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The Discrimination of the Oxidation States of Neptunium in Sodium Hydroxide Solutions by Means of Chromatography on Alumina

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A method of discriminating the oxidation states of Np in a NaOH solution by means of chromatography on alumina is proposed. In a NaOH solution of 0.5—1.7 M(1 M = 1 mol dm^{-3}), the separation of Np(VI) from Np(VII) can be made effectively by means of chromatography on alumina. Only a little Np(VI) is adsorbed on alumina the Np(VII) adsorbed to some extent, and the Np(V), strongly, under the same conditions. By applying this chromatographic method, the method of preparing Np(VI) and Np(VII) of a tracer quantity in 1 M NaOH is established.

It has been found by polarography that the possible oxidation states of Np in a NaOH solution are the penta-, hexa-, and heptavalent states.[1] In a basic solution, the color of the Np(VII) is green, and its existence is easily confirmed by spectrophotometry because of its large extinction coefficient and high solubility.[2] On the other hand, since both Np(V) and Np(VI) have a small extinction coefficient and a low solubility,[2] the spectrophotometry cannot be used even for an ordinary concentration of Np. Therefore, a method other than spectrophotometry is required if we are to ascertain the distribution of the oxidation states of Np of a low concentration in a basic solution. However, no such method has yet been established, and the chemical behavior of Np(V), Np(VI), and Np(VII) in a basic solution is not sufficiently clarified.

In a previous paper,[3] we ourselves reported that, in a NaOH solution of 1—2 M, the Np(V) was almost completely adsorbed on zirconium(IV) hydroxide, while the Np(VI) and Np(VII) remained in the supernatant. The present study is an attempt to establish a method for discriminating, in a NaOH solution Np(VI) and Np(VII), which are indistinguishable by adsorption on zirconium(IV) hydroxide. For this purpose, column chromatography on alumina is found to be excellent. A method of preparing Np(VI) and Np(VII) of a tracer quantity in a NaOH solution is also proposed by the application of this method.

Experimental

The sodium hydroxide solution of Np was prepared from a 0.5 M nitric acid solution of Np by adding an adequate oxidant or reductant after the addition of NaOH. The NaOH stock solution was prepared by filtering its saturated solution through a Millipore Mitex filter with a pore size of 5 μm, the necessary experimental procedures were carried out in a polyethylene bag filled with nitrogen gas to avoid contamination with carbon dioxide.

Alumina (Merck aluminium oxide 60, active basic 70—230 mesh) was heated in a 2 M NaOH solution containing bromine at 80—100 °C for 1 h. After cooling, the alumina was transferred into a black glass tube with a carbon dioxide absorber of 0.6 cm in diameter and with its length adjusted to 10.0—10.2 cm. Then the alumina bed was rinsed with water and the eluent used in each run. NaOH solution of various oxidation states of Np of 1 cm^3 was carefully transferred to the top of the bed and allowed to flow through. After the tube had been washed, the eluent was allowed flow through at 0.2—0.3 cm/min.

The ^{237}Np was obtained from The Radiochemical Centre, Amersham, while the ^{239}Np tracer was prepared by milking from ^{243}Am through a cation exchanger. By measuring the ^{239}Np activity by means of a NaI scintillator or Ge detector, the neptunium was determined. The optical density was measured by means of a Hitachi 330 spectrophotometer.

Results and Discussion

Chromatographic Behavior of Np(VII) and Np(V). The chromatographic behavior of Np(VII), prepared by a conventional ozone oxidation,[4] is shown in Fig. 1 for its ordinary concentration of 4.3×10^{-4} M in 1.2 M NaOH. In this figure, the ordinate represents the ratio of the amounts of Np found in each fraction of the effluent to the total amount placed in the column. In the first peak of the chromatogram, the effluent was colorless, but in the second peak the color was the green characteristic of a heptavalent state. Moreover, the recovery of Np was 99%, which showed that almost all the Np loaded on the column was eluted. As is shown in Fig. 1, the Np(VII) of an

