

Rapid Determination of U Isotopic Ratios in Environmental Sample Matrix Using by ICP-MS

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1. Introduction

It is important to assure the radiological safety for the general population. As an attempt to reduce the social costs and apprehension arising from the radioactivity in environmental media, an accurate and rapid assessment of radioactivity is highly desirable. Hence, it is important to develop a series of evaluation of rapid procedures for efficient radioactivity management.

Uranium and its salts are both toxic and radioactive. And it is also well known that soluble uranium compounds are more toxic to the kidneys. Alpha-emitters (e.g., ²³⁵U, ²³⁸U, ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, etc.) in the environment are known to have a relatively high toxicity. For this reason, alpha-emitters have been a focus of interest not only in the waste management field from nuclear power plants, but also in environmental studies for the origin of the nuclear materials.

In general, α -spectrometry has a prominent measurement capability at a very low activity level of ²³⁸U, ²³⁵U, and ²³⁴U, it has a major disadvantage of a long counting time (especially ²³⁵U) for the determination of α -nuclide activity. Contrary to the α -spectrometry method, some high sensitivity mass spectrometric methods including thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS), and isotope dilution mass spectrometry (ID-MS) could be applied to determine U ratio in environmental samples. Typically, measurement technique using ICP-MS with an advanced sample introduction and mass counting system allows radioactivity in many samples to be measured within a short time period with a high degree of accuracy and precision. However, all of analytical methods for U ratios encounter the most significant difficulties during pretreatment (e.g., purification, speciation, and dilution/enrichment).

An analysis of solid matrix samples is especially complicated owing to a destruction of the matrix and digestion into a liquid phase. These procedures are usually very time consuming and do not fully recover target isotopes. For this reason, a rapid and accurate analytical method that can be used to evaluate the radioactivity of U isotopes should be developed and validated.

In this study, in order to immediately response, the rapid digestion and purification procedure for U

isotopes in environmental sample media such as soil and sediment were developed using LiBO₂ fusion and ICP-MS measurement. In order to concentrate and purify the U isotopes, the rapid selective extraction chromatography process was developed and applied using automatic sample separation system. Finally, the evaluated method in this study were applied for quantitative determination of U isotopes of the sediments CRMs (Certified reference materials) samples.

2. Experimental

2.1 Apparatus and reagents

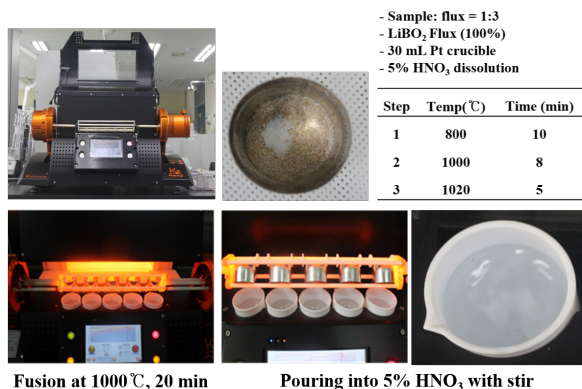
A reagent of analytical grade and deionized water (>18 M Ω) were used for each process. For the alkali-fusion of solid powder samples, lithium metaborate and lithium bromide (XRF scientific Limited) with an automatic fusion machine (K2 Prime, Katanax, Canada) were used. For an analysis of the radioactivity, ICP-MS (ICAP RQ, ThermoFisher, Germany) with an APEX nebulizer, and α -spectrometry (Alpha AnalystTM, CANBERRA, USA) were used. For the concentration and purification of U isotopes UTEVA resin (EICHROM, USA) was used. The purification of U isotopes for ICP-MS measurement was applied extraction chromatography method with automated radio-nuclides separation system (Fast and Intelligent Radionuclide Separation Technique, KAERI, KOREA)

