32 5
10/2/64

MASTER

Argonne National Laboratory

ANION EXCHANGE CHARACTERISTICS OF THE ELEMENTS IN NITRIC ACID AND NITRATE SOLUTIONS AND APPLICATION IN TRACE ELEMENT ANALYSIS

by

J. P. Faris and Robert F. Buchanan

10/7

LEGAL NOTICE

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60440

ANION EXCHANGE CHARACTERISTICS OF THE ELEMENTS IN NITRIC ACID AND NITRATE SOLUTIONS AND APPLICATION IN TRACE ELEMENT ANALYSIS

by

J. P. Faris and Robert F. Buchanan

Chemistry Division

July 1964

TABLE OF CONTENTS

4

LIST OF FIGURES

ANION EXCHANGE CHARACTERISTICS OF THE ELEMENTS IN NITRIC ACID AND NITRATE SOLUTIONS AND APPLICATION IN TRACE ELEMENT ANALYSIS

by

J. P. Faris and Robert F. Buchanan

ABSTRACT

I. Nitric Acid

The adsorption of most metal ions onto a strongly basic anion exchange resin from nitric acid solution has been determined. Distribution coefficients are given for some 70 elements in acid concentrations ranging from 0.1M to 14M. A comprehensive list of references to similar studies and to some typical uses of anion exchange separation in a nitric acid medium is included.

II. Nitrate Media

The increased absorption of some elements from nitrate solutions of low acidity offer additional possibilities for analytical separations by anion exchange resins. Past work in inorganic nitrate solutions and in water-miscible organic solvent mixtures is reviewed briefly from the standpoint of possible use in trace element analysis.

III. Analytical Applications

Some analytical procedures are outlined whereby trace impurities were concentrated by anion exchange in a nitrate medium and then determined by an emission spectrographic technique. Methods developed for the analysis of thorium, plutonium, and neptunium have utilized the large separation factors from most other ions in a nitric acid medium; differences in adsorption from methanol-nitric acid mixtures have been applied to the analysis of the rare earths. Limits of detection by the copper spark method are given for more than 50 elements.

I. NITRIC ACID

Introduction

Anion exchange adsorption from a nitric acid medium has many specific uses and much has been published about the characteristic behavior of various metallic ions in such media. To gain more complete information and to gather data necessary for analytical application, the Analytical Group of the Chemistry Division at Argonne made a series of studies in which the adsorption of most metal ions from nitric acid solutions of concentration ranging from 1 to 14M has been determined.[13,14] This work has now been extended to include the behavior of some 70 elements in acid concentrations ranging down to 0.1M. Both column elution and batchwise techniques were used in the experiments, as well as radiochemical, chemical, and optical emission spectrographic methods of analysis.

Experimental

Analytical grade Dowex 1 x 10, 200-400 mesh strong-base anion-exchange resin was oven-dried for several hours at approximately 100°C, weighed in the chloride form, and then converted to the nitrate form by washing thoroughly with nitric acid and water. The rated capacity was 3 meq/g, and the approximate density, determined from displacement of benzene by the dry resin, was 1.67 g/cm³. All work was at room temperature (about 25°C).

In column experiments the elements were added in microgram quantities to a series of equilibrated columns and then eluted with nitric acid of appropriate molarity. The effluents were collected in fractions that ranged from 2 ml for a 3.5-mm-ID column containing 0.4 g of resin to 10 ml for a 6-mm-ID column containing 2 g of resin. Flow rates were from 2 to 10 ml/hr.

Whenever a radioactive tracer was added to a column, the effluent was analyzed by counting the alpha, beta, or gamma activity, depending on the decay characteristics of the element being determined. The alpha and beta activities were stippled on to stainless steel planchets and counted in a 2π flow proportional counter using a 90% argon and 10% methane gas mixture. The counting efficiency for alphas was 50.5%; that for beta was about 70%. The gammas were counted in solution on a well-type scintillation counter with a NaI(Tl) crystal.

For most elements the elution was determined by emission spectrographic examination of effluent fractions by the copper spark method.[36,42] This procedure was rapid and convenient because it permitted a mixture of elements to be added to a column and kept the number of tracer preparations or time-consuming chemical analyses to a minimum. Since ionic species

were present at only trace concentrations, distribution coefficients (K_d) could be derived from $K_d = V/M$,[108] where V is the number of ml required to reach the elution curve maximum (less the first-column volume of displaced liquid) and M is the weight of resin in grams.

In the batch method, a known amount of an element was equilibrated with weighed amounts of resin and acid. Distribution coefficients were derived from analysis of the aqueous phase by the relationship

$$K_d = \frac{\text{concentration per gram dry resin}}{\text{concentration per ml solution}}.$$

Results and Discussion

Distribution coefficients obtained from the column elution and batchwise experiments are presented in Fig. 1 as a function of nitric acid molarity. Elements placed in the "no adsorption" category were those spectrographically estimated to be quantitatively eluted in the first effluent fraction and not detected in subsequent fractions, as well as those found to have values of K_d of less than about one or two as determined by use of a radioactive tracer in column or batchwise experiments. A negligible percentage of an element appearing in a second effluent fraction from a column was indicated by "slight adsorption."

In some cases a valence change may have taken place on the resin; as a rule, the addition of excess oxidant or reductant to an eluting solution or to a batch was avoided. An exception was in the case of neptunium, for which the tetravalent state was maintained with 0.1M ferrous sulfamate. Ruthenium may exist in nitric acid as neutral, anionic, or cationic species.[80] Although Ru(IV) can be adsorbed,[15,57,122] we found that without a holding oxidant most of the ruthenium added to a column broke through early. For Tl(III), both column and batchwise experiments suffered from lack of reproducibility, and the adsorption function has not been definitely established. Also, Ce(IV), for which excellent adsorption has been reported,[25,72,94,95] was eluted to about the same extent as Ce(III), owing to a reduction by the resin in the columns.

Particular care was taken to exclude the presence of chloride ions during adsorption measurements of the platinum metals and Au(III), because these elements are strongly adsorbed as the chloro complexes.[72] Platinum has not been included in Fig. 1 because the distribution measurements by the batchwise method did not agree with those made by the column elution technique. The reason for this difference has not been fully resolved; probably the higher batchwise values could be attributed to some extent to the difficulty of removing completely all traces of chloride. On the other hand, the adsorption of Pd(II) was found to increase only slightly when an equivalent

NO ADS. – NO ADSORPTION FROM 0.1–14 M HNO_3

SL. ADS. – SLIGHT ADSORPTION

LOG DISTR. COEFF.

