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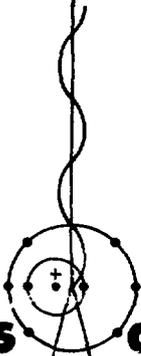
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Issued: February 1978

MASTER

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DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

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ANION EXCHANGE OF 58 ELEMENTS IN HYDROBROMIC ACID AND IN HYDRIODIC ACID

by

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ABSTRACT

Anion exchange distributions of 58 elements have been measured from 0.1-8.7M HBr and from 0.1-7.4M HI onto three strong-base resins, 8 and 4% cross-linked and macroporous. Data were obtained by 16- to 18-h dynamic batch contacts. Anion exchange in these media is compared to that in HCl. The effect of resin cross-linkage is considerably greater in HI media than in HBr and HCl media. Examples are presented of potentially useful separations using HBr and HI media alone and in combination with HCl.

INTRODUCTION

Anion exchange has become an increasingly useful chemical separation technique since Kraus¹ demonstrated its value using aqueous HCl. The combined strong anion-complexing and reductive properties of HBr and HI can be expected to produce unique distributions and separations.

Distribution data are available for many aqueous media, including HNO₃,² HF,³ acetic acid,⁴ and H₂PO₄.⁵ Also available are data for many organic solvents, exemplified by organic acids⁶ and mixed aqueous and organic solvents.⁷ Conspicuously absent are comprehensive anion exchange data from aqueous HBr and HI media. No multielement study of HI media has been published. The only study⁸ covering a broad range of aqueous HBr concentrations gives data for 15 ions but does not state the concentrations of the ions in contact with the resin. Although these data generally agree with ours, no basis for valid comparison is considered to exist. Another study⁹

provides data for 19 elements over the limited aqueous HBr range of 0.15-0.9M. The data for all ions except In³⁺ agree with ours.

In this measurement of distribution from aqueous HBr and HI media, we have included the effect of resin cross-linkage by using strong-base resins of 4 and 8% cross-linkages, as well as macroporous resin (MP1). The latter resin, with its open pore structure, is an excellent substitute for conventional microporous resin in anion exchange separations that involve aqueous HCl media or a mixed methanol and HNO₃ solvent.¹⁰ In addition to providing fast equilibrium, its use lessens the differing elution properties typical of different batches of microporous resin.

Distribution data for 58 elements in 0.1-8.7M HBr and 0.1-7.4M HI are given for each resin. Our major intent is to provide relative distribution data that will lead to practically useful separations. We hope that other investigators' considerations of the differing distributions onto the three resin types will lead

to better understanding of ion exchange mechanisms.

REAGENTS

Resin. Dowex resins, 50- to 100-mesh, from Bio-Rad Laboratories were used. Batch designations, provided because of possible batch-to-batch differences, are 12908 (AG 1 x 4), 12618 (AG 1 x 8), and 9881 (AG MP1).

Hydrobromic Acid. AR grade, 47-49% (8.7M) acid was used. It was diluted with distilled water to 0.1, 1, 3, and 6M concentrations.

Hydriodic Acid. AR-grade, 57% (7.4M) acid, without holding reductant, was used. (The usual H_2PO_4 preservative and its oxidation products could affect distribution). The acid was diluted with distilled water to 0.1, 1, 3, and 5.7M concentrations.

Elements and Radioactive Tracers. The distribution data for most elements were obtained using 0.01M element solutions plus radioactive tracer (see the Experimental section). Metals of >99% purity were dissolved directly in HBr or HI where feasible. Selected compounds, also >99% pure, were converted to bromide or iodide salts without introduction of other potentially interfering anions.

Most radioactive tracers were prepared by thermal neutron activation in the Los Alamos Scientific Laboratory (LASL) Omega West Reactor. Exceptions were ^{90}Zr , ^{99}Tc , ^{66}Ge , and 7Be obtained commercially, and ^{210}Po and ^{226}Ra obtained from other LASL projects.

EXPERIMENTAL

Resin Conversion to Bromide and Iodide Forms and Measurement of Halide Contents

Hydriodic acid is available with or without a holding reductant of H_2PCl_2 . We selected HI without H_2PCl_2 to avoid competitive complexes involving oxyphosphorous anions. Without a holding reductant, air oxidation slowly produces elemental iodine which is sorbed on resin. Elemental iodine also forms during equilibration with ions that oxidize iodide.

The three resins were obtained in the chloride form. To convert the resins to the bromide and iodide forms, several hundred grams of each was washed free of fines and water-soluble components and transferred to a 3.7-cm-diam by 50-cm-long glass column. Then an amount of HBr or HI equal to at least six times the theoretical capacity of the resin (based on the meq/g value stated by the supplier) was passed through. Each column was rinsed with water until the effluent pH increased to 3. Additional 1-liter volumes of water were passed through until the pH remained constant. The resin was air-dried in a Buchner funnel and heated at 70°C to constant weight. Nearly 100 h of heating was required.

The dried resin weights could not be correlated with the as-received resin weights, because of their high and undetermined 42-52% water contents. Therefore the distribution data are based on dried weights.

The residual chloride content relative to bromide or iodide was determined by thermal neutron activation analysis of each converted, dried resin. The measured <0.015 Cl/Br and Cl/I mole ratios are considered too low to affect the measured distribution data significantly.

The total bromide and iodide contents were determined by eluting 1 g of resin with 4M HClO₄ and potentiometrically titrating the effluent with AgNO₃. Elution (and titration) was repeated to completeness. The measured iodide content per gram of converted resin includes an uncertainty caused by sorption of elemental iodine. The measured contents were 3.5 ± 0.2 meq of bromide and 3.0 ± 0.3 meq of iodide per gram of each resin.

Selection of 0.01M as Element Concentration Level

The exchange behavior of an ion at very low concentration often differs significantly from that at moderate concentration. Rieman and Walton¹¹ explain that exchange between a resin and $\leq 0.001N$ solution generally is controlled by film diffusion, whereas at $\sim 0.01N$ concentrations both film and bead diffusion prevail. Kim¹² reports substantially

different behavior of some ions with ion exchange resins copolymerized from styrene and m-divinylbenzene and from styrene and p-divinylbenzene. Because the resins used are mixtures of m- and p-divinylbenzene, it seems reasonable that ions at very low concentration would interact preferentially with the most accessible exchange sites, or those capable of enhanced bond stability. For this reason and perhaps others, distributions of ions at very low concentrations do not represent distributions at higher concentrations. Also, distributions at high ion concentrations can differ as saturation of exchange sites is approached. The element solutions in this study were 0.01M, except for lower, tracer-only, levels of ^{95}Nb , ^{210}Po , ^{226}Ra , ^{233}Pa , and ^{241}Am . Solubilities of some elements were exceeded at the 0.01M level, especially at the higher acid levels. These exceptions are noted in the Discussion section.

