REFERENCES

1. P. Zikolov, A. Astrug and O. Budevsky, Talanta, 1975, 22, 511.
2. P. Zikolov and O. Budevsky, ibid., 1973, 20, 487.
3. T. A. Khudyakova and A. P. Kreshkov, J. Electroanal. Chem., 1971, 29, 181.
4. J.-P. Escarfail, Untersuchungen an Säure-Basen-Gleichgewichten in organischen Lösungsmitteln, Promotionsarbeit, ETH, Zürich, 1963.
5. F. Seel, Grundlagen der analytischen Chemie, IV Aufl., Chemie, Weinheim, 1968.
6. O. Budevsky, Fundamentals of Analytical Chemistry, (in Bulgarian), Medicina i Fizkultura, Sofia, 1974.
7. S. R. Palit, M. N. Das and G. R. Somayajulu, Non-aqueous Titration, (in Russian), Goskhimizdat, Moscow, 1958.
8. F. J. Rossotti and H. Rossotti, J. Chem. Educ., 1965, 42, 375.
9. L. G. Sillén, Graphic Presentation of Equilibrium Data, in Treatise on Analytical Chemistry, eds. I. M. Kolthoff and P. Elving, Part I, Vol. I. Interscience, New York, 1959.
10. G. Hägg, Die theoretischen Grundlagen der analytischen Chemie, Birkhäuser, Basel, 1950.
11. J. N. Butler, Ionic Equilibrium; (in Russian), Khimia, Leningrad, 1973.
12. N. A. Izmailov, Selected Works, (in Russian), ed. Naukova Dumka, Kiev, 1967.
13. K. K. Kundu and M. N. Das, J. Chem. Eng. Data, 1964, 9, 82.

Summary—Theoretical titration curves are used for the selection of appropriate conditions for the acid–base volumetric determination of weak bases in ethylene glycol medium. The theoretical curves for titration of some alkaloids are deduced graphically on the basis of the logarithmic concentration diagram. The acid–base constants used for the construction of the theoretical titration curves were determined by potentiometric titration in a cell without liquid junction, equipped with a glass and a silver–silver chloride electrode. It is shown that the alkaloids investigated can be determined accurately by visual or potentiometric titration. The same approach for the selection of titration conditions seems to be applicable to other non-aqueous amphiprotic solvents.

CONCENTRATION AND SEPARATION OF TRACE METALS WITH AN ARSONIC ACID RESIN*

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Because of their selectivity for heavy metals, chelating resins have been used for the concentration and separation of trace metals in food extracts,[1,2] oil-field brine,[3] industrial waste waters,[4] geological samples,[5] and sea-water.[6-8] Most of this work was performed on Dowex A-1 (Chelex 100), which has an iminodiacetic acid functional group. Dowex A-1 is a gel-type resin which undergoes pronounced swelling and shrinking. This resin has rather slow kinetics and a comparatively high affinity for calcium and magnesium.[6,9]

To meet the growing needs of ecological research in pollution control[10] and elsewhere, new chelating resins are continually being developed. Among those showing promise for trace metals are dithiocarbamate,[11,12] natural polymer,[13] 8-aminoquinoline,[14] polyamine–polyurea[15] and isothiouronium[5] exchangers. Hirsch et al.[16] started with a macroporous polystyrene–DVB resin and prepared a resin containing the iminodiacetic acid functional group and another containing an arsonic acid group. Macroporous resins are much less susceptible to swelling and shrinking and appear to have faster reaction kinetics than gel-type chelating resins.

A series of macroporous arsonic acid resins has now been prepared by a synthetic method similar to that used by Hirsch et al.[16] The effect of varying pore diameter and surface area on the properties of the final resins has been studied. These arsonic acid resins are now proposed for the concentration of trace metal ions from hard water and sea-water.

EXPERIMENTAL

Apparatus

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

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

Plasma emission analyses were performed on the ICP-OES system built at Ames Laboratories.

Reagents

XAD-1, -2, and -4 macroporous resins were obtained from Rohm and Haas. The 150–200 mesh resin was prewashed with acetone and concentrated hydrochloric acid.

For all trace analyses 0.5 g of resin IV was packed in a column measuring 2.8 × 0.6 cm.

^{54}Mn, ^{65}Zn, and ^{59}Fe gamma-emitters with 99% radiometric purity were obtained from New England Nuclear

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Co. Synthetic sea-water was made according to Lyman and Fleming.[17]

All chemicals were of the highest available purity.

Synthesis

The synthesis used was adapted from methods used by Hirsch.[16] The resin was nitrated with a 60/40 v/v mixture of sulphuric and nitric acids at 65–70° after addition at 0 . It was reduced to the amine with mossy tin in conc. hydrochloric acid at 70–75°. The reduction product was slurried with 1M sodium hydroxide to remove tin salts, chilled to 0° in conc. hydrochloric acid, and diazotized by slow addition of 1M sodium nitrite. The resin was washed with sodium carbonate solution and coupled with sodium arsenite in aqueous soln at 70–75°. All reactions other than diazotization were allowed to proceed for half a day.