MOLARITY HNO_3
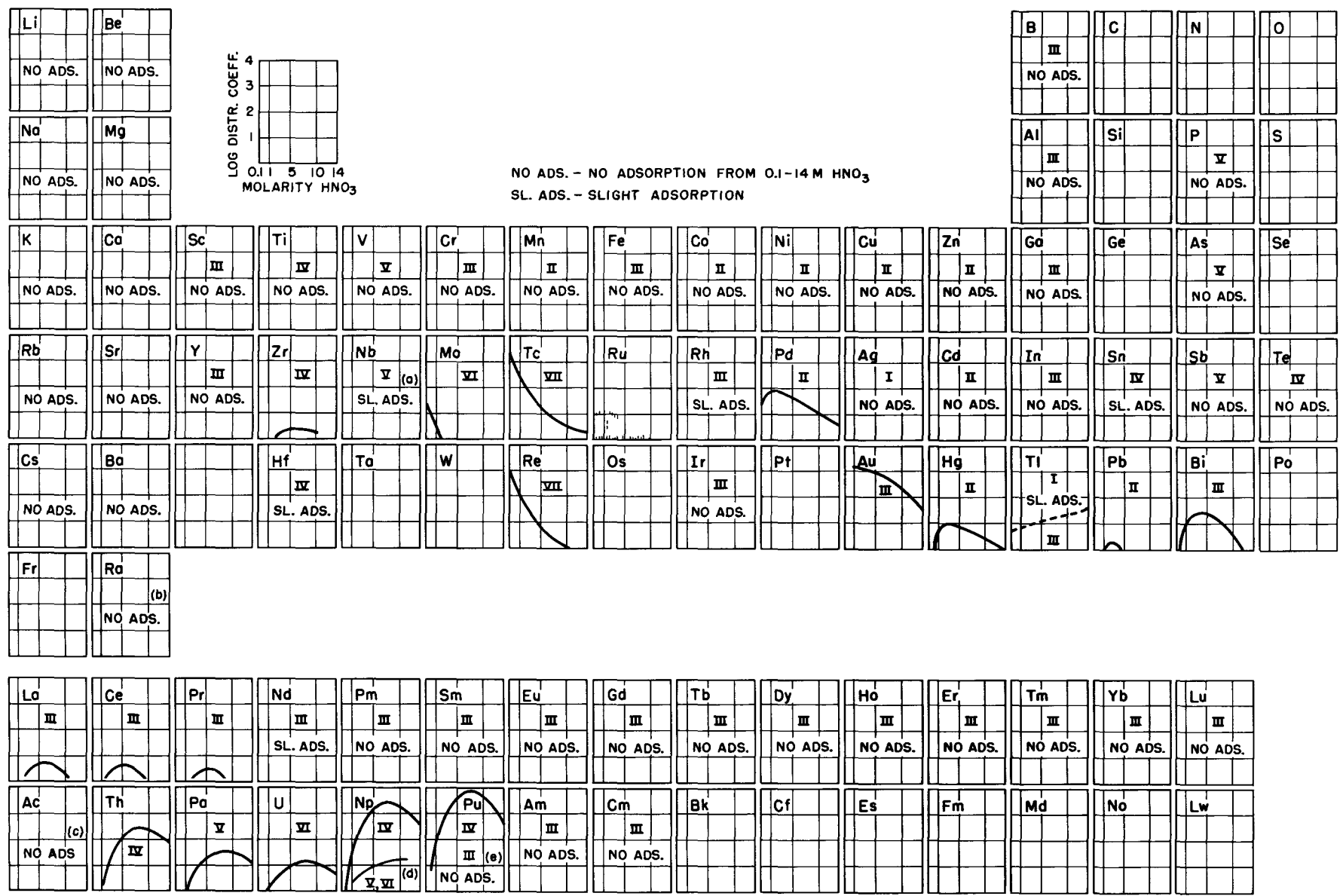
Fig. 1. Removal from Solution of Elements in 0.1 to 14M Nitric Acid with Strongly Basic Anion Exchange Resin. (a) Nb(V) - Bunney et al.,[15] James,[58] Phillips and Jenkins,[86] Prevot et al.[88] (b) Ra(II) - Choppin and Sikkeland.[23] (c) Ac(III) - Choppin and Sikkeland,[23] Hyde.[54] (d) Np(V), (VI) - Hardy,[46] Ichikawa et al.,[57] Tober,[107] Wish and Rowell.[122] (e) Pu(III) - Roberts and Brauer,[95] Wish and Rowell.[122]

amount of chloride was deliberately added to a batch. When ten times the equivalence of chloride was added, distribution coefficients at 1M and at 2M nitric acid were higher by a factor of two to four.

Adsorptions of several elements investigated by the spectrographic procedure were also determined at the tracer level with radiometric methods of analysis or in macro quantities by the use of chemical analyses. Results of some single batchwise equilibration measurements of Th^{230} and U^{233} adsorptions and of Pd(II) and Hg(II) adsorptions by spectrophotometric analyses are compared with spectrographically determined adsorptions in Table I. Similar agreement was found in column elution experiments with U^{233}, Ce^{144}, and Mo^{99} tracers. It will be noted that the variation of results between the different procedures was less than that obtained for Hg(II) when resin from different lots was used.

Table I

EXPERIMENTAL DISTRIBUTION COEFFICIENTS BY SPECTROGRAPHIC METHOD COMPARED WITH OTHER PROCEDURES AT VARIOUS NITRIC ACID CONCENTRATIONS[13]

Element	Method	Anal.	M HNO$_3$							
			1	2	4	6	8	10	12	14
Th^{230}	Batch	R. C.[b]	1.0	6.0	51	216	303	227	130	67
Th	Column	Spec.	1.0	3.3	47		323		93	51
U^{233}	Batch	R. C.	1.3	3.3	6.7	13	15	9.7	7.2	6.2
U^{233}	Column	R. C.	3.8	3.8	9.2	17	16	13	12	7.3
U	Column	Spec.	<2	3.0	7.2	12	12	7.2	5.6	5.4
Pd	Batch	Chem.	45	57	41	29	12	6	14	4.0
Pd	Column	Spec.	50	52	54	38	18-25	10-18	8.0	4-7
Hg	Batch[a]	Chem.	11	23	20	18.4	5.7	2.5	2.0	<2
Hg	Batch	Chem.		7.8		8.6				
Hg	Column	Spec.	3.5	8.0	6-9	5.0	3.5	3.0	1.5	<1.5

[a] Resin from different lot.

[b] R. C. = radiochemical; Spec. = spectrographic; Chem. = chemical.

For the most part the adsorptions in Fig. 1 were in satisfactory agreement with those which have been reported in the literature referred to below, although many of the comparisons can only be qualitative because of variations in physical properties or type of resin used. After the early reports from Chalk River,[5,6,29] the strong adsorption of plutonium was much investigated, and a detailed study of the exchange kinetics was made by Ryan and Wheelwright.[101] The adsorption of thorium has also been studied extensively.[15,20,21,24,25,72] The present values found for the adsorption of Pb(II) and Bi(II) are in good agreement with those reported by Nelson and Kraus,[83] and those found for Re(VII) and Tc(VII) agree with the results of Huffman et al.[53] The batchwise measurement of Pa(V)

adsorption confirmed the published data.[15,47,105,122] The elution of Zr(IV)[15,89,122] and of Mo(VI)[15,57] could be compared qualitatively. A general agreement of results was found with the K_d values which have been reported in the literature for Zn(II),[51,72] U(VI),[15,21,72,88,122] Np(IV),[46,92,95,107] Am(III),[15,95] Cm(III),[95] and the rare earths.[25,56,72,74] Adsorptions of numerous elements from nitric acid have been studied by Kraus and Nelson,[72] and in an extensive survey by Ichikawa et al.[57] adsorptions were presented for a large number of radioactive tracers. James[58] has reported distribution coefficients for many elements on Dowex 1 x 4 from 7M nitric acid.

Some literature values for anion exchange adsorption in nitric acid are also included in Fig. 1. From the data published for the adsorption of Np(V)[22,46,107,122] and Np(VI)[22,46,57,107] a maximum distribution coefficient of about 15 can be expected. Negligible adsorption has been reported for Nb(V),[15,58,86,88] Ra(II),[23] Ac(III),[23,54] and Pu(III).[95,122]

Polonium adsorption in nitric acid was studied by Danon and Zamith,[27] who reported distribution coefficients for Po(IV) ranging from 120 to 90 in nitric acid from 0.8M to 5M. In the presence of an effective reductant the adsorption decreased to give a curve similar to that of Bi(III) in nitric acid. Ichikawa et al.[57] later found Po(IV) to be only slightly adsorbed. Starik and Amplelogova[104] studied the sorption of polonium ions from nitric acid. In 7M acid, Ir(IV) was adsorbed, whereas Se(IV) and Ta(V) were not.[58] For Ge(IV), both negligible adsorption[58,72] and strong adsorption[57] have been reported. It has been implied that francium and the transcurium elements would not be adsorbed on anion exchange resins from nitric acid solution.[54,55]

James[59] has studied the synergistic effect of thorium on the distribution coefficients of several elements. Ryan[98] has studied the species involved in the anion exchange adsorption of quadrivalent actinide nitrates. Kazantsev[61] has compared the chemical resistance of several anion exchangers in nitric acid solutions. Fernandez[39] has reported on the rate of diffusion for alpha emitters in some anion exchange resins.

