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# Determination of Uranium Isotopes in highly Contaminated Soil Samples

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## Abstract

An accurate and reliable technique of uranium isotopes determination in highly contaminated soil samples was developed and applied to the IAEA-Reference samples. The conventional TBP method of uranium isotopes can not be completely separate uranium from the actinide such as the plutonium and americium isotopes. For overcoming the demerits of the conventional TBP extraction method, sample materials was decomposited with $HNO_3$ and HF and uranium isotopes were purified by TBP extraction and anion exchange columns. Among the modified TBP extraction methods, with TRU Spec resin column after TBP solvent extraction, uranium was completely separated from the radionuclides in highly contanimated sample. With the modified TBP extraction method, it was found that the concentrations of uranium isotopes consistent with reference values reported by IAEA.

# 1. Introduction

The accurate and reliable determination of the uranium isotopes in the environment is important because of the public health impact of any releases of the uranium isotopes to the environment. The determination of the uranium isotopes in the soil and sediment is generally complicated, because soil have a complex chemical matrix as well as organic and inorganic materials. The problem of separating small quantities of uranium isotopes from chemically similar elements such as the rare earths and from the transition elements, including titanium, manganese, zirconium and vanadium sometimes happens in the determination of the uranium isotopes. Also, soil contains the bulk elements such as silicon, aluminium, iron and calcium, which are present in amount between $10^6$ - $10^{10}$ greater than those of the uranium isotopes.

Recently, several investigators have reported on the method of analysis for the uranium isotopes analysis in environmental samples.[1-11] Sill et al carried out a detailed study on the simultaneous determination of alpha-emitting nuclides in soil.[1] Anderson and Fleer reported on the determination of $^{227}$Ac, $^{228}$Th, $^{230}$Th, $^{232}$Th, $^{234}$Th, $^{231}$Pa, $^{234}$U and $^{238}$U in samples of suspended marine particles materials and sediments.[4] Singh et al reported on the simultaneous determination of uranium, thorium and plutonium in bone.[5] Among these methods, the radiochemical assay of uranium with TBP has been used largely for environmental samples.[9] However, though the conventional TBP extraction method is more simple and rapid than other methods, sometimes, this method can not completely separate the uranium isotopes from the the actinides such as the plutonium and americium isotopes in high contaminated soil samples.

In this study, to overcome the disadvantages of the conventional TBP extraction method, modified TBP extraction method combining TBP extraction and anion exchange step was developed for accurately and reliably determining uranium isotopes in environmental samples. The optimized analytical method of uranium isotopes was validated by application to IAEA-Reference soils.

## 2. Experimental methods

### Conventional TBP method of uranium

An aliquot of 5 g soil and IAEA-Reference soils was calcined at at 550 $^{o}$C for 24h to eliminate organic matter. After adding $^{232}$U as a yield tracer, the calcined samples were dissolved with 50 ml concentrated $HNO_3$ and evaporated to dryness. About 2 ml concentrated $HClO_4$ and 1 ml $H_2O_2$ were added into the residue. After the residue is dissolved with $HNO_3$ (3 + 11), uranium isotopes were extracted from the dissolved sample materials into TBP (tributyl phosphate) in carbon tetrachloride. The radiochemical purification of the U fraction was performed with HCl (1 + 1). With HCl (1 + 11), uranium isotopes were then back-extracted to the aqueous phase from the organic phase. The obtained U fraction was electroplated on stainless steel platelets. Detailed procedure of the analytical methods of uranium with TBP was presented in elsewhere.[9]

### Modification of conventional TBP method of uranium

To modify the conventional TBP 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, an anion exchange column was used for removing the transuranium elements such as plutonium and americium. A flow sheet of the modified TBP method developed in this study was shown in Fig. 1.

