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The Chemistry of Americium. III. The Coprecipitation of Am(III), Am(V), and Am(VI) by Some Fluorides and Phosphates

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The radiochemical behavior of americium in the coprecipitation process involving a precipitate such as lanthanum, thorium, and ceric fluorides, zirconium, and bismuth phosphates was investigated at the tracer concentrations of americium. All the precipitates except zirconium phosphate completely carried the Am(III), leaving the Am(VI) in the supernatant. The lanthanum and thorium fluorides carried portions of the Am(V) in proportion to the amounts of the metal ion of the carrier added under any given conditions. Then, the analytical conditions were established for determining the distributions of the oxidation states of americium.

The recognized oxidation states of americium in an ordinary aqueous solution are the tri-, penta-, and hexavalent states. They can usually be identified by means of spectrophotometry.[1] However, this method is not sensitive enough here because of the low molar extinction coefficients of both Am(V) and Am(VI) ions. The development of an oxidation-state separation scheme at low americium concentrations is often beset by certain inherent difficulties. The properties of a trace amount of an element (tracer) can often be observed by means only of its chemical behavior, which in most cases closely resembles the chemical behavior of the element at a macro concentration. In some cases, however, it is necessary to pay attention to such peculiarities of the tracer behavior as the radiocolloid formation, the adsorption on the container walls, and the oxidation-state perturbation caused by small amounts of impurities.

A few workers have reported methods for the separation of Am(III) and the higher oxidation states of americium at low concentrations utilizing these differences in the chemical properties: the solubility in the lanthanum-fluoride[2] and calcium-fluoride systems,[3] the adsorbability on a chromatographic column consisting of bis(2-ethylhexyl)phosphoric acid[4,5] or on a column consisting of zirconium phosphate,[6] and the extractability in liquid-liquid extraction using 2-thenoyltrifluoroacetone as the extractant.[7,8]

The methods involving the organic agents substantially perturb the oxidation states of americium in the course of the separation process, and the column operations take much time. The coprecipitation technique involving the lanthanum fluoride is based on the facts that the actinoid(III,IV) ions are carried, while the actinoid(VI) ions are not carried, by the lanthanum fluoride.[2,9] However, the behavior of the actinoid(V) ions in this system has not yet been confirmed.

In a previous work the present authors investigated the instability of Am(V) in several media and found that Am(V) at tracer concentrations was stable within a few hours after preparation in a nitric acid solution, *etc.* at 0—5 °C.[8] In order to develop the solution chemistry of the higher oxidation states of americium, it is necessary to establish a method for determining the oxidation-state distributions of americium. For this purpose, the coprecipitation technique was chosen because of its rapidity and convenience. In this work, the coprecipitation of americium by lanthanum, thorium, and ceric fluorides and by zirconium and bismuth phosphates was investigated under various conditions. The results will be discussed from the standpoints of the coprecipitation process and the oxidation-state analysis.

Experimental

Reagents. The independent solutions of Am(III), Am(V), and Am(VI) were prepared by the methods reported previously;[5,8] in some cases, they were arbitrarily mixed in order to prepare the multi-component solutions. The initial concentration of ^{241}Am was of the order of 10^{-6} M. Solutions of lanthanum, thorium, cerium(IV), bismuth, and zirconium nitrates were used as the metal ion of the carrier. The precipitants were solutions of ammonium fluoride and phosphoric acid and also, if necessary, hydrofluoric acid and ammonium dihydrogenphosphate solutions. These and other chemicals were all of a G. R. grade.

Apparatus. The experiments prior to centrifuging were carried out in an Onishi Netsu-Kagaku thermostated box at 0—5 °C. For the centrifugation, a Sakuma Model SMC 30-1 centrifuge was used. The γ-ray assay was performed by the use of a Kobe Kogyo Model PS-500 flat-type NaI(Tl) scintillation probe connected with a Kobe Kogyo Model SA-400 scaler.

