Studies on Solvent Extraction using Radioactive Isotopes. IX[1]. *Solvent Extraction of Carrier-free Cerium-144 with Acetylacetone*

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Several methods for the extraction of cerium have been developed[2,3]. A few applications have also been made to the separation of carrier-free ^{144}Ce from fission products[4]. The separation of a daughter nuclide of a short half-life such as ^{144}Pr from her parent is a very difficult problem on account of the requirement of rapidity. For this purpose, solvent extraction is one of the most proper methods.

In a previous paper[1] the solvent extraction of cerium with acetylacetone was studied. In the course of the work, the carrier-free ^{144}Ce was found to show peculiar features. The authors intend not only to investigate the solvent extraction of ^{144}Ce from fission products, but also to visualize the outlines of the peculiar behaviors of the carrier-free ^{144}Ce compared with cerium of the ordinary concentration reported on in the previous paper.

In addition, because of the rapidity and the simplicity of the method, the separation of ^{144}Pr was found to be possible with acetylacetone.

Experimental

Reagents and Apparatus.—Reagents and apparatus were the same as those of the previous paper. The hydrogen ion concentration of the aqueous phase was adjusted with an acetate buffer solution (ca. 0.1 M for sodium acetate), sodium hydroxide (1 M), and/or nitric acid (1 M). The washing solution for the organic phase consisted of an 0.1 M acetate buffer solution with or without sodium bromate (ca. 0.3 M); this solution was pre-saturated with 20% acetylacetone in carbon tetrachloride or in benzene.

General Procedure.—Unless otherwise stated, the general procedure was as follows: To 5 ml. of an acetate solution containing ^{144}Ce in a separatory funnel, 1 ml. of a 1 M sodium bromate solution was added, and the pH of the aqueous phase was adjusted to 5～6, after which 3 ml. of 20% acetylacetone in carbon tetrachloride or in benzene solution was added. Equilibration was achieved by shaking. After the phases had disengaged the phases were transferred into two test tubes. If necessary, the organic phase was washed with the washing solution.

Results and Discussion

Shaking Time.—^{144}Ce is completely extracted by shaking for about 3 min., especially in the presence of bromate (Table I). It is strange that carrier-free ^{144}Ce is extracted without an oxidizing agent such as bromate. Smith and Pitzer have noticed that tracer amounts of cerium were oxidized by dichromate, but this phenomenon is not expected from the oxidation potential data of a cerous-ceric couple. Cerous cerium can not be extracted with acetylacetone[1], so it may be considered that ^{144}Ce is oxidized to a ceric state without an oxidizing agent and is extracted as acetylacetonate. This is very characteristic behavior of tracer amounts of cerium. This problem is now being examined. It may be noticed in Table I that it takes a longer shaking time for complete extraction without bromate.

TABLE I. THE EFFECT OF SHAKING TIME

Shaking time min.	% Extracted With $NaBrO_3$	Without $NaBrO_3$
1	97.5	92.4
2	98.6	93.4
4	99.3	91.9
8	99.3	96.8
15	99.0	95.3

Concentration of Reagents.—The effect of the concentration of the reagents was examined. The results are summarized in Table II, but the relation between the amounts of bromate and the yield is not clear.

TABLE II. EFFECTS OF CONCENTRATIONS OF ACETYLACETONE AND BROMATE

Concn. of acetylacetone	% Extracted Amounts of 1 M $NaBrO_3$ added, ml.			
%	0	0.5	1.0	2.0
5	83.0	97.0	90.6	97.0
10	88.9	98.0	98.9	98.6
20	94.5	98.9	99.3	98.2

Extraction Solvents.—It is expected that extractability would vary with different solvents.

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[1] Part VIII of this series, This Bulletin, 35, 233 (1962).

[2] E. C. Pitzer, U. S. Pat. 2615798 (Oct. 28, 1952).

[3] D. F. Peppard, G. W. Mason and S. W. Moline, *J. Inorg. Nucl. Chem.*, 5, 141 (1957).

[4] G. W. Smith and F. L. Moore, *Anal. Chem.*, 29, 448 (1957).