About 2 dpm of $^{232}$U, $^{229}$Th, $^{239}$Pu and $^{241}$Am was dropped into calcined soil and blank samples. The sample material was dissolved with concentrated $HNO_3$ and HF (48 %). The chemical separation steps are the same to the conventional TBP method. After uranium isotopes were back-extracted to the aqueous phase from the organic phase with HCl (1 + 11), about 1 ml $H_2O_2$ and 0.25 ml 1.5 M $NaNO_2$ added into the aqueous solution to oxidizing U (VI) and evaporated to dryness. For purifying uranium, additional step with an anion exchange column was adapted. Three kind of anion exchange column such as Dowex ($NO_3^-$ form), Dowex ($Cl^-$ form) and TRU Spec. column is used in this study.

Dowex ($NO_3^-$ form): The residue was dissolved in 10 ml 7.2 M $HNO_3$, then the sample was passed through a pre-conditioned anion exchange column (Dowex 1x2, 50-100 mesh; 2 g, height; 15 cm, inner diameter; 8 mm) with 7.2 M $HNO_3$ at a rate of 1 ml/minute. The column was then washed with 20 ml 7.2 M $HNO_3$. The passing and washing solutions are collected and reserved for uranium analysis.

Dowex ($Cl^-$ form): The residue was dissolved in 10 ml 9 M HCl, then the sample was passed through a pre-conditioned anion exchange column with 9 M HCl at a rate of 1 ml/minute. The column was washed with 50 ml 9 M HCl. For elution of uranium 50 ml 1 M $HNO_3$ was used.

TRU Spec resin: The residue was dissolved in 10 ml 2 M $HNO_3$ with heating on the hot plate. The sample was passed through a pre-conditioned anion exchanger column with 2 M $HNO_3$ at a rate of 1 ml/minute. The column was washed with 5 ml 9 M HCl and 10 ml 4 M HCl for removing Am and Th fraction, respectively. For removing Pu fraction 10 ml 0.1 M hydroquinone/4 M HCl was passed through the TRU Spec resin column. 20 ml 0.1 M ammonium oxalate was used for the elution of the uranium isotopes.

The elute solutions were evaporated to dryness in a crystallizing dish. The purified uranium isotopes were electrodeposited from the electrodeposition solution on a polished stainless steel disc.[12]

### Measurement of uranium isotopes

The alpha spectrometer (EG&G ORTEC, Model 676A) was composed of an ion-implanted silicon detector (ORTEC, size : 450 $mm^2$; alpha resolution : 25 keV FWHM at 5.486 MeV of $^{241}Am$) 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 vaccum below $10^{-2}$ Torr was maintained with a vacuum pump.

## 3. Results and discussion

## Analysis of uranium isotopes with the conventional TBP method

Using the conventional TBP method, the results of concentrations of $^{238}$U in IAEA-Reference samples were represented in Table 1. The concentrations of uranium isotopes in IAEA-Reference samples obtained by the conventional TBP method was somewhat lower than reference values. 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, an accurate and reliable analytical procedure for the uranium isotopes should give complete decomposition of the siliceous matrix with complete elimination of insoluble material before chemical separations are attempted.

The alpha spectrum of uranium isotopes in the IAEA-367 Sediment sample analyzed with the conventional TBP method was shown in Fig. 2. The radionuclides levels of IAEA-367 Sediment sample, collecting at the Enewetak Atoll in the Marshall Islands (Central Pacific Ocean), was known to be high due to its contamination by nuclear weapon tests by U.S.A. from 1948 to 1958 in the Marshall Islands. 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 $^{241}$Am, 38 Bq kg$^{-1}$ for $^{239,240}$Pu, 0.08 Bq kg$^{-1}$ for $^{238}$Pu, respectively. As shown in Fig. 2, the peak of $^{239,240}$Pu, which should have 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 small than that of $^{239,240}$Pu. From these results, it is supposed that the conventional TBP method can not completely separate uranium from the transuranium elements such as the plutonium and americium isotopes in the highly contaminated samples. Therefore, for getting the precise and accurate data of uranium isotopes for highly contaminted samples as well as environmental samples, it is necessary to completely separate the uranium isotopes from the transuranium elements.

