Distribution of Various Elements between Nitric Acid and Anion Exchange Resin

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Previous studies showed that successful separation of plutonium[1] or neptunium[2,3] from fission products was carried out using anion exchange techniques in nitric acid solution. In these cases, plutonium or neptunium(IV) was strongly adsorbed on anion exchange resin from 7.5 M nitric acid while the bulk of fission products were eluted. The anion exchange of thorium[4], lead and bismuth[5] in nitric acid solution has been studied by other researchers. Authors previously reported the anion exchange behaviors of neptunium[3], thorium, uranium, protactinium[6] and rare earth elements[7] in nitric acid.

In the present paper, the distribution of some metallic elements between anion exchange resin and nitric acid is studied and results are shown in a periodic table as is shown in Kraus and Nelson's work[8].

Experimental

Resin. — A strongly basic anion exchange resin Dowex 1, X8 100~200 mesh, was used as an exchanger. The resin was treated with 10% sodium hydroxide solution, washed with water and then converted into nitrate form with nitric acid. The used resin was dried in a desiccator with silica gel at room temperature.

Half a gram of dried resin was used for each experiment.

Radioactive Tracers. — For the measurement of distribution coefficient, the radioactive isotopes were used as nitric acid solution of desirable concentration. Some of these isotopes were imported from U. S. A. or the United Kingdom. The others were prepared by neutron irradiation of each element in J. R. R.-1 Reactor. The radiochemical purity of these isotopes was determined by γ-ray spectrum, γ-ray decay or absorption curve of β-ray with aluminum plates. The used nuclides and the method of their preparation are shown in Table I.

Nitric Acid.—Reagent grade nitric acid was diluted with distilled water to a desirable concentration varying from 0.1 to 14.5 M.

Determination of Distribution Coefficient (K_d). —Half a gram of the dried resin was immersed in 5 ml. of the nitric acid solution of the given element for 24 hr. at room temperature. The solution was filtered and the radioactivity of 1 ml. of the filtrate was compared with that of the reference solution which contains no resin. K_d was calculated by the following equation,

$$K_d = \frac{C_1}{C_2}$$

where C_1 means the adsorbed radioactivity on 1 g. of resin and C_2 means the radioactivity of 1 ml. of the filtrate.

Experimental Error.—Polyethylene beakers were used for equilibrium experiments in order to avoid the adsorption of radioactive element on a glass wall. In all cases, a slight increase in the concentration of radioactive element in the supernatant solution occurred. This would be due to the absorption of swelling water by dried resin. But this effect was so small that the K_d value was not corrected.

After the resin was treated with concentrated nitric acid for 24 hr., the color of resin changed from light yellow to dark yellow, but it was found from the results of titration that the decrease of exchange capacity was very small.

Results and Disscusion

Results are shown in Fig. 1. K_d values were plotted against the concentration of nitric acid both in logarithmic scale. The oxidation state of each element is considered to be the most stable one in nitric acid and is noted in the figure. Based on the periodic table, the feature of K_d curves for each group is described as follows.

Alkali Metals. — The adsorption of alkali metals did not occur practically from any concentration of nitric acid.

Because of the absence of available radioisotopes, lithium and francium were not examined, but it was suggested that the resin did not adsorb these elements from nitric acid. K_d value increased slowly with increasing concentration of nitric acid for sodium, potassium, rubidium and cesium and decreased again at a concentration above 8~10 M nitric acid. This trend is one of the typical features of K_d curve.

Beryllium, Magnesium and Alkaline Earths. —Beryllium and magnesium were not examined

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[1] C. Philips and E. N. Jenkins, *J. Inorg. Nucl. Chem.*, **4**, 220 (1957).

[2] J. S. Nairn et al., A/Conf. 15/p/1458 (1958).

[3] F. Ichikawa, This Bulletin, **31**, 778 (1958).

[4] J. Danon, *J. Am. Chem. Soc.*, **78**, 5935 (1956).

[5] F. Nelson and K. A. Kraus, ibid., **76**, 5916 (1954).

[6] F. Ichikawa and S. Uruno, This Bulletin, 33, 569 (1960).

[7] F. Ichikawa, ibid., **34**, 183 (1961).

[8] K. A. Kraus and F. Nelson, A/Conf. 8/p/837.

