

Development of Radiochemical Analysis of Uranium Isotopes in Soil Samples with Extraction Chromatography

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크로마토 그래피 추출법을 사용한 토양시료중 우라늄 동위원소 화학분석법 개발

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Abstract - An accurate and rapid analytical technique of uranium isotopes in highly contaminated soil samples was developed and validated by application to the IAEA-Reference samples. For overcoming the demerits of the TBP extraction method, sample materials were decomposed with HNO_3 and HF, and uranium isotopes were purified by an anion exchange resin and a TRU Spec resin. With the extraction chromatography method, the hindrance elements were completely removed from the uranium fraction. The chemical yields with the extraction chromatography method were more 10 % higher than those with the TBP extraction method. The concentrations of uranium isotopes in soil samples using the extraction chromatography method were consistent with the reference values reported by the IAEA.

Key words : radiochemical analysis, uranium isotopes, TBP extraction, extraction chromatography

요약 - 방사성 동위원소에 오염된 토양시료에 대하여 정확하고 신속한 U 동위원소 분석법을 개발하였고 IAEA 표준시료에 적용하여 분석법의 타당성을 검증하였다. TBP 용매추출법의 단점을 보완하기 위해서 토양시료를 질산 및 불산을 사용하여 매트릭스 성분으로부터 우라늄을 완벽하게 추출하였고 이온교환수지와 TRU Spec 수지를 이용하여 우라늄 동위원소를 악티나이드 원소로부터 순수분리하였다. 크로마토 그래피 추출법을 사용하여 토양시료에서 우라늄 동위원소 화학수율은 TBP 용매추출법의 경우보다 10% 정도 증가하였다. 크로마토 그래피 추출법을 사용한 IAEA 토양시료에 분석결과는 IAEA에서 보고된 수치와 일치하였다.

중심어 : 방사능 분석, 우라늄 동위원소, TBP 추출, 크로마토 그래피 추출

INTRODUCTION

The determination of the uranium isotopes in soil and sediment is generally complicated, because chemical recoveries are variable due to interferences from major salt ions, the so-called

"matrix effects". These effects are especially troublesome because there is a strong sample-dependency involving the composition and mineralogy of soil samples. The problem of separating small quantities of uranium isotopes from chemically similar elements such as the

rare earths and from the transition elements sometimes happens in the determination of the uranium isotopes. Many methods have been described in the literature on the radiochemical procedures for uranium isotopes[1-17]. Only a few of them are suitable for uranium determination in the environmental samples. Among these methods, the solvent extraction method with TBP (tri-butyl-phosphate)[12] is simple and still has been used widely, but organic solvent material effects on electrodeposition and results in a poor energy resolution. Also, the anion exchange resin method[5,6] and the combined method using organic solvent and anion exchange resin[14] also have been used in the environment samples. Though the anion exchange resin method has an advantage of separation of uranium isotopes from interfering elements completely in natural soil samples, only the use of an anion exchange resin can not completely purify uranium isotopes from transuranium elements in the highly contaminated soil. Also, it is somewhat difficult to adjust column size, elution speed and pH control. The combined method using organic solvent and anion exchange resin can overcome disadvantages of solvent extraction method and anion resin method, but this method is relatively complicated and takes long a time.

Recently, a novel extraction chromatographic resin (TRU Spec resin), which is available from Eichrom Industries Inc., has been shown to retain U efficiently and separate selectively from interfering elements[17]. However, when larger amounts (5 g +) of soil and sediment samples are used for uranium isotopes, only TRU Spec resin is insufficient to purify uranium fraction in the matrix elements. Hence, it is necessary to remove hindrance elements in the leaching solution, before passing the sample solution through a TRU Spec resin. In this study, to overcome the disadvantages of the conventional uranium separation methods, extraction chromatography method using anion exchange resin and TRU Spec resin was developed to determine accurately and reliably uranium isotopes in environmental samples. The developed analytical method of uranium isotopes was validated by application to IAEA-Reference soils.

EXPERIMENTAL METHODS

Reagents and apparatus

All chemicals were of analytical reagent grade. Anion exchange resin (Dowex 1 × 8, 100 - 200 mesh; NO₃⁻ form, height; 6 cm, inner diameter; 8 mm) and prepacked columns of TRU Spec resin (bed volume; 1.3 ml, column length; 2.6 cm) were used in the experiments. The alpha spectrometer (EG & G, ORTEC, Model 676 A) 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.