Infrared spectra of the phenylarsonic acid resins I, II and IV and the monomeric acid were taken on a Beckman IR7.

The 2.9 μm arsonic acid O–H stretch was visible for each of the three resins and matching bands in the region of 11.0–13.0 μm were found in the resins and the monomer that can be ascribed to the arsonic acid group.

Recovery

The recovery of trace metal ions was determined as a function of the effluent pH. One litre of distilled demineralized water containing 0.5 ppm of the metal ion was buffered to the appropriate pH and passed through the resin at a flow-rate of 7 ml/min. After collection and washing, the adsorbed metals were stripped from the column with 25 ml of 4.0M perchloric acid and determined by plasma emission, atomic absorption or colorimetrically with Arsenazo I.

Complexing agents

To 250 ml of distilled demineralized water containing 10 ppM (parts per milliard) of metal ion (including radiotracer) and 10 ppm of complexant, 5 or 6 drops of orthophosphoric acid were added. The phosphoric acid was added as a buffer and was necessary for 100% recovery of iron(III). The pH was adjusted to 5.0 and the solution was passed through the column at 7 ml/min. The metals were then stripped from the column with 25 ml of 4M perchloric and the activity of an aliquot of the effluent was measured.

Recovery of trace metals

One litre of distilled demineralized water, tap-water, or synthetic sea-water at pH 5 and containing 0.5 ppm of heavy metals was passed through the resin at 7 ml/min, followed by 100 ml of metal-free pH-5.0 solution, and the metals were eluted with 25 ml of 4M perchloric acid and determined by plasma emission or atomic absorption.

For trace metals at sub-ppM level, the procedure was similar, but with 5 ml of 2 μCi/ml tracer solution replacing the 0.5 ppm of heavy metals. Detection was by gamma emission.

In the analysis of the tap-water, no metal ions were added.

Separation of uranium(VI) from other heavy metals

A 1-litre sample containing 0.5 ppm of uranium(VI) and other heavy metals and 0.01M in EDTA was buffered to pH 5.0 with orthophosphoric acid and ammonia and passed through the resin column at 7 ml/min. The column was then washed with 100 ml of 0.01M EDTA at pH 5.0 and 100 ml of pH-5 wash-solution (both solutions buffered with phosphoric acid and ammonia). The column was then stripped with 25 ml of 4M perchloric acid. The uranium was determined colorimetrically and the other heavy metals were determined by plasma emission.

Separation of thorium(IV) from other heavy metals

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

Batch abstraction of trace metals

Resin IV, 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, or 24 hr before collection of the resin. The adsorbed metals were washed from the resin with 25 ml of 4M perchloric acid.

RESULTS AND DISCUSSION

Arsonic acid resins were prepared from XAD-1, -2, and -4, which are macroporous polystyrene–DVB resins of varying pore size and surface area. The arsonic acid resins are designated I, II and IV, corresponding to the numbers of the XAD-resin starting material. The physical properties of the three resins are summarized in Table 1. Each of the three resins contains a nitrogen-containing group as an impurity although less than reported by Hirsch.[16] The resin IV synthesis was repeated and the yield in each step was estimated by analysis for the appropriate functional group. Nitration gave approximately 1.2 nitro groups per benzene ring. Reduction to the amine gave approximately 0.8 amine group per benzene ring, 67% yield. Conversion into the arsonic acid then gave approximately 0.6 arsonic acid group per benzene ring for an overall yield of about 50%.

The ratios of arsonic acid group per benzene ring and acidic hydrogen atoms per benzene ring were calculated from the arsenic and hydrogen analyses, the average molecular weight per resin unit being based on the calculated arsonic acid content and the remainder assumed to be 50% styrene and 50% DVB. The acidic hydrogen content is more than the 2:1 ratio of H:As expected for an arsonic acid group and probably represents titratable protonated amine. Although the exact values may be somewhat in question the trend seems clear; conversion into the arsonic acid is highest in resin I and lowest in resin II. The large pores in XAD-1 appear to lead to high reactivity. In XAD-4 the very high surface area is able to compensate for the smaller pores and good conversion into the arsonic acid was obtained.

