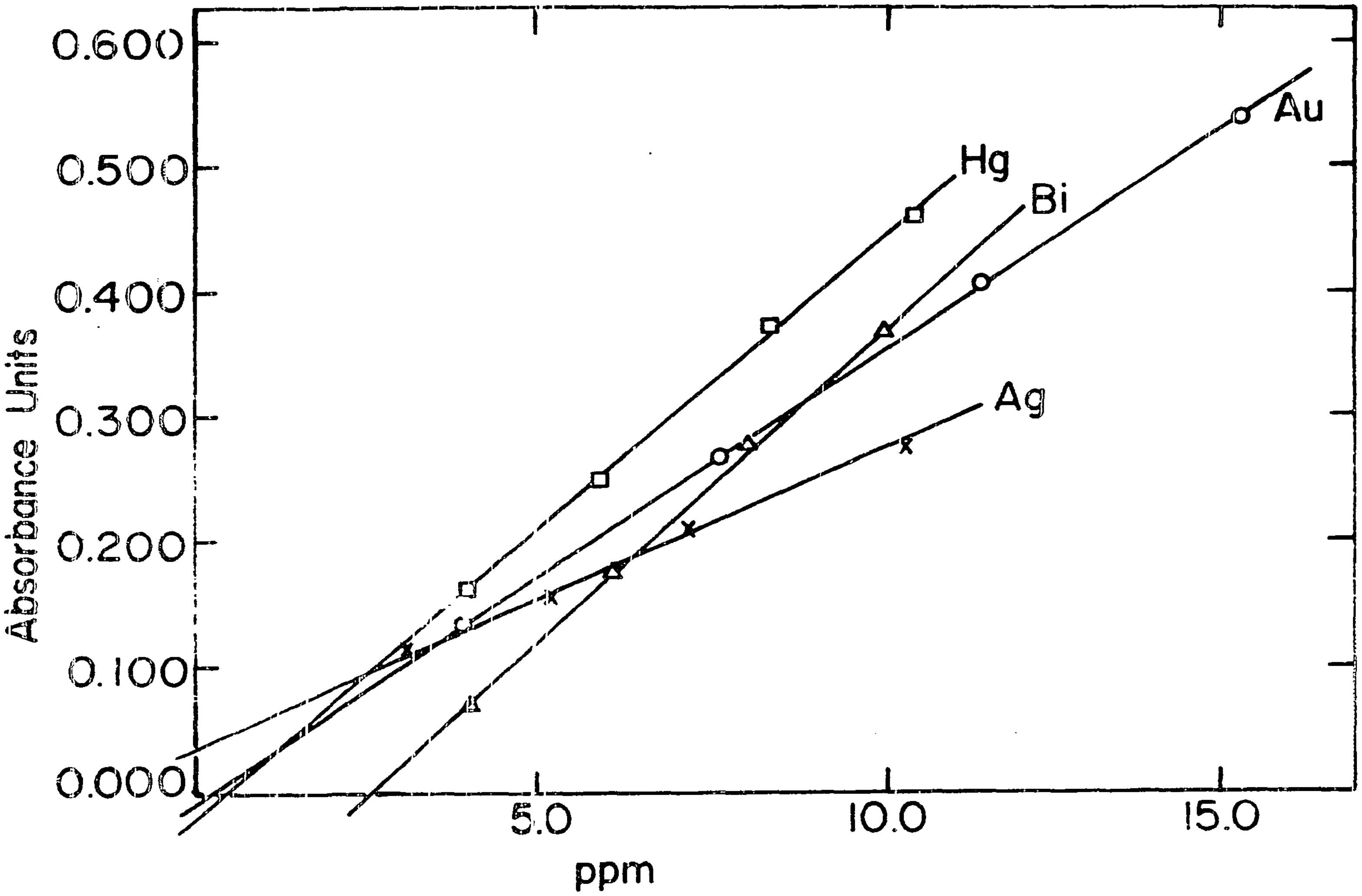


Figure 12. Typical calibration curves for bismuth(III), gold(III), mercury(II), and silver(I)

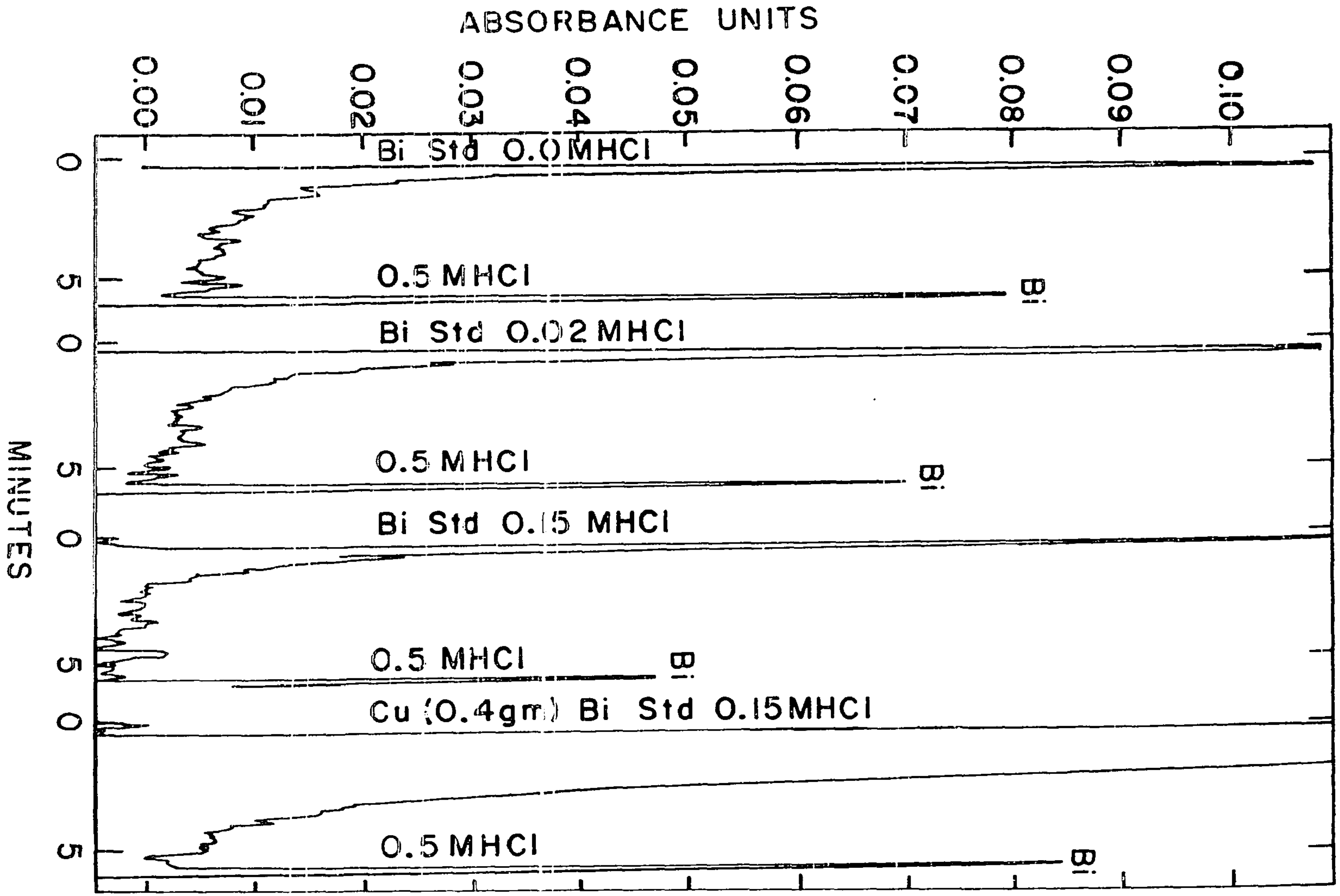
Table 8 presents data for separation of bismuth (III) from a ten-fold excess of each of 5 different metal ions. In Table 9 data are given for quantitative separation of gold from fifteen-fold excess of various metal ions. The gold separations were performed both in 2 M and 6 M hydrochloric acid. The only interference at these levels is platinum (II), palladium (II), and rhenium (III) with gold. These ions are partially retained in 0.1 M perchloric acid-2 x 10^{-4} M tartrate and are not eluted at any concentration of hydrochloric acid. However, they are eluted by pH 3.0-0.001 M thiourea and absorb in the 256 nm region.

Bismuth (III) is retained quantitatively by the HTG-4 resin up to 0.2 M hydrochloric acid. However, when the bismuth (III) sample solution contains 0.0002 M sodium hydrogen tartrate, the bismuth is partially eluted even in 0.02 M hydrochloric acid (see Figure 13). This is evidenced by the reduced bismuth peak on elution with 0.5 M hydrochloric acid. It is likely that this decrease results from the competition of the tartrate with the resin ligand for the bismuth. As shown by the last chromatogram in Figure 4, this problem is solved by adding 0.3 to 0.4 g of copper to all samples containing hydrochloric acid.