## Analysis of uranium isotopes with modified TBP method

The determination of the uranium isotopes in environmental and biological materials often depends on completely separation of the uranium isotopes from a bulky matrix containing interfering radioelements. In this study, for overcoming the disadvantages of the conventional TBP extraction method and getting reliable data of uranium isotopes, sample materials was decomposited with $HNO_3$ and HF and uranium isotopes were completely purified by the TBP extraction and the ion exchange step with an anion exchange column, as presented in Fig. 1.

Using the conventional TBP method and anion exchange columns, recoveries of $^{229}$Th, $^{242}$Pu, $^{241}$Am and $^{232}$U in the purified U fraction were presented Table 2. In the conventional TBP method, more than 10 % of $^{242}$Pu and 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 conventional TBP method is insufficient to clearly purify uranium isotopes from the radionuclides in the highly contaminated samples. Also, after passing the back-extracted solution (HCl, 1+11) through the Dowex columns ($NO_3^-$ or $Cl^-$ form), a trace level of $^{229}$Th, $^{242}$Pu and $^{241}$Am was detected in the uranium fraction. This result means that the Dowex column is insufficient for purifying the uranium isotopes from the radionuclides such as thorium, plutonium and americium in the contaminated samples. However, in the use of TBP solvent with TRU Spec resin column, the hindrance elements was completely removed from the uranium fraction, as presented in Table 2.

In the calculating the recovery of $^{232}$U, the peak of $^{232}$U (5.32 MeV) has to be analyzed immediately following source preparation to minimize interference due to the daughter $^{228}$Th (5.42 MeV) which grows back into $^{232}$U at a rate of about 0.1 % of equilibrium activity per day,[13] even if uranium is completely separated from Th, Am and Pu isotopes in the chemical separation step. The recovery of $^{232}$U in the use of TBP solvent with TRU Spec resin column was found to be more than 60 % for the blank and soil samples, as presented Table 2. This value is a little lower than that with the conventional TBP method. It is reasonable that the chemical yields with the modified TBP method were a little lower than those with the conventional TBP method, because an anion exchange step was added to the conventional TBP method. However, this value is not bad for reliably assessing the data of the uranium isotopes.

**Validation of the modified TBP method**

The modified TBP method for the determination of uranium was validated by its application to several IAEA-Reference samples. As shown in Table 1, the concentrations of uranium isotopes using the modified TBP method were consistent with reference values reported by IAEA. Also, 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 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 the radionuclides were encountered.

# 4. Conclusions

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

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

| | Concentration of $^{238}$U (Bq/kg) | |
|---|---|---|
| Sample material | Recommended Value | Conventional TBP method[a] |
| IAEA-367 | 20.3 | 17.4 ± 2.1[b] |
| IAEA-300 | 64.7 | 57.4 ± 3.8 |
| IAEA-375 | 24.4 | 22.1 ± 1.9 |

[a] Number of aliquots analyzed is 4

[b] Error is 1σ

Table 2. Comparison of chemical yields between conventional TBP extraction method and the modified TBPextraction method in the purified U fraction

| Method | Sample Material | Recoveies of radionuclides in the purifie | | |
|---|---|---|---|---|
| | | $^{229}$Th | $^{242}$Pu | $^{241}$A |
| Conventional TBP | Blanks | 3.8 ± 0.7[b] | 15.7 ± 4.4 | 6.3 ± |
| | Soil | 4.0 ± 1.1 | 10.5 ± 3.1 | 5.5 ± |
| TBP + Dowex ($NO_3^-$ form) | Blanks | 1.1 ± 0.2 | 2.1 ± 0.3 | 1.1 ± |
| | Soil | 2.4 ± 0.8 | 2.0 ± 0.2 | 4.1 ± |
| TBP + Dowex ($Cl^-$ form) | Blanks | 2.9 ± 0.6 | 4.2 ± 3.2 | N. |
| | Soil | 3.1 ± 0.8 | 3.8 ± 2.1 | 0.5 |
| TBP + TRU-Spec | Blanks | N. D. | N. D. | N |
| | Soil | N. D. | N. D. | N |