Procedure. Suitable aliquots of the americium, the metal ion of the carrier, and nitric acid solutions were transferred into a polyethylene test tube; a precipitant was then added, and the volume and the acidity were adjusted to the desired values. The mixture was then shaken mechanically for enough time to obtain an apparently constant fraction of americium carried. The recommended shaking time was 10 and 30 min for the fluoride and phosphate systems respectively. The final concentration of ^{241}Am in the mixture was $(0.5-5)\times 10^{-6}$ M. By measureing the ^{241}Am activity in both the mixture and the supernatant obtained by centrifuging the mixture at about 6000 rpm for 5 min, the fraction of americium carried was determined. When thorium was used, the correction for the γ-activity from the daughters of ^{232}Th was performed, but the interference from them was negligibly small in most cases. The acidity of the supernatant was stoichiometrically calculated. In the preliminary experiments it was confirmed that no oxidation state of americium was centrifuged under the conditions examined when neither the metal ion of carrier nor the precipitant was added.

Results

The fraction of americium carried generally depended on the volume and composition of the mixture, the amounts of the metal ion of the carrier, and the molar ratio of the precipitant to the metal ion of the carrier added. For instance, under the same conditions except for the volume, 14, 65, and 95 % of Am(III) were carried by the thorium fluoride by the use of 0.1 mg Th^{4+} per 3.5, 3.0, and 2.5 ml respectively of the mixture at an acidity of 0.1 M. Therefore, the volume of the mixture was adjusted to 2.5 ml except when otherwise noted.

Coprecipitation by the Insoluble Fluorides. The relation between the fraction of americium carried and the amounts of a metal ion of the carrier was investigated at the acidity of 0.2 M, as is shown in Fig. 1. In the range of the amounts of the thorium ion examined, more than 95 % of the Am(III) and less than 12 % of the Am(VI) were carried, but the fraction of Am(V) carried increased from 1 to 100 % with an increase in the amount of the thorium ion from 0.15 to 75 mg per 2.5 ml of the mixture. The coprecipitation behavior with the lanthanum fluoride showed a tendency similar to that with the thorium fluoride. On the other hand, in the ceric-fluoride system the fractions of Am(V) and Am(VI) carried were both very small, irrespective of the amounts of the ceric ion, while the coprecipitation of Am(III) was complete when more than 0.2 mg Ce^{4+}/ml was used.

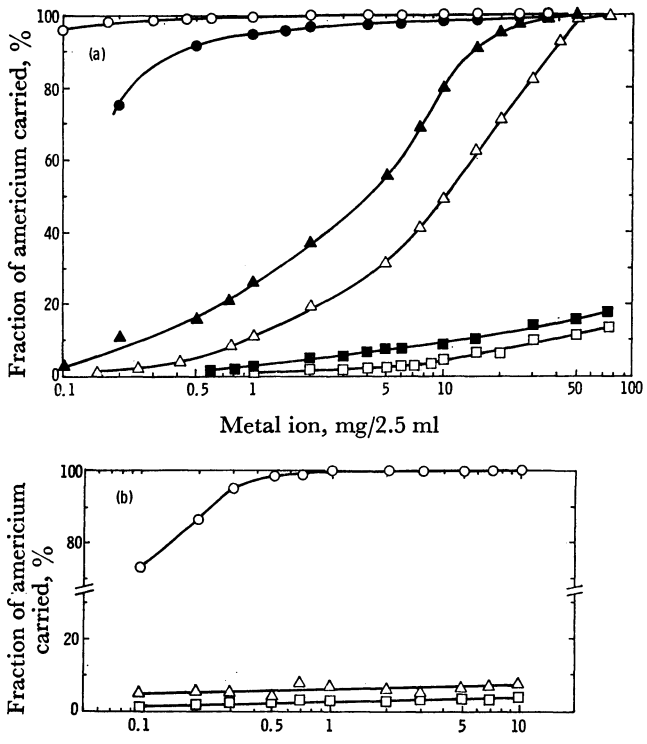

Fig. 1. The dependence of the coprecipitation of americium on the amounts of metal ion of carrier in the lanthanum, thorium, and ceric fluoride systems.
(a) Thorium fluoride system: ○, Am(III); △, Am(V); □, Am(VI). Lanthanum fluorides system: ●, Am(III); ▲, Am(V); ■, Am(VI).
(b) Ceric fluoride system: ○, Am(III); △, Am(V); □, Am(VI).
In each system, the acidity of the mixture is 0.2 M and $F/M > 10$.