Radiochemical separation

5 g of soil were weighed into a porcelain dish and ashed in a muffle furnace with a gradual heating program up to 600 °C to eliminate organic matter. After adding ²³²U as a yield tracer, the calcined samples were dissolved with 50 ml concentrated HNO₃ and 10 ml HF (48 %), and evaporated to dryness. Above step was carried out once more. The residue was dissolved with 50 ml 8 M HNO₃. About 2 ml H₂O₂ were added into the solution to oxidizing U (VI). After heating the solution, the sample solution was passed through a pre-conditioned anion exchange column with 8 M HNO₃ at a rate of 1 ml/minute. The column was then washed with 20 ml 8 M HNO₃. The passing and washing solutions were collected and evaporated to dryness. For removing organic substances about 2 ml HClO₄ was added to the residue and evaporated to dryness. The residue was dissolved with 30 ml 2 M HNO₃.

The column of TRU Spec resin (bed volume; 1.3 ml, column length; 2.6 cm) was conditioned with 30 ml 2 M HNO₃. Samples were loaded to the column followed by washing with 30 ml 2 M HNO₃. The column was washed with 5 ml 9 M HCl and 15 ml 4 M HCl for removing Am fraction. Finally uranium fraction was eluted with 20 ml 0.1 M ammonium oxalate. The obtained U fraction was electroplated on stainless steel platelets[18]. A flow chart of the entire chemical procedure improved in this study was shown in Fig. 1.

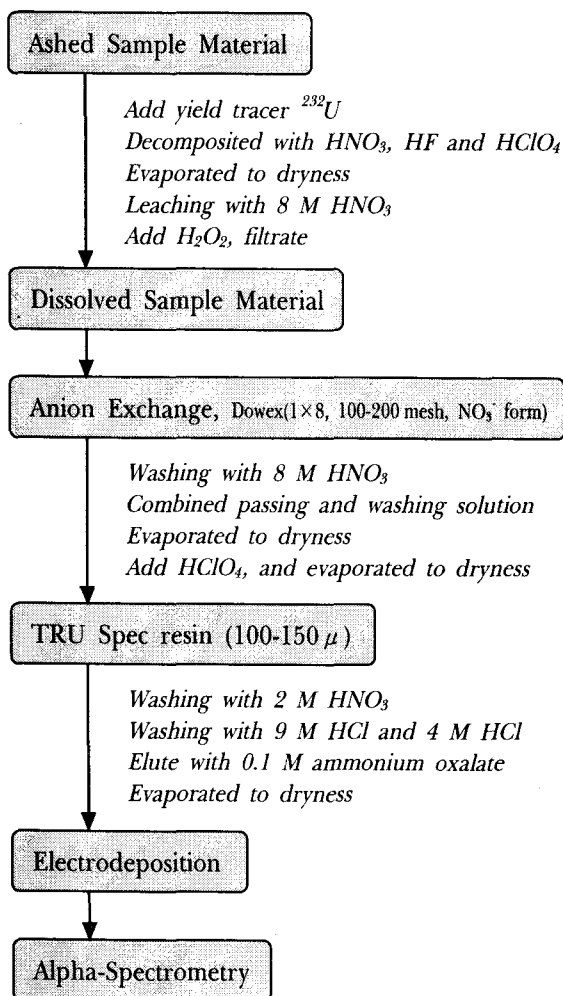


Fig. 1. Analytical procedure for separation of uranium isotopes with extraction chromatography method

Performance test of radio-analytical methods of uranium isotopes

For comparing performance of radio-analytical methods of uranium isotopes, about 2 dpm of ^{232}U , ^{229}Th , ^{239}Pu and ^{241}Am was dropped into calcined soil and blank samples. Radiochemical separation of uranium isotopes from hindrance elements was carried out by TBP extraction[12], TOPO extraction[14] and extraction chromatography described above.