Application

The strong anionic adsorption of the tetravalent complex has been used to advantage in fuel processing for plutonium recovery and separation from fission products.[2,6,17,18,88,89,99,100,101,107,118,120] In similar processes which have been described for the concentration and purification of neptunium, [16,17,62,81,90,97,107] the tetravalent state was usually maintained with the addition of reductants such as semicarbazide, ferrous sulfamate, or hydrazine. Procedures for sequential separation of the actinide elements[95,121,122] and their isolation from fission

products[14,82,86,92,100,120,122] have incorporated anion exchange adsorption from nitric acid. Similar use in analytical methods has been described for the quantitative recovery of plutonium[60,73] and of thorium,[43,59] for the chemical assay of plutonium alloys,[8,41] and for the removal of interfering ions in chemical or radiochemical analyses.[5,9,14,87,121]

II. NITRATE MEDIA

Anion exchange of the lanthanides and actinides from inorganic nitrate solutions have been studied in considerable detail. In slightly acidified solutions of lithium nitrate Marcus and Nelson[78] found increasing adsorption with increasing nitrate concentration. The lighter rare earths were more strongly adsorbed than the heavier and could be readily separated. Further work provided more data for the heavier lanthanides[75,76] and compared the effect of nitrate ion concentration for several nitrate salts. Distribution coefficients were highest for the lighter lanthanides in nitrate solutions of lithium, and decreased in magnitude for solutions of aluminum, calcium, ammonium, and hydrogen. Adar et al.,[1] and Marcus et al.,[77] have measured distribution coefficients for a number of the trivalent actinide ions in lithium nitrate solutions and reported an efficient separation of americium and curium. Danon[26] separated trace amounts of actinium from weighable quantities of lanthanum by elution with lithium nitrate solution. Edge[31] found the adsorption of thorium varied with the nature of the cation of supporting nitrate solution in the order aluminum > lithium > calcium > hydrogen. He also developed a procedure for separation and spectrographic determination of trace rare earths.[32] The strong adsorption of uranium from a solution nearly saturated with aluminum nitrate was used by Okenden and Foreman[85] for an analytical separation from large amounts of iron. Vita et al.,[112] similarly separated uranium from many elements and compared distribution ratios for uranium in solutions of several nitrate salts, including those of aluminum, sodium, nickel, and zinc. Higgins[48] recovered uranium from calcium nitrate solutions. Foreman et al.,[40] found that the addition of inorganic nitrates increased the uptake of uranium onto an anion exchange resin in the order aluminum > calcium > lithium > ammonium at constant nitrate molarity. Caracciolo[19] adsorbed thorium from nitric acid-sodium nitrate solutions on an agitated bed of anion exchanger. In a detailed study by Nelson and Kraus[83] the strong adsorption of bismuth permitted a ready separation from lead in ammonium nitrate solutions of low acidity. Kraus and Nelson[72] also found a marked increase in the adsorption of uranium and the rare earths in the same medium but not for thorium. Korkisch et al.[71] collected uranium from a solution half-saturated with ammonium nitrate. The adsorption of a number of elements from ammonium nitrate solutions has been reported in studies made at this Laboratory,[13] including the effect of free acid on the adsorption functions of uranium, bismuth and the rare earths (see Fig. 2).

The elution of several radioelements from nitrate-loaded columns containing a complexing agent were studied by Schonfeld et al.[102] At about pH 8, lead, yttrium, and bismuth were adsorbed, while strontium was eluted with a 0.1M sodium nitrate, 0.0005M, 8-hydroxyquinoline sulfonate solution.
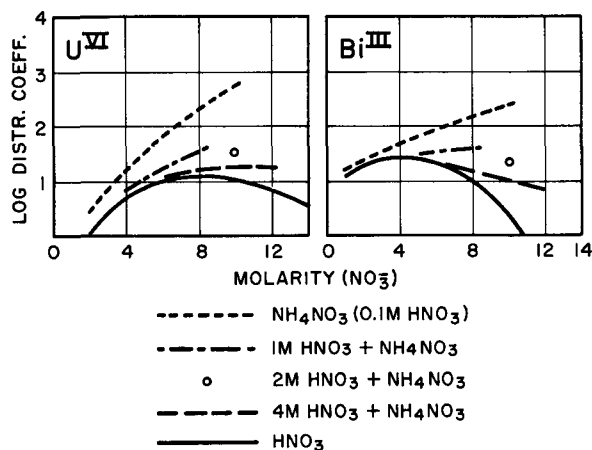
Fig. 2 area (chart labels):

LOG DISTR. COEFF.

U^{VI} Bi^{III}

4

3

2

1

0   4   8   12   0   4   8   12   14

MOLARITY (NO_3^-)

------- NH_4NO_3 (0.1M HNO_3)

—·—·— 1M HNO_3 + NH_4NO_3

o   2M HNO_3 + NH_4NO_3

— — — 4M HNO_3 + NH_4NO_3

——— HNO_3

Fig. 2. Anion Adsorption of U(VI) and Bi(III) in NH_4NO_3-HNO_3 Mixtures (see Ref. 13)

Halide ions were separated by Atteberry and Boyd[10] and by Rieman and Lindenbaum,[91] who used a strongly basic anion exchange resin in the nitrate form. Elution with a sodium nitrate solution first displaced fluoride, then chloride, bromide, and finally iodide. DeGeiso, Rieman, and Lindenbaum[28] later improved the procedure, especially for iodide elution.

The adsorption of some elements by anion exchange resins can be much greater from nitrate solutions containing a high proportion of a miscible organic solvent than from aqueous nitric acid. At the Analytical Institute of the University of Vienna, Korkisch and coworkers have made extensive studies of the adsorption of ions from mixtures of mineral acids and aliphatic alcohols or other solvents, such as ethers or ketones. This work has been recently summarized and the general theoretical aspects discussed.[68] In earlier work[7,65,106] they used to advantage the strong adsorption of thorium in nitric acid-ethanol mixtures for a ready separation from zirconium and from uranium, and later compared other alcoholic solutions[70] for thorium-uranium separations. Their work with nitric acid-methanol mixtures[69] demonstrated that a number of elements could be quantitatively separated from thorium and that the rare earths, barium, and lead were adsorbed strongly. Akaishi[3] prepared carrier-free Th^{234} by anion exchange from mixed solvents and studied thorium adsorption in the presence of phosphate.[4] Solvent mixtures of diethyl ether or dioxane with nitric acid have been employed in a column separation of uranium from the more strongly adsorbed ions of thorium, aluminum, and iron.[110] The adsorption of uranyl nitrate from several organic solvents has been reported.[11,111] Tuck and Welch[109] found a maximum adsorption for Pu(IV) at about 0.4M nitric acid from diethylene glycol dibutyl ether.

Enhanced adsorption of the rare earth nitrates from mixed solvents containing ethanol or acetone was demonstrated by Marcus and Abrahamer.[76] Edge[30] separated yttrium, neodymium, and lanthanum by using ethanol as the added solvent. Work at this Laboratory has shown that the rare earth nitrates can be adsorbed from a number of miscible organic solvents,[38] and distribution coefficients have been presented as a function of both the volume percentage of methanol and the acidity (see Fig. 3 and 4). Edge[33] separated the light rare earth group from the heavy in a methanol-nitric acid mixture. Korkisch et al.[67] gave detailed data for the rare earths in several aliphatic alcohols and proposed individual separation techniques that included some other elements. As a general rule, the light rare earths,

lanthanum, and thorium could be quantitatively isolated in the above systems, whereas the rare earths heavier than terbium were eluted from a column practically as a group.

Fig. 3. Variation of Distribution Coefficient with Acid Molarity in Mixtures of 10% Nitric Acid-90% Methanol. Dowex 1 x 4, 200-400 Mesh Resin (see Ref. 38).

Fig. 4. Variation of Distribution Coefficient with Proportion of 7M Nitric Acid. Dowex 1 x 4, 200-400 Mesh Resin (see Ref. 38).