Distribution Measurement Experiments

Distributions were measured after 16- to 18-h batch contacts of 0.25 g of resin and 2.5 ml of the element solution. The 16- to 18-h contact period substantially gave equilibrium. It was held constant to permit comparison of sorptions, which can be affected by rate-dependent reactions, by the three resins. Total uptake by the resin of the element in a 0.01M solution was 3-10% of the resin capacity.

The resin and solution (plus tracer) were placed in 20-ml glass vials and shaken mechanically. After the resin had settled, the solution was analyzed for the element relative to an identical solution that had not contacted resin. For experiments with gamma-emitting radiotracers, 1 ml of solution was transferred to a glass vial that was counted using a NaI(Tl) detector. Beta and alpha radiotracers were measured by counting measured aliquots evaporated on glass or dissolved in solution appropriate for liquid scintillation counting. Multichannel gamma spectrometry was used to resolve gamma-emitting parent and daughter pairs.

No suitable radiotracers were available for 6 of the 58 elements. Of these, vanadium and rhodium were determined by atomic absorption spectrophotometry and aluminum, magnesium,

calcium, and nickel were determined by chelometric titrimetry.

Data Presentation

Distribution data generally are expressed in terms of the distribution ratio, D, the ion concentration on the resin relative to that in solution at equilibrium, for equal weights of resin and solution. Computation of D from batch experimental data is inexact because the resin phase, even after filtration, contains a significant amount of the aqueous phase. For liquid-liquid extraction equilibrium, Morrison and Freiser¹⁸ recommend that distribution data be expressed in terms of "percent extraction" for practicality. In their words, "When the extraction efficiency approaches 100%, the distribution ratio approaches infinity as a limit. Thus, for differences in extraction in the range of 99 to 100%, the distribution ratio will vary from 99 to infinity. Initial observation of such widely differing distribution ratios might erroneously suggest a serious discrepancy when in reality the extraction would be nearly complete in both instances."

The distribution data are in percentages of ion sorbed on resin. Measurements of the solutions after batch contact are not highly accurate when the ion concentration is either very high or very low. Therefore, reporting batch-contact data in units of distribution coefficient, Kd, can be misleading.

After the 16- to 18-h batch contact of 0.25 g of resin and 2.5 ml of solution, 1 ml of solution, free of resin particles (termed S_{post}), was measured for element content by radiometric assay or by chemical analysis relative to 1 ml of the identical solution that had not contacted resin (termed S_{pre}). The percentage of element sorbed was computed using

$$\text{per cent on resin} = \% S = 100 \frac{S_{pre} - S_{post}}{S_{pre}}$$

The 0.25 g of resin and 2.5 ml of solution provided convenient quantities for measurement. The tenfold ratio of solution to resin gives a lower sorption percentage than would have been measured using equal quantities of resin and solution. Because we wanted

to show relative ion exchange, we reported the sorption percentages computed using the above relationship, rather than adjusting to an equal-volume basis as was done by Kraus and Nelson.¹ The % S data can be converted to Kd values by using

$$Kd = \frac{(\% S)(R)}{100 - (\% S)}$$

where R = 10, the liquid-to-resin ratio of our measurements.

The distributions from HBr solutions are presented in Figs. 1-3; those from HI solutions, in Figs. 4-6.

DISCUSSION

The distribution data are considered in periodic groupings, first with 1 x 8 resin as a function of the type of halide acid, then as a function of resin cross-linkage. We also discuss how a nonisotopic carrier affects sorption of tracer-level elements, on the basis of data from radium with and without barium carrier.

Elements in their usual and stable oxidation states were added to HBr and HI. The resulting oxidation states are predicted, for discussion, from standard oxidation potentials.¹⁴

Distribution as a Function of Acid Type

Distributions of elements from HBr and HI are compared with Kraus and Nelson's¹ HCl distribution data, reproduced as Fig. 7. (We have added a % S equivalent scale for R = 10 to the right of the key in Fig. 7 to facilitate comparison with Figs. 1-6).

Alkalies. The alkalies are not sorbed from HBr, HI, or HCl.

Alkaline Earths. Unexpectedly, barium is sorbed onto the resins from strong HBr. Tracer levels of radium are not sorbed from any acid. However, when 0.01M barium is present as a nonisotopic carrier (shown by broken lines), radium is sorbed from HBr like barium. This topic is discussed later.

Scandium, Yttrium, and Lanthanides. These trivalent ions are not sorbed from HBr, HI, or HCl. Tetravalent cerium is reduced by HBr and HI.

Titanium, Zirconium, and Hafnium. The sorption order is Hf > Zr > Ti, sorption being strongest from HCl and weakest from HI.

Vanadium, Niobium, and Tantalum. Vanadium, reduced to V³⁺ by HBr and HI in the presence of resin, is not sorbed from these media. Sorption of V⁵⁺ from HCl starts at about 8M and increases to nearly 100% at 12M.

Niobium, tested only at tracer levels, is sorbed considerably more from HBr than from HI, with nearly 100% sorption from 8.7M HBr, as from 9M HCl.

Tantalum, highly insoluble in both media, was not evaluated.

Chromium, Molybdenum, and Tungsten. Slight sorption of Cr³⁺ occurs from HI and HCl, and moderate sorption occurs from 0.1M HBr. Chromium(VI), strongly sorbed from HCl, is reduced to Cr³⁺ by HBr and HI.

Molybdenum, added as Mo⁶⁺, is sorbed completely from strong HBr, as from HCl. Reduction of Mo⁶⁺, evidenced by development of a blue color, probably explains the low sorption from HI.

Tungsten, highly insoluble in acid media, was not tested.

Technetium, Manganese, and Rhenium. Technetium, tested at the 0.01M level initially as Tc⁷⁺, is sorbed strongly from HBr, as from HCl. Reduction to nonsorbing oxidation states occurs in HI.

Sorption of manganese, greater from HBr than from HCl, increases with increasing acidity. Sorption of rhenium, on the other hand, decreases with increasing acidity. This trend and the rhenium sorption order of HCl > HBr > HI may be due to its reduction by the latter two media.

Iron, Cobalt, and Nickel. Sorption of iron from HBr, as from HCl, approaches 100% with increasing acidity. Sorption of cobalt from HBr and HI approaches 100% at high acidity, compared to about 70% from HCl. Sorption of iron, reduced to Fe²⁺ by

