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Development of Analysis of Uranium Isotopes in Environmental Samples

Myung Ho Lee, Hyun Sang Shin, Mi Kyung Kim, Gun Sik Choi, Kwang Hee Hong, Yung Hyun
Cho, Chang Woo Lee,

Korea Atomic Energy Research Institute

ABSTRACT

Using TBP extraction and anion exchange step, a precise and quantitative technique of uranium isotopes determination was developed. For overcoming the demerits of the conventional TBP extraction method, sample materials was decomposed with HNO_3 and HF and uranium isotopes were purified by TBP extraction and ion exchange step. Using the modified method step, the concentrations of uranium isotopes in the IAEA-Reference sample were so consistent with reference values reported by IAEA. The concentrations and activity ratios of uranium isotopes at the different sample were similar to those in the natural conditions.

1. Introduction

Natural radionuclide existing in the environment is an important in the general study of radionuclide migration, and the results of behavior of radionuclides may be used as a reference data in the case of an accident in a radioactive waste repository or in a nuclear fuel plant. Among the natural radionuclides occurrence in the environment, uranium isotopes are good tracers to study the behavior

of these radionuclides, because natural uranium can be easily detected in nearly all materials from the environment.

There are many radiochemical procedures for uranium isotopes analysis[1-6]. However, only a few of them are suitable as well for environmental samples as for waste samples. One of these methods, the radiochemical assay of uranium with TBP has been used largely for environmental samples[7]. However, though the conventional TBP extraction method is more simple and rapid than other methods, sometimes, this method can not completely separate from plutonium isotopes in high contaminated soil samples.

In this study, to overcome the disadvantages of the conventional TBP extraction method, using TBP extraction and anion exchange step, a precise and quantitative technique of uranium isotopes determination was developed. The optimized analytical method of uranium isotopes was validated by application to IAEA-Reference soils as well as environmental samples.

2. Description of radiochemical procedures

A flow sheet of the conventional analytical methods of uranium with TBP is given in Fig. 1. In the following section the main steps of the radiochemical procedure developed in this study are described in detail and individual steps are discussed. A flow sheet of the developed radiochemical assay of uranium is presented in Fig. 2.

Decomposition of the ashed sample material

As tracer for determination of the yield, known amounts of ^{232}U activity are added into the sample material ashed at $550\text{ }^{\circ}\text{C}$. 40 ml concentrated HNO_3 and 10 ml HF (48 %) are added and evaporated to dryness. 2 ml concentrated HClO_4 and 1 ml H_2O_2 are added. This procedure is repeated once more. After the residue is dissolved with 50 ml (), the sample is heated for 30 minutes. After cooling the solution is filtered and the re

Separation of uranium isotopes

The sample solution is transferred into a 250 ml separatory funnel. As a salting agent, 15 ml NaNO_3 (50 W/V %) and 5 ml $\text{Al}(\text{NO}_3)_3$ (50 W/V %) done uranium blank test are added into the sample solution. 15 ml TBP- CCl_4 (1 + 9) is dropped into the sample solution and shaken for 15 minutes. After phase separation, the TBP- CCl_4 phase is transferred into a 250 ml separatory funnel. The aqueous phase is shaken once more for 15 minutes with 15 ml TBP- CCl_4 (1 + 9). The organic phase is added to the phase obtained in the first extraction step in the 250 ml separatory funnel and the aqueous phase is discarded. In this step, the matrix elements such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , and Fe^{3+} , are remained in the aqueous phase and the uranium fraction is extracted into the TBP- CCl_4 phase. The organic phase containing uranium fraction is purified by shaken for 5 minutes with 20 ml NaNO_3 (50 W/V %) and the aqueous phase is discarded. For removing thorium isotopes, the organic phase is shaken for 15 minutes with 30 ml HCl (1 + 1) and the aqueous phase is discarded. The organic phase is shaken for 15 minutes with 15 ml HNO_3 (1 + 11). This procedure is repeated once more. Uranium is backextracted to the aqueous phase and the organic phase is discarded.

Radiochemical purification of the uranium fraction

The aqueous solution is transferred into a 50 ml beaker. 1 ml H_2O_2 is added and the solution is evaporated to dryness. The residue is dissolved in 10 ml 9 M HCl, then the sample is passed through a conditioned anion exchanger column at a rate of 1 ml/minute. The column is 15 cm long, its inner diameter is 8 mm, and it contained 2 g Dowex 1x2, 50-100 mesh, which had been filled into the column together with 10 ml 7.2 M HNO_3 and then wash with 50 ml 9 M HCl. The washing solution is discarded. For elution of uranium 50 ml 1 M HNO_3 are used. The elute solution is evaporated to dryness in a crystallizing dish.