Within the alkaline earth group, Korkisch and Tera[69] found barium to be strongly adsorbed from a 90% methanol-10% 5M nitric acid mixture and thus separated from strontium, calcium, and magnesium. Fritz and Waki[44] used a similar mixture with isopropyl alcohol as the added solvent for a quantitative separation of magnesium and calcium, and also demonstrated a calcium-strontium-barium separation. Calcium and strontium could be quantitatively separated in a methanol-nitric acid mixture.[45] Column elution experiments have been made at this Laboratory with microgram quantities of alkaline earths in solutions of nitric acid with methanol (see Fig. 5) and some other solvents similar to those tested for rare earth separations.[38] Adsorption onto a strong base anion exchange resin was in the order Be $\leq$ Mg < Ca < Sr < Ba. Radium would presumably be adsorbed to an even greater degree.
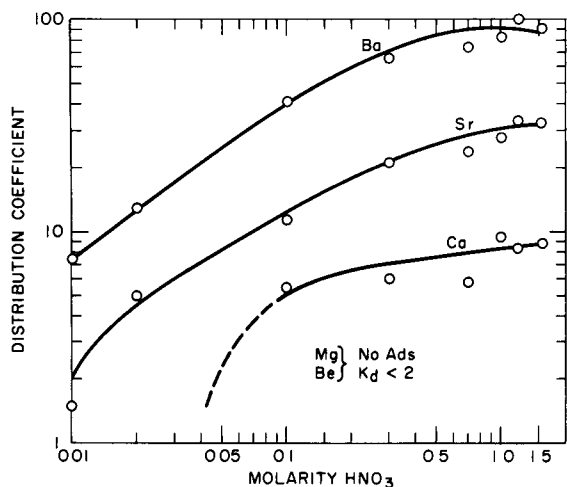
Fig. 5. Approximate Distribution Coefficients
of Alkaline Earths as a Function of Acid
Molarity in Mixtures of 10% Nitric
Acid-90% Methanol. Dowex 1 x 4,
200-400 Mesh Resin

Anion exchange separation of some actinides in a methanol-nitric acid medium has been accomplished by Hines, Wahlgren and Lawless[49] (see Figs. 6 and 7). The same general behavior as that of the rare earths was observed. Californium was eluted from a column before curium, then followed by americium (see Fig. 8). A separation factor for americium and curium of 3.25 was found in a 90% methanol-10% nitric acid mixture. Elements heavier than californium were not expected to fractionate to any extent.

Recently, Korkisch and Arrhenius[66] found that a number of ions, including the rare earths, bismuth, lead, and cadmium, were strongly retained by an anion exchange resin from a mixture of 90% acetic acid and 10% 5M nitric acid, and thus separated from many nonadsorbed elements.
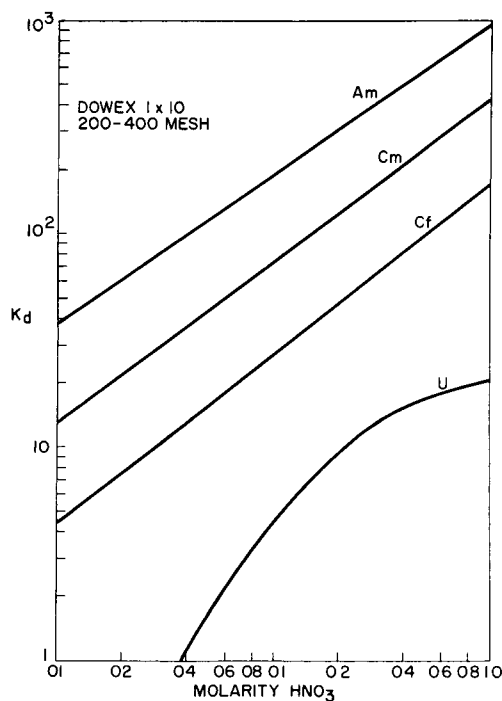
Fig. 6. Distribution Coefficients of Actinides
as a Function of Acidity in 10% Nitric Acid-90% Methanol (from Hines, Wahlgren, and Lawless, Ref. 49)
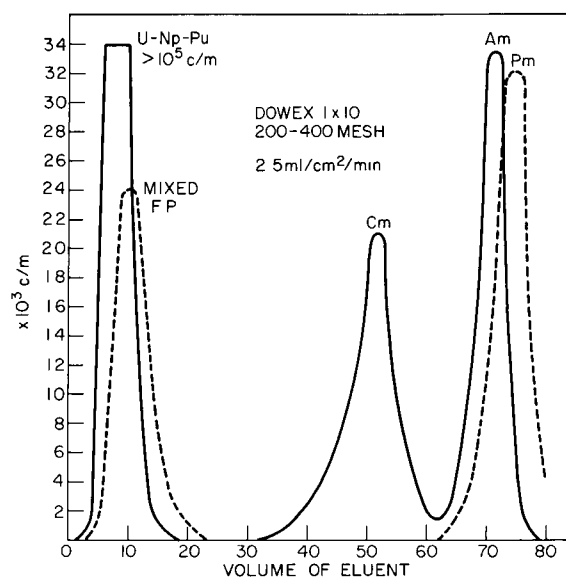
Fig. 7. Elution Curves for the Separation of Americium and Curium from Other Common Actinides in a 10% Nitric Acid-90% Methanol Mixture (from Ref. 49)
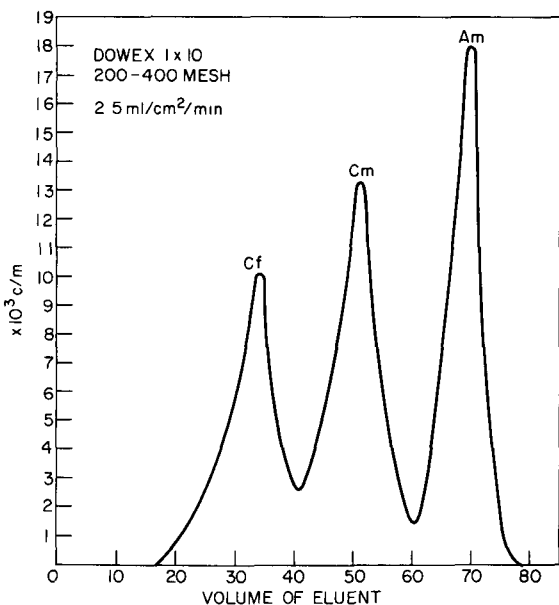
Fig. 8

Elution Curve for the Separation of Californium from Americium and Curium in a 10% Nitric Acid-90% Methanol Mixture (from Ref. 49)

Although anion exchange in inorganic nitrate media can be of advantage in purification or concentration processes, in radiochemical separations, and in the presence of high levels of radiation, application of these systems to analysis for general trace impurities is not simple. Further separation or concentration may be necessary to attain the necessary sensitivity or analytical precision, and preparation of reagents of acceptable purity could be time-consuming. On the other hand, the use of water-miscible organic solvents offers a good advantage in that most solvents can be readily purified and subsequently volatilized to concentrate the separated trace impurities.

III. ANALYTICAL APPLICATIONS

The current interest in high-purity materials frequently requires considerable analytical effort to provide good values for metallic impurities present in extremely low concentration. Among the methods used, various emission spectrographic techniques are excellent for trace-element determinations; there is, however, no universal method. Norris[84] has reviewed the spectrographic determination of trace elements in metals and has outlined separation methods as a means of extending the detection limits for impurities. The advantages of using ion exchange for this purpose have been discussed.[35] Spectrochemical methods using anion exchange in a nitrate medium are particularly effective for the analysis of plutonium, and procedures have been described for the determination of zirconium,[64] americium,[116] and most other impurities.[63,113-115] Similar procedures have been used to separate impurities from neptunium[37,117] for spectrochemical determination. Mixed solvents have been used in the spectrographic analysis of the rare earths.[33,96]

Anion exchange resins are routinely employed at Argonne to concentrate trace elements for determination by the copper spark method of analysis.[36] The method of Brody, Faris, and Buchanan[12] for the analysis of uranium and plutonium has been modified by Huff[52] for the analysis of plutonium metal. This procedure, now in routine use at Argonne in the Fuels Technology Center analytical laboratory, is described below in detail. Some other procedures in which adsorption from a nitrate medium has been particularly effective[37] have also been outlined.

Plutonium

All operations were carried out in a series of enclosed chemical fume hoods equipped with glove ports. Samples other than the metal were converted to a hydrochloric acid solution; plutonium oxide was dissolved by the sealed tube technique of Wichers, Schlecht, and Gordon.[119] Reagent solutions were prepared and stored in polyethylene containers as was practical.

a) Materials

Pure 13M HCl: Prepared by passing hydrogen chloride gas into chilled, deionized water.

Pure 8M HNO_3: Prepared by distilling reagent-grade nitric acid from a quartz still.