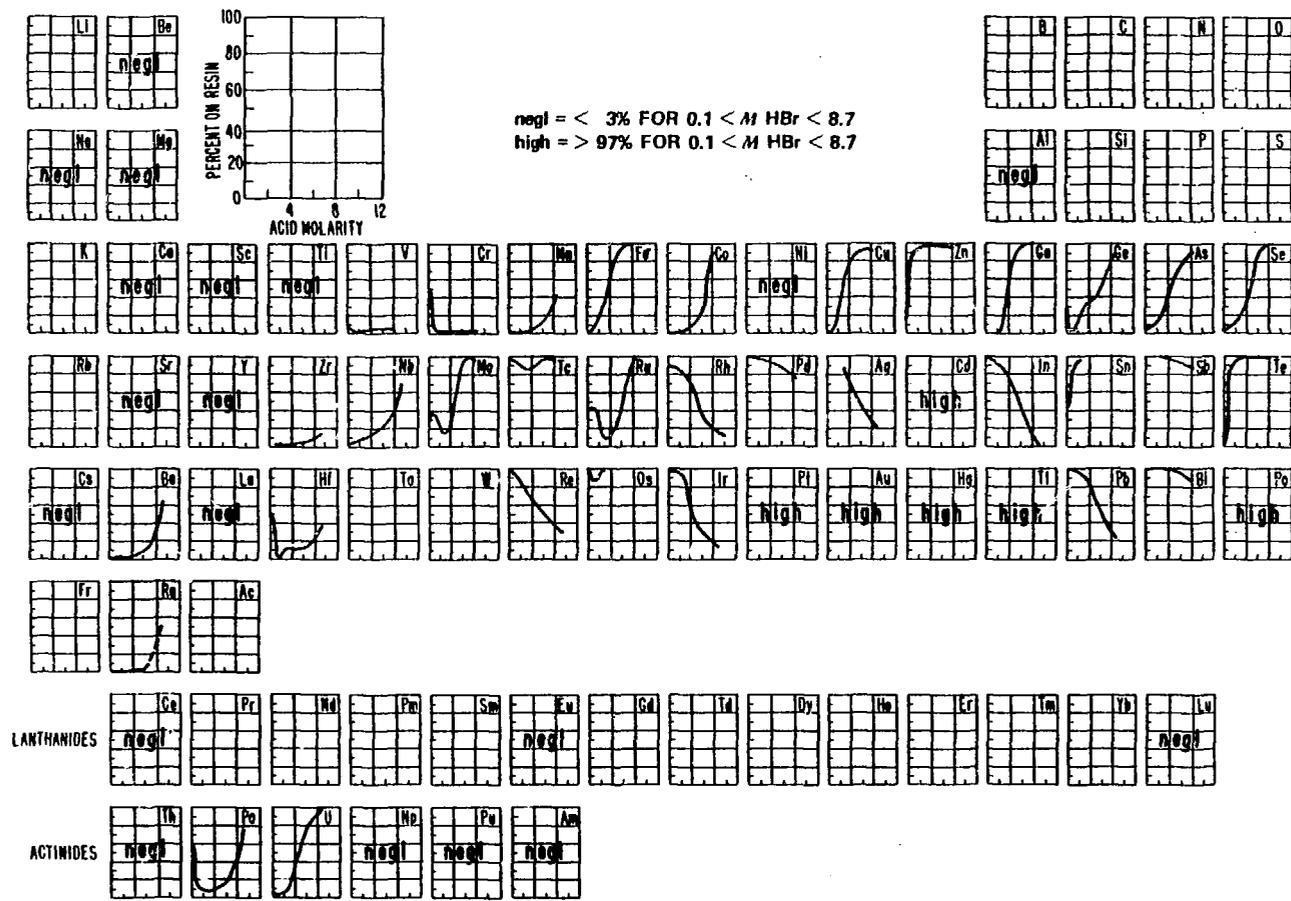


Fig. 1.

Sorption of elements by 1 x 8 anion exchange resin from hydrobromic acid (acid volume/resin weight = 10).

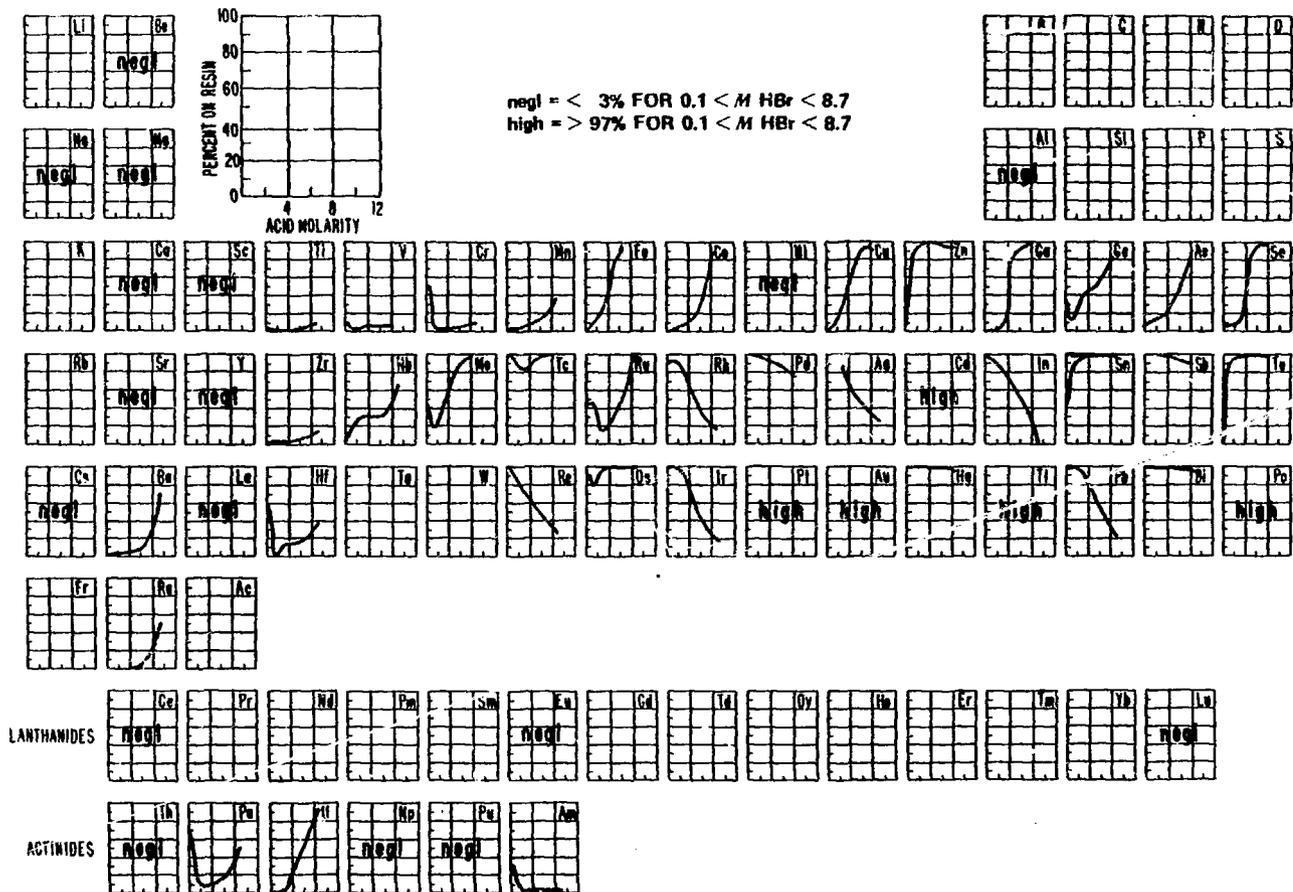


Fig. 2.

Sorption of elements by 1 x 4 anion exchange resin from hydrobromic acid (acid volume/resin weight = 10).