Table 9. Gold recovery in the presence of other metals (1.32 μmoles Au(III) and 19.80 μmoles interfering ion in each sample)

Interfering Ion	μmole Au(III) Found 2 M HCl	Diff.	μmole Au(III) Found 6 M HCl	Diff.
Bi (III)	1.34	+0.02	1.32	0.00
Cd (II)	1.35	+0.03	1.33	+0.01
Cu (II)	1.33	+0.01	1.30	-0.02
Fe (III)	1.57	+0.25	1.31	-0.01
Hg (II)	1.35	+0.03	1.31	-0.01
Pb (II)	1.29	-0.03	1.29	-0.03
Ru (III)	1.29	-0.03	1.31	-0.01
Sb (III)	1.56	+0.24	1.33	+0.01
Sn (IV)	1.30	-0.02	1.30	-0.02

Figure 13. Effects of hydrochloric acid and copper(II) on the recovery of bismuth(III) in the presence of 0.0002 M sodium hydrogen tartrate-0.1 M perchloric acid


ABSORBANCE UNITS
0.00
0.01
0.02
0.03
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0.06
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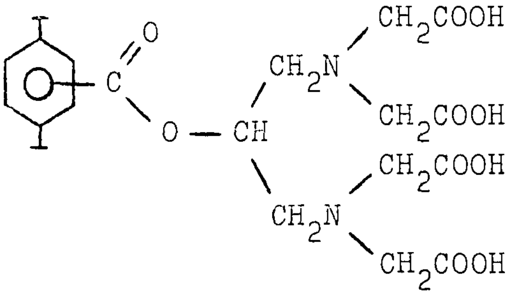
MINUTES
0
5
0
5
0
5
0
5
Bi Std 0.0 MHCl
0.5 MHCl
Bi
Bi Std 0.02 MHCl
0.5 MHCl
Bi
Bi Std 0.15 MHCl
0.5 MHCl
Bi
Cu (0.4gm) Bi Std 0.15MHCl
0.5 MHCl
Bi

THE SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A DIAMINOTETRAACETIC ACID RESIN

Alpha amino carboxylic acid resins are the most widely used and studied chelating ion exchangers. Dowex A-1 (Chelex 100), an iminodiacetic (IDAA) acid resin, is a standard for theoretical and application studies (8,33,54, 63,64). It is also widely used for concentrating and separating trace metal ions (18, 21-32). A new macroporous IDAA resin, XE-318, is also available with superior physical properties that allow its use in automated methods (35). In addition, a large number of other IDAA resins are being synthesized and used in various ways (1,67,72,112,113).

More novel resins have multiple IDAA groups and alpha amino triacetic acid groups. Blasius and Olbrich (114) used a resin containing two IDAA groups per benzene ring in meta configuration to separate cobalt and nickel. Morris _et al_. (115) synthesized a resin containing N,N,N-benzylamine triacetic acid. Blasius and Bock (113) synthesized a N,N,N'-ethylenediamine triacetic acid resin for separating transitional metals from the alkaline earths. Klyatschko (116) fixed EDTA as a solid solution within a phenol formaldehyde condensate for chromatographic work.

The strength of EDTA for complexing many metal ions at high pH and its selectivity for a few metal ions at low pH make it a desirable ligand for a chelating resin. Therefore, a similar ligand, propylenediamine tetraacetic acid, was chemically bonded to XAD-4 by an ester linkage to study such a resin. The structure of this resin is



BPDTA-4

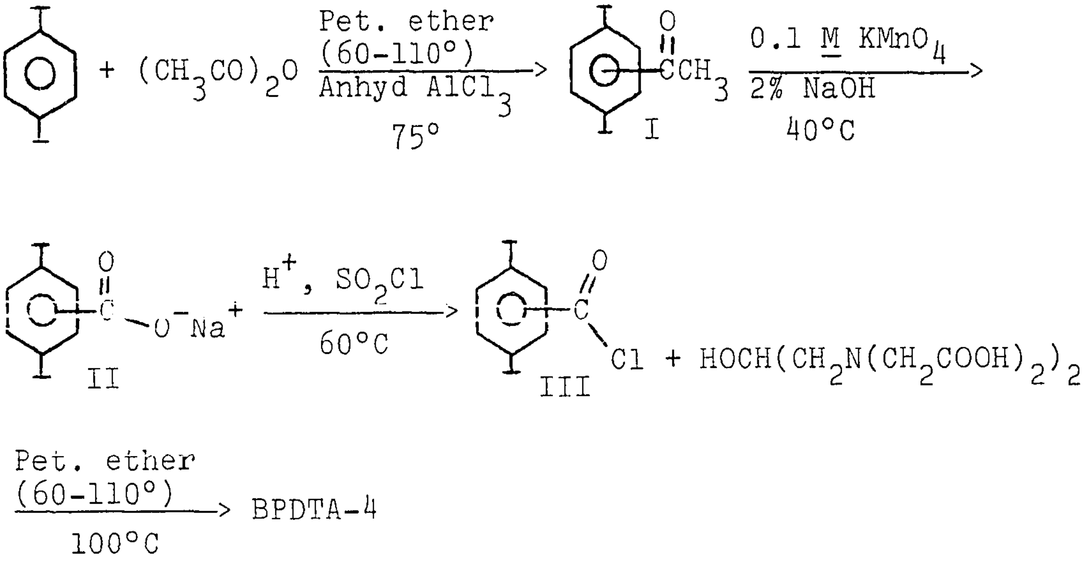
BPDTA-4 was used to separate uranium (VI), thorium (IV), and zirconium (IV) from other metal ions and each other. The effect of various cations and ligands on their recovery was studied. The quantitative determination of uranium in low grade ores and thorium in monazite sands was demonstrated. Several other separations were performed or suggested.

A selectivity order for the resin was determined by column distribution coefficients. In addition, the stability constants for four ions were determined by the method of Lewenschuss and Schmuckler (64). A study was made to determine at what pH values the resin acted as an ion-exchanger and as a complexer.

The quantitative recovery of 16 metal ions on a sub-ppm level demonstrated the resin's usefulness in concentrating trace metal ions. Radiotracers were used to test further the resin's ability to concentrate both free and bound trace cations in sea water. Also, the effect of pH and complexing agents on the recovery of trace metals was studied.

Experimental

Synthesis



The synthesis up to the formation of II was cited in the experimental section of the HTG-4 resin.

To 2.0 g of II was added 20 ml of thionyl chloride. The mixture was reacted at 60°C for 30 minutes. The resin was taken to near dryness so that little thionyl chloride would remain to react with the 1,3 Diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid.

III was slurried in 20 ml of petroleum ether to which 10 g of the aminoacid was added. The mixture was reacted at 100°C for 12 hours. The final product was collected by suction filtration and washed with 12 M hydrochloric acid, water, and acetone.

Distribution coefficients

The selectivity order of the resin was determined by use of column distribution coefficients (D_c). The equation of analysis was

$$D_c = \frac{(FE_e)(RT) - V_d}{W}$$

For the determinations, 51.4-μl aliquots of 10^{-3} M metal ion solutions were injected onto a 2.8 x 0.6 cm column of BPDTA-4 in various hydrochloric acid eluents ranging from 10^{-3} to 1.0 M in concentration. The time from injection to the appearance of the peak maximum was measured as RT. The flow rate of the eluent through the column was measured as FR_e. Detection was accomplished by mixing 12 M hydrochloric acid, pH 0.5-4 x 10^{-4} M Arsenazo III, 5 x 10^{-3} M PAR in 4 M ammonium hydroxide or 4 x 10^{-4} M Arsenazo I in 0.25 M THAM-0.25 M hydrochloric acid on-line 1:2, dye to eluent, with the column effluent and measuring the absorbance at 225, 635, 495, or 590 nm, respectively. The dead volume (V_d) was taken as the volume to elute magnesium (II) from the column in 1.0 M hydrochloric acid.

After these measurements were completed the resin was removed from the column; washed with 12 M hydrochloric acid, water, and acetone; and dried over calcium carbonate for 24 hours. The resin was then weighed in the acidic form. Batch 1 was used for these determinations.

Stability constants

The procedure of Lewenschuss and Schmuckler (64) was followed to determine the stability constants of the resin for manganese (II), zinc (II), copper (II), and calcium (II).

From 0.05 to 0.20 mmoles of EDTA, the external complexing agent, and 0.05 to 0.15 mmoles of the metal ion were mixed with 0.[illegible] g of resin. For zinc and manganese a small quantity of radiotracer was also added. After the pH was adjusted to 10.0, the mixtures were equilibrated for 2.0 hours in a [illegible] water bath and for a further 2.0 hours at room temperature. The samples were filtered and washed thoroughly with deionized water. The quantity of metal ion remaining in the effluent was determined by gamma emission or atomic absorption. The metal ion solutions were standardized with 0.025 M EDTA by standard procedures.