TABLE III. EXTRACTION BY VARIOUS SOLVENTS

Solvent	% Extracted
Carbon tetrachloride	98.5
Benzene	98.9
Chloroform	97.8
Xylene	96.9
Isoamyl acetate	94.6
Methyl isobutyl ketone	93.0
Isopropyl ether	78.6

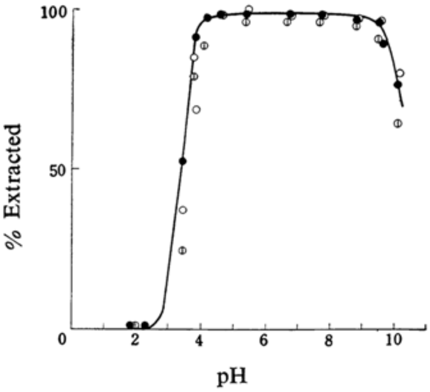

Fig. 1. Extraction curve of ^{144}Ce.
○ Benzene
● Carbon tetrachloride
⌽ Xylene

The results of the extraction with 20% acetylacetone in various solvents are summarized in Table III. Carbon tetrachloride and benzene are found to be more effective for extraction.

Extraction and Back-extraction.—The extraction curves of ^{144}Ce by the general procedure with carbon tetrachloride, benzene and xylene are shown in Fig. 1. ^{144}Ce is completely extracted in the range of pH 4∼9, and the range is wider than the case of the extraction of carrier cerium[1], but the pH range in the back extraction curve in the latter case is similar to that of the extraction curve of carrier-free ^{144}Ce.

In order to investigate the suitable conditions for the stripping of ^{144}Ce, an aliquot of the organic solution containing the chelate prepared by the general procedure was shaken with mineral acid or a hydrogen peroxide solution for one minute. After the aqueous phase had been removed, the remaining organic phase was shaken again with fresh mineral acid (second stripping). The results are summarized in Tables IV and V. ^{144}Ce in organic phase is readily stripped by dilute acid or hydrogen peroxide solution of about 10%.

TABLE IV. BACK-EXTRACTION WITH MINERAL ACIDS

Stripping soln.	CCl$_4$ as solvent 1st stripping %	CCl$_4$ as solvent 2nd* %	Benzene as solvent 1st %	Benzene as solvent 2nd* %
0.1 N H_2SO_4	99.0	100.0	95.1	99.1
1 N H_2SO_4	99.4	100.0	92.8	98.2
0.1 N HCl	99.3	100.0	96.5	99.7
1 N HCl	99.8	100.0	93.7	99.5
0.1 N HNO_3	99.9	100.0	97.2	100.0
1 N HNO_3	98.8	100.0	96.7	99.8

* The total of 1st and 2nd stripping.

TABLE V. BACK-EXTRACTION WITH HYDROGEN PEROXIDE

Concn. of H_2O_2, %	Back-extracted, %
2	20.1
4	36.9
6	76.9
8	96.6
10	95.0

Decontamination from Fission Products.—The elements found in fission products were tested for their degree of separation from ^{144}Ce. Each pure nuclide was examined individually by the general procedure, and after the completion of this procedure the organic phase was washed with an equal volume of acetate buffer solution (pH 5.6) containing bromate, then the organic phase was shaken with 2 ml. of 0.1 M nitric acid. The results are summarized in Table VI. Decontamination from ^{90}Sr (^{90}Y), ^{106}Ru, ^{137}Cs and rare earth nuclides (e. g., ^{152,154}Eu), except ^{95}Zr (^{95}Nb), is complete. ^{95}Zr (^{95}Nb) is extracted in the range of pH 2∼7[5]; therefore, it is unavoidable that some ^{95}Zr (^{95}Nb) is joined with ^{144}Ce.

For the separation of ^{144}Ce from ^{95}Zr (^{95}Nb), the authors devised two tentative schemes;

TABLE VI. BEHAVIOR OF OTHER NUCLIDES (EXPRESSED AS PERCENTAGE FOUND IN 0.1 M HNO_3 PHASE)

Nuclide	CCl$_4$ as solvent	Benzene as solvent
Sr-Y-90	0.07	0.01
Zr-Nb-95	22.5	—
Ru-106	0.1	0.1
Cs-137	0.2	0.1
Eu-152, 154	0.01	0.07
Ce-144	99.1	99.6

TABLE VII. THE EFFECT OF $NaNO_3$ ON STRIPPING

Nuclide	Concn. of $NaNO_3$ M	Remained in org. phase
Ce-144	1	1.0
	2	1.2
Zr-Nb-95	1	70.5
	2	82.1

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[5] N. Suzuki and T. Omori, This Bulletin, unpublished.