Electrodeposition

Electroplating solution was prepared as follows[8]: 43 g ammonium oxalate, 53 g ammonium sulfate, 18 g hydroxylammonium sulfate and 2 g diethyl triamino pentaacetic acid (DTPA) are

dissolved in one liter of H₂O and then the pH is adjusted to exactly 1.8 with H₂SO₄. The crystallizing dish containing uranium isotopes was rinsed with 3 ml electroplating solution and transferred the rinsing solution into an electrodeposition cell. The crystallizing dish was washed three times with 3 ml electroplating solution and transferred it to the cell. The distance between the two electrodes was adjusted to about 5 mm. Darkening of the cathode occurred at a spacing of 2 mm, and excessive voltage was required at a spacing of about 8 mm, resulting in boiling and electrolyte loss. The electrodeposition of the uranium isotopes on a stainless steel disc was performed at a current of 950 mA for 2 hours.

Alpha spectrometry system

The alpha spectrometer (EG&G ORTEC, Model 676A) was composed of an ion-implanted silicon detector (ORTEC, size : 450 mm²; alpha resolution : 25 keV FWHM at 5.486 MeV of ²⁴¹Am) in a vacuum chamber (Edwards Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier and a multichannel pulse-height analyzer. During the measurement inside the chamber a vacuum below 10⁻² Torr was maintained with a vacuum pump.

3. Results and discussion

Validation of radiochemical procedure

Using the conventional TBP method, uranium isotopes spectra in the IAEA-367 SEDIMENT sample were presented in Fig. 3. The IAEA-367 SEDIMENT sample was highly the radionuclides level contaminated by nuclear weapon tests by U.S. from 1948 to 1958, collecting at the Enewetak Atoll in the Marshall Islands (Central Pacific Ocean). The reference activity values were reported as 102 Bq kg⁻¹ for ⁹⁰Sr, 195 Bq kg⁻¹ for ¹³⁷Cs, 26.4 Bq kg⁻¹ for ²⁴¹Am, 38 Bq kg⁻¹ for ^{239,240}Pu, 0.08 Bq kg⁻¹ for ²³⁸Pu, respectively. As presented in Fig. 3, with the conventional TBP method, peak of ^{239,240}Pu was shown distinctly in the spectrum of uranium isotopes. Also, in the region of ²³²U, the weak peaks of ²⁴¹Am and ²²⁸Th were overlapped with the peak of ²³²U. This means that the conventional TBP method can not completely separate from the actinide such as the plutonium,

americium and thorium isotopes. However, as shown in Fig. 4, the alpha peaks of uranium isotopes spectra in the IAEA-367 SEDIMENT sample were well resolved (FWHM; 27 keV) and the spectrum was free from contributions due to various plutonium, americium and thorium isotopes, using the developed analytical method of uranium isotopes.

In Table 1, the chemical yields obtained for IAEA-Reference samples were compared between the conventional TBP method and the modified method. The chemical yields of the developed method in this study was a little lower than those of the conventional TBP method. As described above, the peak of ^{232}U as a yield tracer was overlapped with the peaks of ^{241}Am and ^{228}Th . In the spectrum analysis of uranium isotopes, the peak of ^{232}U can not be distinguished from the peaks of ^{241}Am and ^{228}Th that the peak of ^{232}U was overestimated. Therefore, the chemical yield calculating the peak of ^{232}U sometimes is increased in the conventional TBP method.

The modified method for the determination of uranium in environmental samples was validated by its application to several IAEA-Reference soils. As shown in Table 1, the concentrations of uranium isotopes using the modified method step are so consistent with reference values reported by IAEA that this method can be applied to different soils with reliable results. However, the concentrations of uranium isotopes with the conventional TBP method was somewhat lower than reference values, though the chemical yields were a little higher than those with modified method. The reason for the lower activity values of uranium isotopes with the conventional TBP method may be incomplete decomposition of sample material. In the conventional TBP method, only HNO_3 was used for decomposition of sample material that uranium isotopes in the inner soil were seldom leached into HNO_3 solution. Therefore, the concentrations of uranium isotopes with the conventional TBP method was a little lower than reference values reported by IAEA. However, in the modified method, HF was used to completely destroy of soil matrix that most of uranium in the sample material was leached into HNO_3 solution. Also, in the spectrum analysis with the conventional TBP method, overestimated ^{232}U peak due to incomplete separation from the actinide affects on lower concentration values of uranium isotopes.