The equation used to determine K_{MR}, the stability constant of the resin for the metal ion, was

$$\log K_{overall} = \log K_{MR} - \log K_{MY} = \log \frac{(MR)(Y)}{(MY)} - \log (R)$$

Mechanism of attraction

A 214-µl aliquot of 10^{-2} M magnesium (II) was injected onto a 2.8 x 0.6 cm column of BPDTA-4 in various eluents. These were pH 3.0 hydrochloric acid, and pH 8.0 ammonium hydroxide with and without 0.1 M sodium nitrate and pH 10.0 ammonium hydroxide with 0.1 M sodium nitrate. The time for the elution of the magnesium (II) in each instance was recorded for an eluent flow rate of 1.8 ml/min. The detection procedure was given in the distribution coefficient study using Arsenazo I in THAM-hydrochloric acid.

The same procedure was followed for zinc (II) in 10^{-3} M hydrochloric acid and in pH 8.0 ammonium hydroxide with 0.1 M sodium nitrate present in each case.

Separation procedures

A 0.214-ml sample loop, a 2.8 x 0.6 cm column of BPDTA-4, and a flow rate of 2.0 ml/min were used in all separations. The column was washed for 10 minutes with the initial eluent used in the separation. Detection procedure was given in the distribution coefficient study.

A sample containing 4 x 10^{-3} M zinc (II) and 2 x 10^{-3} M magnesium (II) was injected onto the column in pH 8.0 - 0.1 M sodium nitrate. After injection, the column was washed for 5 minutes with this eluent and then with pH 3.0 - 0.1 M sodium nitrate. Arsenazo I in THAM-hydrochloric acid was used for detection.

A sample containing 2 x 10^{-4} M manganese (II), 1 x 10^{-3} M zinc (II), and 1 x 10^{-3} M cadmium (II) was injected onto the column in pH 2.25 hydrochloric acid. After injection, the column was washed for 5 minutes with this eluent. PAR was used for detection.

A sample containing 5 x 10^{-4} M copper (II) and 5 x 10^{-3} M manganese (II), nickel (II), cadmium (II), zinc (II), cobalt (II), and lead (II) was injected onto the column in pH 2.0 hydrochloric acid. After injection, the column was washed for 2 minutes with this eluent then with pH 1.5 hydrochloric acid. PAR was used for detection.

A sample containing 1.2 x 10^{-3} M uranium (VI), 4.0 x 10^{-4} M thorium (IV), and 4.0 x 10^{-3} M zirconium (IV) was injected onto the column in 0.01 M hydrochloric acid. After injection, the column was washed for 5 minutes with this eluent. The ions were then sequentially eluted with 0.1 M hydrochloric acid, 4.0 M hydrochloric acid, and 1.0 M sulfuric acid. pH 0.5 - Arsenazo III was used for detection.

Interference studies

A 3.0 x 0.6-cm column of BPDTA-4 was used in interference studies for the three ions. Samples were made by adding the metal ion or ligand to be tested to 25, 100, or 200 µmoles of thorium (IV), uranium (VI), or zirconium (IV), respectively, and diluting to 25 ml with 0.1 M hydrochloric acid. The species were tested at a 1000-fold molar excess to the analyte or at the highest ratio solubility allowed. If found to interfere, the ratio was dropped by a factor of 10 and retested.

Pre-equilibration of the column, sample injection, and the washing procedure and detection were described in the separation procedure. In addition for thorium (IV) and zirconium (IV) samples, the resin was washed for a further 5 minutes with 0.1 M hydrochloric acid. Three measurements of the peak height in the presence and absence of the potential interfering species were taken and the relative deviation of the two recorded.

Ore samples

To 10.0 mg of monazite sand, NBL-7a, was added 10 ml of concentrated sulfuric and 10 ml of concentrated nitric acid. The sample was digested and allowed to go to dryness. It was then readily dissolved in 50 ml of deionized water leaving behind a small silica residue.

The low grade uranium ores, uraninite and carnotite, were digested by the procedures recommended by Hildebrand *et al*. (117). The 0.1 g uraninite samples were digested in 15 ml each of concentrated nitric and sulfuric acids. The 0.1-g carnonite samples were digested in 20 ml concentrated hydrochloric acid followed by a digestion in 15 ml each of concentrated nitric and hydrochloric acids. The samples were taken to dryness and dissolved in 50 ml of deionized water.

The analysis procedure for all samples was identical to that given in the interference studies.

Concentration of trace metals

The percentage recovery of 22 trace metals was determined as a function of effluent pH. A 0.5-g, 3.2 x 0.6-cm column of BPDTA-4 resin was washed with 25 ml of a pH 6.0 ammonium hydroxide-acetic acid buffer then with 100 ml deionized effluent at the pH to be tested. The column effluent was checked to make sure it was the proper pH; if not, it was further adjusted. The samples were made with deionized water buffered to the appropriate pH with hydrochloric acid, phosphoric acid and/or ammonium hydroxide. Each 500-ml sample which was 0.5 ppm in each metal ion tested was passed through the column at 5 ml/min. The column was then washed with two 25-ml portions of metal-free effluent and stripped with 25 ml of 2 M hydrochloric acid. The recovered ions were determined by plasma emission or colorimetrically with Arsenazo III.

The procedure for determining the percentage recovery of trace metals in the presence of citrate, tartrate, phosphate, carbonate, and EDTA was identical to the above except that sufficient ligand was added to the solution so that the ratio of L:M was 1000:1.

The recovery of metal ions from sea water was determined both by use of radiotracers and spectrophotometrically. A 1.0-ml aliquot of 25 μCi zinc-65, manganese-54, iron-59, or 100 μCi chromium-51 or 2.0 to 3.0 ml-aliquot of 1.02×10^{-3} M uranium (VI) was added to 250 ml of Pacific Ocean sea water. These solutions were equilibrated for 30 days at pH 8.0 then passed through a 3.2 x 0.6 cm column of BPDTA-4 which had been pre-equilibrated to pH 8.0. After passage of the samples at 5 ml/min, the resin was washed further with 100 ml of pH 8.0 ammonium buffer. The tracer ions were eluted with 25 ml of 2.0 M hydrochloric acid. Subsequently, 5-ml aliquots were measured for gamma emission. The uranium (VI) was eluted from the column with 25 ml of 0.1 M hydrochloric acid and determined by reinjection onto a BPDTA-4 column following the interference studies procedure.

Results and Discussion

Evaluation of resin

A chelating resin containing 1,3-diamino-2-hydroxypropane-N,N',N'-tetraacetic acid, HPDTA, was synthesized. It is light brown in color and is stable to acid and base under normal experimental conditions. Temperatures in excess of 150° must be avoided as the resin decarboxylates. Analysis shows the two batches of resin to have 1.54 and 1.21% nitrogen, respectively. Assuming all nitrogen present to belong to the unaltered functional group, the resin batches have capacities of 0.55 and 0.45 mmole/g, respectively.

The closeness of the ionization constants of the polymeric ligand and of the carboxylic acid impurity from the synthesis procedure prevent a useful titration of the resin. Based on the close agreement of monomeric and polymeric ligand ionization constants for the HTG-4 resin however, it is suggested that the pK values for the polymeric ligand are close to those for HPDTA itself. Data obtained by Marhol and Cheng (67) support this theory. The pK values are cited by Thompson and Kundra (118) as 1.6, 2.60, 6.96, and 9.49.

The selectivity order of the resin is Mg(II) < Mn(II) < Cd(II) < Zn(II) < Co(II) < Ni(II) < Pb(II) < Cu(II) < Cr(III) < Fe(III) < V(V) < Bi(III) < U(VI) < Th(IV) < Zr(IV) as determined by column distribution coefficients in hydrochloric acid. This is in good agreement with the selectivity order of the HPDTA monomer of Mg(II) < Mn(II) < Zn(II) < Cd(II) < Co(II) < Ni(II) < Cu(II) (119).

The distribution coefficients for 11 of the ions are given in Table 10. In addition, zirconium (IV) is retained by the resin at all concentrations of hydrochloric acid, while tin (IV) is not retained at any concentration nor in any other medium tested. The latter fact indicates that the resin might be used to purify tin (IV) of many trace impurities.

The stability constants for calcium (II), copper (II), manganese (II), and zinc (II) are given in Table 11. They are compared with the stability constants found for the HPDTA monomer and EDTA. As expected from the studies of Schmuckler, Hering and others (9-12, 33,47,64, 70-72), the complex between the metal ion and the polymer ligand is stronger than that of the monomer but follows the same order.

The first acidic hydrogen of the resin is fully ionized by pH 2.2, enabling the resin to function as an ion exchanger as well as a complexer above this pH. To determine which of these mechanisms predominates at pH values of 3.0, 8.0, and 10.0, the retention of magnesium (II) and zinc (II) on BPDTA-4 was tested with and without 0.1 <u>M</u>

Table 10. Column distribution coefficients for metal ions on BPDTA-4 in hydrochloric acid

Ion/pH	0.00	0.50	0.75	1.00	1.50	2.00	2.25	2.50	2.75
Bi(III)				0.3		0.7	22.3		
Cd(II)				0.2		1.3	7.4	24.1	>200
Co(II)				0.0		1.5	9.4	28.2	>200
Cu(II)				5.7	12.2	82.0	(111.0)[a]	>200	
Fe(III)				1.3		4.1	11.9	44.0	>200
Mg(II)				0.0		0.5	3.5	12.3	34.5
Mn(II)				0.0		0.7	4.4	13.5	76.5
Ni(II)				0.1		2.7	17.5	57.4	>200
Th(IV)	13.2	21.8	80.1	>200					
U(VI)	0.2	0.8		3.9	17.9	(90.0)[a]	>200		
Zn(II)				0.2		1.3	10.8	32.7	>200

[a] These ions bleed from column.