[a] Number of aliquots analyzed is 3

[b] Error is 1σ

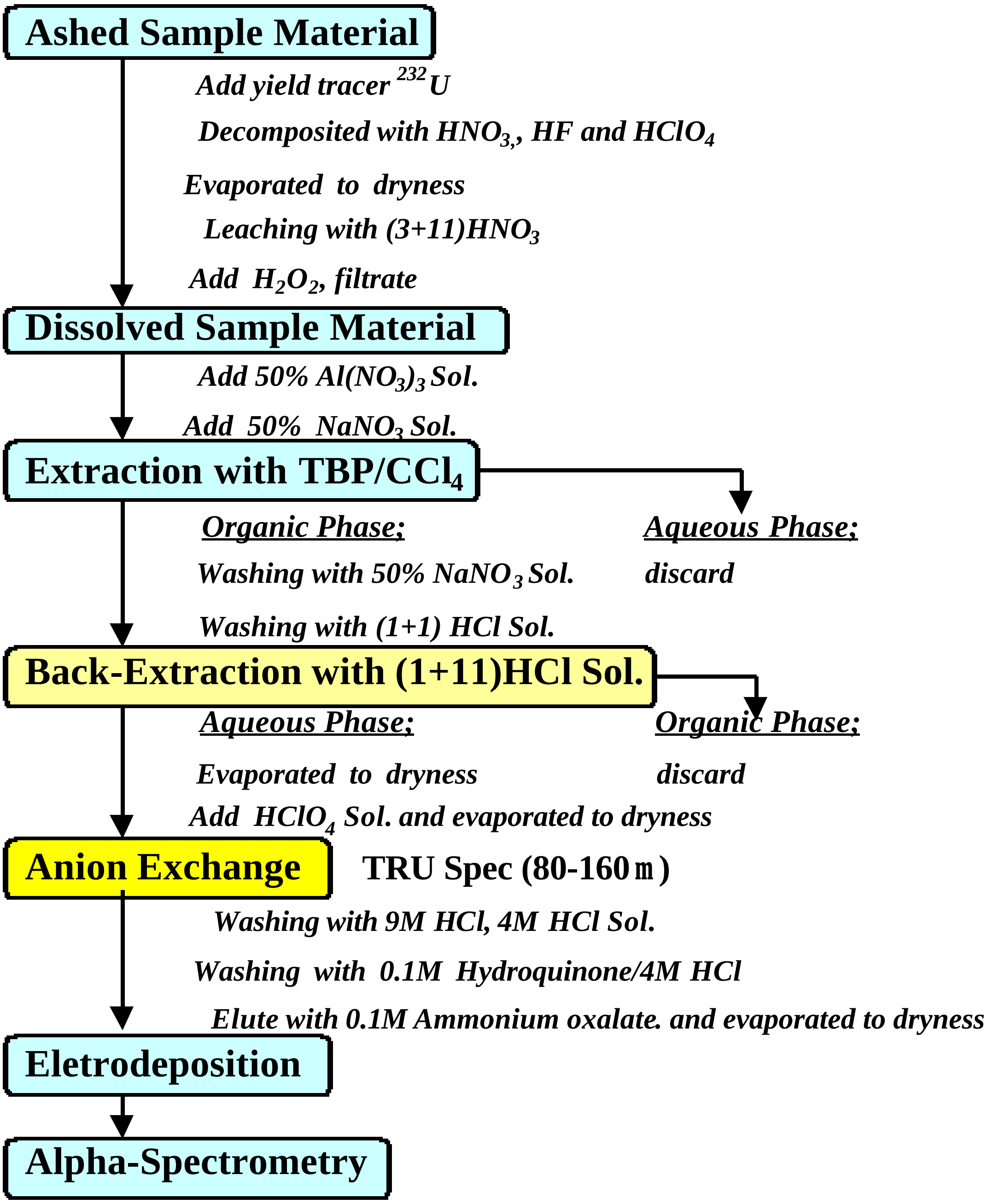

Fig. 1. Modified analytical procedure for uranium isotopes with TBP extraction and anion exchange column