

Rapid Analysis of U isotopic ratios in Food Stuff samples using Fusion and ICP-MS measurement: For radiation monitoring program in the vicinity of nuclear facilities

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1. Introduction

It is very important to assure the radiological safety of food stuff for protection of the general population from internal radiation exposure. In general, the sources of radioactivity in food can be divided into both natural (e.g., solar radiation and natural decay) and anthropogenic sources (e.g., human activities such as accidents, the nuclear power industry and weapon tests). As an attempt to reduce social costs and apprehension arising from the radioactivity in food, an accurate and rapid assessment of radioactivity is highly desirable. Hence, it is very important to develop a series of evaluation of rapid procedures for efficient radioactivity management in food.

Alpha-emitters (e.g., ²³⁵U, ²³⁸U, ²³⁹⁺²⁴⁰Pu, ²⁴¹Am, etc.) in the environment are known to have a relatively high toxicity. Thus these nuclides have been a focus of interest not only in waste management field from nuclear power plants, but also in environmental studies for the origin of the nuclear materials.

While 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, a measurement technique using ICP-MS with an advanced sample introduction and mass counting system allows radioactivity in many samples to be measured with a short time period with a high degree of accuracy and precision. It should be noted that ICP-MS technique has proved the advanced abilities to determine very low levels of activity concentration for the long half-lived radionuclides such as ²³⁸U, ²³⁵U, ²³⁷Np, ²³²Th, ⁹⁹Tc, ²³⁹⁺²⁴⁰Pu, etc.

However, both methods encounter the most significant difficulties during pretreatment (e.g., purification, speciation, and dilution/enrichment). Since the pretreatment process consequently plays an important role in the measurement uncertainty, a method of development and validation should be performed.

In this study, a rapid digestion and separation method for U isotopes was developed in food stuff matrix such as cabbage and rice. The dry-ashed food stuff samples were digested using LiBO₂ fusion and the target nuclides were extracted through Fe(OH)₃ co-

precipitation. The selective extraction chromatography process was developed for concentrating of U isotopes for ICP-MS measurement. Finally, the results from evaluated method in this study were compared to those from previous acid digestion and α -spectrometry determination.

2. Experimental

2.1 Apparatus and reagents

All of reagent with analytical grade and deionized water (>18 M Ω) was used for all the process. For the alkali-fusion of raw materials and by-product samples, lithium metaborate and lithium bromide (XRF scientific Limited) with automatic fusion machine (K2 Prime, Katanax, Canada) were used. For analysis of radioactivity, ICP-MS (SPECTROMS, SPECTRO, Germany) with an APEX nebulizer, and α -spectrometry (Alpha AnalystTM, CANBRR, USA) were used.

For the concentration and purification of U isotopes the UTEVA resin (EICHROM, USA) was used.

2.2 Procedure

The analysis in solid matrix samples such as food stuff is especially complicated owing to a destruction of the matrix and digestion into a liquid phase. These procedures are usually very time consuming and not fully recovered target isotopes. Thus a rapid and accurate analytical method that can be used to evaluate the radioactivity of U isotopes should be developed and validated.

The analytical process of ²³⁴U, ²³⁵U, and ²³⁸U in the food stuff samples and fusion process are shown in the Fig. 1. First, approximately 10 kg of rice and cabbage sample was heated and controlled stepwise slowly up to 650°C for 2 days, separately. The samples were then ashed during 3 days. The ashed residues were digested using alkali-fusion method and concentrated by iron hydroxide co-precipitation. The co-precipitation was conducted by adding Fe-carrier and adjusting to the pH 7 with concentrated ammonia solution. After the precipitate was allowed to settle down by centrifuging, the supernatant was discarded and the precipitate was dissolved with 20 mL of concentrated HNO₃. To determine the ²³⁸U concentration, the solution was diluted about 200 times and initially measured by ICP-MS. For the removal of fusion flux matrix elements (e.g., Li, B, Si, etc), the solution was heated to the

dryness at 250°C on the hot plate after adding 10 mL of 28 M of HF. Finally, the residue was re-digested with 5 mL of 8 M HNO₃ and washed 5 times, repeatedly.