Table 11. Stability constants for metal ions with BPDTA-4 resin, HPDTA monomer, and EDTA monomer

	BPDTA-4 Resin (log K)	HPDTA Monomer (log K)	EDTA Monomer (log K)
Ca(II)	10.0	6.69	11.0
Cu(II)	17.4	17.21	18.7
Mn(II)	13.0	9.06	13.8
Zn(II)	15.8	13.70	16.4

sodium nitrate present. Since sodium does not form a complex with the resin and nitrate does not form a complex with the ions, the only effect the salt can have is through mass action. Thus, it has a much greater effect on ions held by ionic bond than those held by complexation.

In pH 3.0 - 0.1 M salt, magnesium (II) is rapidly eluted (Figure 14b) even though it is slightly retained in the absence of any salt (Figure 14a). The mechanism of attraction appears to be ion exchange. Zinc (II) behaves similarly though it is held slightly longer in the presence of sodium nitrate than is magnesium (II) (Figure 14c). Again, the mechanism of attraction appears to be predominately ion exchange.

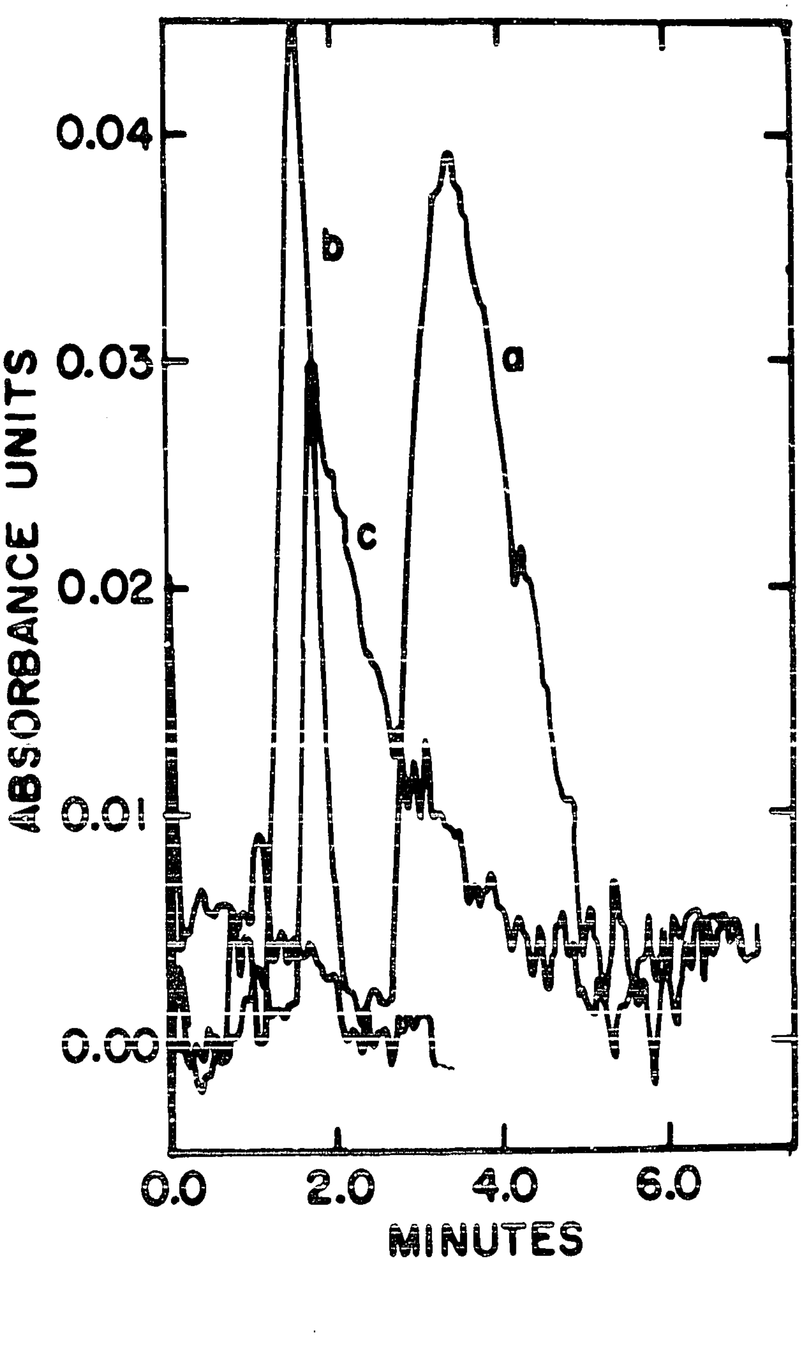
Figure 14. The elution curves on BPDTA-4 for magnesium (II)

(a) in 10^{-3} M hydrochloric acid,

(b) in 10^{-3} M hydrochloric acid - 0.1 M sodium nitrate

and for zinc (II)

(c) in 10^{-3} M hydrochloric acid - 0.1 M sodium nitrate


ABSORBANCE UNITS
0.04
0.03
0.02
0.01
0.00
b
a
c
0.0
2.0
4.0
6.0
MINUTES

At pH 8.0, the magnesium (II) is eluted faster in the presence of a high salt concentration (Figure 15b) than in its absence (Figure 15a). However, the magnesium is held longer than at pH 3.0 in 0.1 M salt indicating that the complexation mechanism does play a significant role here. Zinc (II) is apparently held fast at pH 8.0 in 0.1 M salt (Figure 15c) indicating that the complexation mechanism predominates. Magnesium (II) is held fast at pH 10.0 in 0.1 M salt (Figure 15d) indicating again that the complexation mechanism now predominates.

Resin separations

The difference in mechanism of attraction for the alkali earths and the transition metals at lower pH values can be used for their separation. Figure 16 shows a separation of magnesium (II) and zinc (II). The addition of 0.1 M sodium nitrate to the pH 8.0 eluent allows only the zinc (II) to be retained by the resin while the magnesium (II) is eluted quickly. The zinc (II) can then be stripped from the column with pH 3.0 - 0.1 M sodium nitrate or any other suitable eluent.

A separation of manganese (II) from the zinc (II) and cadmium (II) at a 1:1 molar ratio is shown in Figure 17. A separation of copper (II) from a number of transition metals at a 1:10 molar ratio is shown in Figure 18. Separations of this type are possible though difficult. Conditions must be