Table 1. Properties of the XAD-arsonic acid resins

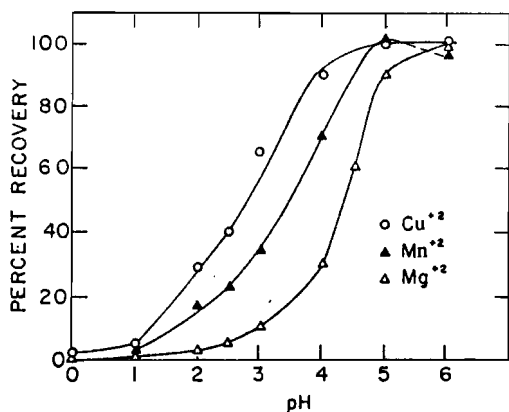|	Surface area, m^2/g	Pore diam., Å	As/benzene ring	H/benzene ring	C, %	H, %	N, %	Kinetics
AsO₃H₂-XAD I	100	205	2.4	5.2	52.8	5.2₅	3.3	Slow
AsO₃H₂-XAD II	300	90	0.3	0.8	58.1	5.4	5.0	Rapid
AsO₃H₂-XAD IV	784	50	0.75	1.8	51.3	5.2	3.2	Rapid

Fig. 1. Effect of pH on recovery of Cu(II), Mn(II) and Mg(II).

Column experiments with various metal cations indicated that the kinetics of resins II and IV are excellent and those of resin I somewhat slow. Because of this and the higher capacity of resin IV (compared to resin II), resin IV was chosen for all subsequent experiments. This resin has little swelling tendency and is stable even in the concentrated acid and base solutions used to wash the resin and to strip some metal ions from the resin.

Small columns packed with resin IV were equilibrated with buffered aqueous solutions. Then solutions of various metal ions buffered to the same pH were passed through the column and the amount of metal ion retained by the column was determined. The degree of retention as a function of pH is plotted for various metal ions in Fig. 1–3. The selectivity order for metal ions, based on the assumption that the more stable complexes are retained at lower pH, is as follows: $Th^{4+} > UO_2^{2+} > RE^{3+} > Cu^{2+} > Pb^{2+} > Al^{3+}, Fe^{3+} > Zn^{2+} > Ni^{2+}, Co^{2+} > Cd^{2+}, Mn^{2+} > Mg^{2+}$ (RE = rare earths). This is in agreement with the order reported by Hirsch[16] of $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$.

Separation of thorium(IV) from all other metal ions studied was possible because of the affinity of resin IV for thorium at low pH values. Recovery of thorium at
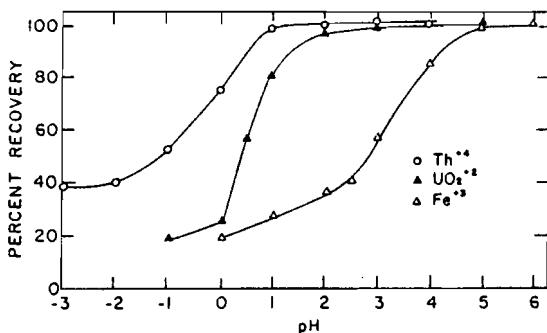

Fig. 2. Effect of pH on recovery of Th(IV), U(VI) and Fe(III).
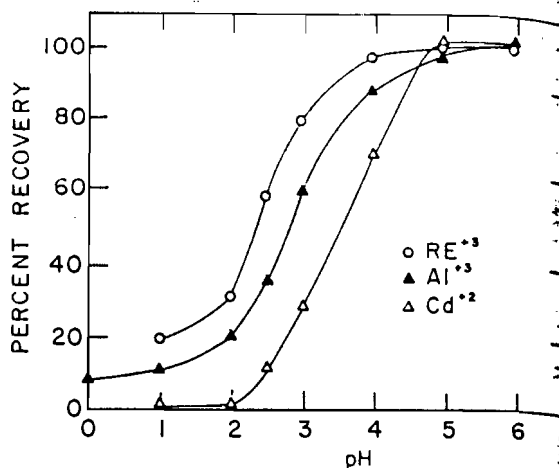

Fig. 3. Effect of pH on recovery of RE(III), Al(III) and Cd(II). (RE = rare earths).

pH 1.0 was 102.5% (from spectrophotometric determination), with less than 1% of any of the other metal ions being retained. A successful separation of uranium(VI) from other metal ions was accomplished by adding EDTA to complex the foreign metal ions. Spectrophotometric analysis showed 98.3% recovery of uranium(VI) at pH 5.0 in 0.01M EDTA medium. Chromium(III) was the only interference (11% recovery).

Eight trace metals were added to demineralized water, tap-water and synthetic sea-water, the pH was adjusted to 5.0 and 1-litre samples were passed though a resin IV column. The sorbed metal ions were then eluted with 25 ml of 4M perchloric acid and the metal ions determined by plasma emission or atomic-absorption spectroscopy. The results, shown in Table 2, indicate excellent recovery except for chromium(III), which has a very slow reaction rate with ligands. With use of radiotracers, the experiment was repeated for three metal ions at the ppb (parts in 10^{12}) level. As shown in Table 3, the recovery is still quantitative within experimental error, even in the presence of a large

Table 2. Recovery of trace metals in aqueous media with resin IV

Metal ion	Recovery,* % Pure water	Recovery,† % Tap-water	Recovery,† % 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

* Plasma emission.
† Atomic absorption.