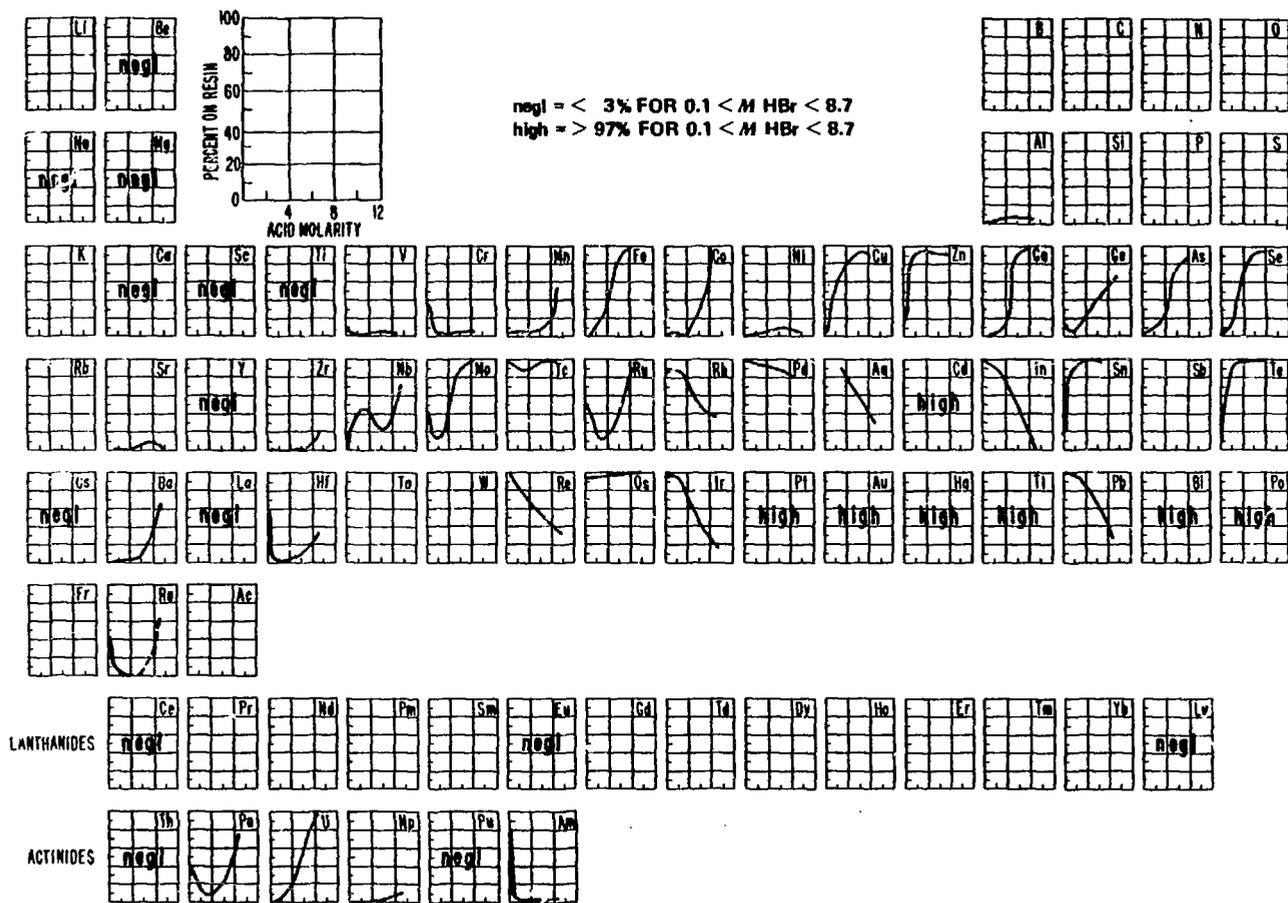


Fig. 3.

Sorption of elements by MP1 (macroporous) anion exchange resin from hydrobromic acid (acid volume/resin weight = 10).

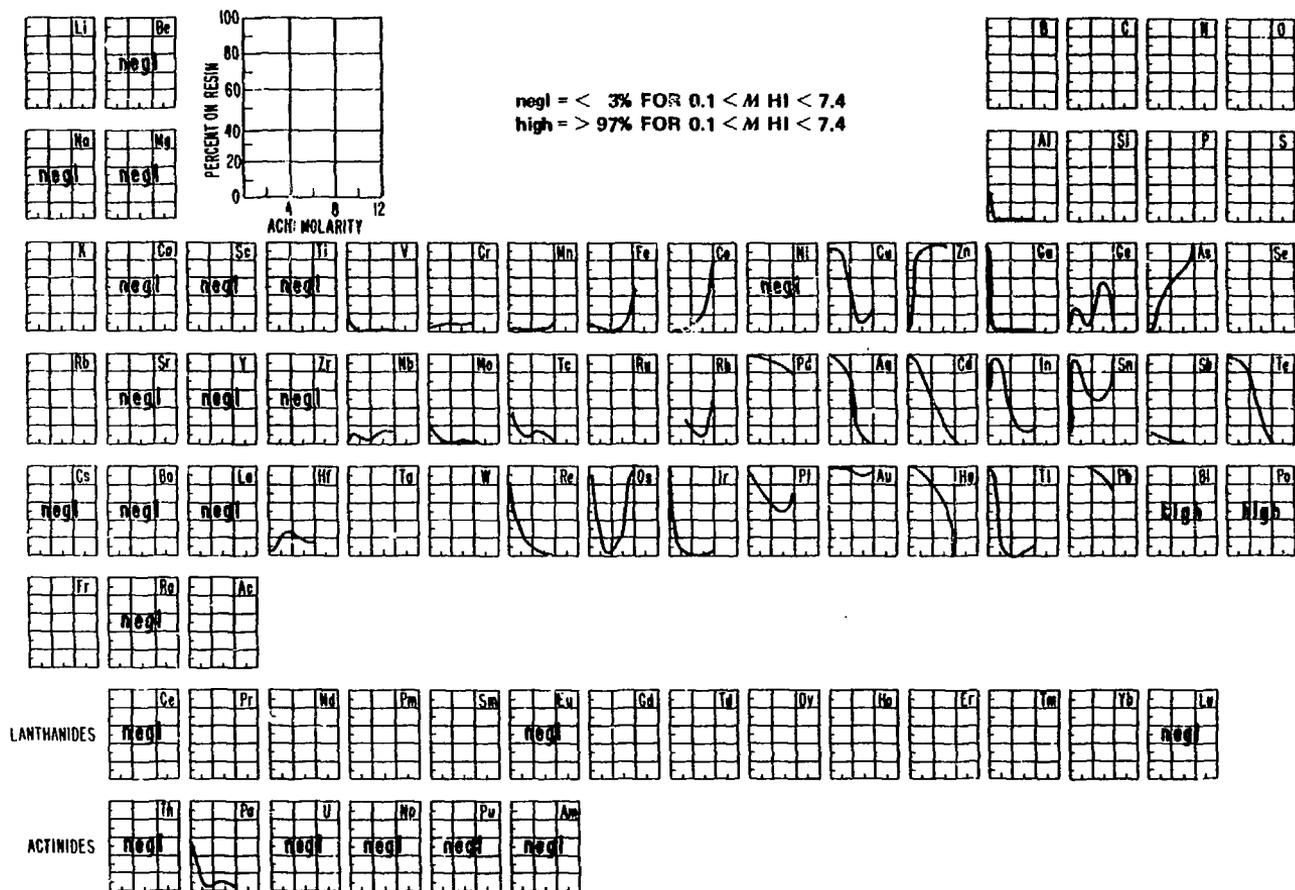


Fig. 4.