Figure 15. The elution curves on BPDTA-4

(a) for magnesium (II) in pH 8.0 ammonium hydroxide,

(b) for magnesium (II) in pH 8.0 - 0.1 M sodium nitrate,

(c) for zinc (II) in pH 8.0 - 0.1 M sodium nitrate

(d) for magnesium (II) in pH 10.0 - 0.1 M sodium nitrate

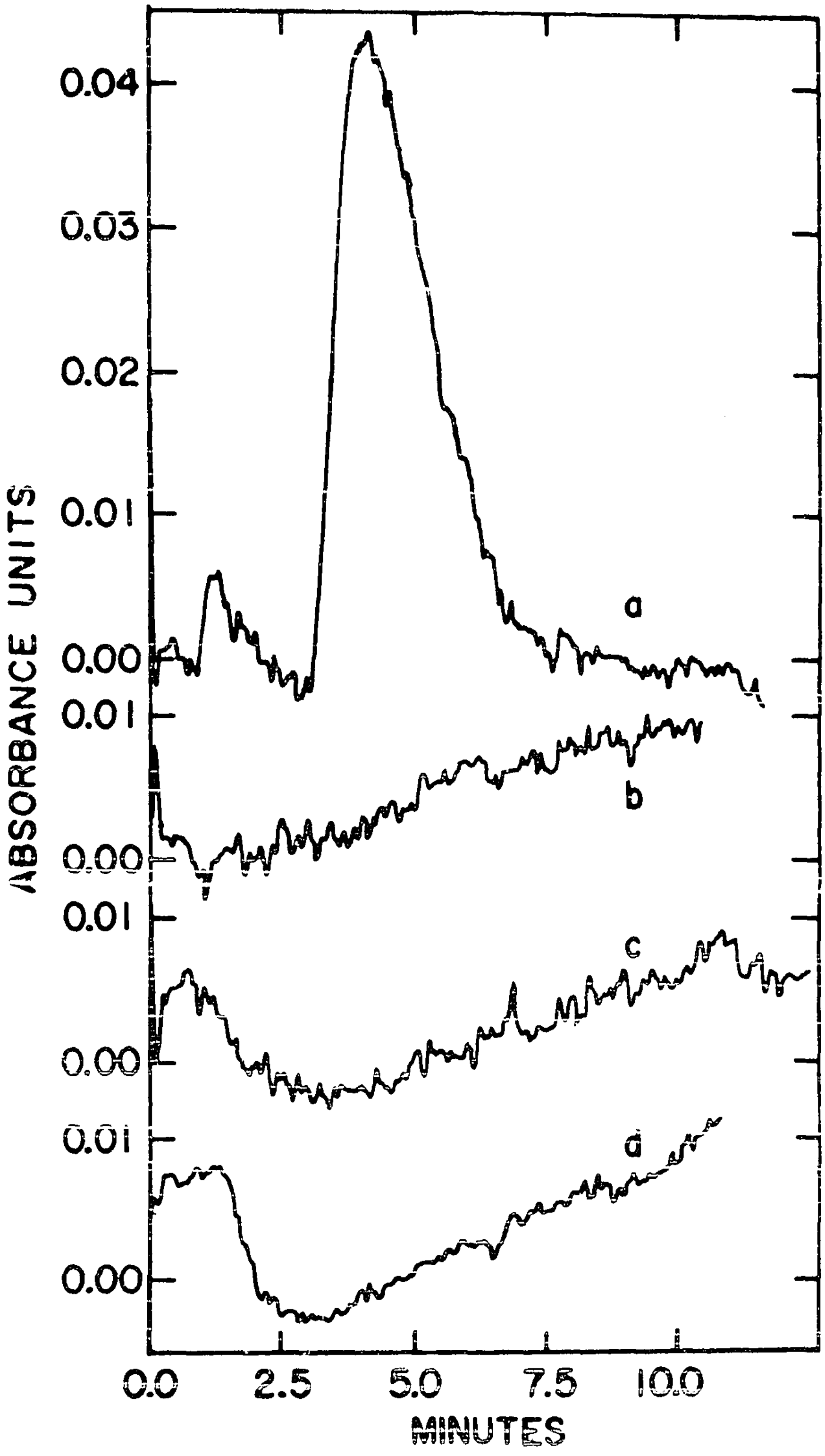

ABSORBANCE UNITS
0.04
0.03
0.02
0.01
0.00
0.01
0.00
0.01
0.00
0.01
0.00
a
b
c
d
0.0
2.5
5.0
7.5
10.0
MINUTES

Figure 16. Separation of manganese (II) and zinc (II)

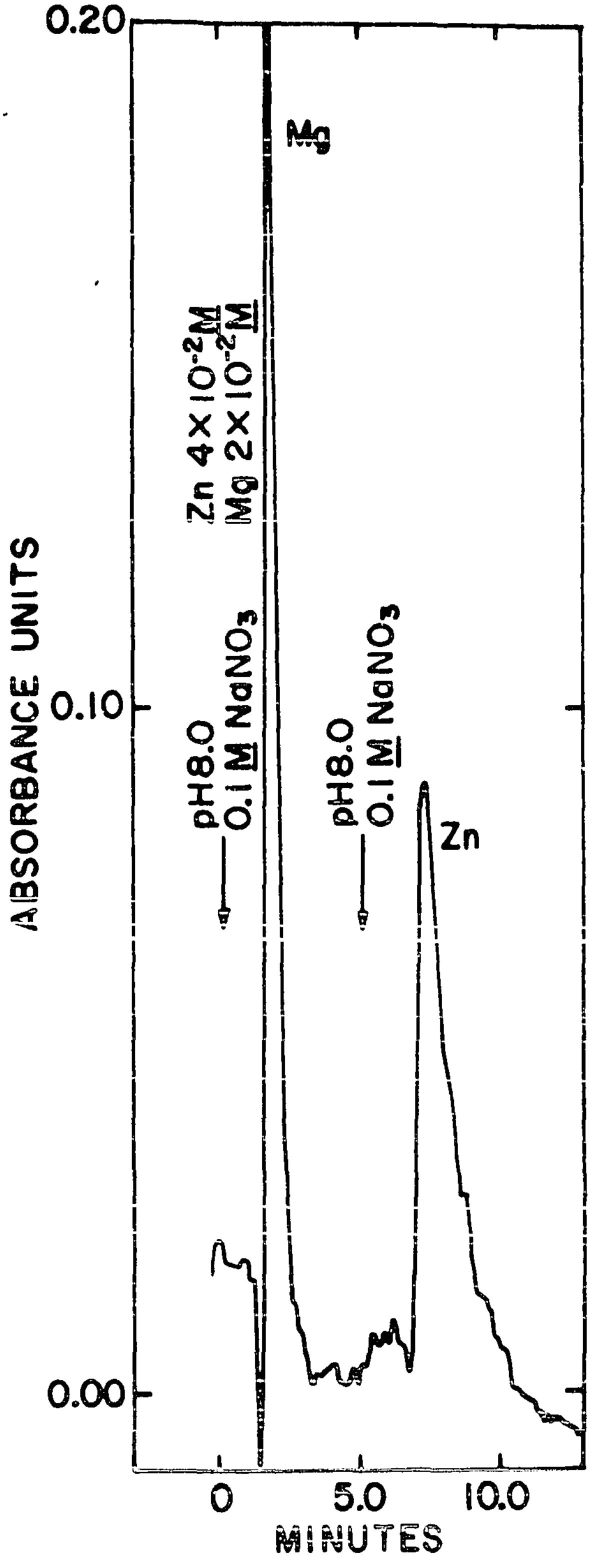
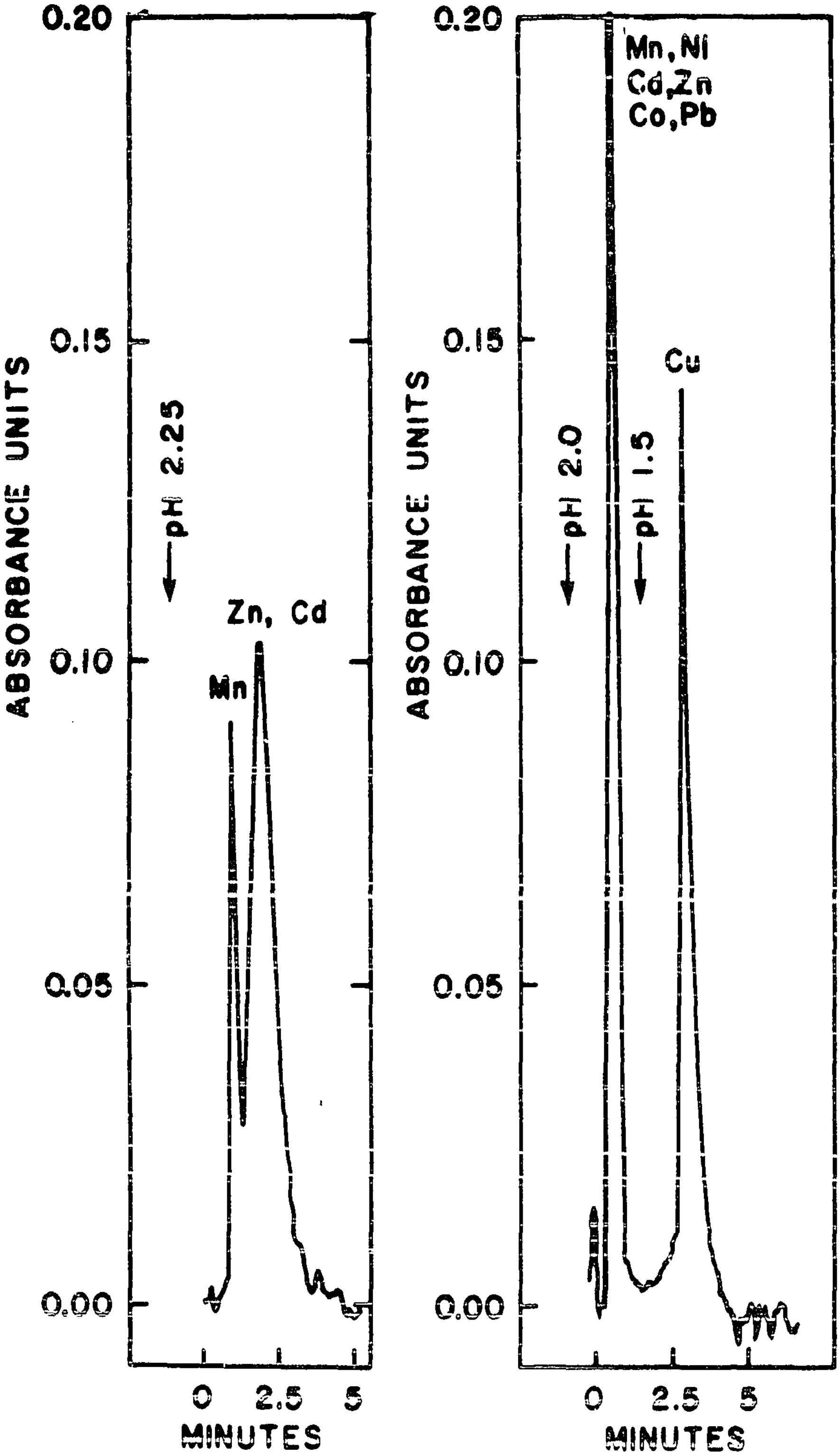

0.20
0.10
0.00
ABSORBANCE UNITS
Mg
Zn 4×10^{-2}M
Mg 2×10^{-2}M
pH8.0
0.1 M NaNO$_3$
pH8.0
0.1 M NaNO$_3$
Zn
0
5.0
10.0
MINUTES

Figure 17. Separation of 2×10^{-4} M maganese(II) from 1×10^{-3} M of zinc(II) and cadmium(II)

Figure 18. Separation of 5×10^{-4} M of copper(II) from 5×10^{-3} M of other ions


ABSORBANCE UNITS
0.20
0.15
0.10
0.05
0.00
pH 2.25
Mn
Zn, Cd
0
2.5
5
MINUTES
ABSORBANCE UNITS
0.20
0.15
0.10
0.05
0.00
pH 2.0
pH 1.5
Mn, Ni
Cd, Zn
Co, Pb
Cu
0
2.5
5
MINUTES

very strictly adhered to because the selectivity coefficients for the ions are very similar. There is also greater chance of interference at these higher pH values especially from ligands.

