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Studies on treatment methods of the safeguards swipe samples for uranium isotope ratio measurement

Masato Takahashi*, **Masaaki Magara, Satoshi Sakurai, Setsumi Kurosawa, Takaaki Sakakibara,**
Yukiko Hanzawa, Fumitaka Esaka, Kazuo Watanabe, Shigekazu Usuda and Takeo Adachi
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

In the environmental sampling and analyses for safeguards, precise and accurate isotope ratio determination of uranium at trace levels is required for detection of undeclared nuclear activities. Currently, swipe (smear) samples are being taken by IAEA from the nuclear facilities. The amount of uranium collected on the cotton swipe is expected to be in the wide range including the order of nano-gram or less. In order to measure the isotope ratios by ICP-MS, we have studied sample preparation procedures for the trace amount of uranium. Elements causing spectroscopic and non-spectroscopic interferences in ICP-MS measurement were sufficiently removed by anion-exchange of hydrochloric acid media. The uranium contamination introduced throughout the process of sample preparation was below 10 pg uranium per sample. The applicability of the treatment process for uranium isotope measurement up to 100 pico-grams was proposed.

KEYWORDS: uranium isotope, trace analysis, ICP-MS, safeguards

I. Introduction

Environmental analysis method was introduced for the strengthened safeguards system based on the Program 93+2 of the IAEA[1).]The wide range amount of uranium are collected on the swipe sample taken by IAEA from nuclear facilities. Since precise and accurate isotope ratio determination of uranium at trace levels is required for detection of undeclared nuclear activities, the analysis methods of the swipe samples are being examined at JAERI clean facility (CLEAR).

Inductivity Coupled Plasma mass spectrometer (ICP-MS) has two large merits in the measurement of isotope ratio for these trace elements: It is possible to treat a large number of samples because of simple sample preparation and short measurement time. Compared with thermal ionization mass spectrometry (TIMS), relatively small amounts of sample are required for system tuning. Since these merits are based on the fact that the samples for ICP-MS are in solution form, establishment of the sample treatment method is important.

On the other hand, in the swipe sample analysis by ICP-MS, it is necessary to remove the concomitant elements inducing two effects as below. One is spectroscopic interference on uranium ions caused by polyatomic ion such as $PtAr^+$. Since the polyatomic ion increases objective signal intensity, it is necessary to reduce these elements producing polyatomic ion. Another is the matrix effect (non-spectroscopic interference)[3,4)]. The matrix effect induced by concomitant elements, the mechanism of which is not yet clarified, is to suppress the objective signal intensity.

Therefore, it is necessary to establish the treatment method of ICP-MS samples with sufficient removal of concomitant elements causing interferences. In the case of the treatment of ultra-trace uranium samples, the estimation of uranium contamination during chemical purification process is also important.

In this work, at first, the treatment method of the swipe samples and measurement method for uranium isotope ratio by ICP-MS are examined using a few samples with swiped uranium and the tracer such as a few nano-gram of natural uranium.[5)] Then, we have estimated the degree of uranium contamination from outside during the chemical purification process.

II. Experimental

In order to dissolve the sample and remove the concomitant elements with the lowest uranium contamination, dry ashing, acid digestion, and anion-exchange in hydrochloric acid media were carried out, as shown in **Fig.1**[6,7)]. A sample together with blank sample was dry ashed using quartz beaker covered with watch glass in muffle reactor. The ashing temperature was set on 550°C (10 hours) which did not produce the sparingly soluble plutonium oxide. The sample after dry ashing was transferred into Teflon beaker. The sufficiently dissolution by the repetition of acid digestion for sample was carried out. The solution sample after acid digestion was purified by anion-exchange in hydrochloric acid media. In order to

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[*] Corresponding author, Tel. +81-29-282-5761,
Fax.+81-29-284-3665
takahashi@sglsun.tokai.jaeri.go.jp

estimate the degree of sample dissolution and the removal of concomitant elements, the sample solution after dry ashing, acid digestion, and anion-exchange were divided into small portions for analysis.