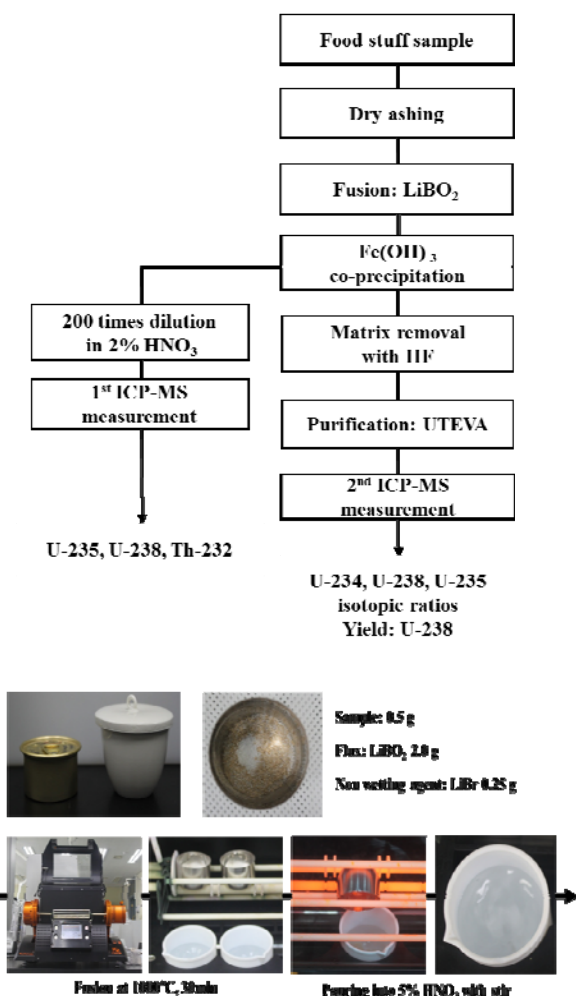


Fig. 1 Analytical procedure (Top) and LiBO₂ fusion for ashed food stuff samples (bottom)

3. Results and Discussions

3.1 Establish the pretreatment process for food stuff sample

In order to satisfy the method detectable activity (MDA) for the regulation of radioactivity monitoring program the analysis of U isotopes always require the extremely large sample amount. These procedures make usually the food stuff sample to carbonize during dry ashing process. The ashed residues have been especially complicated into a liquid phase because of their carbonization. This process are very time consuming and not fully recovered target isotopes.

Thus, a digestion method for ashed-residue was developed for a rapid analysis of U isotopes using LiBO₂ fusion and Fe co-precipitation. For an evaluation of the accuracy and precision of the method, certified reference materials (CRMs) were analyzed using an

established process. The analytical results of CRM samples were in agreement with the certified concentration values.

Since the prepared the solution using LiBO₂ have enriched amount of Li, B, Si, etc., which usually make serious problems (e.g., pore clogging, exceed of resin capacity, etc.) throughout column purification process, relatively easy and rapid treatment step using HF was applied. As the result from this step the Si, B, and some elements were removed over than 90% as volatile form with fluoride complexes. And Ca and actinide like as Th also removed as form of non-dissolved salt.

3.2 Purification and concentration of U isotopes

The prepared 20 mL of solution was loaded into the 2 mL bed volume of preconditioned UTEVA. The matrix elements (e.g., Fe, lanthanides, alkali earth metals, etc.) was almost removed at the stage of loading and rinsing. The actinide except U isotopes were eliminated by loading 9 M HCl and oxalic acid, stepwisely. The elution profile of U isotopes in UTEVA resin was shown in Fig. 2. The solution of the extraction process using UTEVA effectively provide the matrix-free and high concentration of U.

Finally, the mass concentrations and isotopic ratios of U were determined using sector-field ICP-MS system with an APEX nebulizer.

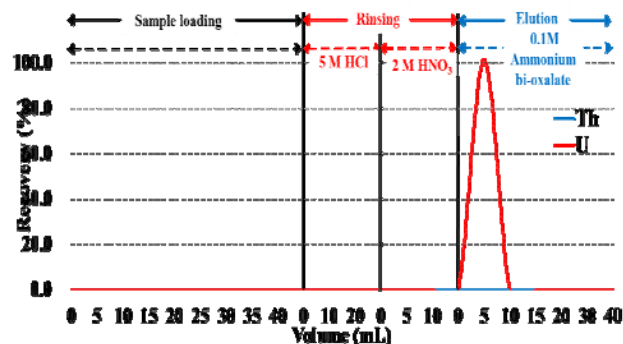


Fig. 2 Elution profile of U in UTEVA resin

For an evaluation of the accuracy and precision of evaluated method, various reference materials (RMs) from IAEA and NIST were analyzed. Based on the analytical results, one may draw conclusions that the evaluated method for actinides using alkali-fusion, Fe co-precipitation, the extraction chromatography process, and ICP-MS measurements is fast and fairly reliable owing to its recovering efficiencies.

REFERENCES

[1] G. Jia, M. Belli, U. Sansone, S. Rosamilia, R. Ocone, S. Gaudino, Determination of uranium isotopes in environmental samples by alpha-spectrometry, Journal of Radioanalytical and Nuclear Chemistry, 253(3), 395-406, 2002.