Verification of the Bulk Analysis Procedure of Safeguards Environmental Samples by Thermal Ionization Mass Spectrometry in KAERI

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1. Introduction

Highly precise analysis of nuclear materials in swipe and environmental samples plays essential roles in monitoring undeclared nuclear activities [1]. The Korea Atomic Energy Research Institute (KAERI) had been qualified as a member of the Network of Analytical Laboratories (NWAL) for bulk anal`ysis on environmental samples (ES) in 2012. Recently a new clean facility had been constructed and opened in KAERI, which caused the validation issue as the analytical environment and the main analytical instrument had been changed after the qualification.

This study is to verify the capability of KAERI to performed bulk analysis on environmental sample under the new analytical environment using thermal ionization mass spectrometry (TIMS).

2. Methods and Results

All of the analytical processes were performed in a newly constructed clean facility in KAERI (CLASS, Clean Laboratory for Analysis of Safeguards Samples) and complied with the QA/QC system (ISO/IEC 17025). All chemical processes were conducted in ISO 5 area while the isotopic measurements were performed in ISO 6 area where a thermal ionization mass spectrometer (TRITON Plus, Thermo Scientific Co.) is installed.

2.1 Sample Preparation

A simulated swipe sample (named as KA-SS) was prepared with a cotton swipe containing a certain amount of uranium (NBS U030) and plutonium (IRMM290A1) standard reference materials. For background correction, an open swipe blank (named as KA-SB) followed the whole sample analytical process as KA-SS did.

2.2 Chemical Treatment

Ashing process of the simulated swipe sample and the open swipe blank was carried out at 600 °C until complete decomposition of the samples. Highly pure nitric acid (Seastar, all metal impurities under 10 ppt) was used for acid digestion of the ashed samples. The resulting solution known as the "mother solution" was precisely weighed, and then, was divided into two portions for isotope ratio analysis and quantification by isotope dilution mass spectrometry (IDMS) by adding appropriate spike reference materials, respectively. Fig. 1 shows the detailed process for chemical treatment.
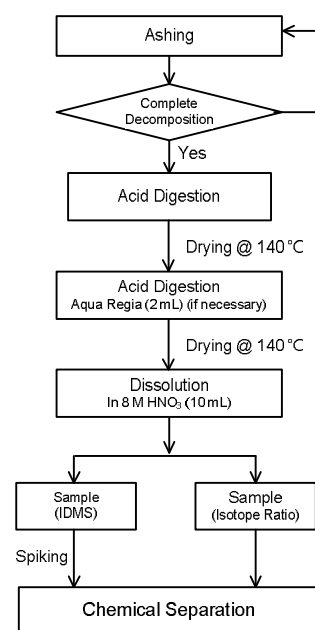

Fig. 1. Flow diagram of the chemical treatment for bulk analysis of swipe samples

2.3 Chemical Separation

A double column system consisting of UTEVA resin (Eichrom, 100 − 150 mesh) and anion exchange resin (Bio-Rad, AG MP-1, Cl⁻ form, 100 − 200 mesh) was utilized for chemical separation of the solution samples [2]. The plutonium portions were eluted by a combination of nitric acid (HNO_3), ascorbic acid, and hydrochloric acid (HCl), followed by a further purification process with MP-1 resin. A weak HCl solution enabled us to collect the uranium portions finally. Each sample was loaded on a pre-degassed zone-refined rhenium filament for TIMS measurements. Fig. 2 shows the detailed process for chemical separation.

2.3 Isotopic Measurement by TIMS

TIMS was utilized for isotopic measurement using the continuous heating method [3,4]. Mass bias correction of uranium isotopic ratio was carried out

based on the isotopic measurement of NBS U100, while no correction was made for plutonium measurement.
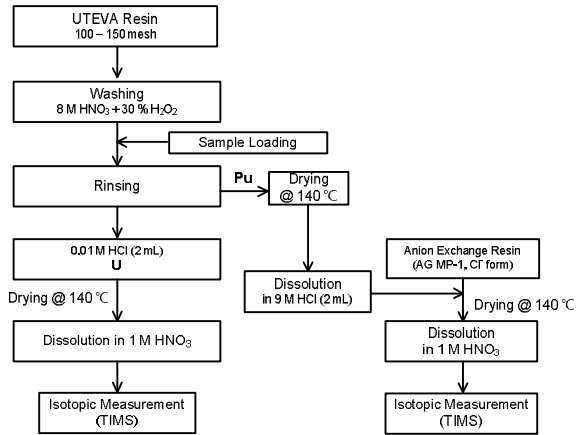

Fig. 2. Flow diagram of the chemical separation for bulk analysis of swipe samples

The amounts of uranium in the samples were determined by IDMS using the following equation [5,6];

$$c(^{238}U,x) = \frac{R_y - R_b}{R_b - R_x} \cdot \frac{1}{R_y} \cdot \frac{m_y}{m_x} \cdot c(^{233}U,y) \quad (1)$$

where,

R_b : amount ratio $n(^{233}U)/n(^{238}U)$ in the blend
R_x : amount ratio $n(^{233}U)/n(^{238}U)$ in the sample
R_y : amount ratio $n(^{233}U)/n(^{238}U)$ in the spike
m_x : mass of the sample
m_y : mass of the spike
$c(^{238}U,x)$: amount content of ^{238}U kg^{-1} in the sample
$c(^{233}U,y)$: amount content of ^{233}U kg^{-1} in the spike

The same mathematical process was applied for quantification of plutonium. The isotope ratios of uranium and plutonium in KA-SS were determined based on the isotopic measurements and the amounts of nuclear elements in KA-SB.

The uncertainty was estimated in compliance with GUM (Guide to the expression of Uncertainty in Measurement).

Table I: Corrected values of the bulk analysis of KA-SS

	Values
U amount (ng)	9.87(20)
$n(^{235}U)/n(^{238}U)$	0.03224(22)
Pu amount (pg)	45(8)
$n(^{242}Pu)/n(^{239}Pu)$	0.968(17)

2.4 Analytical Resutls

The result of the bulk analysis on the simulated swipe sample (KA-SS) by TIMS measurement is shown

in Table 1, which was corrected from the contribution of the open swipe blank, KA-SB. The result agreed well with the certified value of the corresponding standard reference materials.

3. Conclusions

The verification of the quality assurance of the bulk analysis of environmental samples was performed by TIMS measurement of a simulated swipe sample. The analytical results for the determination of the isotopic ratios and the amount contents of nuclear materials in the simulated environmental samples were in good agreement with the certified values. Therefore, we believe that our laboratory can produce reliable results for the bulk analysis on environmental swipe samples performed in CLASS and contribute the analytical services as a member of NWAL.

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