Application to environmental samples

The results of concentrations and activity ratios of uranium isotopes in environmental samples were

represented in Table 2. The concentrations of uranium isotopes at the different sample were similar to natural value of uranium. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ were found to be within the narrow range of 1.06 - 1.12 with a mean value of 1.11. This means that the activity of ^{238}U is nearly equal to that of ^{234}U in different samples, because of radioactive equilibrium in natural conditions. Also, the mean activity ratio of $^{235}\text{U}/^{238}\text{U}$ was close to 0.051, which was the same as that for natural uranium.

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Table 1. Comparison of chemical yields between the modified and the conventional TBP extraction method

Sample material	Chemical yield (%)	
	Modified method*	Conventional TBP
IAEA-367	68.1 ± 5.4**	78.4 ±
IAEA-300	70.2 ± 5.9	71.4 ±
IAEA-375	67.4 ± 6.1	73.2 ±
Surface Soil	72.2 ± 6.8	73.2 ±

* Number of aliquots analyzed is 4

** Error is 1 σ

Table 2. Comparison of concentrations of ^{238}U between the modified and the conventional TBP extraction method in

IAEA-Reference samples		
Sample material	Concentration of ^{238}U (Bq/kg)	
	Recommended Value	Modified method*
IAEA-367	20.3	19.9 ± 2.1**
IAEA-300	64.7	65.2 ± 2.9
IAEA-375	24.4	24.0 ± 2.3

* Number of aliquots analyzed is 4

** Error is 1 σ

Table 3. Activity concentration of uranium isotopes together with activity ratios in the environmental samples

Sample material	Concentration of uranium isotopes (Bq/kg)		
	²³⁸ U	²³⁵ U	²³⁴ U
Surface Soil(0-5 cm)	23.3 ± 1.3*	1.39 ± 0.29	24.8 ± 5.4
Deep Soil(10-20 cm)	24.4 ± 0.8	1.27 ± 0.18	27.3 ± 1.2
Sea Sediment	20.1 ± 2.1	0.86 ± 0.21	21.2 ± 2.4
Lake Sediment	25.1 ± 1.9	1.18 ± 0.21	27.4 ± 2.1