Sorption of elements by 1 x 8 anion exchange resin from hydriodic acid (acid volume/resin weight = 10).

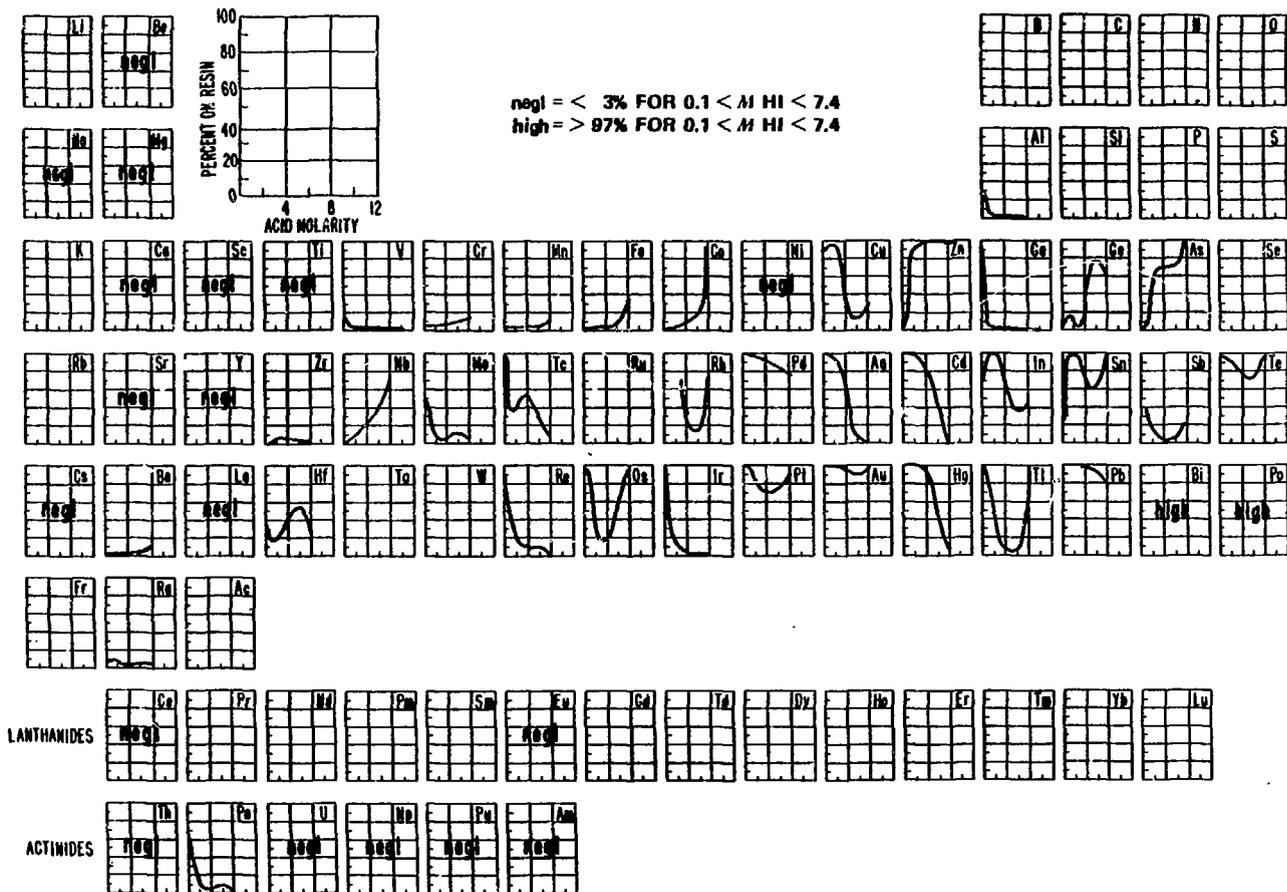


Fig. 5.

Sorption of elements by 1 x 4 anion exchange resin from hydriodic acid (acid volume/resin weight = 10).