Ion exchange resin: Analytical grade Dowex 1 x 8, 100-200 mesh (Bio-Rad Laboratories, Berkeley, California).

Ion exchange columns: 1.5-cm-diameter polyethylene tubing drawn to a tip. The columns were 20 cm long, and the reservoir sealed to the top was 5 cm in diameter and 5 cm high. Polypropylene wool was moderately packed at the tip to support the resin.

Beakers: Naglene PR polypropylene; Teflon.

Electrodes: $\frac{1}{4}$-in.-diameter commercial electrolytic hard copper rods cut to $1\frac{1}{4}$-in. lengths.

Apiezon solution: 1 g Apiezon-N grease dissolved in 1 liter of distilled low-boiling petroleum ether.

b) Procedure

A sample of plutonium metal, generally received as a solid piece, was cleaned (by filing and brushing) and weighed in a nitrogen atmosphere gloved box designed for this purpose. About 0.5 g was placed in a clean vial and then sealed in a plastic pouch for transport to the analytical hood train. After transfer to a plastic beaker, the sample was dissolved in about 0.5 ml of 8M nitric acid. The solution was heated gently under infrared heat lamps for at least 10 min to effect a complete oxidation to Pu(IV).

Ion exchange columns were prepared from resin washed alternately with water and dilute hydrochloric acid and added as a slurry to an approximate height of 15 cm. The resin bed was conditioned with 30 ml of 13M hydrochloric acid.

After cooling, the sample solution was poured onto the column and the plutonium allowed to adsorb as the chloride complex. The impurities were then eluted with 120 ml of 8M nitric acid. The wash solution was evaporated to dryness to remove the free nitric acid and the residue redissolved in 1 ml of 5M distilled hydrochloric acid. This solution was saved for the copper spark analysis. A column could be conditioned for reuse after stripping off the plutonium with 1M hydrochloric acid.

c) Spectrographic Determination

Copper electrodes were prepared as needed by machining the end and side surfaces on a lathe to a smooth, clean finish. A drop of Apiezon solution was dried on the end of each electrode. Then 0.1-ml aliquots of the sample solution were divided equally on electrode pairs and evaporated to dryness under infrared heat lamps. An additional pair of graphite electrodes were used for a determination of copper. Also, a 1 to 10 dilution of the sample solution was usually included, particularly for

those samples known to have a high impurity content, to provide subsequently a better evaluation of matrix effects on line intensities and to give a better estimation of major impurities.

The samples were sparked and the spectra photographed under standard conditions. By visual comparison with standard spectra the presence of almost 60 impurity elements could be detected with the limits given in Table II. Values could usually be estimated to within a factor of two. Standard photometric techniques[79] have been applied when a more precise determination was desired, cobalt or some other suitable element being added to serve as an internal standard. Silicon was determined on a separate sample portion by the method of Holt.[50]

Table II

LIMITS OF DETECTION[a] (ppm) FOR ION EXCHANGE-COPPER
SPARK METHOD (see Ref 36)

Element	In Th,Np (HNO₃)	In U,Np, Pu(HCl)	Add'l in Pu(HNO₃)	Element	In Th,Np (HNO₃)	In U,Np, Pu(HCl)	Add'l in Pu(HNO₃)
Am	0 5	0 5		Mn	0 05	0 05	
Ag	2		2	Mo	0 05		0 05
Al	0 5[b]	0 5[b]		Na	1[b]	1[b]	
B	0 5	0 5		Nd	0 3	0 3	
Ba	0 1	0 1		Ni	0 2	0 2	
Be	0 002	0 002		P	20	20	
Ca	1[b]	1[b]		Pb	0 5	0 5	
Cd	0 4		0 4	Pr	0 3	0 3	
Ce	0 3	0 3		Rb	0 3	0 3	
Co	0 2		0 2	Re	1		1
Cr	0 2	0 2		Rh	0 2		0 2
Cs	5	5		Ru	0 5		0 5
Cu	1	1		Sc	0 01	0 01	
Dy	0 2	0 2		Sm	0 5	0 5	
Er	0 1	0 1		Sr	0 002	0 002	
Eu	0 02	0 02		Tb	1	1	
Fe	1		1	Te	5		5
Ga	0 1		0 1	Th		0 5	
Gd	0 2	0 2		Ti	0 05	0 05	
Hf	0 5	0 5		Tl	1		1
Ho	0 2	0 2		Tm	0 2	0 2	
In	0 5			U	2		2
Ir	1		1	V	0 1	0 1	
K	0 5[b]	0 5[b]		Y	0 005	0 005	
La	0 02	0 02		Yb	0 01	0 01	
Li	0 001	0 001		Zn	2		2
Lu	0 01	0 01		Zr	0 1	0 1	
Mg	0 5[b]	0 5[b]					

[a]For a 0 1-ml aliquot of effluent from 1-g sample concentrated to 1 ml
[b]Limited by residual in blank

Thorium

A solution of a one-gram thorium sample in approximately 8M nitric acid was passed through a previously conditioned column containing about

20 g of strong-base anion exchange resin. After washing with about 50-70 ml of 8M nitric acid, the effluent was evaporated to dryness, taken up in hydro-chloric acid, and the impurities determined by the copper spark method. Limits of detection and elements determined are given in Table II. Densitometric procedures have been used for rare earth determinations.[34]

Analysis for silicon and boron was made with a separate sample portion by the carrier distillation method.[103]

Neptunium

A procedure similar to that described for thorium was applied to the analysis for neptunium. Samples of from 25 to 100 mg were reduced to Np(IV) by heating for at least an hour in an 8M nitric acid, 0.2M hydrazine solution. After adding a sample to a conditioned column the impurities were eluted with a similar mixture. Although the dark band of adsorbed neptunium was larger than expected, more than 99% was retained by the resin. For convenience, the limits of detection in Table II are given for a sample of one gram, although sample weights have usually not exceeded 0.1 g.

In some instances, particularly for a determination of thorium impurity, adsorption of neptunium from hydrochloric acid was desirable. Satisfactory separation of the nonadsorbed elements[72] were made in 8 to 10M hydrochloric acid by a procedure similar to that applied to the analysis of uranium.[12]

Rare Earths (Light)

The strong adsorption of lanthanum, cerium, praseodymium, and neodymium from a nitric acid-methanol medium permitted their ready separation from the heavier rare earths as well as from most other elements. For analysis of a light rare earth, a 0.5-g sample was dissolved in a few ml of strong nitric acid and methanol added to give a solution of about 90-95% alcohol. The sample was then allowed to adsorb slowly on a $\frac{3}{4}$-in.-ID resin column containing about 20 g conditioned Dowex 1 x 4. The weakly adsorbed impurities, including yttrium and the heavy rare earths, could then be eluted with a mixture of methanol (90-80%) and nitric acid (1-0.1M). Distribution coefficients varied with the acidity, and separation factors were influenced by the proportion of alcohol.[38] Recovery experiments[96] have demonstrated that the heavier rare earths, including gadolinium, could be quantitatively separated. In the most difficult case, the recovery of samarium impurity from neodymium samples was consistently low, ranging from 40 to 75% for samples of about 0.5 g. A more quantitative separation could be made by use of smaller samples, but with a corresponding loss in sensitivity. Similar detection limits relative to sample size as given in Table II could be achieved for the nonadsorbed metals.[69]

Separations could also be made within the light group of rare earths that were useful for extending the limits of detection. Sample weights of from 10 mg to 50 mg were adsorbed on smaller columns and chromatographically eluted with a 75-80% alcohol, dilute nitric acid mixture.

Rare Earths (Heavy)

For a general analysis of an yttrium or a heavy rare earth sample, about 100 mg were dissolved and adsorbed as described above from a 95% methanol-5% 7M to 10M nitric acid solution. Column sizes from about 3 to 5 g of resin have been used. The nonadsorbed impurities could readily be separated and were recovered for analytical determination in the effluent after adsorbing the sample. This was verified in experiments in which two nonadsorbed elements, gallium and cobalt, were added to samples of yttrium oxide and lutetium oxide, and then recovered from a column before an appreciable breakthrough of the matrix. In addition, the presence of several heavier rare earths could be detected in samples of samarium, europium, and gadolinium from an examination of the combined effluent fractions collected before the matrix broke through.