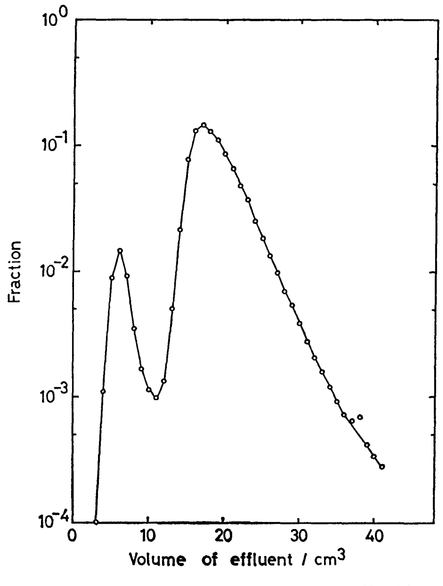

Fig. 1. Column chromatogram of Np(VII) on alumina.
Influent: 4.3×10^{-4} M Np(VII) in 1.2 M NaOH, eluent: 1.1 M NaOH, recovery: 99%.

ordinary concentration prepared by ozone oxidation is separated into two parts by means of alumina chromatography.

The chromatographic behavior of Np(V), prepared by the addition of hydrazine,[3] was investigated for an extremely low concentration of 5×10^{-12} M. However, no neptunium was eluted at all, even by the use of 60 ml of the eluent (1 M NaOH+10^{-3} M $N_2H_4\cdot2HCl$). Also, the adsorption of Np(V) on 100 mg of alumina was found to be above 98% by the agitation of 4 ml of Np(V) in a 1 M NaOH solution containing hydrazine. Thus, the Np(V) in a 1 M NaOH solution may be said to be strongly adsorbed on alumina.

Chromatographic Behavior of Np(VI). A basic Np(VI) solution of an ordinary concentration is usually prepared by alkalizing an acidic Np(VI) solution without any foreign oxidants,[5] by dissolving Np(VI) salt in a solvent of interest,[2] or by electrolyzing a basic Np(VII) solution.[6] However, there is some probability of a partial formation of a pentavalent state in the basic Np(VI) solution prepared by the abovementioned method. Here we prepared not pure Np(VI), but various mixed solutions of Np(VI) and Np(VII) by adding hydrazine to Np(VII) solutions prepared by ozone oxidation, as is tabulated in Table 1. This table shows the fraction of Np(VII) as calculated from the optical densities at 618 nm before and after the addition of hydrazine. In these mixtures of Np(VII) and Np(VI), there is no probability of the existence of the pentavalent state at all, because the reaction of Np(V)+Np(VII)→2Np(VI) is rapid and complete.[2]

The chromatographic behavior of Np(VII) and Np(VI) can be examined without any consideration of Np(V). The elution chromatograms of the mixtures are shown in Fig. 2, in which the numbers correspond to the index numbers in the first column of Table 1. As the fraction of Np(VII) in a mixture decreases, the intensity of the first peak in Fig. 2 becomes larger, and that of the second peak, smaller. The fractions of the second peak, observed by means of chromatograms, are shown in the sixth column of Table 1. These values agree fairly well with the fractional values of Np(VII) in the mixtures obtained by spectrophotometry. From Table 1 and Fig. 2, it may be concluded that the first peak in the chromatogram is due to Np(VI), and the second peak, to Np(VII), and that the intensity ratio of the two peaks corresponds to the concentration ratio of Np(VI) and Np(VII).

The difference between the D_1/D_0 ratio and the second peak fraction may result either from the reduction of Np(VII) during chromatography or from an incomplete preparation of pure Np(VII) in 1 M NaOH, as shown by controlled potential coulometry.[6]

Preparation of Tracer-scale Np(VII) and Np(VI) in a 1 M NaOH Solution. As is shown in Table 1 and Fig. 2, Np(VII) and Np(VI) of an ordinary concentration can easily be discriminated by chromatography on alumina. Here, we are concerned with the preparation of Np(VII) and Np(VI) of a tracer quantity in a 1 M NaOH solution.