TABLE I. THE PREPARATION AND COUNTING METHOD OF USED RADIOISOTOPES

Atomic number	Nuclide	Half life	Preparation	Counting method
11	^{24}Na	15.0 h.	Irradiation of Na_2CO_3	γ
19	^{42}K	12.7 h.	Irradiation of K_2CO_3	γ
20	^{45}Ca	164 d.	Imported	β
21	^{46}Sc	85 d.	Irradiation of Sc_2O_3	γ
24	^{51}Cr	27.8 d.	Imported	γ
25	^{56}Mn	2.58 h.	Irradiation of MnO_2	γ
26	^{55}Fe+^{59}Fe	30 y., 45.1 d.	Imported	γ
27	^{60}Co	5.2 y.	Imported	γ
28	^{63}Ni	85 y.	Imported	γ
29	^{64}Cu	12.8 h.	Irradiation of Cu metal	γ
30	^{65}Zn	245 d.	Imported	γ
31	^{72}Ga	14.2 h.	Irradiation of Ga_2O_3	γ
32	^{71}Ge	11.4 d.	Irradiation of Ge metal	γ
34	^{75}Se	119.9 d.	Imported	γ
37	^{86}Rb	19 d.	Imported	γ
38	^{90}Sr	28 y.	Imported	β
39	^{90}Y	64 h.	Milking from ^{90}Sr	β
41	^{94}Nb	35 d.	Separation from ^{95}Zr	γ
42	^{99}Mo	67 h.	Irradiation of molybdic acid	γ
43	^{99m}Tc	6.04 h.	Separation from irradiated $HMoO_4$	γ
44	^{106}Ru+^{106}Rh	1.0 y., 30 s.	Imported	γ of ^{106}Rh
46	^{109}Pd	13.6 h.	Irradiation of Pd metal	γ
47	^{110m}Ag	233 d.	Irradiation of Ag metal	γ
48	^{115}Cd	53 d.	Irradiation of Cd metal	γ
49	^{114m}In	49 d.	Imported	γ
50	^{113}Sn	112 d.	Irradiatton of Sn meial	γ
51	^{124}Sb	60 d.	Imported	γ
55	^{137}Cs	30 y.	Imported	γ
56	^{140}Ba	12.8 d.	Imported	γ
57	^{140}La	40.2 d.	Milking from ^{140}Ba	γ
58	^{141}Ce	33 d.	Irradiation of Ce_2O_3	γ
59	^{143}Pr	13.7 d.	Irradiation of Pr_2O_3	γ
60	^{147}Nd	11.3 d.	Irradiation of Nd_2O_3	γ at 0.092 MeV.
61	^{147}Pm	2.6 y.	Imported	β
62	^{153}Sm	47 h.	Irradiation of Sm_2O_3	γ
63	^{152}Eu	13 y.	Irradiation of Eu_2O_3	γ
64	^{159}Gd	18.0 h.	Irradiation of Gd_2O_3	γ at 0.364 MeV.
65	^{160}Tb	73 d.	Irradiation of Tb_2O_3	γ
66	^{165}Dy	2.3 h.	Irradiation of Dy_2O_3	γ
67	^{166}Ho	27.3 h.	Irradiation of Ho_2O_3	γ
68	^{165}Er	10.0 h.	Irradiation of Er_2O_3	γ
69	^{170}Tm	129 d.	Irradiation of Tm_2O_3	γ
70	^{175}Yb	4.2 d.	Irradiation of Yb_2O_3	γ at 0.394 MeV.
71	^{176}Lu+^{177}Lu	6.8 d.	Irradiation of Lu_2O_3	γ
75	^{186}Re	3.87 d.	Irradiation of Re metal	γ
76	^{191}Os	15 d.	Imported	γ
77	^{192}Ir+^{194}Ir	74.4 d., 19 h.	Irradiation of Ir metal	γ
78	^{193m}Pt+^{197}Pt	3.5 d., 18 h.	Irradiation of Pt metal	γ
79	^{198}Au	2.72 d.	Irradiation of Au metal	γ
80	^{203}Hg	4.54 d.	Imported	γ
81	^{204}Tl	4.0 y.	Imported	β
82	^{212}Pb	10.6 h.	Separation from imported ^{228}Th	γ
84	^{210}Po	138.4 d.	Separation from irradiated Bi	α
90	^{234}Th	24.1 d.	Separation from natural U	γ
91	^{233}Pa	27.4 d.	Separation from irradiated Th	γ
92	nat. U			Colorimetric
93	^{239}Np	2.33 d.	Separation from irradiated U	γ