** Error is 1σ

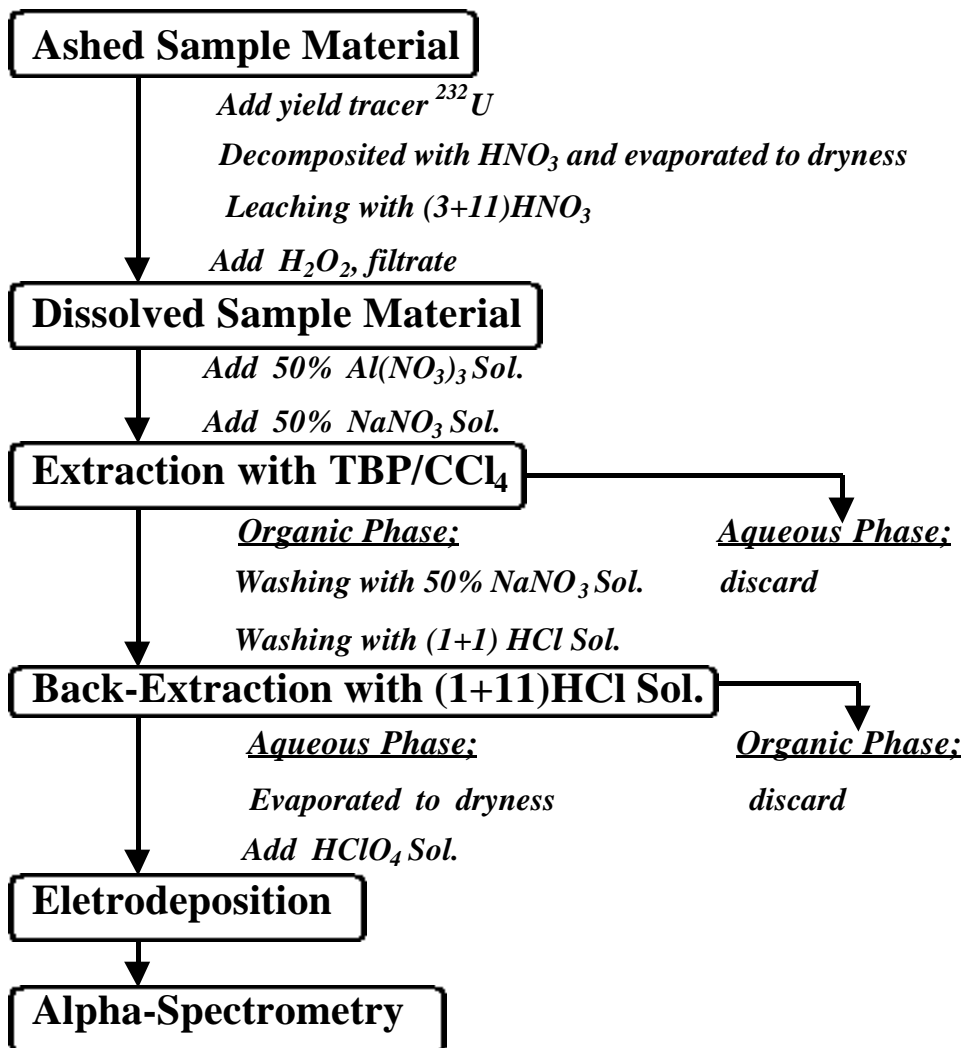


Fig.1. Conventional analytical procedure for uranium isotopes with TBP extraction

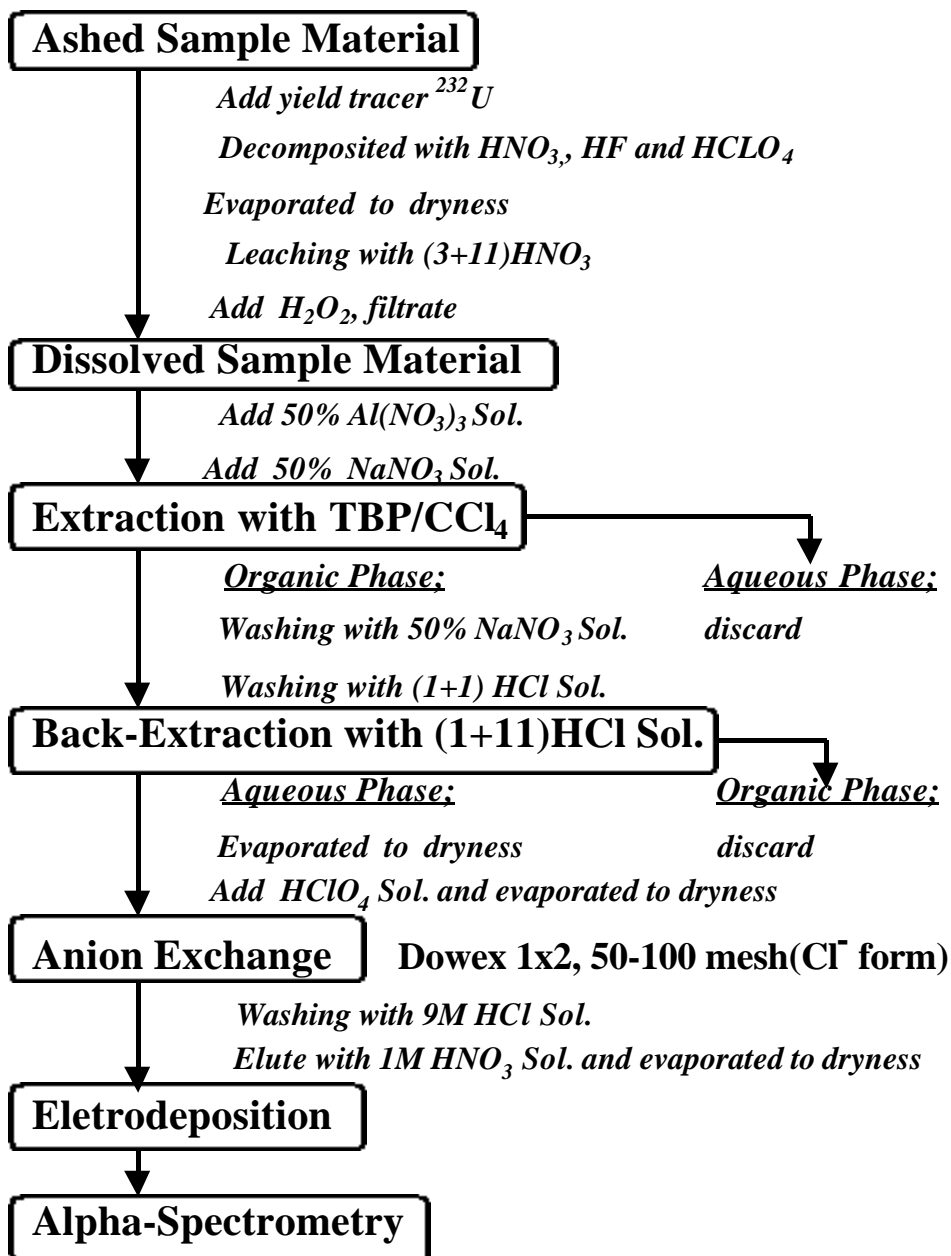


Fig.2. Modified analytical procedure for uranium isotopes with TBP extraction and anion exchange column