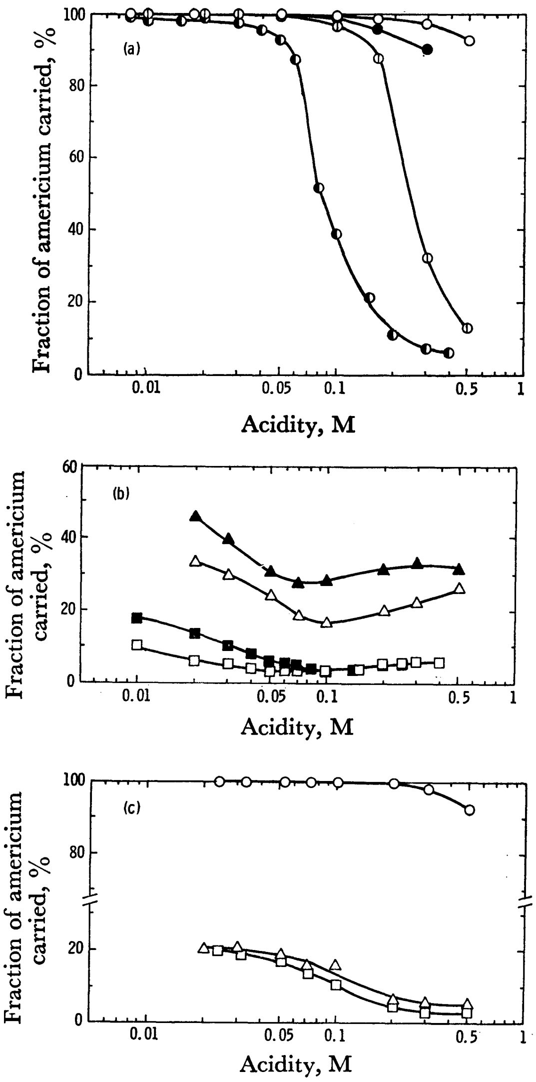

Fig. 2. The acidity-dependence of the coprecipitation of americium by the lanthanum, thorium, and ceric fluorides.
(a) Am(III): ○, F/Th=115; ⦶, F/Th=23; ●, F/La=70; ◐, F/La=14.
(b) Am(V): △, F/Th=115; ▲, F/La=70. Am(VI): ■, F/Th=115; □, F/La=70.
(c) F/Ce=14: ○, Am(III); △, Am(V); □, Am(VI).
In each system, 1 mg of metal ion per 2.5 ml of the mixture was used.

The acidity dependence of the coprecipitation of americium was also studied at a constant amounts of the carrier-metal ion and at a constant molar ratio of the precipitant to the metal ion of the carrier added (F/M). The results are shown in Fig. 2. The larger fractions of americium were carried at the lower acidities, and the coprecipitation of Am(III) was less complete at the higher acidities, especially at smaller F/M values. The fractions of Am(III), Am(V), and Am(VI) carried by the insoluble fluoride under the given conditions are summarized in Table 1.

Coprecipitation by the Insoluble Phosphates. The acidity dependence of the coprecipitation of americium by the zirconium and bismuth phosphates was also investigated. The experiments with the latter were per-

Table 1. Summary of the coprecipitation of americium

Run	Experimental condition[a)]			Fraction carried, %		
	Precipitate	Metal ion, mg[b)]	Precipitant, mM[b)]	Am(III)	Am(V)	Am(VI)
1	Thorium fluoride	1	0.5	99±1	11±2	1±1
2	Thorium fluoride	50	2.5	99±1	99±1	11±1
3	Lanthanum fluoride	1	0.5	94±2	26±3	3±2
4	Lanthanum fluoride	50	2.5	98±2	98±3	16±2
5	Ceric fluoride	1	0.5	99±1	5±2	4±2
6	Bismuth phosphate	10	2.5	99±1	0[c)]	1±1

a) Acidity of the mixture is 0.2 M. b) Amounts per 2.5 ml of the mixture. c) Not investigated.