To detect the presence of any light rare earth or thorium impurity, the adsorbed sample was removed from the column with a 90% methanol-10% 0.5M nitric acid eluant and discarded. Then dilute nitric acid was added to the column to elute the remaining strongly adsorbed impurities. Determination was made by the copper spark method after evaporating the effluent. Similar detection limits relative to sample size as given in Table II could be achieved for thorium, lanthanum, cerium, praseodymium, and neodymium.

ACKNOWLEDGMENT

REFERENCES

1. Adar, S., Sjoblom, R. K., Barnes, R. F., Fields, P. R., Hulet, E. K., and Wilson, H. D., Ion-exchange Behaviour of the Transuranium Elements in $LiNO_3$ Solutions, J. Inorg. Nucl. Chem. 25, 447 (1963).

2. Aikin, A. M., Ion Exchange Recovers Plutonium from Irradiated Fuels, Chem. Eng. Prog. 53, 82F (1957).

3. Akaishi, J., The Preparation of Carrier-free $^{234}Th(UX^1)$ by Anion Exchange from Nitric Acid-Alcohol Mixed Solution of Uranyl Nitrate, Bull. Chem. Soc. Japan 34, 1198 (1961).

4. Akaishi, J., Adsorption of Thorium on the Anion Exchange Resin in Nitric Acid-Alcohol Mixed Solution in the Presence of Phosphate, Nippon Genshiryoku Gakkaishi 4, 154 (1962); Nucl. Sci. Abs. 16, 17606 (1962).

5. Allison, G. M., The Spectrophotometric Determination of Plutonium as Pu(III), Atomic Energy of Canada, Chalk River, Ontario, PDB-57 (1952); reissued as AECL-1371 (1961).

6. Allison, G. M., and Hart, R. G., The Separation of Plutonium by Anion Exchange in 10M Nitric Acid Solution, ibid, PDB-86, 87 (1953); reissued as AECL-1372 (1961).

7. Antal, P., Korkisch, J., and Hecht, F., Distribution of Thorium, Zirconium and Titanium in Inorganic-acid Solutions Containing Alcohol, and the Strongly Basic Anion Exchanger Dowex-1, J. Inorg. Nucl. Chem. 14, 251 (1960).

8. Atkins, D. H. F., and Jenkins, E. N., The Chemical Analysis of Binary Alloys of Plutonium with Aluminum, Iron or Uranium, AERE-C/R-2161 (1960).

9. Aubouin, G., and Laverlochere, J., Separation Par Resines Echangeuses D'Ions Appliquees a L'Analyse Par Activation (Ion-exchange Resin Separation Applied to Activation Analysis) CEA-2359 (1963) (in French).

10. Atteberry, R. W., and Boyd, G. E., Separation of Seventh Group Anions by Ion-exchange Chromatography, J. Am. Chem. Soc. 72, 4805 (1950).

11. A Method of Concentrating Compounds of Uranium, British Patent 904,569 (1962); Nucl. Sci. Abs. 16, 30484 (1962).

12. Brody, J. K., Faris, J. P., and Buchanan, R. F., Ion Exchange Spectrographic Method for Determination of Impurities in Uranium and Plutonium, Anal. Chem. 30, 1909 (1958).

13. Buchanan, R. F., and Faris, J. P., "Adsorption of the Elements from Nitric Acid by Anion Exchange," Radioisotopes in the Physical Sciences and Industry, Vol. 2, p. 361, International Atomic Energy Agency, Vienna (1962).

14. Buchanan, R. F., Faris, J. P., Orlandini, K. A., and Hughes, J. P., Analytical Application of the Nitric Acid Anion Exchange System to Plutonium-Fissium and Plutonium-Binary Alloys used in Metallurgical Studies, TID-7560, p. 179 (1958).

15. Bunney, L. R., Ballou, N. E., Pascual, J., and Foti, S., Anion Exchange Behavior of Several Metal Ions in Hydrochloric, Nitric, and Sulfuric Acid Solutions, Anal. Chem. 31, 324 (1959).

16. Burney, G. A., Anion Exchange of Neptunium in Nitrate Solution, DP-531 (1960).

17. Burney, G. A., Separation of Neptunium and Plutonium by Anion Exchange, DP-689 (1962).

18. Campbell, W. M., Canadian Fuel Reprocessing, Nucleonics 14, 92 (Sept. 1956).

19. Caracciolo, V. P., Anion Exchange in a Large-scale Agitated Bed, DP-624 (1961).

20. Carroll, J. L., Absorption of Thorium on an Anion Exchange Resin, HW-70536 (1961).

21. Carswell, D. J., Separation of Thorium and Uranium Nitrates by Anion Exchange, J. Inorg. Nucl. Chem. 3, 384 (1957).

22. Chen, Y., Anion-Exchange Behavior of Neptunium Ions in Nitric Acid System, Nippon Genshiryoku Gakkaishi 4, 665 (1962). Nucl. Sci. Abs. 17, 2992 (1963).

23. Choppin, G. R., and Sikkeland, T., NAS-NS-3004 (see Ref. 55).

24. Danon, J., Adsorption of Thorium by Anion-exchange Resins from Nitric Acid Media, J. Am. Chem. Soc. 78, 5953 (1956).

25. Danon, J., Separation of Thorium and Rare-earth Elements in Nitric Acid Media by Anion Exchange, J. Inorg. Nucl. Chem. 5, 237 (1958).

26. Danon, J., Anion-exchange Studies with Actinium and Lanthanides in Nitrate Solutions, J. Inorg. Nucl. Chem. 7, 422 (1958).

27. Danon, J., and Zamith, A. A. L., Ion Exchange and Solvent-extraction Studies with Polonium, J. Phys. Chem. 61, 431 (1957).

28. DeGeiso, R. C., Rieman, W., and Lindenbaum, S., Analysis of Halide Mixtures by Ion-exchange Chromatography, Anal. Chem. 26, 1840 (1954).

29. Durham, R. W., and Mills, R., Adsorption of Plutonium by Anion Resins, Atomic Energy of Canada, Ltd., Chalk River, Ontario, CEI-62 (1953); reprinted 1961.

24

30. Edge, R. A., The Anion Exchange Behaviour of Yttrium, Neodymium and Lanthanum in Dilute Nitric Acid Solutions Containing Ethanol, J. Chromatog. 5, 526 (1961).

31. Edge, R. A., The Adsorption of Thorium on a Strong Base Anion Exchange Resin from Nitrate Media, J. Chromatog. 6, 276 (1961).

32. Edge, R. A., A Combined Anion Exchange-Solvent Extraction Procedure for Separating Trace Amounts of Eu, Gd, Dy, Sm and Er from Thorium Tetrafluoride, Anal. Chim. Acta 28, 278 (1963).

33. Edge, R. A., The Removal of Ce, Nd, Pr and La from Er, Dy, Gd, Eu and Sm by Anion Exchange, Anal. Chim. Acta 29, 321 (1963).

34. Faris, J. P., Spectrographic Determination of Scandium, Yttrium, and the Rare Earths in Thorium, Applied Spectroscopy 12, 157 (1958).

35. Faris, J. P., "Ion Exchange-Spectroscopic Procedures, Trace Element Analysis,' The Encyclopedia of Spectroscopy, G. L. Clark, Ed., Reinhold, New York (1960) p. 204.

36. Faris, J. P., Applications of the Copper Spark Method for Spectrographic Analysis, 6th Conf. on Anal. Chem. in Nuclear Reactor Technology, Gatlinburg, Tenn., TID-7655, p. 193 (1962).

37. Faris, J. P., Buchanan, R. F., Anion Exchange Characteristics of the Elements in Nitric Acid Medium, 4th Conf. on Anal. Chem. in Nuclear Reactor Technology, Gatlinburg, Tenn., TID-7606, p. 185 (1960).

38. Faris, J. P., and Warton, J. W., Anion Exchange Resin Separation of the Rare Earths, Yttrium, and Scandium in Nitric Acid-Methanol Mixtures, Anal. Chem. 34, 1077 (1962).