The resin is highly selective for uranium (VI), thorium (IV), and zirconium (IV) below pH 2.5. They are separated from other metal ions by complexation on the resin in 0.01 M hydrochloric acid. Once retained, they are separated from each other by sequential elution with 0.1 M hydrochloric acid, 4.0 M hydrochloric acid, and 1.0 M sulfuric acid. A typical separation is shown in Figure 19.

The results of an interference study for a number of cations and ligands is given in Table 12. Species for which greater than 0.030 relative deviation is found are considered to interfere. In most cases species could be present at least to a 100:1 molar excess to the analyte. However, citrate, tartrate, bismuth (III), and molybdenum (VI) must be avoided totally when zirconium (IV) is to be determined. Additionally, iron (III), EDTA, and sulfate must be limited for zirconium (IV), and iron (III) and molybdenum (VI) for thorium (IV) and uranium (VI).

The quantitative recovery of thorium (IV) by the resin in the presence of a 400:1 molar excess of uranium (VI) is demonstrated in Figure 20. It can be seen that the height of the thorium peaks in the presence and absence of

Figure 19. Separation of 1.2×10^{-3} $\underline{M}$ uranium(VI), 4.0×10^{-4} $\underline{M}$ thorium(IV), and 4.0×10^{-3} $\underline{M}$ zirconium(IV)

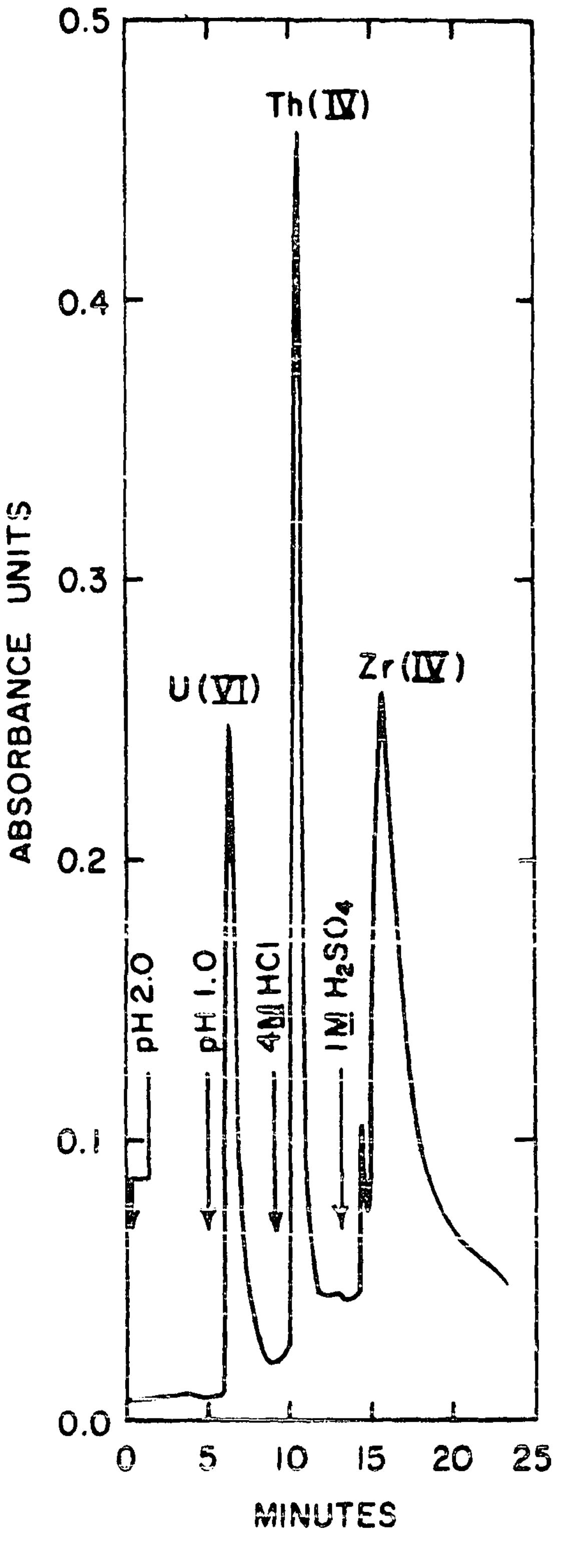

ABSORBANCE UNITS
0.0
0.1
0.2
0.3
0.4
0.5
MINUTES
0
5
10
15
20
25
pH 2.0
pH 1.0
4M HCl
1M H_2SO_4
U(VI)
Th(IV)
Zr(IV)

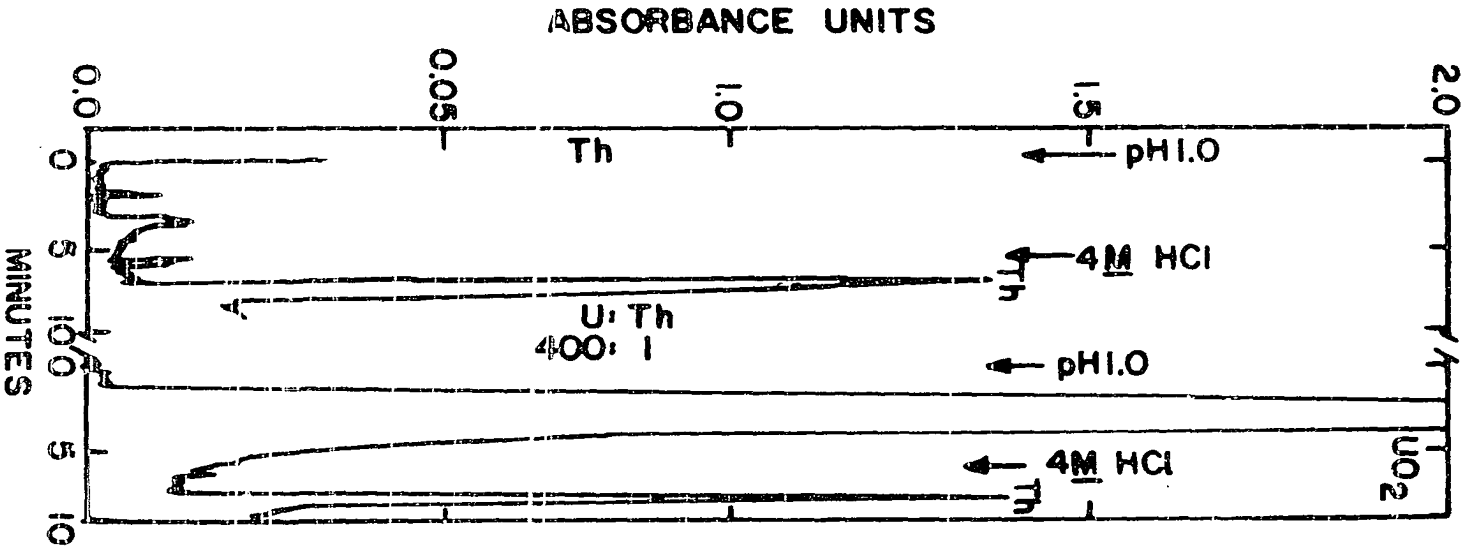
Table 12. Interference of metal ions and ligands with the determination of uranium, thorium, or zirconium

Interfering Species	Molar Ratio interf/Th	Rel dev	Molar Ratio interf/U	Rel dev	Molar Ratio interf/Zr	Rel dev
Bi(III)	1000	-0.004	100	0.000		
Cr(III)	1000	+0.004	1000	+0.026		
Cu(II)	1000	0.000	1000	-0.003		
Fe(III)	1000	-0.045	100	+0.203	200	+0.121
			10	+0.025	20	+0.024
Mo(VI)	1000	-0.490	50	+0.007		
	50	-0.002				
Pb(II)	1000	+0.006	1000	-0.011		
Hg(II)	1000	-0.005	1000	-0.251		
			100	-0.022		
U(VI)	500	-0.002			1000	0.000
Zr(IV)	1000	>+100	1000	+0.010		
	100	-0.002				
Th(IV)			100	+0.014	1000	-0.039
Zn(II)	1000	+0.001	1000	-0.002		