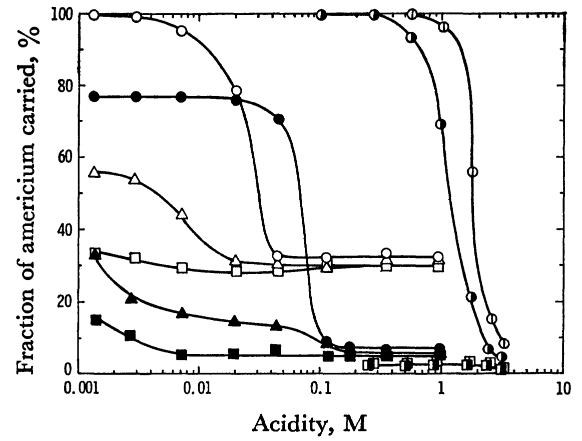

Fig. 3. The acidity-dependence of the coprecipitation of americium by the zirconium and bismuth phosphates at PO_4/M 20.
1 mg Zr^{4+}/3.5 ml: ●, Am(III); ▲, Am(V); ■, Am(VI).
10 mg Zr^{4+}/3.5 ml: ○, Am(III); △, Am(V); □, Am(VI).
1 mg Bi^{3+}/2.5 ml: ◑, Am(III); ◨, Am(VI).
10 mg Bi^{3+}/2.5 ml: ⦶, Am(III); ◫, Am(VI).

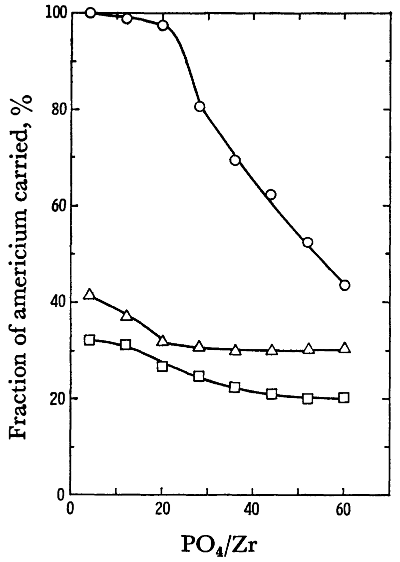

Fig. 4. The variation of the coprecipitation of americium by zirconium phosphate with the molar ratio PO_4/Zr by using 10 mg Zr^{4+} per 3.5 ml of the mixture at the acidity 0.01 M.
○, Am(III); △, Am(V); □, Am(VI).

formed at acidities above 0.1 M because the hydrolysis products of a bismuth ion were precipitated at lower acidities without the addition of any precipitant. Significant coprecipitation of americium took place with amounts of zirconium and bismuth ions of more than 0.3 and 0.5 mg/ml respectively. Some typical results with a constant amount of the carrier-metal ion are shown in Fig. 3. The fractions of Am(III) and Am(V) carried by the zirconium phosphate increased with a decrease in the acidity below 0.1 M, while the acidity dependence of the fraction of Am(VI) carried was small. The complete coprecipitation of Am(III) by bismuth phosphate took place at the higher acidities, at which not so much Am(III) was carried by the zirconium phosphate, while the fraction of Am(VI) carried remained constant at lower levels. The behavior of Am(V) in the bismuth-phosphate system was not investigated, since the method of preparation and the stability of the Am(V) ion have not been established at higher acidities.

The molar ratio, PO_4/M, had a remarkable effect on the coprecipitation of americium, especially in the zirconium-phosphate system. As is shown in Fig. 4, 97—100 % of the Am(III) was carried at ratios less than 20, using a constant amount of zirconium ions, but the fraction of Am(III) carried decreased strikingly when the ratio increased to more than 20. On the other hand, the variations in the fractions of Am(V) and Am(VI) carried were very small, even at ratios more than 20. The separation of the precipitate and the supernatant by centrifuging was not complete at ratios less than 2, since the fine suspension of the zirconium phosphate could hardly be centrifuged at all. The fraction of americium carried by the bismuth phosphate under the given conditions is also postulated in Table 1.

Analysis of the Multi-component Solutions. The multi-component solutions, which were prepared by mixing independent solutions of Am(III), Am(V), and Am(VI), had the following compositions with respect to the oxidation state of americium: Sample 1: Am(III) 55.4±0.3 % and Am(V) 44.6±0.2 %; sample 2: Am(III) 48.5±0.3 % and Am(VI) 51.5±0.3 %, and Sample 3: Am(III) 34.1±0.2 %, Am(V) 30.7±0.2 %, and Am(VI) 35.2±0.2 %.