(a) and (b). Scheme (a) was designed on the basis of the following experimental results: ^{95}Zr (^{95}Nb) extracted in the organic phase is not practically stripped with the mixed solution of 0.01 M nitric acid and 2 M sodium nitrate; on the other hand, ^{144}Ce is stripped quantitatively with the same solution (cf. Table VII). ^{95}Zr (^{95}Nb) stripped in the aqueous phase is extracted again less than 60%, while ^{144}Ce is re-extracted more than 90%. By repeating the extraction-washing cycle twice, the radiochemically pure ^{144}Ce can be prepared from fission products.

In scheme (b), thiocyanate ion serves as a complete masking agent for cerium in the case of acetylacetone extraction[6], while ^{95}Zr (^{95}Nb) is not affected by the presence of thiocyanate[5]. Thiocyanate ions are easily destroyed with nitric acid. Then ^{144}Ce is extracted from the aqueous phase by adjusting the pH with an acetate buffer solution.

By either of the methods nearly 90% of the ^{144}Ce was recovered, while ^{95}Zr (^{95}Nb) was present less than 1% of the initial amount. Fortunately, fission products aged for two years or so have a smaller content of ^{95}Zr (^{95}Nb) than ^{144}Ce; therefore, the contamination by ^{95}Zr (^{95}Nb) is practically negligible. The purity of the ^{144}Ce obtained from such fission products by these methods is expected to be higher than that of ^{144}Ce separated from the mixture (ca. 1 : 1) of ^{144}Ce and ^{95}Zr (^{95}Nb). ^{144}Ce of a radiochemical purity of over 99% was obtained from the fission products with a high yield.

Separation of ^{144}Pr from ^{144}Ce. — As praseodymium is not extractable, the effective separation of a short-life daughter ^{144}Pr from its parent ^{144}Ce is possible. After the radioactive equilibrium of ^{144}Ce (^{144}Pr) in the organic phase has been established, an aliquot of the organic phase is shaken with 3 ml. of the washing solution with or without bromate, and then ^{144}Pr is brought into the aqueous phase. The aqueous phase is washed with carbon tetrachloride; then the radioactivity is measured by a well-type scintillation counter. The radiochemical purity of ^{144}Pr is measured at more than 99.5%. The separation takes only 3 min. or so. The results are summarized in Table VIII, together with the elapsed time after the preparation of the organic phase containing ^{144}Ce. As is shown in Table VIII, bromate is not always necessary to avoid the contamination of ^{144}Ce, and, for practical purposes, it is better not to add bromate to the washing solution. Milking of ^{144}Pr is possible succesively, and the results of the half life of ^{144}Pr show a good agreement with the literature's value (17.5 min), as shown in Fig. 2.

TABLE VIII. RADIOCHEMICAL PURITY OF Pr-144 OBTAINED BY WASHING

Solvent	Standing time after preparation, hr.	Purity %
Benzene	8	99.4
	15	99.2
	22	98.6
	50	97.6*
CCl_4	25	99.1
	33	99.8*
	50	99.6*

* The washing solution contains $NaBrO_3$.

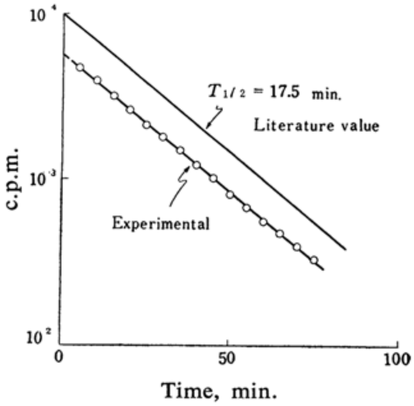

Fig. 2. Decay of ^{144}Pr.

Summary

^{144}Ce was extracted with acetylacetone in a benzene or in a carbon tetrachloride solution by shaking for 3 min. at a pH range of $4\sim9$. Though an oxidizing agent such as bromate was not always necessary, the presence of bromate makes the time for extraction shorter. Decontamination from other fission products, ^{90}Sr (^{90}Y), ^{106}Ru, ^{137}Cs, and rare earths (e.g., ^{152,154}Eu), except ^{95}Zr (^{95}Nb), was found to be negligible. The contamination of ^{95}Zr (^{95}Nb) was reduced to a negligible amount by repeating the cycle of extraction and stripping or by masking ^{144}Ce with thiocyanate. The separation of ^{144}Ce from fission products with acetylacetone was attempted. ^{144}Pr with a radiochemical purity of more than 99% was easily obtained by washing the organic phase with an acetate buffer solution of pH $5\sim8$.

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[6] At the concentrations of 1 and 2 M KSCN, ^{144}Ce is extracted at only 3 and 2% respectively.