The Mutual Separation of ^{227}Ac, ^{227}Th, ^{223}Ra, and ^{223}Fr by the Solvent Extraction Technique Using Bis(2-ethylhexyl)phosphoric Acid as an Extractant

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The separation and purification of ^{227}Ac, ^{227}Th, ^{223}Ra, and ^{223}Fr were studied by the solvent extraction method using HDEHP (bis(2-ethylhexyl)phosphoric acid) as an extractant. The mutual separation of Ac, Th, and Ra was achieved, and new milking processes for ^{223}Fr and ^{228}Ac are presented.

The cyclic relation between ^{227}Ac, ^{227}Th, ^{223}Fr, and ^{223}Ra in natural actinium decay series is shown in Fig. 1. These nuclides are important as radioactive tracers, and interesting from the viewpoint of investigation of natural radioactive substances. Measurement of the radioactivity of ^{227}Ac is especially difficult, since its γ-activity and α-activity are very weak and the energy of β-rays are too low for quantitative detection. Many authors have reported on the application of radiation of its daughter nuclides to the detection and determination of ^{227}Ac. The separation of these nuclides is very important for the chemistry of natural radioactive substances.

The separation of Ac and Ra has been attempted by the cation exchange[1] and solvent extraction methods utilizing the TTA-TBP synergistic effect,[2] but these methods have certain drawbacks.

The cation exchange method,[1] because of its rather prolonged elution time, is not suitable for the separation of short-lived tracers such as ^{228}Ac ($t_{1/2}$=6.13 h)[3] and ^{223}Fr ($t_{1/2}$=21 min)[3] from each other. In the solvent extraction method using TTA as an extractant, it is necessary for the aqueous solution to have acidity of 4—5 pH, in spite of the remarkable tendency of Ac and Th toward hydrolysis in such a low acidic solution. The separation coefficient of Ac and Ra is expected to increase with the decrease in acidity of the aqueous solution, and there is a possibility of the hydrolysis of Ac also increasing in such a low acidic solution. Once the hydrolysis of Ac occurs, the separation coefficient should decrease because of the decrease in the proportion of the native ion Ac^{3+} in aqueous solution. It would be better to extract Ac from the solution whose acidity is as high as possible. Since HDEHP can extract some multivalent metal elements selectively from a highly acidic solution,[4] it is expected that Ac, Ra, and Th can be effectively separated from each other by HDEHP extraction. We have studied the application of HDEHP as an extractant to the separation of ^{227}Ac, ^{227}Th, ^{223}Ra, and ^{223}Fr.

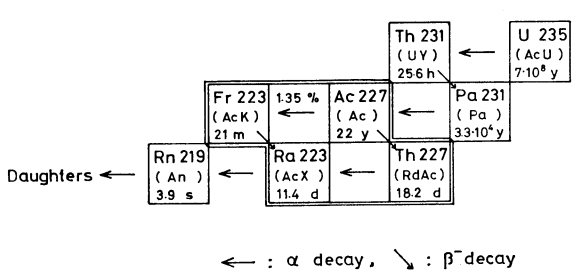

Fig. 1. Cyclic relation of ^{227}Ac, ^{227}Th, ^{223}Ra, and ^{223}Fr in natural actinium decay series.

It is well known that Th is quantitatively extracted by 1 M HDEHP–benzene solution from 0.2—0.5 M HCl solution. However, the extraction behavior of Ac, Ra, and Fr in the HDEHP extraction system is not known as yet. From the difference in the charge of the native ions Ac^{3+}, Ra^{2+}, and Fr^{+}, we can expect that Ac can most easily be extracted. Thus, the extraction conditions of Ac in the HDEHP extraction system were investigated first. It was found that Th is much more extractable than Ac and the separation of Ac and Th is easy. Thus the main problem was to separate Ac and Ra or Fr, and we tried to find the exact conditions for the separation of Ac and Ra. Fr goes to the Ra-fraction in our separation method, and there remains the problem of separating ^{223}Ra and ^{223}Fr. However, the difference in their half-lives is too large, and makes our procedures feasible. It is rather worthwhile to establish a new milking method of ^{223}Fr by which we can easily get ^{223}Fr grown from ^{227}Ac.