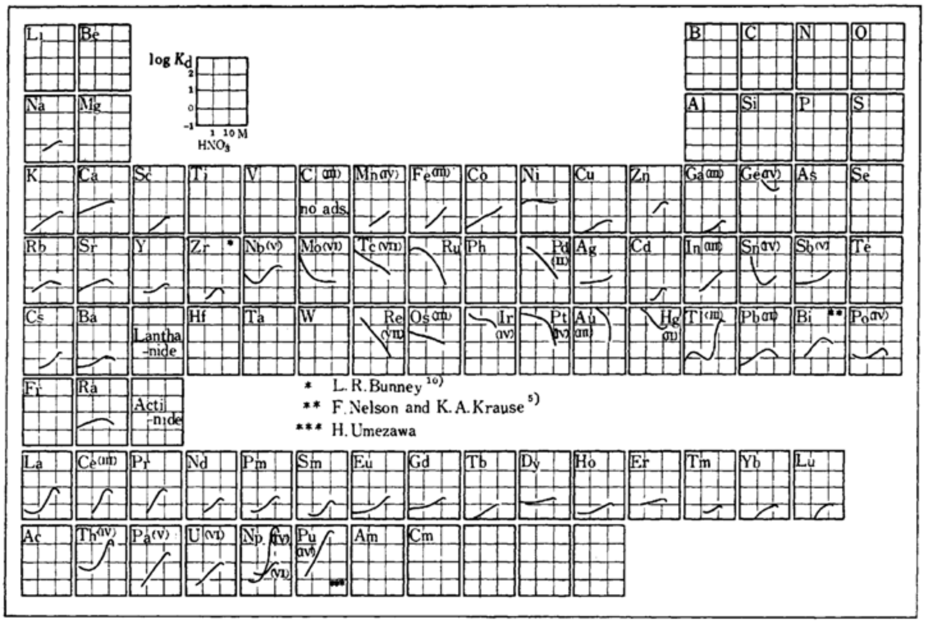

Fig. 1. Distribution coefficients between anion exchange resin and nitric acid.

for the same reason as lithium. Alkaline earths were not adsorbed practically at lower concentration of nitric acid, but they were slightly adsorbed at a concentration above 4 M nitric acid.

Scandium, Yttrium and Lanthanide Elements. —In every case, there was a maximum K_d value at 8 M nitric acid. Scandium and yttrium were scarcely adsorbed at all. As was shown in the previous paper⁽⁷⁾, there is an interesting trend in the K_d values of lanthanide elements. The K_d values of lanthanide elements at 8 M nitric acid decrease with increasing atomic number.

Actinide Elements.—Of the actinide elements thorium(IV), protactinium(V), uranium(VI), neptunium(IV) and neptunium(VI) were examined. The data on plutonium(IV), which was reported by Umezawa⁽⁹⁾, is also shown. As in the case of neptunium, the high adsorbability in tetravalence state was already reported, and was applied to the separation of neptunium from fission products and uranium. Thorium and protactinium were strongly adsorbed on the resin from 8 M nitric acid solution. Uranium was slightly adsorbed under the same condition. From these facts this method may be applied to the separation of uranium-233 from irradiated thorium.

Zirconium and Niobium. — The data of zirconium were cited from the report⁽¹⁰⁾ of Bunney et al., who used Dowex 2 as an anion exchanger. Both zirconium and niobium were slightly adsorbed on the resin and therefore, a long column will be needed for the separation.

Molybdenum, Technetium and Rhenium. — These elements showed similar K_d curves. From a very dilute nitric acid, these elements were adsorbed strongly on the resin and the adsorbability decreased with increasing concentration of nitric acid. This is probably due to the decrease of the dissociation of these oxy acids. For instance, rhenium is present in water as ReO_4^- and is adsorbed on the resin as an anion, but when the acidity of nitric acid increases the dissociation of $HReO_4$ becomes small, resulting in desorption from anion exchanger.

Chromium(III), Manganese, Iron(III), Cobalt and Nickel.—Only nickel was slightly adsorbed and the others were not practically adsorbed. If a more detailed discussion is permitted, K_d values of manganese and iron(III) increase with a slope of 1 and this means the formation of anionic species which has one negative charge.

Ruthenium, Paradium, Osmium, Iridium, Platinum and Gold. — These elements were strongly adsorbed from nitiric acid of lower concentration and desorbed from nitric acid of higher concentration. The metals of these elements were dissolved in aqua regia, evaporated to dryness and redissolved in nitric acid. Therefore it is likely that these elements exist as chloro metallic acid in nitric acid, and that the anionic chloro complexes are adsorbed on

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9) H. Umezawa, *J. Atomic Energy Soc. Japan*, **2**, 478 (1960).

10) L. R. Bunney et al., *Anal. Chem.*, **31**, 325 (1959).

the resin from nitric acid of low concentration.

Silver, Copper, Zinc, Cadmium and Mercury. — Copper and cadmium were not adsorbed. Zinc and silver were slightly adsorbed at higher concentration of nitric acid. Mercury was strongly adsorbed from dilute nitric acid and K_d value decreases at concentrated nitric acid.

Gallium, Indium, Germanium and Tin(IV).— Gallium and indium were not adsorbed from nitric acid of any concentration. Germanium and tin(IV) were strongly adsorbed in dilute nitric acid and the K_d value showed a negative slope with increasing concentration of nitric acid.

Thallium, Lead, Bismuth and Polonium. — These elements exist as daughter products of natural radioactive decay series. The data on bismuth is cited from Kraus-Nelson's report[5]. Lead and polonium were slightly adsorbed on the resin from 8 M nitric acid. Thallium was strongly adsorbed at a concentration above 10 M nitric acid, but it was scarcely adsorbed at lower concentration of nitric acid.

Summary

Distribution coefficient of some metallic elements between nitric acid and anion exchange resin were measured. From the results described above, the fundamental data on the separation of each element in nitric acid were obtained.

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