Suitable aliquots of a sample solution were simultaneously taken for the six kinds of coprecipitation experiments under the conditions presented in Table 1; the results are shown in Table 2. If the Am(III), Am(V),

TABLE 2. ANALYSIS OF THE MULTI-COMPONENT SOLUTIONS OF AMERICIUM

Run i[a)]	Y^i, %					
	Sample 1		Sample 2		Sample 3	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
1	59.3±0.7	59.8±1.1	48.8±0.7	48.5±0.8	37.4±0.6	37.5±0.8
2	98.9±0.6	99.0±0.8	55.5±0.7	53.7±1.2	66.6±0.8	68.0±0.9
3	63.3±1.5	63.7±1.8	46.6±1.7	47.1±1.4	37.9±1.5	41.1±1.4
4	96.2±1.7	98.0±1.5	60.4±1.5	55.8±1.4	66.6±1.5	69.1±1.2
5	57.6±0.8	57.1±1.1	53.1±0.7	50.1±1.2	40.9±0.7	36.7±1.0
6	56.6±0.3	54.9±0.6	48.0±0.4	48.5±0.8	34.6±0.5	34.1±0.5

a) Experimental conditions are given in Table 1.

and Am(VI) in the multi-component solution all behave independently in the course of the coprecipitation process, the fraction of americium carried under the i condition may be given as:

$$Y^i = f_{III}Y^i_{III} + f_V Y^i_V + f_{VI} Y^i_{VI}, \quad (1)$$

where Y^i_x is the fraction of Am(x) carried which is obtained in the independent system, and where f_x is the mole fraction of Am(x) in the multi-component solution. Then, the fraction of americium carried from the multi-component solution was calculated according to Eq.(1) by the use of the Y^i_x given in Table 1 and the f_x described previously; it is also presented in Table 2. The calculated values nearly agree with the observed values in all cases. Therefore, the assumption that Y^i_V in the bismuth-phosphate system is very small is reasonable.

By the way, Eq.(1) can also be written as Eq.(2), for instance, because $f_{III}+f_V+f_{VI}=1$:

$$Y^i = f_{III}(Y^i_{III} - Y^i_{VI}) + f_V(Y^i_V - Y^i_{VI}) + Y^i_{VI} \quad (2)$$

Therefore, if the Y^i_x is reproducibly established under the given condition, i, the mole fraction, f_x, in the multi-component solution can be deduced by solving two simultaneous equations like Eq.(2) with two unknowns. For instance, when two pairs of data obtained for the same sample solution in both lanthanum- and thorium-fluoride systems were analyzed, it was found that the calculated mole fractions satisfactorily agreed with those known previously, especially in the thorium-fluoride system (*cf.* Table 3).

TABLE 3. DISTRIBUTION OF THE OXIDATION STATE OF AMERICIUM IN THE MULTI-COMPONENT SOLUTIONS

Sample	State	Percentage of the oxidation state		
		Taken	Calcd[a)]	Calcd[b)]
1	Am(III)	55.4±0.3	54.9±4.4	55.6±9.9
	Am(V)	44.6±0.2	45.0±4.4	42.2±9.5
	Am(VI)	0	0.1±0.1	2.2±2.2
2	Am(III)	48.5±0.3	48.6±3.4	47.0±7.0
	Am(V)	0	2.0±2.0	3.5±3.5
	Am(VI)	51.5±0.3	49.4±4.5	49.5±11.4
3	Am(III)	34.1±0.2	34.2±3.1	30.4±7.2
	Am(V)	30.7±0.2	29.0±3.8	31.3±7.9
	Am(VI)	35.2±0.2	36.8±4.3	38.3±10.4

a) Values calculated by using the couple of data with runs 1 and 2. b) Values calculated by using the couple of data with runs 3 and 4.

Discussion

It has been found that the coprecipitation behavior of Am(III) and Am(VI) with lanthanum fluoride agree essentially with that reported previously.[2)] On the other hand, the present work revealed the chemical behavior of Am(V) in the lanthanum-fluoride system for the first time. Portions of the Am(V) were carried by the lanthanum fluoride in proportion to the amounts of lanthanum ions of more than 0.04 mg/ml. Nearly the same results have been obtained in the thorium-fluoride system.

The processes by which the tracer is carried by a precipitate formed in the presence of the tracer have been discussed by many workers–for instance, by Bonner and Kahn[10)] and by Starik.[11)] The coprecipitation processes can be classified as follows:

(a) Isomorphous replacement.

(b) Adsorption. Chemical adsorption and ion-exchange adsorption.

(c) Anomalous-mixed-crystal formation.

(d) Internal adsorption.