Experimental

Reagents. All the chemicals used were of analytical grade. HDEHP was purified by the procedures reported previously.[5]

Radioisotopes and Their Detection. *Ac*: ^{228}Ac was used as a tracer of Ac, whose γ-activity is very easy to detect,[3] and was prepared by the cation exchange chromatography method from ^{228}Ra isolated from ^{232}Th. When a sample of ^{228}Ac contains any amount of ^{228}Ra that is a parent nuclide of ^{228}Ac, the γ-activity of the sample does not vanish because of the radio-equilibrium between ^{228}Ac and ^{228}Ra. Thus, the purity of the sample of ^{228}Ac could be confirmed by checking the decay out of the γ-activity of the sample in each experiment.

Ra and Th: ^{223}Ra and ^{227}Th isolated from ^{227}Ac in their radio-equilibrium by cation exchange chromatography were used as the tracers. These two nuclides were determined by measuring their γ-spectra by Ge(Li) detector and calculating the peak area of their characteristic γ-ray peaks.

pH Buffer Solution. Considering the fact that the distribution ratios of multivalent metal ions in HDEHP extraction system are expected to be a sensitive function of the acidity of the solution, the pH value of the aqueous phase must be fixed in order to keep the reproducibility of the extraction. Thus, we used "Clark-Lubbs pH buffer solution"[6] which consists of KCl and HCl in the range of pH$\leq$ 2.2, and KH phthalate and HCl in the range of pH$\geq$2.2, where the concentration of both salts in each solution is 0.05 M. Solutions, the pH values of which were 1.0—3.6 were prepared using this buffer solution in this work. Since there might be difference in their behavior between KCl-system and KH phthalate-system, two kinds of solutions made from two different salts were prepared in the range of 2.1$\leq$pH$\leq$

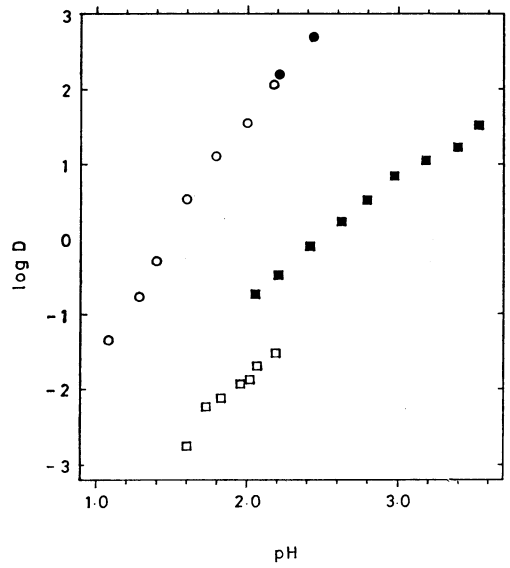

Fig. 2. Relations between D_{Ac}, D_{Ra} and the acidity of the aqueous phase.
○● : D_{Ac} when KCl (○) and KH phthalate (●) buffer solution was used. □■ : D_{Ra} when KCl (□) and KH phthalate (■) buffer solution was used.

2.2, and the data were compared with each other.

Apparatus. The apparatus used are as follows. *Separatory Funnel Shaker*: IWAKI KM type (200—400 rpm), *Ge(Li) Detector*: ORTEC model number 8101-1820 (the effective volume is about 60 ml), *Multichannel Pulse Height Analyser*: TOSHIBA USC-1 4096 ch (controlled by a mini-computer TOSBAC-40 A), *NaI Scintillation Counter*: HITACHI well type $1^3/_4'' \times 2''$, *Digital pH Meter*: ORION 801-A type.

Procedures. The back extraction behavior of Ac was investigated according to the following procedures. The pH value of the ^{228}Ac solution was adjusted to 3.0 and ^{228}Ac was extracted with a 1M HDEHP-benzene solution. Then a 5 ml portion of the organic phase containing ^{228}Ac was poured to the another separatory funnel and shaken for 20 min with 5 ml of buffer solution.

The forward extraction of ^{223}Ra was investigated with the shaking time of 20 min.

In both cases of Ac and Ra, the pH value of the aqueous phase was checked after extraction with a digital pH meter. A 2 ml portion of each phase was taken into a polyethylene test tube and their γ-rays were measured. The calculation of the peak area of the characteristic γ-rays of ^{223}Ra and ^{227}Th were carried out with a mini-computer system[7] connected to the multichannel pulse height analyzer.

For the final experiment to check the separation method, a mixed solution of ^{227}Ac, ^{227}Th, and ^{223}Ra in radio-equilibrium was used. A radio-equilibrium mixture of ^{227}Ac and ^{223}Fr was used for the check of the milking of ^{223}Fr.