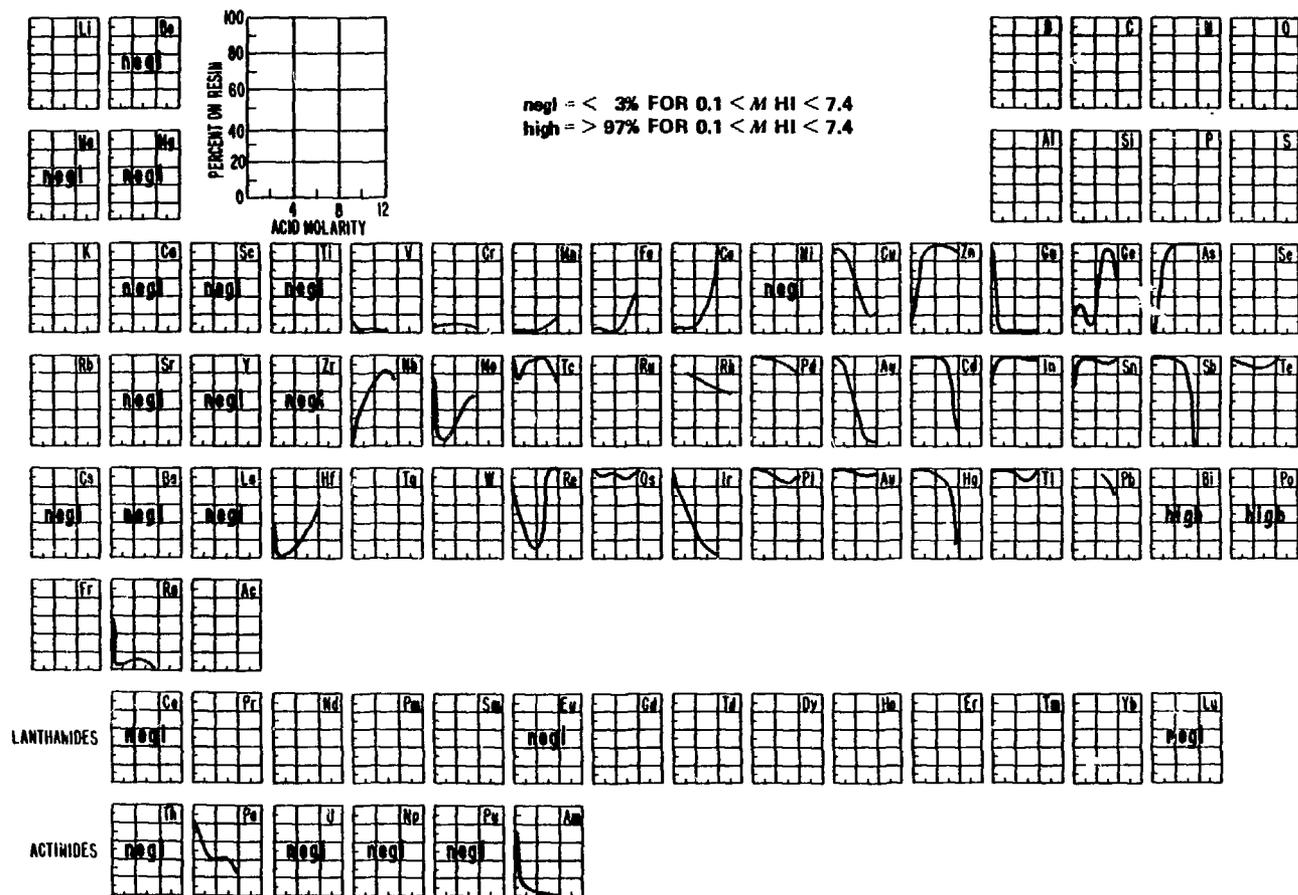


Fig. 6.

Sorption of elements by MPI (macroporous) anion exchange resin from hydriodic acid (acid volume/resin weight = 10).

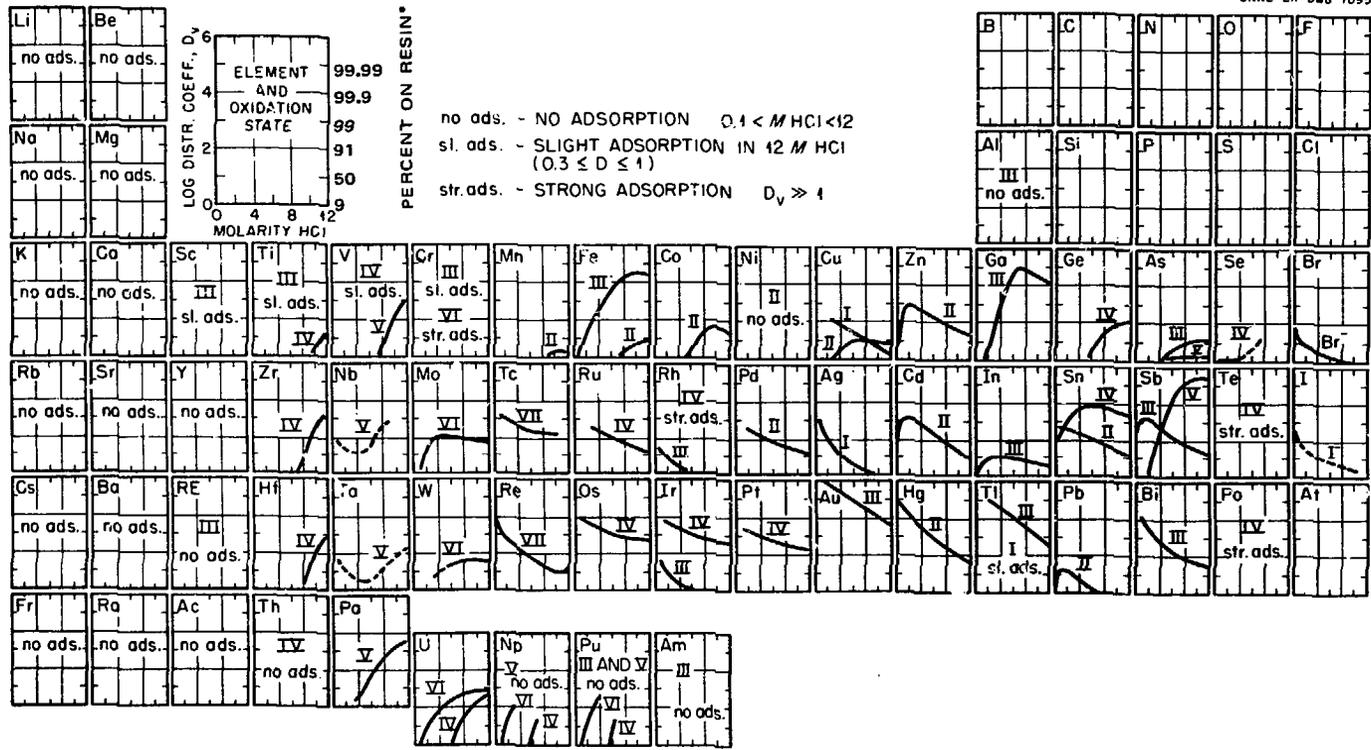


Fig. 7.
 Adsorption of elements from HCl solutions by an anion exchange resin (supplied by F. Nelson). *Percent on resin" scale added to facilitate comparison with Figs. 1-6.

HI, increases with increasing acidity, like that from HCl. Nickel is not sorbed from any of the three acids.

Ruthenium and Osmium. Ruthenium, insoluble in HI, was not tested in it. Sorption of ruthenium, expected to be Ru^{3+} in HBr, is minimal at 3-4M, then approaches 100% at 8M. This behavior differs from that in HCl media from which sorption of ruthenium, identified as Ru^{4+} , continuously decreases with increasing acidity.

Osmium, probably as Os^{4+} (or higher oxidation states) is sorbed strongly from all HBr levels. Osmium, as Os^{3+} , is sorbed strongly from all HCl levels. Osmium, reduced to Os^{2+} by HI, partially precipitated as OsI_2 . The filtrates, containing osmium at saturation levels $<0.01M$, were tested. Sorption from HI is least at 3 to 4M, then approaches 100% with increasing acidity.

Rhodium and Iridium. Because rhodium is insoluble in 0.1 and 1M HI, no data were obtainable at these levels. The oxidation state of rhodium in both HBr and HI is no higher than +3, perhaps +2 in HI. The rhodium pattern of decreasing sorption with increasing HBr acidity is similar to that of Rh^{3+} in HCl. Rhodium is sorbed partially from 3-7.4M HI.

The pattern of decreasing iridium sorption with increasing HBr acidity is more like that of Ir^{3+} than of Ir^{4+} in HCl. Iridium, reduced to Ir^{2+} by iodide, is sorbed appreciably only from 0.1M HI.

Palladium and Platinum. Palladium, as Pd^{2+} , approaches 100% sorption from all three media at low acidity. Sorption decreases with increasing acidity.

Sorption of platinum, as Pt^{4+} , is essentially complete from 0.1-8.7M HBr, like that from HCl. Sorption of platinum from HI, in which it should reduce to Pt^{2+} , decreases with increasing acidity to a minimum of 50% from 6M HI, then slightly increases in stronger acid.