Table 12. (Continued)

Interfering Species	Molar Ratio interf/Th	Rel dev	Molar Ratio interf/U	Rel dev	Molar Ratio interf/Zr	Rel dev
EDTA	1000	-0.003			100	-0.260
					10	-0.065
Tartrate	1000	+0.004	1000	+0.413	200	-0.528
			100	-0.005	20	-0.299
Citrate	1000	+0.005	1000	-0.030	200	-0.386
			100	-0.008	20	-0.205
Sulfate	1000	-0.006	1000	-0.202	200	+1.52
			100	0.000	20	-0.008
Phosphate	1000	-0.151	1000	+0.005	200	0.000
	100	+0.013				
Sulfosalicylate			1000	-0.008		
Phenylarsonic acid	1000	-0.016	1000	-0.175		
			100	-0.025		
Citrate			1000	-0.010		

Figure 20. Spectra of 1.5 x 10^{-4} $\underline{M}$ thorium(IV) and of 1.5 x 10^{-4} $\underline{M}$ thorium(IV) in the presence of uranium(VI)


ABSORBANCE UNITS
0.0
0.05
1.0
1.5
2.0
MINUTES
0
5
10
0
5
10
Th
pH1.0
4M HCl
Th
U: Th
400: 1
pH1.0
4M HCl
Th
UO2

uranium (VI) are the same within experimental limits. This demonstrates the ability of the resin to purify uranium (VI) of small amounts of thorium (IV).

The quantitative recovery of thorium (IV) from monazite sand and uranium (VI) from low grade ores as determined by triplicate analysis is demonstrated in Table 13. The method is thus applicable to samples high in silica and rare earth concentration. Another low grade uranium ore, torbernite, was also tried but the uranium peak was masked by an unknown interfering species.

Table 13. Analysis of ore samples

Sample	Species Determined	% Found	% Previously Reported
Uraninite Ore	U (U_3O_8)	0.373 ± 0.025	0.375
Carnotite Ore	U (U_3O_8)	0.408 ± 0.017	0.418
Monazite Sand	Th (ThO_2)	9.61 ± 0.04	9.65

Trace metal studies

In recent years, there has been increasing concern over the health hazard caused by pollution of our food and water supplies by heavy metals. Increasing awareness to the toxic effects of excess quantities of these metals has led to development of methods for their elimination.

Chelating ion exchange resins have proved more effective purifiers than extraction, electrodialysis, evaporation and precipitation methods (17). The strength of EDTA-metal complexes makes an EDTA resin the prime choice for removing the heavy metals from our contaminated waterways. Thus, it was decided to make a resin with a closely related ligand, HPDTA, which also forms strong bonds with a number of metal ions to test this theory.

A study of pH <u>versus</u> percentage recovery was performed for 22 metal ions at a 0.5 ppm level. Figure 21 gives the pH range for quantitative recovery of 16 of these ions. The maximum recovery and pH for the other ions are as follows: Ti(III) 80% at pH 6-9, As(V) 40% at pH 8-9, Mo(VI) 40% at pH 5-5.5, Sb(V) 40% at pH 6.0, Se(IV) 30% at pH 5-5.5, and Sn(IV) no retention.

Florence and Batley (16) have used anodic stripping voltammetry to show that the chelating resin, Chelex 100, collects 100% of the free metals in sea water but not the "bound metals". By "bound metals", they are referring to

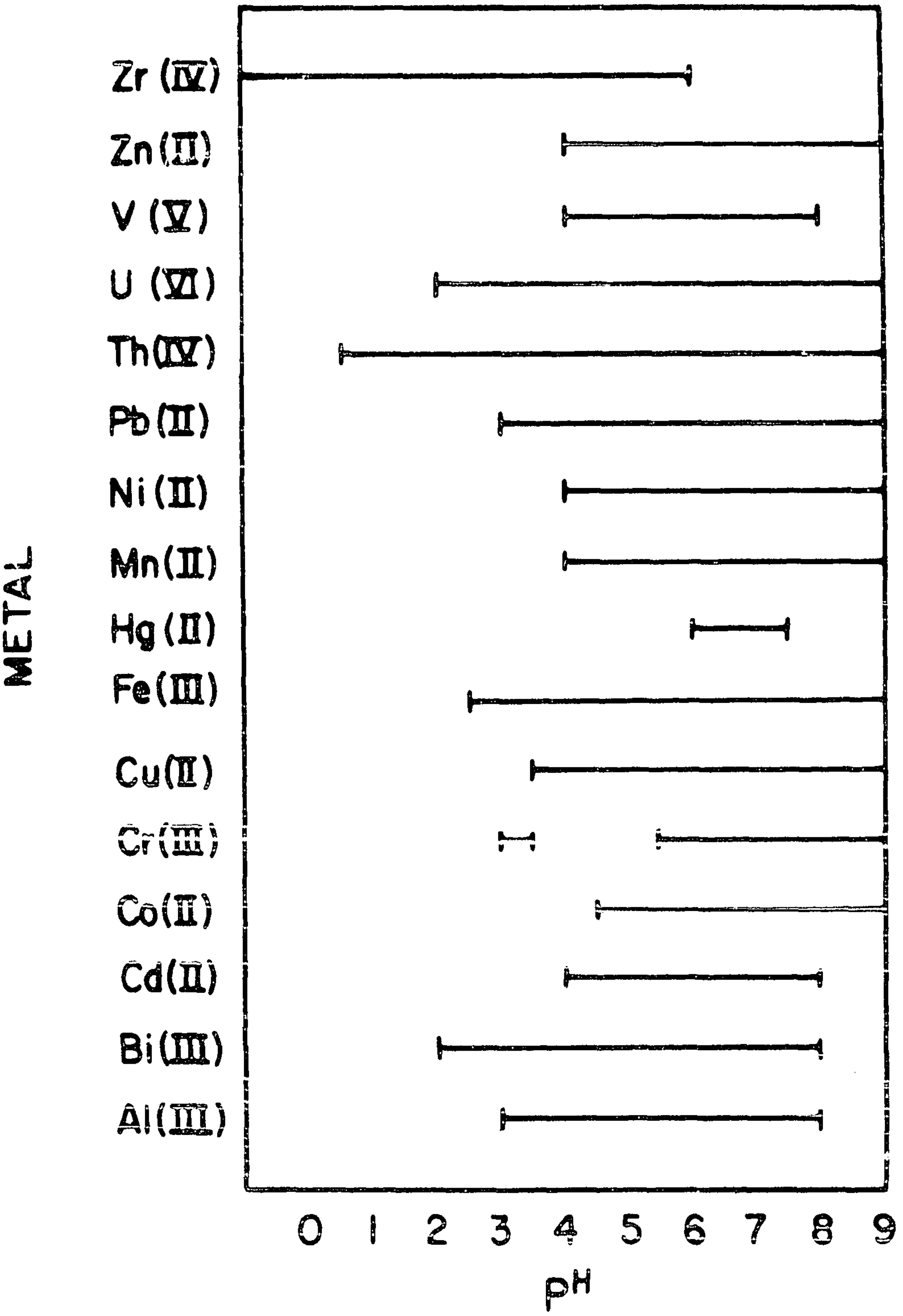


Figure 21. Recovery of trace metals as a function of pH in hydrochloric acid

adsorbed or occluded metal ions in collodial organic or inorganic particles. Only in the cases of chromium (III) and iron (III) do they consider any significant amount of the ions to be complexed.

The method used here to test the recovery of 5 ions added to sea water was designed to determine whether the BPDTA-4 resin could recover 100% of the elements whether they were free, complexed, occluded, or adsorbed. By equilibrating the samples for 30 days, it was hoped that the added metal ions would assume the same percentages of free and bound as the metal ions already present. Thus, if quantitative recovery could be accomplished, it would imply that the total metal concentration could be recovered. This study was performed at pH 8.0 because earlier studies had shown this to be the only pH at which the resin could quantitatively recover metal ions in the presence of large concentrations of sodium, calcium, and magnesium.

The results of this study are given in Table 14. Three ions, zinc (II), manganese (II), and uranium (VI) presented no problems. However, iron (III) and chromium (III) recoveries are low. This indicates that the resin can recover free, adsorbed, and occluded metal ions but not complexed. This might be corrected by the use of a digestion procedure to remove the organics (16,119).