Neptunium solutions from 5×10^{-4} M to an extremely low concentration were oxidized by ozone in a 1 M NaOH solution containing bromine. The chro-

Table 1. The composition of a mixture of Np(VI) and Np(VII) in a 1.1 M NaOH solution and the results of the chromatography

No.	[Np]/M	D_0[a]	D_1[b]	Np(VII) fraction[c]/%	The 2nd peak fraction/%	Recovery of Np/%
1	4.78×10^{-4}	0.186	0.186	100	92	101
2	4.81×10^{-4}	0.183	0.137	75	71	103
3	4.74×10^{-4}	0.187	0.095	50	46	101
4	4.97×10^{-4}	0.187	0.042	22	18	99

a) D_0: The optical density at 618 nm for the solution of Np(VII) prepared by ozone oxidation. b) D_1: The optical density at 618 nm for the mixture of Np(VI) and Np(VII). c) D_1/D_0.

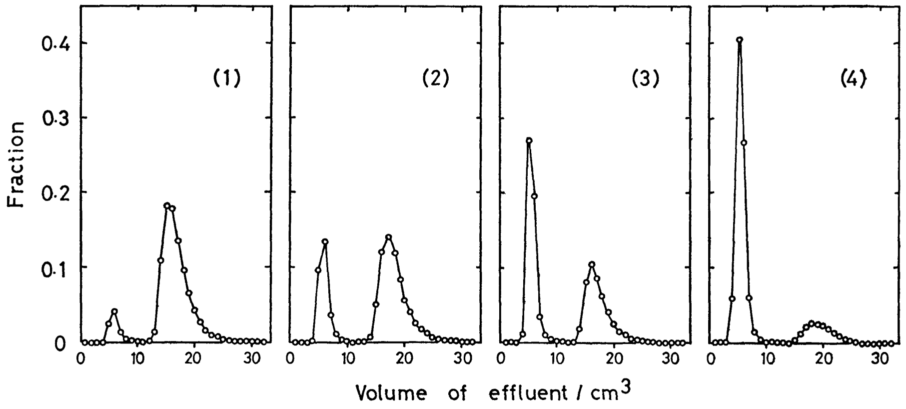

Fig. 2. Chromatogram of the mixture of Np(VI) and Np(VII). Influent: see Table 1, eluent: 1.1 M NaOH.

matogram is shown in Fig. 3. A comparision of Fig. 3-(1) with Fig. 1, makes it obvious that Np(VII) of a higher purity is obtained by ozone oxidation in a NaOH solution containing bromine; the contamination of Np(VI) is estimated to be about 1% from the chromatogram of Fig. 3-(1). Figure 3 shows that the distribution coefficient of Np(VII) on alumina grows larger as its concentration decreases, though that of Np(VI) is apparently constant from an ordinary to an extremely low concentration. Also, Np(VII) of a tracer quantity in 1 M NaOH can be prepared by ozone oxidation in a 1 M NaOH solution containing bromine, as is shown in Fig. 3-(4).

Np(VI) in a 1 M NaOH solution may be obtained by the use of an oxidant with a formal electrode potential of about 0.45 V, because the potential in a 1 M NaOH solution is 0.59 V for a Np(VII)/Np(VI) couple[6] and 0.30 V for a Np(VI)/Np(V) couple.[7] However there are not any suitable oxidants in basic solutions. Therefore, we tried to prepare Np(VI) by oxidation with mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$. For a $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple, the standard electrode potential is 0.36 V and the formal electrode potential is 0.46 V at 0.01 M NaOH and 0.52 V at 5 M NaOH.[8] By oxidation with this mixture, Np(VI) must be obtained, because the potential of the mixture will vary with the concentration ratio, Q, where $Q=[[Fe(CN)_6]^{4-}]/[[Fe(CN)_6]^{3-}]$. The preliminary spectrophotometric experiments showed that the concentrations of $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$

