A new method of americium and curium extraction from nitric acid solutions using diphenyl[dibutylcarbamoylmethyl]phosphine oxide

Yurii M. Kulyako,* Dmitrii A. Malikov, Marina K. Chmutova and Boris F. Myasoedov

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975 Moscow, Russian Federation. Fax: +7 095 938 2057

For the first time diphenyl[dibutylcarbamoylmethyl]phosphine oxide (PBCPO) has been shown to effectively extract americium and curium from nitric acid solutions into the reagent phase without the usual use of organic solvents.

An alternative approach to the safe disposal of highly radioactive wastes is their separation in order to selectively isolate long-lived highly radioactive α-emitting nuclides (Pu, Np, Am, Cm). The use of bidentate neutral organophosphorus compounds (BNOC) is the most promising for these purposes.[1–5]

For the first time diphenyl[dibutylcarbamoylmethyl]phosphine oxide (PBCPO) has been shown to extract effectively transplutonium elements (TPE) from acidic solutions without preliminary dissolution of this reagent in an organic solvent. Hereafter we conditionally call this method 'ER' (extraction by reagent). It was of interest to compare the relative characteristics of TPE extraction by the ER method and the usual liquid extraction technique (LE) using the reagent previously dissolved in organic solvent. It was also of interest to investigate the behaviour of americium in higher oxidation states (VI and V) during the processes of ER and LE. The data obtained are shown below.

A mixture of ^{243}Am, ^{241}Am, ^{244}Cm and ^{242}Cm isotopes was used in these experiments. The α-activity due to Am isotopes was 25.4±1.8% and that of Cm isotopes 74.6±1.8% of the total. The specific activity of the mixture due to the Am isotopes was 9.07×10^{6} Bq mg^{-1} and Cm 2.99×10^{9} Bq mg^{-1}. The concentration of Am in the tested solutions was *ca.* 10^{-3} M, and Cm *ca.* 10^{-5} M. The Am$^{\mathrm{III}}$ was oxidized to Am$^{\mathrm{VI}}$ by $(NH_4)_2S_2O_8$ (74 mg ml^{-1} of solution) in 0.12 M HNO_3 by heating to 95 °C for 20 min. A check of the total radionuclide contents was carried out by radiometry. A flow-type methane counter 'Protoka' was used for measurement of the total α-activity. The specific isotopic measurements were carried out by α-spectrometry. The concentrations of Am in various oxidation states were determined by a Shimadzu recording spectrophotometer connected to a PC. The PC allowed control of the spectrophotometer and processing of the light absorption spectra obtained.

The experiments on liquid extraction were carried out by a conventional method. A volume of americium solution ranging from 1 to 1.5 ml in an appropriate acid was introduced into a centrifuge test-tube with a conic bottom (5 ml). Each extraction was carried out by an equal volume of 0.2 M PBCPO solution in dichloroethane. As has been previously established, 3 min of extraction were enough to achieve the greatest possible degree of radionuclide extraction. Centrifugation was carried out after extraction to maximize the separation of phases. In experiments involving the ER method a weighed sample of PBCPO in the form of a powder (74 mg ml^{-1} of solution, corresponding to 0.2 M) was introduced into the solution and the solution was shaken. After being centrifuged the aqueous phase was removed. The PBCPO remaining in the test-tube was dissolved in a volume of dichloroethane equivalent to the water phase volume. Water and organic phases were analysed for metal content.

Table 1 Extraction of Cm$^{\mathrm{III}}$, Am$^{\mathrm{III}}$ and Am$^{\mathrm{V}}$ from nitric acid solutions by 0.2 M PBCPO in dichloroethane.

[HNO$_3$]/M	Distribution coefficient			Extraction %		
	Cm$^{\mathrm{III}}$	Am$^{\mathrm{III}}$	Am$^{\mathrm{V}}$	Cm$^{\mathrm{III}}$	Am$^{\mathrm{III}}$	Am$^{\mathrm{V}}$
0.12		0.12	0.184		11	15.6
1.0	5.8	2.8	0.74	85	71	42.6
2.0	22.2	22.6	1.15	95.7	95.8	53.5
3.0		32.5	–		97.0	–
4.1	41.4	41.5	–	97.6	97.6	–

Table 2 Extraction of americium in various oxidation states by diphenyl[dibutylcarbamoylmethyl]phosphine oxide. [PBCPO] = 74 mg ml^{-1} of aqueous solution.

[HNO$_3$]/M	Solution	Americium concentration/10^{-4} M			
		Am$^{\mathrm{VI}}$	Am$^{\mathrm{V}}$	Am$^{\mathrm{III}}$	Am
0.12	initial solution	10.6	0.7	4.35	15.6
	aqueous solution after contact with PBCPO	2.55	4.31	2.135	9.0
	PBCPO dissolved in 1 ml DCE	–	3.51	3.09	6.6
3.0	initial solution	6.63	1.51	3.26	11.4
	aqueous solution after contact with PBCPO	–	1.74	0.405	2.145
	PBCPO dissolved in 1 ml DCE	–	2.34	7.145	9.485
4.1	initial solution	3.418	4.666	1.774	9.858
	aqueous solution after contact with PBCPO	–	1.86	–	1.86
	PBCPO dissolved in 1 ml DCE	1.64	2.62	3.45	7.69

The extraction of Cm$^{\mathrm{III}}$ and Am in various oxidation states from nitric acid solutions by PBCPO solution in dichloroethane. The distribution coefficients and degree of extraction from nitric acid solutions for Cm$^{\mathrm{III}}$, Am$^{\mathrm{III}}$ and Am$^{\mathrm{V}}$ by 0.2 M PBCPO in dichloroethane are given in Table 1.