39. Fernandez, L. P., A Method for Determining the Diffusion Coefficient of an Alpha Emitter in a Solid, DP-727 (1962).

40. Foreman, J. K., McGowan, I. R., and Smith, T. D., Some Aspects of the Anion-exchange Behavior of Uranyl Nitrate in the Presence of Other Inorganic Nitrates, J. Chem. Soc., 738 (1959).

41. Foster, E., and Phillips, G., The Chemical Analysis of Ternary Alloys of Plutonium with Uranium and Molybdenum, AERE-R-3147 (1960).

42. Fred, M., Nachtrieb, N. H., and Tomkins, F. S., Spectrochemical Analysis by the Copper Spark Method, J. Opt. Soc. Am. 37, 279 (1947).

43. Fritz, J. S., and Garralda, B. B., Anion Exchange Separation of Thorium Using Nitric Acid, Anal. Chem. 34, 1387 (1962).

44. Fritz, J. S., and Waki, H., Anion Exchange Separation of Magnesium and Calcium with Alcohol-Nitric Acid, Anal. Chem. 35, 1079 (1963).

45. Fritz, J. S., Waki, H., and Garralda, B. B., Anion Exchange Separation of Calcium and Strontium, Anal. Chem. 36, 900 (1964).

46. Hardy, C. J., "Ion-exchange Data for the Actinide Elements in Nitric and Hydrochloric Acid Solutions," Progress in Nuclear Energy, Series III, Vol. 2, p. 357; Bruce, F. R., Fletcher, J. M., and Hyman, H. H., Eds., Pergamon, New York (1958).

47. Hardy, C. J., Scargill, D., and Fletcher, J. M., Studies on Protactinium (V) in Nitric Acid Solutions, J. Inorg. Nucl. Chem. 7, 257 (1958).

48. Higgins, I. R., Recovery of Uranium from Calcium Nitrate, Ind. and Eng. Chem. 53, 999 (1961).

49. Hines, J., Wahlgren, M. A., and Lawless, F., Ion-exchange Separation of Actinides with Nitric Acid-Methanol and with EDTA, 6th Conf. on Anal. Chem. in Nuclear Reactor Technology, Gatlinburg, Tenn., TID-7655, p. 247 (1962).

50. Holt, B. D., Determination of Silicon by Distillation-Colorimetric Method, Anal. Chem. 32, 124 (1960).

51. Horne, R. A., Holm, R. H., and Meyers, M. D., The Adsorption of Zinc (II) on Anion-exchange Resins. III., J. Phys. Chem. 61, 1661 (1957).

52. Huff, E. A., Anion Exchange-Copper Spark Method for the Analysis of Impurities in Plutonium Metal, ANL, unpublished (1963).

53. Huffman, E. H., Oswald, R. L., and Williams, L. A., Anion-exchange Separation of Molybdenum and Technetium and of Tungsten and Rhenium, J. Inorg. Nucl. Chem. 3, 49 (1956).

54. Hyde, E. K., The Radiochemistry of Francium, NAS-NS-3003 (1960). Available from the Office of Technical Services, Dept. of Commerce, Washington, D. C.

55. Hyde, E. K., The Radiochemistry of Thorium, NAS-NS-3004 (1960). Available from the Office of Technical Services, Dept. of Commerce, Washington, D. C.

56. Ichikawa, F., A Study on Anion Exchange and Amine Extraction of Rare Earth Elements in Nitric Acid, Bull. Chem. Soc. Japan 34, 183 (1961).

57. Ichikawa, F., Uruno, S., and Imai, H., Distribution of Various Elements between Nitric Acid and Anion Exchange Resin, Bull. Chem. Soc. Japan 34, 95 (1961).

58. James, D. B., The Processing of Plutonium by Ion Exchange - I. The Concentration Dependence of Distribution Coefficients on Dowex 1 x 4 from 7M Nitric Acid, J. Inorg. Nucl. Chem. 25, 711 (1963).

59. James, D. B., _The Synergistic Effect of Thorium on the Distribution Coefficients of Several Elements with Anion-exchange Resin from 7M Nitric Acid_, LA-2836 (1963).

60. Jones, R. J., Ed., _Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle_, p. 410-419, TID-7029 (1963).

61. Kazantsev, E. I., _Chemical Resistance of Anion Exchangers in Nitric Acid Solutions_, J. Applied Chem. USSR, English Trans., Consultants Bureau, N. Y. 35, 2463 (1962).

62. Kazantsev, E. I., Kondratov, P. I., Kalinichenko, B. S., and Gel'man, A. D., _Elution of Neptunium from the Anionite AM_, Soviet Radiochemistry, English Trans., Consultants Bureau, N. Y. 4, 70 (1962).

63. Ko, R., _The Use of Anion Exchange in the Spectrographic Determination of Impurities in Plutonium_, HW-57873 (1958).

64. Ko, R., _Determination of Zirconium in Plutonium by Ion Exchange and Spectrography_, Applied Spectroscopy 13, 10 (1959).

65. Korkisch, J., Antal, P., and Hecht, F., _Distribution of Uranium in Inorganic-acid Solutions Containing Alcohol, and Strongly Basic Anion Exchanger Dowex-1_, J. Inorg. Nucl. Chem. 14, 247 (1960).

66. Korkisch, J., and Arrhenius, G., _Separation of Uranium, Thorium, and the Rare Earth Elements by Anion Exchange_, Anal. Chem. 36, 850 (1964).

67. Korkisch, J., Hazan, I., and Arrhenius, G., _Adsorption Behaviour of the Rare Earths and Some Other Elements on a Strong-base Anion-exchange Resin from Nitric Acid-Alcohol Media_, Talanta 10, 865 (1963).

68. Korkisch, J., and Janauer, G. E., _Adsorption Behaviour of Uranium and Thorium on Strong-base Anion-exchange Resins from Mineral Acid-Alcohol Media_, Talanta 9, 957 (1962).

69. Korkisch, J., and Tera, F., _Separation of Thorium by Anion Exchange_, Anal. Chem. 33, 1264 (1961).

70. Korkisch, J., and Tera, F., _The Distribution of Hexavalent Uranium between Alcohol-Nitric Acid Solutions and the Strongly Basic Anion Exchanger Dowex-1_, J. Chromatog. 7, 564 (1962).

71. Korkisch, J., Zaky, M. R., and Hecht, F., _Schnellbestimmung von Mikrogrammengen Uran in Mineralen_, Mikrochem. Acta, p. 485 (1957).

72. Kraus, K. A., and Nelson, F., "Metal Separations by Anion Exchange," _Symposium on Ion Exchange and Chromatography in Analytical Chemistry_, ASTM Spec. Tech. Pub. No. 195, p. 27 (1956).

73. Kressin, I. K., and Waterbury, G. R., _The Quantitative Separation of Plutonium from Various Ions by Anion Exchange_, Anal. Chem. 34, 1598 (1962).

74. Kriss, E. E., and Sheka, Z. A., Complex Compounds of Lanthanide Nitrates with Nitric Acid, Soviet Radiochemistry 4, 279 (1962). Trans. from Radiokhimiya 4, 312 (1962).

75. Marcus, Y., Anion Exchange of Lanthanides and Actinides in Inorganic Media, Israel Atomic Energy Comm. Rept. R-20 (1959).

76. Marcus, Y., and Abrahamer, I., Anion Exchange of Metal Complexes - VII; The Lanthanides-Nitrate System, J. Inorg. Nucl. Chem. 22, 141 (1961); Israel Atomic Energy Comm. Rept. IA-608 (1961).

77. Marcus, Y., Givon, M., and Choppin, G. R., Anion Exchange of Metal Complexes - XIII; The Actinide(III)-Nitrate System, J. Inorg. Nucl. Chem. 25, 1457 (1963).

78. Marcus, Y., and Nelson, F., Anion-exchange Studies. XXV. The Rare Earths in Nitrate Solutions, J. Phys. Chem. 63, 77 (1959).

79. Methods for Emission Spectrographic Analysis, Third ed., ASTM, Philadelphia, Pa., 1960.

80. Minami, E., Honda, M., and Sasaki, Y., Ion Exchange Separation of Fission Products, Bull. Chem. Soc. Japan 31, 372 (1958).