Copper, Silver, and Gold. Sorption of copper, as Cu^{2+} , is higher from HBr than from HCl. It increases with increasing HBr concentration to $>90\%$ at 6M. Copper behavior in HI, in which it is Cu^+ , is like that of Cu^+ in HCl. Sorption is $>90\%$ at low acidity and decreases with increasing acidity.

No data were obtainable for silver from 0.1 and 1M HBr and 0.1M HI, in which it precipitated. At higher acid concentrations, silver behaved similarly in all three media; sorption, high at low acidity, decreases with increasing acidity.

Gold, as Au^{3+} , is sorbed strongly from both HCl and HBr over the complete acidity range. It also is sorbed strongly, as Au^+ , from HI.

Zinc, Cadmium, and Mercury. Zinc is sorbed strongly from all three media above 1M. Sorptions are strongest from HBr and HI.

Cadmium approaches 100% sorption from HBr up to about 9M, whereas its sorption from HCl decreases with increasing acidity to $<90\%$ at 9M. Its sorption from HI decreases rapidly from nearly 100% at low acidity to zero at 7.4M.

Mercury, as Hg^{2+} , is sorbed more strongly from HBr than from HCl. Its sorption as Hg^+ from HI decreases rapidly with increasing acidity.

Aluminum, Gallium, Indium, and Thallium. Surprisingly, aluminum is about 30% sorbed from 0.1M HI, but it is not significantly sorbed from the other two media.

Gallium sorption from HCl and HBr approaches completeness with increasing acidity, whereas gallium is not sorbed from HI.

The sorption pattern of indium, as In^{3+} , is similar from HBr and HI, decreasing from nearly 100% at low acidity to essentially zero at high acidity. From HCl, the pattern of low sorption at low acidity, increasing to about 50% maximum at 3M, is different.

Thallium, as Tl^{3+} , is sorbed strongly from both HBr and HCl. Sorption of thallium, reduced to Tl^+ , from HI decreases rapidly from nearly 100% at low acidity to zero at 3M.

Germanium, Tin, and Lead. Germanium precipitated in HBr and HI. We tested the filtrates containing germanium at saturation levels $<0.01M$. Germanium sorption is similar from HBr and HCl, increasing with increasing acidity to $>90\%$ at high acidity. Two maxima are obtained in HI, about 15% sorption at 1-2M and about 50% at 6M.

Sorption of tin, as Sn^{4+} , is nearly 100% from HBr and HCl above about 1M. Tin precipitated at the higher HI concentrations, and we tested the filtrates. Tin sorption shows a minimum of about

50% from 5-6M HI, but is essentially complete from <1 and 7.4M.

Lead, very insoluble in dilute HI, was not tested at 0.1 and 1M. At the higher HI levels and all HBr levels, we tested lead at 0.01M rather than the usual 0.01M. The sorption order from the three media is HI > HBr > HCl, with sorption decreasing as acidity increases. Nearly 100% sorption occurs from <3M HBr and HI.

Arsenic, Antimony, and Bismuth. Sorption of arsenic from both HBr and HI approaches completeness with increasing acidity. It is higher than the sorption of As^{3+} from HCl. Sorption of As^{3+} is much lower from HCl. Arsenic initially was dissolved in HBr and HI as As_2O_3 and is believed to have remained as As^{3+} .

Data for antimony from 0.1 and 1M HBr, and 0.1M HI, were not obtainable owing to its insolubility. Sorption of antimony, as Sb^{3+} , from HCl and from HBr differs considerably. Sorption from HBr is nearly complete at 2M, then decreases slightly at 8.7M. From HCl, sorption increases continuously with increasing acidity, from 10% at <2M to nearly 100% above 4M. Antimony, reduced to Sb^{3+} by HI, is sorbed weakly from it.

The sorption order of bismuth as Bi^{3+} is HI > HBr > HCl. Sorption from all three media is strong, especially at low acidity levels.

Selenium, Tellurium, and Polonium. Selenium, reduced to the metal by HI, could not be tested in it. Its sorption from HBr approaches completeness at about 6M. This is considerably greater sorption than from HCl.

Tellurium was partially reduced to metal by HI. We used the filtrates containing saturated tellurium iodide at <0.01M to get distribution data. The decreased tellurium sorption with increasing HI concentration is not understood. Tellurium precipitated increasingly with increasing HBr concentration; the filtrates were tested. Tellurium is sorbed strongly from HBr, as from HCl, approaching 100% sorption above about 2M.

Tracer levels of polonium were sorbed completely from all concentrations of all three acids.

Actinides. All actinides except protactinium and americium tracers were evaluated at the 0.01M level.

Thorium is not sorbed from any of the three acids.

Sorption of protactinium is similar from HCl and HBr, increasing with acidity to >90% at about 9M. There is no sorption from HI except that at low acidity which is suspected to be deposition of a hydrolyzed species. Hydrobromic acid produces the same effect.

Uranium, as U^{6+} , behaves similarly in HCl and HBr; sorption increases with increasing acidity to nearly 100% at about 8M. No sorption occurs from HI even though uranium does not reduce.

Neptunium is not sorbed from HBr and HI, whereas the +4 and +6 states are sorbed from >6M HCl.¹⁶ The expected oxidation state of neptunium is +4 in HBr and HI in contact with resin.¹⁶

Plutonium also is not sorbed from HBr or HI, whereas the +4 and +6 oxidation states are sorbed strongly from >6M HCl.¹⁶ Hydriodic acid, and HBr above about 6M, reduce plutonium to nonsorbing Pu^{3+} . Apparently there is little formation of negative bromide complexes of plutonium in <6M HBr.

Americium, as tracer level Am^{3+} , is not sorbed on 1 x 8 resin from any of the three acids.

Distribution as a Function of Resin Cross-Linkage

The porosity of the three resins follows the order MP1 \gg 1 x 4 > 1 x 8. Higher porosity facilitates diffusion of ions within resin particles to provide more accessible exchange sites and faster attainment of equilibrium. Significant differences in distribution as a function of resin cross-linkage are most striking in HI, and virtually absent in HBr. This may be due to the larger radii of anionic iodide complexes. If so, the cross-linkage effect on anion exchange in HCl should be insignificant.

Molybdenum, technetium, rhenium, osmium, rhodium, iridium, platinum, cadmium, indium, thallium, germanium, tin, arsenic, antimony, tellurium, and carrier-free protactinium show this

MP1 > 1 x 4 > 1 x 8 sorption pattern from HI. Carrier-free niobium follows this pattern in both HI and HBr. Aluminum follows the reverse of this pattern in 0.1M HI, where the order of sorption, although low, is 1 x 8 ≈ 1 x 4 > MP1. Sorption of carrier-free radium on MP1 resin is about 50% from 0.1M HBr and HI, but it is near zero from other systems.

The greatest sorption of hafnium from HI shifts from 3M with 1 x 8 resin to 6M with 1 x 4 resin and to 7.4M with MP1 resin.

Tracer-level americium is >70% sorbed on MP1 resin from 0.1M HBr and HI. It is about 30% sorbed on 1 x 4 resin from 0.1M HBr. The indicated formation of an anionic complex of americium in dilute acid is unexpected and not understood.