The available information concerning the fluoro-complex formation of americium[12)] or those elements whose chemical properties closely resemble those of americium, such as neptunium and plutonium,[13)] suggests that the predominant species of Am(III), Am(V), and Am(VI) in the floride solutions investigated are the insoluble AmF_3, insoluble AmO_2F (or $NH_4AmO_2F_2$), and soluble $AmO_2F_4^{2-}$(and/or $AmO_2F_3^-$) respectively. The observation that both the amorphous lanthanum and thorium fluorides carried more of the insoluble and neutral species of Am(III) and Am(V) than the ionic species of Am(VI) may be explained by the adsorption process, especially by the chemical adsorption process. This mechanism is based on the phenomenon that a tracer is carried well when it forms an insoluble compound at macro concentrations. In this sense, the fluoride species of Am(V) may not be so insoluble as AmF_3, for Am(V) is less carried than Am(III). The findings obtained in the present studies with regard to the dependence of the coprecipitation of americium on the several parameters can be easily correlated to the extent to which the complex formation of americium occurs.

The coprecipitation behavior of americium in the ceric-fluoride system was considerably different from that in the other fluoride systems, and it could not be explained by the argument presented above. Evidently the precipitate of ceric fluoride was not amorphous, but crystalline. It is known that Am(III) and Ce(IV) fluorides have a hexagonal structure.[14,15] On the other hand, if an $NH_4AmO_2F_2$ crystal is isostructural to $KAmO_2F_2$, it may be rhombohedral.[16] Therefore, it is reasonable that the ceric fluoride carries the isomorphous AmF_3 better than either the heteromorphous $NH_4AmO_2F_2$ or the ionic species of Am(VI), according to the isomorphous replacement process.

On the other hand, the behavior of americium in the zirconium-phosphate system is rather complex. All of the experiments were performed at low temperatures and within a short time, taking into account the instabilities of the higher oxidation states of americium. Such experimental conditions resulted in an ununiform and less reproducible precipitation of the zirconium phosphate. The available information concerning the phosphato-complex formation of americium,[17] neptunium,[18] and plutonium,[19] and the behavior of americium in a phosphoric acid,[20] suggests that the predominant species of Am(III), Am(V), and Am(VI) in the phosphate solutions examined are the Am^{3+} (and/or $AmH_2PO_4^{2+}$), AmO_2^+(and/or $AmO_2H_2PO_4$), and $AmO_2H_2PO_4^+$ ions respectively. It is well known that a crystal of the preliminarily-prepared zirconium phosphate has ability of ion-exchange adsorption.[6] Therefore, the coprecipitation of the ionic species of americium by zirconium phosphate must result mainly from the ion-exchange adsorption. The results obtained in the zirconium-phosphate system suggest that the adsorbability of the species decrease in this order: $Am^{3+} > AmH_2PO_4^{2+} > AmO_2^+ > AmO_2H_2PO_4^+ \gg AmO_2H_2PO_4$. The decrease in the coprecipitation of Am(III) with an increase in PO_4/Zr, as is shown in Fig. 4, can be explained by the formation of less adsorbable phosphate species.

By the way, the fine crystalline bismuth phosphate carried Am(III) completely even at higher acidities at which the zirconium phosphate did not so carry it. It seems that this finding cannot be explained simply by the ion-exchange adsorption process, but can de explained by the argument used in the case of the crystalline ceric fluoride. If this is true, Am(III) may form a phosphate compound which is isostructural to a hexagonal bismuth phosphate[21] as well sɐ lanthanoid(III) ions.[22]

The analytical results obtained for the multi-component solutions demonstrate that the perturbation of the oxidation state in the course of the coprecipitation process was negligible, and that the fraction of americium carried by the precipitates studied was additive and constitutive. Equation (1) or Eq. (2) guarantees that the coprecipitation behavior of each oxidation state of americium must be established under the given conditions. In the lanthanum- and thorium-fluoride systems, two sets of analytical conditions have been established; they are shown in Table 1. Therefore, the distribution of the oxidation state of americium in the multicomponent solutions can be approximately deduced by investigating the coprecipitation of americium by the lanthanum or thorium fluoride under the recommended conditions, followed by solving two simultaneous equations like Eq. (2). However, the sets of such conditions could not be established in the ceric-fluoride and bismuth-phosphate systems alone.

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