RESULTS AND DISCUSSION

Analysis of uranium isotopes with the solvent extraction with TBP

Using the conventional TBP method, the

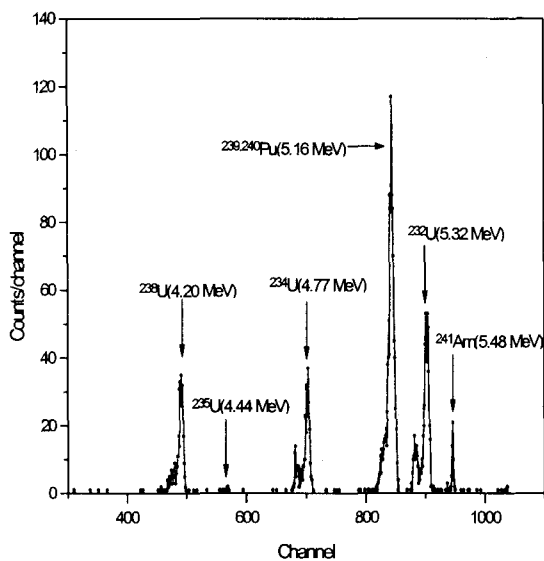


Fig. 2. Alpha spectrum of uranium isotopes in the IAEA-367 Sediment sample with the TBP extraction method

results of ^{238}U concentrations in the IAEA-Reference samples are represented in Table 1. The concentrations of uranium isotopes in the IAEA-Reference samples obtained by the TBP method were somewhat lower than the reference values. The reason for the lower activity values of uranium isotopes with the conventional TBP method may be incomplete decomposition of the sample material. In the TBP method, only HNO_3 was used for the decomposition of sample material that uranium isotopes in the inner soil were seldom leached into the HNO_3 solution. Therefore, an accurate and reliable analytical procedure for uranium isotopes should give the complete decomposition of the siliceous matrix with complete elimination of the insoluble material before chemical separations are attempted.

The alpha spectrum of uranium isotopes in the IAEA-367 Sediment sample analyzed with the TBP extraction method is shown in Fig. 2. The radionuclide levels of the IAEA-367 Sediment sample, collected at Enewetak Atoll in the Marshall Islands (Central Pacific Ocean), were known to be high due to its contamination by nuclear weapon tests in the Marshall Islands by the U.S.A. from 1948 to 1958. The reference activity values were reported as 102 Bq kg^{-1} for ^{90}Sr , 195 Bq kg^{-1} for ^{137}Cs , 26.4 Bq kg^{-1} for

Table 1. Comparison of concentrations of ^{238}U between the TBP extraction method and extraction chromatography method in IAEA-Reference samples

Sample material	Concentration of ^{238}U (Bq/kg) ^a		
	Recommended Value	TBP extraction method	Extraction chromatography method
IAEA-367	20.3	17.4 ± 2.1 ^b	19.8 ± 2.5
IAEA-300	64.7	57.4 ± 3.8	64.1 ± 1.7
IAEA-375	24.4	22.1 ± 1.9	24.9 ± 2.1

^aNumber of aliquots analyzed is 4^bError is 1σ

Table 2. Comparison of chemical yields with different radiochemical methods in the purified in the U fraction

Method	Sample Material	Recoveries of radionuclides in the purified U fraction (%) ^a			
		^{239}Th	^{242}Pu	^{241}Am	^{232}U
TBP extraction	Blanks	3.8 ± 0.7 ^b	15.7 ± 4.4	6.3 ± 1.7	68.4 ± 9.8
	Soil	4.0 ± 1.1	10.5 ± 3.1	5.5 ± 0.9	65.2 ± 10.8
TOPO +Anion exchange	Blanks	N. D.	N. D.	2.3 ± 0.7	66.4 ± 5.1
	Soil	N. D.	N. D.	3.1 ± 0.6	69.2 ± 8.7
Anion exchange + TRU-Spec	Blanks	N. D.	N. D.	N. D.	76.4 ± 5.8
	Soil	N. D.	N. D.	N. D.	74.9 ± 6.7

^aNumber of aliquots analyzed is 3^bError is 1σ

^{241}Am , 38 Bq kg⁻¹ for $^{239,240}\text{Pu}$, 0.08 Bq kg⁻¹ for ^{238}Pu . As shown in Fig. 2, the peak of $^{239,240}\text{Pu}$, which should have been completely removed by the chemical separation procedure, was distinctly shown in the spectrum of uranium isotopes. In addition, the peak of ^{241}Am was found in the spectrum of the IAEA-367 Sediment sample, though the peak area was smaller than that of $^{239,240}\text{Pu}$. From these results, it is supposed that the TBP extraction method can not completely separate uranium from the transuranium elements such as plutonium and americium isotopes in highly contaminated samples. Therefore, for getting precise and accurate data on the uranium isotopes in highly contaminated

samples as well as environmental samples, it is necessary to completely separate the uranium isotopes from the transuranium elements.