The distribution ratio of each element is defined by

$$D_M = C_{M.org}/C_{M.aq}$$

where M denotes metal element, $C_{M.org}$ the concentration of M in the organic phase and $C_{M.aq}$ that in the aqueous phase. The separation coefficient is defined by

$$\alpha_{Ac,Ra} = D_{Ac}/D_{Ra}.$$

Results and Discussion

Dependence of D_{Ac} and D_{Ra} on the pH in 1 M HDEHP–Benzene Extraction System. Figure 2 shows the relation between the logarithm of D_{Ac} or D_{Ra} and the pH value of the aqueous phase. They show linearity with different slopes. The slope for Ac is *ca.* 3.0 and that for Ra, 1.9. In the data of D_{Ra}, there is a large difference between the two kinds of buffer solutions containing KCl and KH phthalate. Two explanations are possible. One is the difference of the stability of the complex ion of Ra with Cl^- or $C_6H_4(COO)_2^{2-}$; the other is the synergistic effect caused by the coordination of the neutral phthalic acid molecules to the extracted compound of Ra. However, we could not decide which explanation is feasible, while it is clear that D_{Ra} shows a larger value when KH phthalate is used than when KCl is used. Considering that there is no difference between the two kinds of buffer solution in the data of D_{Ac}, it is obvious that the separation coefficient of Ac and Ra ($\alpha_{Ac,Ra}$) becomes larger when KCl is used and the KCl-buffer solution is more suitable for the separation of Ac and Ra. The calculated values of $\alpha_{Ac,Ra}$ using the above-mentioned data, are given in Table 1. These values were calculated from the two straight lines drawn by the method of linear least square fitting. There is the tendency that $\log(\alpha_{Ac,Ra})$ increases in proportion to the pH value. The maximum of $\alpha_{Ac,Ra}$ is 4.1×10^3 at pH=2.2 where over 99.4% of Ac is extracted into the orgaic phase and over 99.9% of Ra remains in aqueous phase. Thus, the separation of Ac from Ra can be made by adjusting the pH of the aqueous solution to 2.2 and then shaking it with 1 M HDEHP–benzene solution, as described in the following. Th which is more extractable than Ac can be

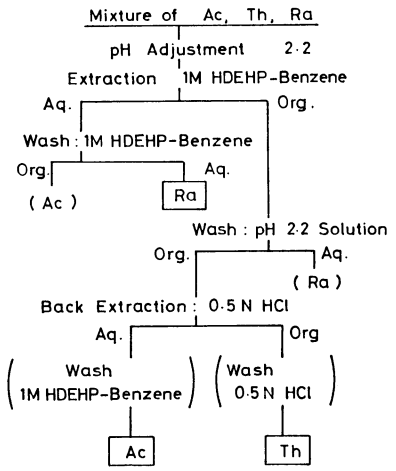

Fig. 3. Separation procedures for Ac, Th, and Ra system.

TABLE 1. SEPARATION COEFFICIENT OF Ac AND Ra IN THE 1 M HDEHP–BENZENE EXTRACTION SYSTEM

pH	D_{Ac}	D_{Ra}	$\alpha_{Ac,Ra}$	$\log \alpha_{Ac,Ra}$
1.6	1.914	0.0024	778.0	2.891
1.7	3.917	0.0038	1025.4	3.001
1.8	8.017	0.00593	1351.9	3.131
1.9	16.405	0.00920	1783.2	3.251
2.0	33.574	0.01429	2349.5	3.371
2.1	68.707	0.02220	3094.9	3.491
2.2	140.61	0.03450	4075.5	3.610