Americium(III) and curium(III) are extracted reasonably effectively from nitric acid solutions in a range of acid concentrations 1–5 M and the results are consistent with the data obtained earlier.[4] Americium(V) is extracted at low acidity similar to the trivalent cation. However, with increasing acidity, the distribution factor increases, but to a smaller degree than for trivalent elements.

Table 3 The results of Cm$^{\mathrm{III}}$, Am$^{\mathrm{III}}$ and Am$^{\mathrm{V}}$ extraction from nitric acid by diphenyl[dibutylcarbamoylmethyl]phosphine oxide using the ER and LE techniques. [PBCPO] is 0.2 M in DCE in the case of LE technique. [PBCPO] is 74 mg ml^{-1} of aqueous solution in the case of the ER technique.

[HNO$_3$]/M	Extraction method	Distribution coefficient			Extraction %		
		Am$^{\mathrm{III}}$	Cm$^{\mathrm{III}}$	Am$^{\mathrm{V}}$	Am$^{\mathrm{III}}$	Cm$^{\mathrm{III}}$	Am$^{\mathrm{V}}$
0.12	ER	1.45	–	0.814	59.1	–	45.0
	LE	0.12	–	0.184	11.0	–	15.6
3.0	ER	56.2	–	1.16	98.3	–	53.7
	LE	32.5	–	–	97.0	–	–
4.1	ER	150	157	1.4	≈100	99.4	58.0
	LE	41.4	41.5	–	97.6	97.6	–

Americium(VI) disappears on contact with an organic phase forming Am^V and Am^{III}, which are then distributed between phases. It was of interest to establish the reason for the Am^{VI} disappearance on contact with organic solution. For this purpose aqueous 1 M nitric acid solution, containing Am^{VI}, was shaken at the beginning with an equal volume of pure dichloroethane for 3 min. After that the phases were separated. The water phase was analysed for Am in various oxidation states. It was established that Am^{VI} is reasonably stable on contact with dichloroethane and its concentration is reduced slightly (by *ca.* 1%) after 3 min contact with the organic phase. At the same time, when introducing PBCPO into the aqueous nitric acid solution containing Am^{VI} and when shaking the solution with this reagent for 3 min, Am^{VI} is also reduced and transforms into Am^V and Am^{III}, as in the case with the LE method.

The extraction of Cm^{III} and Am in various oxidation states from aqueous nitric acid solutions by diphenyl[dibutylcarbamoylmethyl]phosphine oxide.

The results of Cm and Am extraction by the ER technique from nitric acid solutions are presented in Table 2. The transition of Am^{VI} into Am^V is observed on contact of Am^{VI} with PBCPO. Americium(III) will also be formed, probably due to disproportionation of Am^V. At low acidity (0.12–3 M) Am^{VI} is absent in the reagent phase unlike at high acidity (4 M), when it is extracted by the reagent phase. This observation can be explained by the formation of a strong complex of Am^{VI} with nitrate ion causing an increase in Am^{VI} stability under these conditions.

The behaviour of Cm^{III} under the extraction conditions using the reagent is similar to that of Am^{III}. Thus, at 4.1 M acidity and initial content of 9.5×10^{-6} M Cm is distributed between the aqueous phase (0.06×10^{-6} M) and the reagent (9.44×10^{-6} M).

The data obtained for the distribution coefficients and extraction efficiency for trivalent Cm and Am and for Am^V by ER and the usual LE technique are presented in Table 3.

It is seen from the data obtained that the distribution coefficients for trivalent species are higher for the ER technique in comparison with the usual LE technique. Furthermore, the distribution coefficients for Am^V also increase. Back extraction of radionuclides from the PBCPO phase can be carried out with almost 100% efficiency by double shaking with 0.01 M nitric acid solution. It should be noted that the state of aggregation of the reagent introduced into the aqueous acidic solution changes. As has been established earlier,[6] on contact of a number of solid carbamoylmethylphosphine class reagents with nitric acid transition of crystalline reagent into another state of aggregation is observed: it is transformed into an oily yellow-brown liquid immiscible with water. Probably, interaction of the reagent with nitric acid leads to its polymerization and hence to a change in the state of aggregation.

It should also be noted that besides PBCPO, some other carbamoyls and dioxides are also capable of extracting transplutonium elements from acidic solutions without the use of organic solvents.

Thus, the work presented here shows that the extraction of metals with carbamoyls as reagents can be carried out without their preliminary dissolution in an organic solvent. The application of organic solvents, many of which are toxic and environmentally hazardous, can therefore be avoided.

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