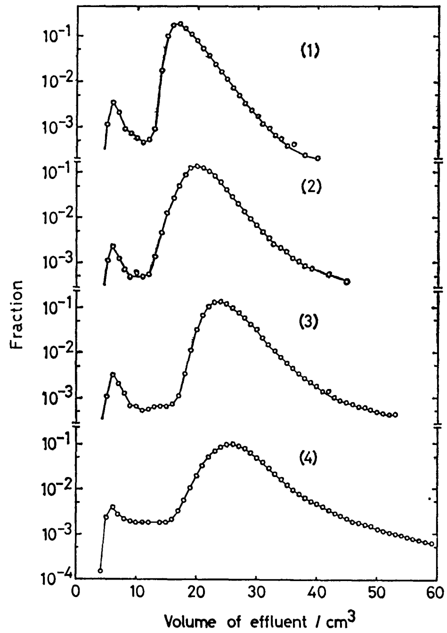

Fig. 3. Chromatogram of Np oxidized by ozone in 1.2 M NaOH+0.16 M Br_2.
Influent: (1) $[Np]=4.6\times10^{-4}$ M, (2) $[Np]=4.3\times10^{-5}$ M, (3) $[Np]=8.9\times10^{-6}$ M, (4) $[Np]=5\times10^{-12}$ M, eluent: 1.1 M NaOH+0.08 M Br_2.

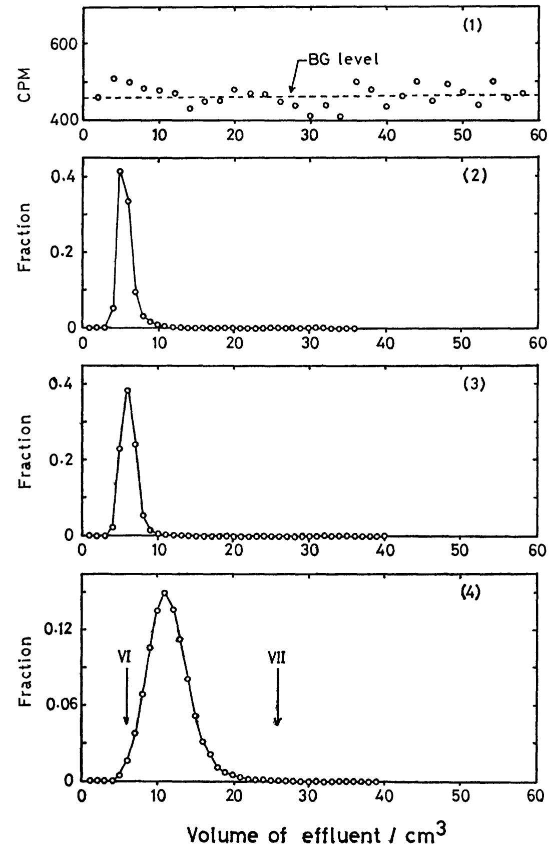

Fig. 4. Chromatogram of Np in the mixture of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.
(1): 1.1 M NaOH+1.0×10^{-3} M $K_4[Fe(CN)_6]$, $R<0.1\%$. (2): 1.1 M NaOH+9.2×10^{-4} M $K_4[Fe(CN)_6]$ +1.0×10^{-4} M $K_3[Fe(CN)_6]$, $Q=9$, $R=99\%$. (3): 1.1 M NaOH+8.1×10^{-4} M $K_4[Fe(CN)_6]$+2.0×10^{-4} M $K_3[Fe(CN)_6]$, $Q=4$, $R=97\%$. (4): 1.1 M NaOH +1.0×10^{-3} M $K_3[Fe(CN)_6]$, $R=100\%$. Where, $Q=[[Fe(CN)_6]^{4-}]/[[Fe(CN)_6]^{3-}]$ and R is recovery of Np.