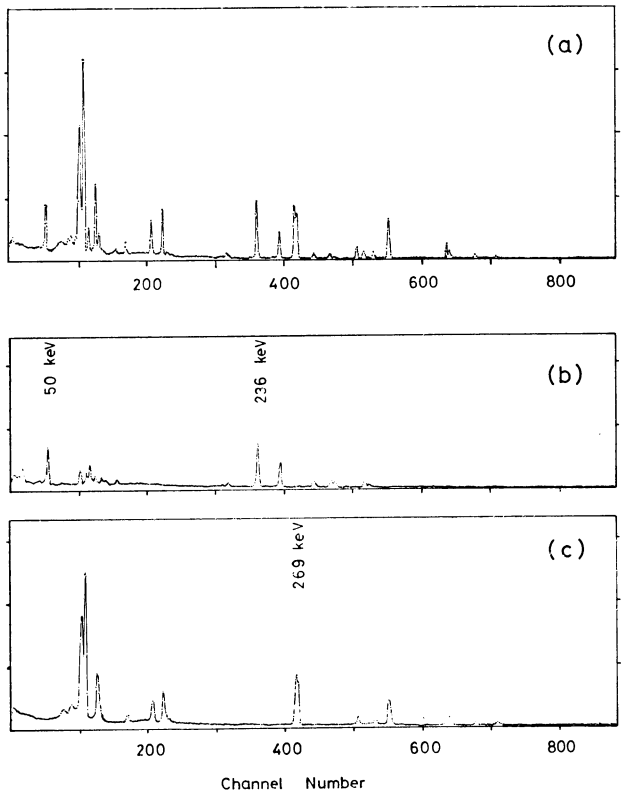

Fig. 4. γ-Spectra of fractions separated.
(a) Starting mixture of ^{227}Ac, ^{227}Th, and ^{223}Ra, (b) ^{227}Th-fraction separated, (c) ^{223}Ra-fraction separated.

separated from Ra and goes to the Ac-fraction.

The Mutual Separation of Ac, Ra, and Th. From the above result, and the fact that Th is quantitatively extracted by 1 M HDEHP–benzene solution from 0.1—0.5 M HCl solution, we propose the following separation method for Ac, Th, and Ra system (Fig. 3).

The acidity of the mixed solution of Ac, Th, and Ra is adjusted to pH=2.2 and the solution is shaken with 1 M HDEHP–benzene solution. Ac and Th are quantitatively extracted to the organic phase while Ra remains in the aqueous phase. Pure Ra solution can be easily prepared by washing the aqueous phase with the same organic solution. The organic phase is washed by the solution of pH 2.2 and shaken with 0.5 M HCl solution. Ac is back-extracted to the aqueous phase while Th remains in the aqueous phase.

Ra is recovered as HCl solution whose pH is equal to 2.2, Ac, as 0.5 M HCl solution, and Th, as 1 M HDEHP–benzene solution. The yield of each element is over 99%.

Figure 4 shows the γ-spectrum of each fraction after the separation of ^{227}Ac, ^{227}Th, and ^{223}Ra which were in radio-equilibrium. Comparing the spectrum of each fraction with that of the original mixed solution, we see that these elements are isolated and purified. No characteristic γ-peaks could be found in the ^{227}Ac-fraction. However, when a sample of ^{227}Ac having a much higher specific activity is used, the growth of the γ-peaks of ^{223}Fr will be detected in a period of about 40 min after purification of ^{227}Ac.

Milking Method for ^{223}Fr Using HDEHP–Solvent Extraction. We can easily carry out the milking of ^{223}Fr from ^{227}Ac by utilizing the principle of the above-mentioned separation method. The procedure is shown in Fig. 5. After recovering ^{227}Ac as 0.5 M HCl solution (Fig. 3), the pH is adjusted again to 2.2 and shaken with 1 M HDEHP–benzene solution to prepare the organic solution of ^{227}Ac to be used as a milking source. Extraction of ^{227}Ac is carried out twice because ^{223}Fr has γ-rays very similar to those of ^{227}Th and it is better to completely eliminate the contamination of ^{227}Th. By shaking the milking source with the solution of pH 2.2 once, ^{223}Fr and a small amount of ^{223}Ra that have grown in the organic phase is back-extracted to the aqueous phase. In a period of 2.5—3.0 h after the first back-extraction, ^{223}Fr whose half-life is 21 min grows and attains radio-equilibrium with ^{227}Ac in the organic phase. Thus, after standing for 2.5—3.0 h, ^{223}Fr should be back-extracted to the aqueous phase by shaking with the same buffer solution. ^{223}Ra also grows in this period. However, because the half-life of ^{223}Ra is 11.4 days and too long compared with that of ^{223}Fr, the growth of ^{223}Ra in this period does not need to be considered, unless the amount of ^{227}Th in the organic phase is not too large. ^{223}Fr is easily isolated from ^{227}Ac by carrying out the same extraction twice. Figure 6 shows the γ-spectrum of ^{223}Fr purified by this milking method. In the second measurement,

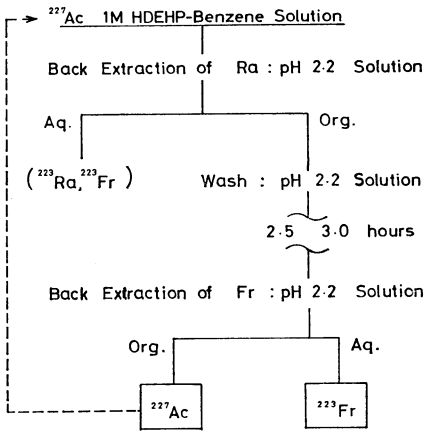

Fig. 5. Milking procedures for ^{223}Fr.