Analysis of uranium isotopes with the extraction chromatography

With the TBP solvent the determination of uranium isotopes in environmental and biological materials often depends on the complete separation of uranium isotopes from a bulky matrix containing interfering radioelements. Also, the solvent extraction with toxic TBP is too cumbersome for use with large numbers of samples. In this study, for overcoming the disadvantages of the TBP extraction method

and getting reliable data on uranium isotopes, sample materials were decomposed with HNO_3 and HF , and uranium isotopes were completely purified by an anion exchange column and TRU Spec resin, as presented in Fig. 1.

Using the different radiochemical separation methods, recoveries of ^{229}Th , ^{242}Pu , ^{241}Am and ^{232}U for the purified U fraction are presented in Table 2. In the TBP extraction method, more than 10 % of ^{242}Pu and a small amount of ^{229}Th and ^{241}Am was found in the purified U fraction, though a large amount of ^{229}Th , ^{242}Pu and ^{241}Am was removed by the washing step with HCl (1 + 1). This means that the TBP extraction method is insufficient to purify clearly uranium isotopes from the radionuclides in highly contaminated samples. Also, the hindrance nuclides such as ^{229}Th and ^{242}Pu were removed from the uranium fraction by TOPO and anion exchange resin method, though trace level of ^{241}Am was found in the uranium fraction. But, time consumed at TOPO and anion exchange resin method is a little longer than extraction chromatography method. In the use of anion exchange resin and TRU Spec resin, the hindrance nuclides were completely removed from the uranium fraction, as presented in Table 2. Also, the chemical yields with the extraction chromatography method were more 10 % higher than those with the TBP extraction method and TOPO and anion exchange resin method. These results mean that the extraction chromatography method with anion exchange resin and TRU Spec resin is more reliable, practical and quantitative method due to simple chemical separation steps than the conventional methods.

Validation of the modified TBP extraction method

The extraction chromatography method was validated by its application to several IAEA-Reference samples. As shown in Table 1, the concentrations of uranium isotopes using the extraction chromatography method were consistent with the reference values reported by the IAEA. Also, with the extraction chromatography method the alpha peaks of uranium isotopes spectra in the IAEA-367 Sediment sample were well resolved (FWHM; 27.5 keV), as shown in Fig. 3. The spectrum of

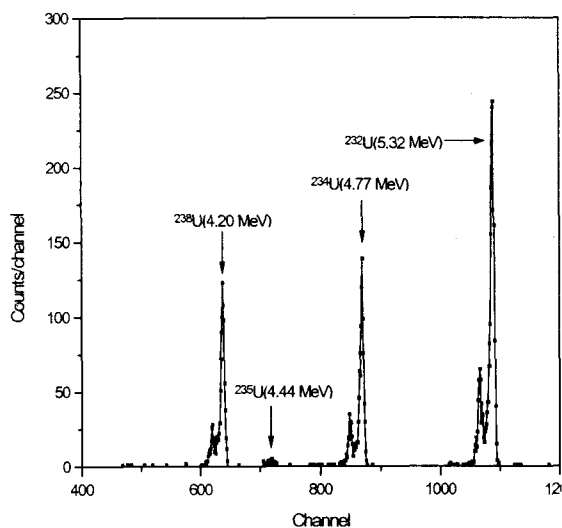


Fig. 3. Alpha spectrum of uranium isotopes in the IAEA-367 Sediment sample using the extraction chromatography method

uranium isotopes in the IAEA-367 Sediment sample was so free from contributions due to various plutonium, americium and other naturally occurring radionuclides that no significant interfering with the radionuclides were encountered.

CONCLUSION

In this study an accurate and rapid analytical technique of uranium isotopes was developed and validated by application to the IAEA-Reference samples. The concentrations of uranium isotopes in the IAEA-Reference samples with the TBP extraction method were somewhat lower than the reference values due to incomplete decomposition of sample material. Using anion exchange resin and TRU Spec resin, the radionuclides, which could not be separated by the TBP extraction method, were completely removed from the uranium fraction. The concentrations of uranium isotopes measured with the extraction chromatography method in the IAEA-Reference samples were close to the reference values reported by IAEA. Therefore, the new extraction chromatography method of uranium isotopes makes it possible to be used for environmental samples as well as highly contaminated samples.

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