Table 3. Recovery of metals at ultra trace level in aqueous media with resin IV

Metal	Conc., ppb*	Recovery, % Pure water	Recovery, % Tap-water	Recovery, % 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

* Parts per billion (10^{12}).

Table 4. Recovery of trace metals in ISU tap-water with resin IV, ppM^*

	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

* Parts per milliard (10^9).

excess of sodium, magnesium and calcium salts. Triplicate analyses of tap-water were also carried out (Table 4).

The effect of complexing agents on the recovery of zinc(II), manganese(II) and iron(III) at 10 ppm concentrations was studied by adding a thousandfold w/w ratio of various complexing reagents. The added reagents included acetate, anthranilate, chloride, citrate, glycine, phosphate, salicylate, succinate, urea and EDTA. The recovery of manganese and zinc was unaffected by any of the complexants except EDTA. The recovery of iron was low in the presence of substances that form complexes having a stability constant greater than 10^8.

Comparative studies showed resin IV to be more effective for retention of trace metal ions when used in a column than for batch collection. For example, by the batch method recoveries were only about 90% for copper(II) and lead, 70% for iron(III), 40% for nickel, and 15% for cadmium.

Some calcium and magnesium is retained by the arsonic acid resin column at pH 5.0. If desired, about 95% of the calcium and magnesium retained by the column can be removed by elution with pH 4.0 buffer before the trace metal ions are stripped with 4–12M perchloric acid.

REFERENCES

1. R. A. Baetz and C. T. Kenner, J. Agr. Food Chem. 1973, 21, 436.
2. Idem. ibid., 1975, 23, 41.
3. O. K. Galle. Appl. Spectry., 1971, 25, 664.
4. D. G. Biechler, Anal. Chem. 1965, 37, 1054.
5. C. W. Blount, T. L. Tomas and S. M. Gwill, ibid., 1975, 45, 1045.
6. J. P. Riley and D. Taylor, Anal. Chim. Acta, 1968, 40, 479.
7. T. M. Florence and G. E. Batley, Talanta, 1975, 22, 201.
8. B. Holynska, Radio Chem. Radioanal. Letters 1974, 17, 313.
9. D. E. Leyden and A. C. Underwood, J. Phys. Chem., 1964, 68, 2093.
10. K. Himsley and F. X. McGarvey, Ion Exchange and Membranes, 1973, 1, 143.
11. D. E. Leyden and G. H. Luttrell, Anal. Chem., 1975, 47, 1612.
12. J. F. Dingman, K. M. Gloss, E. A. Milano and S. Siggia, idem., 1974, 46, 774.
13. R. Muzzarelli and O. Tubertini, Talanta, 1969, 16, 1571.
14. S. B. Savvin, I. I. Antokolskaja, G. V. Myasoedava, L. I. Bolshakova and O. P. Shvoeva, J. Chromatog., 1974, 102, 287.
15. J. F. Dingman, Jr., S. Siggia, C. Barton and K. B. Hiscock, Anal. Chem., 1972, 44, 1351.
16. R. F. Hirsch, E. Gancher and F. R. Russo, Talanta, 1970, 17, 483.
17. J. Lymna and W. H. Fleming, J. Marine Research, 1940, 3, 134.

Summary—Macroporous arsonic acid resins with different pore sizes and surface areas were prepared and the properties compared. One of the resins was used for concentration of trace metal ions from dimineralized water, tap-water, and sea-water. The effect of pH and complexing agents on the recovery of metal ions was studied. A method for separation of uranium(VI) and thorium(IV) from each other and from other metal ions was developed.

ORGANIC ACID SOLUTIONS IN THE CHROMATOGRAPHY OF INORGANIC IONS—IV

CATION-EXCHANGE OF Mn(II), Cd(II), Co(II), Ni(II), Cu(II), Al(III) AND Fe(III) IN TARTRATE MEDIA*

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The ion-exchange behaviour of inorganic ions in citric[1] and formic[2] acid media has been reported. Anion-exchange in tartaric acid media has been studied by Pitstick et al.[3] and Morie et al.[4,5] who describe the separation of some transition metals. Cation-exchange studies[6-9] have resulted in the resolution of a limited number of metal ions. Qureshi et al.[10] have separated Fe(III) and other metal ions in formic, oxalic, tartaric and citric acid media, but the only comprehensive investigation was made by Rouchaud et al.[11] They examined both cation- and anion-exchange and determined distribution coefficients for several ions in tartaric acid media containing nitric acid.