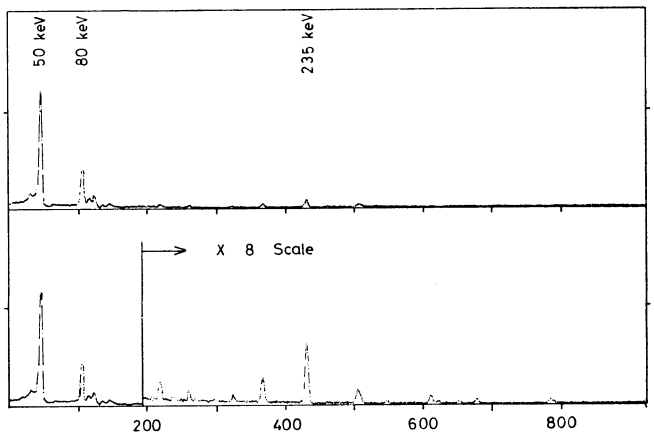

Fig. 6. γ-Spectrum of ^{223}Fr obtained by the proposed milking method.

almost all of the γ-peaks disappeared and a slight growth of the characteristic γ-peaks of ^{223}Ra and the Kx-rays of Rn were observed.

Possibility of the Determination of ^{227}Ac Utilizing the γ-Activity Measurement of ^{223}Fr. It is impossible to detect and determine ^{227}Ac by its γ-activity since it has no characteristic γ-rays that have intensity sufficient for measurement. Thus, the only way to detect and determine ^{227}Ac by the γ-ray measurement is to measure the γ-activity of its daughter nuclides (^{223}Ra, ^{223}Fr, and ^{227}Th). However, for ^{223}Ra and ^{227}Th, because of their long half-lives of 11.4 and 18.2 days respectively, we must wait more than 3 months for the attainment of radio-equilibrium for the determination of ^{227}Ac. For ^{223}Fr, since its γ-rays are similar to those of ^{227}Th, correct measurement of its γ-activity is difficult. However, the proposed separation method can eliminate the contamination of ^{227}Th which prevents accurate measurement of ^{223}Fr, and we can expect a new method to determine ^{227}Ac by measuring the γ-activity of ^{223}Fr in radio-equilibrium with ^{227}Ac. As shown in Fig. 6, the peak of 50 keV of ^{223}Fr has sufficient intensity to be measured and ^{227}Ac can be easily determined by correct measurement of this peak. It is also possible to determine the absolute amount of ^{227}Ac by this γ-ray, if we know the absolute abundance ratio of this γ-transition and its relation with the absolute disintegration rate of ^{227}Ac. The proposed method for the determination of ^{227}Ac is very attractive. However, we must be careful no to allow even a slight contamination of ^{227}Th in ^{223}Fr fraction, since ^{227}Th also has intense γ-ray of 50 keV. Elimination of ^{227}Th is completely done by the separation method, and check of contamination of ^{227}Th could be easily made by checking the relative ratio of the intensity of each γ-peak.

Separation of ^{228}Ac and ^{228}Ra in Natural Thorium Decay Series. The separation method using HDEHP extraction can be applied to the ^{232}Th-^{228}Ra-^{228}Ac chain in the natural thorium decay series. ^{228}Ac is the most useful radioactive tracer of Ac, and is convenient for obtaining ^{228}Ac from ^{228}Ra by applying the simple milking method. The separation of ^{228}Ra and ^{228}Ac can be easily made by HDEHP extraction, and a new milking method for ^{228}Ac utilizing HDEHP extraction was proposed as shown in Fig. 7.

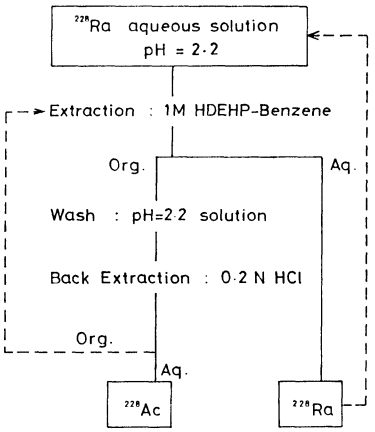

Fig. 7. Milking procedures for ^{228}Ac from ^{228}Ra.

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