Effect of Nonisotopic Carrier

The distribution of an element on ion exchange resin is known to vary as the element concentration changes from tracer to macro levels. Most of the elements in this study were tested at a 0.01M concentration corresponding to 3-10% of the total resin capacity. Distribution data for the few elements measured at tracer levels cannot be considered to represent their distributions at macro levels. However tracer-based distribution data for elements, such as radium, polonium, and protactinium, unlikely to be present in higher concentrations, are valuable.

The effect of another element having similar chemistry was evaluated using radium with and

without 0.01M barium as a nonisotopic carrier. Tracer radium alone, as discussed earlier, is sorbed only from 0.1M HBr and 0.1M HI and only on MP1 resin, somewhat like tracer americium. In the presence of 0.01M barium, however, tracer radium follows the barium distribution pattern by increasing rapidly with increasing HBr molarity above 6M. This indicates that barium and radium chemically interchange so that radium follows the unique anion exchange distribution pattern of barium in HBr.

APPLICATIONS

Anion exchange in HBr and HI should provide versatility to the separation chemist. Examples of potentially useful separations, using a single HBr or HI medium, are given in Table I. Table II presents examples of potentially more selective separations using various combinations of HCl, HBr, and HI as the sorption and elution media. These examples, derived from the data presented in Figs. 1-7, have not been tested experimentally. We expect that readers who consider the data for specific applications will develop other useful separations.

ACKNOWLEDGMENTS

R. D. Gardner, LASL, provided the atomic absorption measurements of vanadium and rhodium. The general assistance of Mrs. Romayne Ortiz is appreciated.

TABLE I
POTENTIALLY USEFUL SEPARATIONS
INVOLVING A SINGLE HBr OR HI MEDIUM

<u>Element Separated</u>	<u>Separated From</u>	<u>Medium</u>	<u>Ion Exchange Resin</u>
Ba	Alkali and Alkaline Earths	Strong HBr	1x4, 1x8
Zr	Hf	Strong HI	MP1
Nb	Zr	Strong HI	MP1
Cr	Mn, Fe, Co, Ni	0.1M HBr	1x8, 1x4
Tc	Re	4M HI	MP1
Ru	Noble Metals	3M HBr	1x8, 1x4, MP1
Ir	Noble Metals	Strong HI	MP1
Ir, Re	Noble Metals	Strong HI	1x4
Zn	Cd, Hg	Strong HI	1x8, 1x4
Ga	In, Tl	>2M HI	MP1
In	Ge, Tl, Many Others	Strong HBr	1x8, 1x4, MP1
Sb	As, Bi	Strong HI	1x8, 1x4, MP1
Po	Te	Strong HI	1x8
Po	Se, Te	0.1M HBr	1x8, 1x4, MP1
Pa	Th	Strong HBr	1x8
U	Th, Np, Pu, Am	Strong HBr	1x8, 1x4, MP1
Am	Th, U, Np, Pu	HBr or HI, 0.1M	MP1

TABLE II
POTENTIALLY USEFUL SEPARATIONS INVOLVING
COMBINATIONS OF HCl, HBr, AND HI MEDIA

<u>Element Separated</u>	<u>Separated From</u>	<u>Sorption Medium</u>	<u>Elutant</u>	<u>Resin</u>
Cr	Most Elements	0.1M HBr	Strong HBr	1x8
V	Cr, Mn, Fe, Co, Ni, Cu, Zr, and Many Others	Strong HCl	Strong HBr	1x8
Sb, As, Bi	Each Sequentially	Strong HI (Sb Elutes)	0.1M HI (As Elutes)	1x8
Ga	Most Elements	0.1M HI	0.1M HBr	MP1
Te	Most Elements	Strong HI Followed By 0.1M HI	0.1M HBr	MP1
Pb	Most Elements Except Noble Metals and Cr	0.1M HBr	Strong HCl	1x8

REFERENCES

1. K. A. Kraus and F. Nelson, "Anion Exchange Studies XXII. Metal Separations by Anion Exchange," in *Am. Soc. Testing Materials, Spec. Tech. Publ. No. 195*, (1958), pp. 27-59.
2. J. P. Faris and R. F. Buchanan, "Anion Exchange Characteristics of Elements in Nitric Acid Medium," *Anal. Chem.* **36**, 1157-1158 (1964).
3. J. P. Faris, "Adsorption of the Elements from Hydrofluoric Acid by Anion Exchange," *Anal. Chem.* **32**, 520-522 (1960).
4. P. Van den Winkel, F. De Corte, and J. Hoste, "Distribution Coefficients for 65 Elements in Acetic Acid on Dowex 1x8," *J. Radioanal. Chem.* **10**, 139-143 (1972).
5. H. Polkowska-Motrenko and R. Dybezyński, "Distribution Coefficients of 52 Elements on a Strongly Basic Anion-Exchange Resin in Aqueous Solutions of Orthophosphoric Acid," *J. Chromatog.* **88**, 387-390 (1974).
6. J. Korkisch, "Ion Exchange of Uranium and Thorium in Mixed and Non-Aqueous Solvents," U. S. Atomic Energy Commission report TID-22402 (October 1965) pp. 93-115.
7. J. M. Peters and G. del Fiore, "Distribution Coefficients for 52 Elements in Hydrochloric Acid-Water-Acetone Mixture of Dowex 1x8," *Radiochem. Radioanal. Lett.* **21**, 11-21 (1975).
8. T. Andersen and A. B. Knutsen, "Anion-Exchange Study. I. Adsorption of Some Elements in HBr Solutions. *Acta Chem. Scand.* **16**, 849-854 (1962).
9. E. Klakl and J. Korkisch, "Cation Exchange Behavior of Several Elements in Hydrobromic Acid-Organic Solvent Media," *Talanta* **16**, 1177-1190 (1969).
10. S. F. Marsh, M. R. Ortiz, R. M. Abernathy, and J. E. Rein, "Improved Two-Column Ion Exchange Separation of Plutonium, Uranium, and Neodymium in Mixed Uranium-Plutonium Fuels for Burnup Measurement," Los Alamos Scientific Laboratory report LA-5568 (June 1974).
11. W. Rieman and H. F. Walton, *Ion Exchange in Analytical Chemistry* (Pergamon Press, New York, 1970), p. 61.
12. K. S. Kim, *Styrene and Divinylbenzene Copolymer*, Ph.D. Dissertation, The City University of New York, 1971, University Microfilms No. 72-13, p. 470.
13. G. H. Morrison and H. Freiser, *Solvent Extraction in Analytical Chemistry* (John Wiley & Sons, New York, 1957), p. 12.
14. W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2nd Ed. (Prentice-Hall Inc., New York, 1952).
15. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, (Pergamon Press, New York, 1969) p. 64.
16. F. Nelson and D. C. Michelson, "Ion-Exchange Procedures IX. Cation Exchange in HBr Solutions," *J. Chromatog.* **25**, 414-441 (1966).