Table 14. Recovery of trace elements from spiked sea water

Ion Added	Amount Added	% Recovered	Stripping Eluent
Cr(III)	100 µCi	83.1 ± 0.7	2.0 M HCl
Fe(III)	25 µCi	94.4 ± 0.2	2.0 M HCl
Mn(II)	25 µCi	102.0 ± 0.6	2.0 M HCl
U(VI)	0.5 ppm	98.5 ± 0.2	0.1 M HCl
Zn(II)	25 µCi	102.8 ± 0.4	2.0 M HCl

The effect of complexing agents on the recovery of metal ions is demonstrated in Table 15. In addition, 60% of chromium (III) at pH 4.0-5.0 was recovered in the presence of EDTA. No other ion was recovered to any significant extent in the presence of this ligand. As can be seen, the optimum pH for determination depends on the ion and ligand in question. In most cases a set of conditions can be found which give acceptable results.

A number of possible separations are suggested from this study. These are evidenced by the large difference in the attraction of the metal ions to the resin. They are as follows: cadmium (II) from zinc (II) in pH 5.0 - citrate; and copper (II), nickel (II), and cobalt (II) from lead (II),

Table 15. Recovery of trace metals in the presence of various ligands (Concentration of each ion - 0.5 ppm; and of each ligand - 500 ppm)

Ligand	pH	Al(III)	Cd(II)	Co(II)	Cr(III)	Cu(II)	Ni(II)	Pb(II)	Zn(II)
Carbonate	4.0	90	34	45	84	290	51	64	83
	5.0	86	22	35	66	286	45	66	96
	6.0	78	95	84	78	---	81	57	--
	7.0	77	88	79	78	---	76	59.6	--
	8.0	53	84	78	77	---	77	59	--
Citrate	4.0	1.8	79	22	80	32	12	81	23
	5.0	0.0	71	3.1	47	20	5	51	7.5
	6.0	0.9	34	3.8	7	9	7	58	10
	7.0	0.0	28	6.5	0.0	3	10	65	20
	8.0	0.5	68	30	0.0	27	32	63	86
	9.0	0.2	94	27	1	21	29	102	105
Phosphate	4.0	84	101	96	83	105	93	81	109
	5.0	78	91	47	82	93	68	79	94
	6.0	89	98	96	78	89	94	78	120
	7.0	85	93	93	81	89	92	72	95
	8.0	85	90	86	84	88	86	72	88
	9.0	41	71	69	43	74	74	88	67
Tartrate	4.0	29	88	52	37	49	35	69	32
	5.0	28	93	79	55	74	57	65	57
	6.0	12	90	58	1.2	91	40	82	63
	7.0	32	88	72	0.0	69	63	59	81
	8.0	32	76	67	0.0	60	72	53	59
	9.0	14	74	62	9.8	71	64	54	50

cadmium (II), and zinc (II) in pH 8.0-9.0 - citrate; and aluminum (III) from other ions, and chromium (III) from other ions in many media.

CONCLUSIONS

Three chelating ion-exchange resins containing arsonic acid, n-hexylthioglycolate, and propylene-diamine-N,N,N',N'-tetraacetic acid functional groups were used to concentrate and separate trace metal ions. Studies were performed on choosing the proper matrix, developing synthetic techniques for polymers, comparing the selectivity of the polymer to the corresponding monomer, and developing the best techniques for the concentration and separation steps.

The macroreticular polystyrene-DVB matrices, designated XAD-1, -2, and -4, are excellent for use under pressure in closed column systems. They do not shrink and swell in various ionic forms, and have superior chemical and mechanical stability. XAD-4 is preferred to XAD-1 or -2 as it gives a product of relatively high yield, of definite structure, and with fast kinetics. In practice, the smaller bead size gives higher product yield but also requires higher pressures in column use. Therefore, as a compromise, the 250-325 mesh fraction is recommended.

For synthesis procedures, reaction times in excess of 12 hours under reflux conditions should be used to effect good synthetic yield. Excess reagent and absence of external solvent should be the rule whenever possible, especially in equilibrium-controlled reactions. If an external solvent must be used, it should be kept at a minimum. All reaction conditions should be as rigorous as possible short of resin or reagent degradation.

Several studies have shown that there is a definite quantitative relationship between the stability constants of metal ions with the monomeric ligands and their analogues in polymeric form (33,62,64). Thus, information as to the selectivity of the monomeric chelating group is useful in designing a resin selective for particular metal ions or in determining for which metals a particular resin will be selective.

This principle is well demonstrated by the three resins examined here. Phenyl arsonic acid is known to be highly selective for thorium (IV) and uranium (VI) (120). The resin maintains this selectivity as demonstrated in the percentage recovery versus pH study. The solvent extraction data on IOTG (109) was used as a preliminary outline for separations on the HTG-4 resin. Finally, the selectivity order of the BPDTA-4 resin is in good agreement with the HPDTA ligand (118).

For the best separation, the dimensions of the column and the amount of the resin required should be as small as possible. For separations of microquantities of metals as performed here low capacity and/or short columns give sharp peaks with little or no tailing. As capacity is increased, metal attraction becomes more generalized and peak overlap and tailing become more pronounced.

Separations are best attained for metals complexed below pH 2-3 where the selectivity of the resin is the greatest. This avoids interference from most other metal ions, external complexing agents and resin impurities. For metals complexed above pH 3.0, the ΔpK_{ML} value should be at least 3 before a separation is attempted. Less than this value usually gives a superficial, nonreproducible separation in which very rigid conditions must be maintained.

Chelating ion-exchange resins are valuable for concentrating trace heavy metals. For this work, the column method is recommended for its speed, its ability to quantitatively concentrate at very low levels of metal ions, and its ability to attain high concentration factors.

The AA-4 resin can be used to concentrate at least 10 metal ions from aqueous media alone and in the presence of various complexing agents. These ions can be freed of 95% of the calcium and magnesium complexed by the resin. However, this is the only advantage AA-4 has over the commercially available XE-318.

The BPDTA-4 resin forms strong complexes with many ions. The resin is able to quantitatively concentrate 16 metals from aqueous media alone and in the presence of various complexing agents. While it does not recover all ions tested quantitatively from fresh water or sea water, it does appear to be an improvement over Chelex 100 (16). Based on the separation of magnesium and zinc on the resin, it should be possible to wash the resin free of calcium and magnesium with a pH 8.0 salt solution prior to the elution of the heavy metals.

FUTURE WORK

More chemically-bonded macroporous resins patterned after well-characterized, selective complexing agents should be synthesized. Ligands containing sulfur and/or phosphorous are especially desirable for their selectivity. Goodkin (77) suggested several possibilities based on the selective behavior of the monomers. Additional possibilities include O-isopropyl-N-ethyl thiocarbamate (93) and thionaphthenic acids (95) which are used in extraction procedures by Zolotov and coworkers. The former is selective for mercury, silver, copper, thallium, gold, and selenium. The latter is selective for the platinum metals, arsenic, antimony, bismuth, silver, mercury, gold, copper, cobalt, and nickel.

It is also suggested that a chelating resin containing 1,3 propylenediamine, made in a similar fashion to the HTG and BPDTA resins, be tried in ligand exchange chromatography. This resin forms a six member ring with metal ions such as copper (II) holding them tightly to the resin but still leaves multiple coordinating sites vacant on the ion for binding external ligands.

Further studies should also be made of the effect of various anions and external ligands on the separations of metal ions. Dingman, Schmuckler, and coworkers (20,54) saw that the equilibrium between the metal ion and resin ligand could be controlled by use of external ligands. By judicious choice of eluent constituents and resin ligand, it should be possible to separate and determine all but the most closely related ions easily.

The study of chelating resins for concentrating trace heavy metals should continue. To attain quantitative recovery of virtually all cations, a combination of resins containing sulfur, oxygen, and nitrogen binders should be used that have selectivity for different ions. To reduce analysis times and attain greater sensitivities, the column should be directly attached to the detector rather than using a collection and determination procedure. Attention should also be given to the suggested methods for oxidation of the organic matter found in estuary and sea water samples that interfere in analyses (16,119).

The actual resin capacity needed for quantitative recovery should be determined. Often the resin capacity is greater than a thousand times that of the total ion content to be collected. Something on the order of ten- to a hundred-fold excess may be more desirable. The resin should still be capable of picking up the heavy metals selectively and the amount of alkali and alkaline earth metals also collected would be greatly reduced.

In the course of this research, it was discovered that gold could be spectrophotometrically determined as the thiourea complex. Unfortunately, the formation of this complex was found to be kinetically slow; and therefore, could not be used conveniently in automated procedures.

In theory, however, there should be many more metal complexes which can be determined in this manner. This could be of particular benefit for hard-to-determine metal ions such as aluminum (III). If a complexer such as thiourea, EDTA, or any of a long list of possible UV absorbing species forms a metal complex, then the absorbance spectrum should be shifted to higher wavelength by a quantity directly related to the strength of the complex. By blanking out any absorbance due to the ligand at this wavelength, it should be possible to determine the metal concentration by use of a Beer's law plot. Thus, the procedure is the same as that used for a variety of dyes in the determination of metal ions in the visible region.

BPDTA-4 forms a strong complex with uranium (VI). This suggests that the monomer, HPDTA, might be used to determine uranium titrimetrically. Based on experimental data attained with the BPDTA-4 resin, Arsenazo I in a pH range of 2-4 is suggested as a first attempt.

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