81. Nairn, J. S., Collins, D. A., "The Recovery of Neptunium-237," Progress in Nuclear Energy, Series III, Vol. 2, p. 518, Bruce, F. R., Fletcher, J. M., and Hyman, H. H., Eds., Pergamon, New York (1958).

82. Nairn, J. S., Collins, D. A., McKay, H. A. C., and Maddock, A. G., The Extraction of Actinide Elements from Wastes, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 17, 216, United Nations, N. Y. (1958).

83. Nelson, F., and Kraus, K. A., Anion Exchange Studies. XI. Lead(II) and Bismuth(III) in Chloride and Nitrate Solutions, J. Am. Chem. Soc. 76, 5916 (1954).

84. Norris, J. A., "Spectrographic Determination of Trace Elements in Metals," Symposium on Spectrochemical Analysis for Trace Elements, ASTM Spec. Tech. Pub. No. 221, p. 23 (1957).

85. Ockenden, H. M., and Foreman, J. K., The Separation of Uranium from Large Amounts of Iron and Aluminum by Anion Exchange in Nitrate Media, Analyst 82, 592 (1957).

86. Phillips, G., and Jenkins, E. N., The Removal of Plutonium before the Analysis of Mixed Fission Products, J. Inorg. Nucl. Chem. 4, 220 (1957).

87. Pietri, C. E., and Baglio, J. A., Ion Exchange Separation and Colorimetric Determination of Microgram Amounts of Iron in Plutonium, NBL-159, 73 (1960).

88. Prevot, I., Corpel, J., and Regnaut, P., Final Treatment of Plutonium at the End of the Fontenay-aux-Roses Pilot Plant, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva 17, 96, United Nations, N. Y. (1958).

89. Prevot, I., and Regnaut, P., "The Purification and Concentration of Solutions of Plutonium by Ion Exchange, Progress in Nuclear Energy, Series III, Vol. 2, p. 377, Bruce, F. R., Fletcher, J. M., and Hyman, H. H., Eds., Pergamon, N. Y. (1958).

90. Prout, W. E., and Fernandez, L. P., Recovery of Neptunium from Purex Waste by an Agitated Bed of Anion Exchange Resin, DP-453 (1960).

91. Rieman, W., and Lindenbaum, S., Analysis of Mixtures of Chloride and Bromide by Ion-exchange Chromatography, Anal. Chem. 24, 1199 (1952).

92. Roberts, F. P., An Analytical Method for Neptunium-237 Using Anion Exchange, HW-59032 (1959).

93. Roberts, F. P., Determination of Small Amounts of Cerium Activity in Strontium-90 Using Anion Exchange, HW-69737 (1961).

94. Roberts, F. P., Separation of Cerium by Anion Exchange, HW-SA-3082 (1963).

95. Roberts, F. P., and Brauer, F. P., Sequential Separation of Some Actinide Elements by Anion Exchange, HW-60552 (1959).

96. Rush, T. A., Analysis of Lanthanum, Cerium, Praesodymium and Neodymium for Trace Amounts of Heavier Rare Earths and Other Impurities, ANL, unpublished (1963).

97. Ryan, J. L., Concentration and Final Purification of Neptunium by Anion Exchange, HW-59193 REV (1959).

98. Ryan, J. L., Species Involved in the Anion-exchange Absorption of Quadrivalent Actinide Nitrates, J. Phys. Chem. 64, 1375 (1960).

99. Ryan, J. L., and Wheelwright, E. J., Application of Anion Exchange to the Reprocessing of Plutonium, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 17, 137, United Nations, N. Y. (1958).

100. Ryan, J. L., and Wheelwright, E. J., Recovery and Purification of Plutonium by Anion Exchange, Ind. Eng. Chem. 51, 60 (1959).

101. Ryan, J. L., and Wheelwright, E. J., The Recovery, Purification, and Concentration of Plutonium by Anion Exchange in Nitric Acid, HW-55893 (1959).

102. Schonfeld, T., Wald, M., and Brund, M., Radiochemical Separations on Anion Exchange Columns with Employment of Strong Complexing Agents, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 28, 48, United Nations, N. Y. (1958).

103. Scribner, B. F., Mullin, H. R., Carrier-Distillation Method for Spectrographic Analysis and Its Application to the Analysis of Uranium-base Materials, J. Research Nat. Bur. Stds., 37, 379 (1946).

104. Starik, I. E., and Amplelogova, N. I., Microquantities of Radioelements in Solutions. XV. Polonium Sorption by Ion Exchange Resins, Radiokhimiya 3, 37 (1961) Nucl. Sci. Abs. Vol. 15, 16954 (1961).

105. Starik, I. Y., Sheidina, L. D., and Il'menkova, L. I., Investigation of the State of Protactinium in Aqueous Solutions-IV. The Ion-exchange Method, Radiochemistry 3, 45 (1962). Trans. from Radiokhimiya 3, 150 (1961).

106. Tera, F., Korkisch, J., and Hecht, F., The Distribution of Thorium between Alcohol-Nitric Acid Solutions and the Strongly-basic Anion Exchanger Dowex-1. Separation of Thorium from Uranium, J. Inorg. Nucl. Chem. 16, 345 (1961).

107. Tober, F. W., Concentration and Purification of Uranium, Plutonium, and Neptunium by Ion Exchange in Nuclearly Safe Equipment, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 17, 574, United Nations, N. Y. (1958).

108. Tompkins, E. R., Laboratory Applications of Ion Exchange Techniques, J. Chem. Educ. 26, 32, 92 (1949).

109. Tuck, D. G., and Welch, G. A., The Ion Exchange Reactions of Quadrivalent Plutonium in Diethylene Glycol Dibutyl Ether, J. Inorg. Nucl. Chem. 9, 302 (1959).

110. Urubay, S., Korkisch, J., and Janauer, G. E., Anion Exchange of Uranium, Thorium, Iron and Aluminum in Mineral Acid-Ether Solutions, Talanta 10, 673 (1963).

111. Vdovenko, V. M., Lipovskii, A. A., and Kuzina, M. G., The Absorption of Uranyl Nitrate from Organic Solvents by Means of Anion-exchange Resins, Radiochemistry 3, 119 (1962). Trans. from Radiokhimiya 3, 365 (1961).

112. Vita, O. A., Trivisonno, C. F., and Phipps, C. W., Analysis of Uranium Solutions Using Anion Exchange in Nitrate Media, GAT-283 (1959).

113. Wenzel, A., and Pietri, C. E., Spectrographic Determination of Impurities in Plutonium, NBL-170, p. 21 (1961).

114. Wenzel, A. W., and Pietri, C. E., Spectrographic Determination of Trace Impurities in High-purity Plutonium, NBL-177, p. 35 (1962).

115. Wenzel, A. W., and Pietri, C. E., Anion-exchange Separation and Spectrographic Determination of Impurities in Plutonium, NBL-188, p. 51 (1962).

116. Wenzel, A. W., and Pietri, C. E., Emission Spectrographic Estimation of Americium in Plutonium, NBL-204, p. 65 (1963).

117. Wheat, J. A., Spectrochemical Determination of Impurities in Neptunium, Applied Spectroscopy 16, 108 (1962).

118. Wheelwright, E. J., Anion Exchange Recovery of Plutonium from the Hanford 234-5 Building Button Line - Task I Oxalate Filtrate, HW-75309 (1962).

119. Wichers, E., Schlecht, W. G., and Gordon, C. L., Preparing Refractory Oxides, Silicates, and Ceramic Materials for Analysis, by Heating with Acids in Sealed Tubes at Elevated Temperatures, J. Research Natl. Bur. Stds. 33, 363, 451 (1944).

120. Winchester, R. S., and Maraman, W. J., Aqueous Decontamination of Plutonium from Fission Product Elements, Second Int. Conf. on Peaceful Uses of Atomic Energy, Geneva, 17, 168, United Nations, N. Y., 1958.

121. Wish, L., Quantitative Ion-exchange Separations for Sequential Radiochemical Analysis, USNRDL-TR-185 (1957).

122. Wish, L., and Rowell, M., Sequential Analysis of Tracer Amounts of Np, U, and Pu in Fission-Product Mixtures by Anion Exchange, USNRDL-TR-117 (1956).