2.2 Procedure

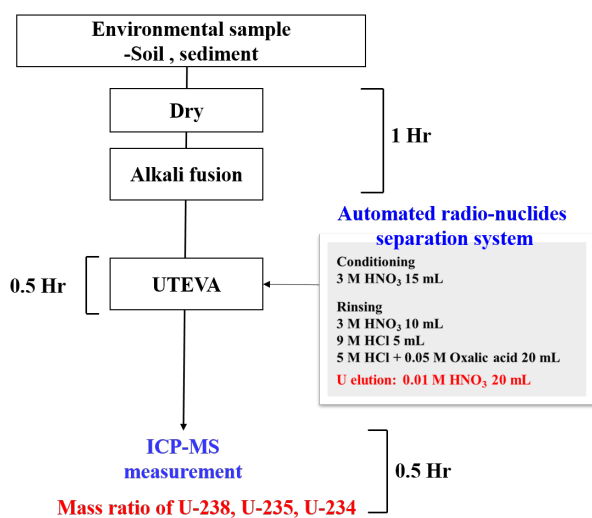
The analytical process for determination of U isotopes in environmental samples are shown in Fig. 1. The process sequentially consists of digestion using LiBO₂ fusion, purification using extraction chromatography, and determination by ICP-MS. In Fig. 1, required time for each step also was shown.

The dried soil and sediment samples were digested in 60mL of 5% nitric acid using an alkali-fusion. For the concentration of U isotopes, the solution was directly passed through UTEVA resin with 3 mL of bed volume. For the samples loading and column rinsing, additionally 40 mL of 3 M HNO₃ was passed through the UTEVA column. To remove the Th, Np, and Pu, which are interfering radio-nuclides, 9 M HCl and 5 M HCl-0.05 M oxalic acid were sequentially pass through the column. Finally, the purified U solution was eluted by 20 mL of 0.01 M HNO₃. Finally, the mass

concentrations and isotopic ratios of U were determined using a quadrupole ICP-MS system with an APEX nebulizer.



(a) Sample digestion using by LiBO₂ fusion



(b) Process of U isotope separation and purification

Fig. 1 Analytical procedure for U isotopes in environmental samples

3. Results and Discussions

Typically, ICP-MS techniques have been well acknowledged to have extremely low detection limit with high resolution. And the technique could analyze the isotopic ratio analysis (e.g., Pu-239/240, U-235/238/234). Therefore, ICP-MS technique has specific benefit for long half-life nuclides with over than 1000 years. The method detection limit of sector field ICP-MS for Pu-240 was approximately 10 ~ 100 fg/ml. However, the polyatomic and isobaric interference in mass spectrometry have significantly affected to accurate determination. It should be noted that the ICP-MS technique has proved advanced capabilities to determine very low levels of activity concentration for the long half-lived radionuclides such as ²³⁸U, ²³⁵U, ²³⁷Np, ²³²Th, ⁹⁹Tc, and ²³⁹⁺²⁴⁰Pu.

For the evaluation of the recovery efficiency for fusion technique, U concentration in various soil and sediment CRMs samples (e.g., NIST SRM 2709a, 1646a, 1944, 8704) were analyzed. The relative error fell below 5% and relative standard deviation were within 3% for all samples. Thus, alkali fusion and ICP-MS measurement derived the good agreement with certified concentration for wide range.

From the elution profile of UTEVA extraction chromatography tests, when the 80 mL of a prepared solution was loaded into the 3 mL bed volume of a preconditioned UTEVA, the matrix elements (e.g., Fe, lanthanides, alkali earth metals, etc.) were almost removed at the stages of loading and rinsing. With the exception of U isotopes, actinides were eliminated by loading 9 M HCl and oxalic acid, in a step-wise manner. The solution of the extraction process using UTEVA effectively provide a matrix-free and high concentration of U.

For an evaluation of the accuracy and precision of the evaluated method, certified reference materials from the IAEA were analyzed. As shown in Table 1, analytical results for the samples show the good agreement to certified isotopic ratio with a very small relative standard deviation. Based on the analytical results for rapid determination of U isotopic ratio, one may conclude that the evaluated method for actinides using alkali-fusion, extraction chromatography process, and ICP-MS measurements is fast and fairly reliable.

Table 1 Analytical results of U isotopes ratios in CRM sample using fusion and extraction chromatography method.

	Mass ratio		Activity ratio	
	U-235/ U-238	U-234/ U-238	U-235/ U-238	U-234/ U-238
IAEA135-1	0.0072647	0.0000524	0.047	0.969
IAEA135-2	0.0074160	0.0000530	0.048	0.980
IAEA135-3	0.0073166	0.0000529	0.047	0.978
Mean	0.0073324	0.0000528	0.047	0.976
SD	0.0000769	0.0000003	0.000	0.006
RSD%	1.05	0.59	1.05	0.59

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