TABLE 2. ADSORPTION OF Np IN A MIXTURE OF $K_4[Fe(CN)_6]$ AND $K_3[Fe(CN)_6]$ ON ZIRONIUM(IV) HYDROXIDE

$[K_4[Fe(CN)_6]]$ / 10^3 M	$[K_3[Fe(CN)_6]]$ / 10^3 M	Q[a]	Adsorption[b]/%			Oxidation state
			RT, 1 h[c]	50 °C, 2 h[c]	RT, 20 h[c]	
0.99	0		70	60		5, (6)
0.94	0.05	19	9	9		(5), 6
0.91	0.10	9	5		4	6, 7
0.81	0.20	4	5		4	6, 7
0.49	0.48	1	4	5		6, 7
0	1.0	0	4	6		6, 7

a) $Q=[K_4[Fe(CN)_6]]/[K_3[Fe(CN)_6]]$. b) [NaOH]=1.1 M, [Zr(IV)]=0.6 mg/ml. c) Time of standing.

in a mixture of them at 1 M NaOH remained almost constant over 2 d. This means that the potential of the mixture in 1 M NaOH is almost constant.

The distribution of the oxidation states of Np in the mixture was examined both by adsorption on zirconium(IV) hydroxide[3] and by chromatography on alumina. The results are shown in Table 2 and Fig. 4. As is shown in Table 2, the adsorption of Np is almost constant, independent of the standing time and the temperature, and the Np in the mixture with the concentration ratio of $Q<10$ is adsorbed a little, though much of the Np in the $[Fe(CN)_6]^{4-}$ solution is adsorbed. Since the oxidation into Np(VII) by $[Fe(CN)_6]^{3-}$ in a NaOH solution is incomplete,[9] the result of adsorption shows that the Np in a mixture with a ratio of $Q<10$ is a pure hexavalent state or a mixture of hexa- and heptavalent states. And also the results show that Np in $[Fe(CN)_6]^{4-}$ solution is a mixture of penta- and hexavalent state. The possible oxidation states of Np are shown in the seventh column of Table 2.

The chromatographic behavior of Np in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ solutions are shown in Figs. 4-(1) and 4-(4) respectively. Though Np(VI) exists in both solutions, Np is not eluted at all in the $[Fe(CN)_6]^{4-}$ solution, as is shown in Fig. 4-(1), while it is eluted at an intermediate position between Np(VI) and Np(VII) in the $[Fe(CN)_6]^{3-}$ solution, as is shown in Fig. 4-(4). The curious behavior can be easily explained by the concept of repeated extractions for chromatography as follows. If there are two different oxidation states of Np which are produced by a reversible redox reaction, these two states of Np are not separated by chromatography, and the elution of Np is observed at the intermediate position between intrinsic positions for each oxidation state, because Np in the mobile and stationary phase is forced to become two different oxidation states by a reversible redox reaction, and it is partly and repeatedly adsorbed or desorbed on alumina between the two phases.

Figures 4-(2) and 4-(3) show the chromatograms of Np in mixtures with the concentrations ratio, Q, of 9 and 4 respectively. Almost all the Np was eluted at an intrinsic peak position for Np(VI). Therefore, in a 1 M NaOH solution Np(VI) in a tracer quantity can be prepared by oxidation with the mixture of $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ having concentration ratio, Q, from 4 to 9.

Effect of the Concentration of Na_2CO_3 and NaOH on the Chromatographic Behavior of Np(VII) and Np(VI). The effects of the concentration of Na_2CO_3 and NaOH on the chromatographic behavior of Np(VII) and Np(VI) were examined. The mixtures of Np(VII) and Np(VI) were prepared by the addition of bromine. Figure 5 shows the effect of the concentration of Na_2CO_3, where Np was been prepared by heating at 80—90 °C for an hour in a 1 M NaOH solution containing bromine, so that the fraction of Np(VII) was rich. As is shown in Fig. 5, the elution peak

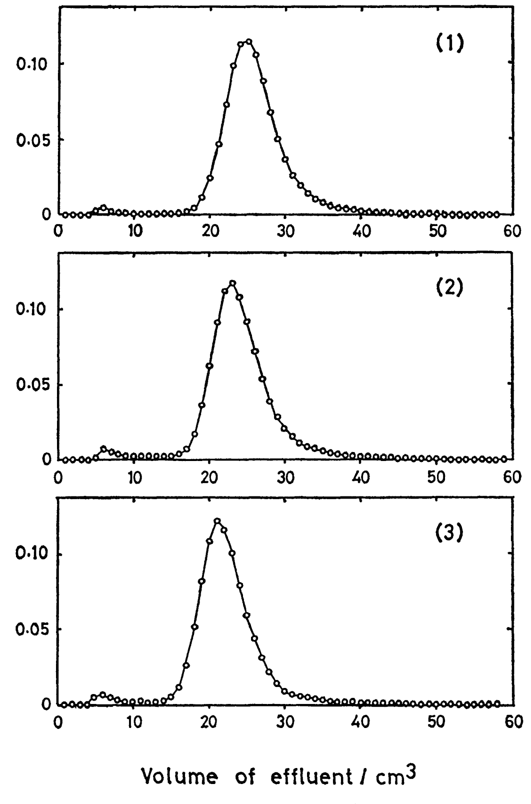

Fig. 5. Influence of the concentration of Na_2CO_3 on the chromatogram of Np(VI) and Np(VII).
(1): 1.1 M NaOH+0.08 M Br_2, (2): 1.1 M NaOH+0.08 M Br_2+0.02 M Na_2CO_3, (3): 1.1 M NaOH+0.08 M Br_2+0.05 M Na_2CO_3.

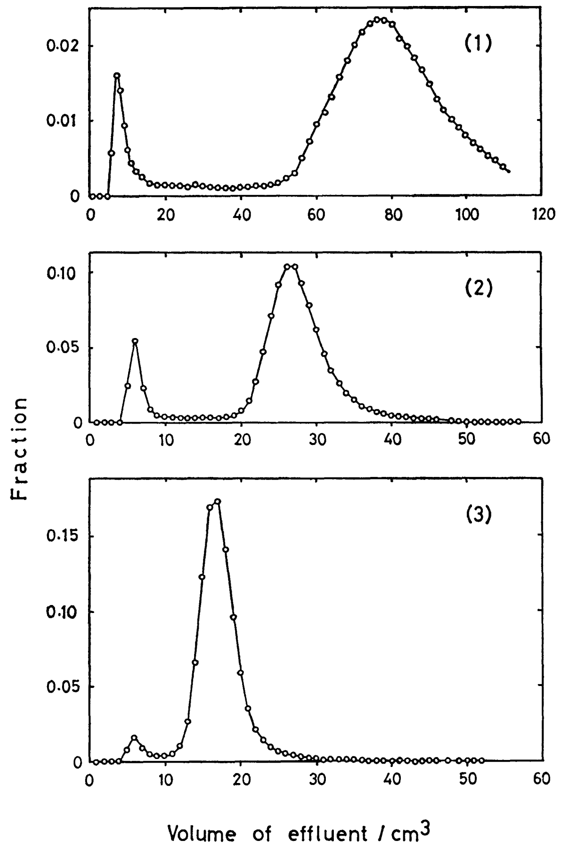

Fig. 6. Influence of the concentration of NaOH on the chromatogram of Np(VI) and Np(VII).
(1): 0.57 M NaOH+0.08 M Br_2, (2): 1.1 M NaOH +0.08 M Br_2, (3): 1.7 M NaOH+0.08 M Br_2.

position on Np(VII) is dependent on the concentration of CO_3^{2-}, but that of Np(VI) is independent of it. It is found that the discrimination between Np(VII) and Np(VI) can be made up to 0.05 M Na_2CO_3 in a 1 M NaOH solution.

Figure 6 shows the effect of the concentration of NaOH, where Np has been prepared by standing at room temperature in a 1 M NaOH solution containing bromine, so that the fraction of Np(VI) was larger. This figure shows that the discrimination can also be made in a NaOH solution of 0.5—1.7 M.

By combining the chromatography on alumina with the adsorption on zirconium(IV) hydroxide, it is possible to analyze the distribution of all the oxidation states of Np, Np(V), Np(VI), and Np(VII) in a 1 M NaOH solution.

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