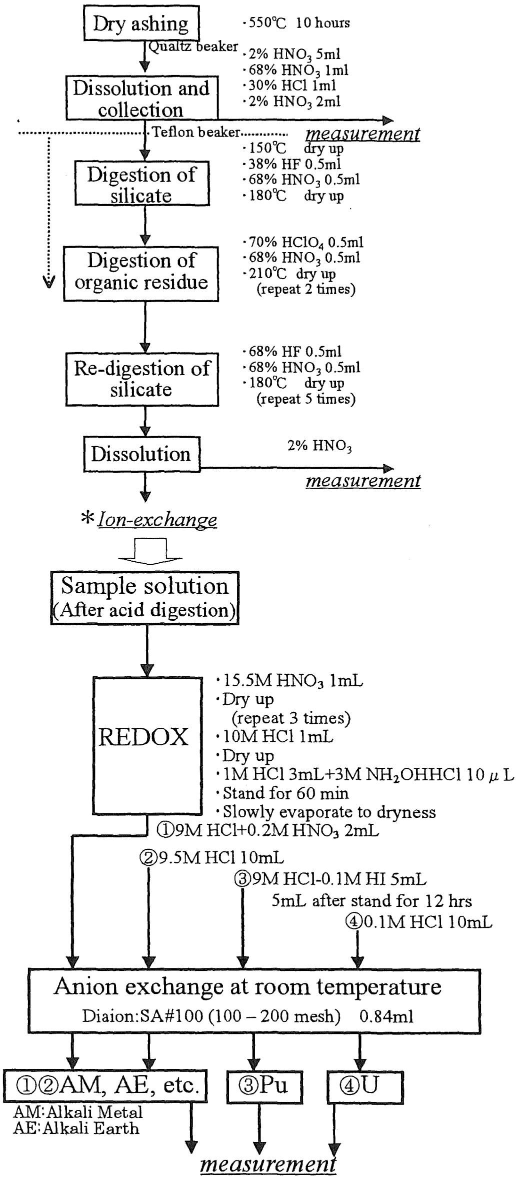

Fig.1 Sample dissolution and uranium purification process[6, 7]

Each sample for measurement by ICP-MS (Thermo Finnigan, Element) was prepared to 2% nitric acid solution. These solution samples were measured by the standard addition method (SAM) using depleted uranium (XSTC-289 (SPEX) 0.295% ^{235}U). On the measurement of SAM, the fixed volume of solution sample was taken, and adjusted by 2% nitric acid at 5ml after adding uranium in a unit of 195pg-U. Since the matrix effect suppress the objective signal intensity by the presence of concomitant elements, the effect was directly estimated by the difference of inclination of calibration curve between signal intensity and uranium concentration measured by SAM.

The uranium contamination from pure water, reagent, vessel, and atmosphere were measured by ICP-MS. High purity acids (HCl, HNO_3, HF and $HClO_4$;TAMAPURE^{TM}) were used throughout the procedure. **Table 1** shows the specification value of uranium concentrations and treatment volume in the ream of process in each acid and pure water.

Table 1 Contribution of uranium contamination from reagent

Reagent	Concentration (ppt)	Volume (ml)	Total (pg)
HNO_3 (68%)	<0.005	5	<0.025
HCl (30%)	<0.1	30	<3
HF (38%)	<0.005	3	0.015
$HClO_4$ (70%)	<0.005	1	<0.005
Pure water	<0.005	16	<0.08

* Specification value on catalogue

The contamination from atmosphere was estimated by the measurement of uranium collected together with air dust under conditions of the Teflon^{TM} bottle (46 mm ϕ) filled with 40ml 2% nitric acid exposed for one week inside and outside of the clean facility. The obtained data were used for examination of uranium contamination from atmosphere during the treatment process after the correction by the treatment time and exposed surface area of sample preparation vessel.

For the estimation of the uranium contamination from vessel surface, Teflon vessel filled with concentrated acid was heated and dried up. Then, the vessel rinsed with 2% nitric solution of measurement solution.

The total uranium contamination from outside during chemical purification procedure was also estimated by the process blank tests.

III. Results and discussion

1. Sample dissolution

The comparison of degree of sample dissolution after each stage of dry ashing, acid digestion, and anion-exchange is shown in **Fig. 2**. These data indicate the variation of signal intensity given by a short time of 50 ms repetitional measurement of ICP-MS. The peculiar peaks of about five percent exist in the sample solution after dry ashing, as shown in **Fig. 2**(a). It is considered that these peculiar peaks are attributed to insoluble components, because it indicates the inhomogeneities in concentration. Since the presence of this composition decreased the precision of analytical results, a series of acidic digestion for the sample was carried out. As a result, the peculiar peak of solution sample after acid digestion was decreased less than 1%, as shown in **Fig. 2**(b). On the anion-exchange process, the peculiar peaks component was removed from uranium fraction by the first elution (9-9.5M HCL) of more

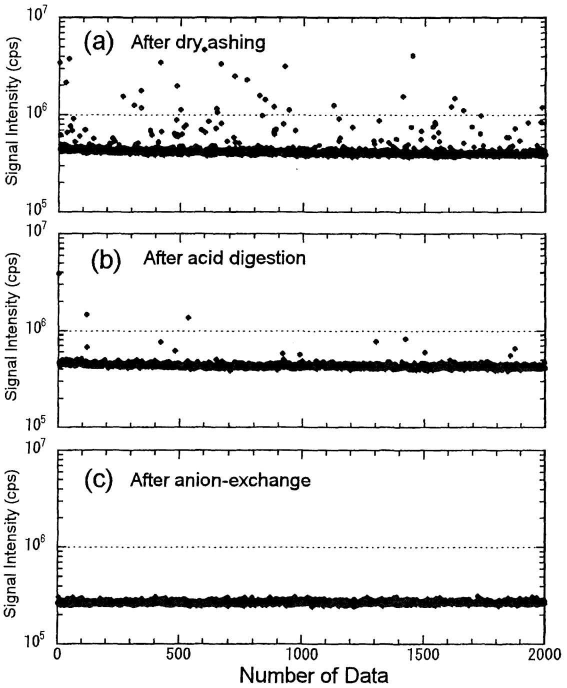

Fig. 2 Comparison of peculiar peak intensity

than 10 columns volume. Therefore, the peculiar peaks were undetected in U fraction, as shown in **Fig. 2**(c).

The chemical yield of uranium after anion-exchange process estimated by the uranium quantity obtained by standard addition method was 57% to 88%.

2. Effect of concomitant elements

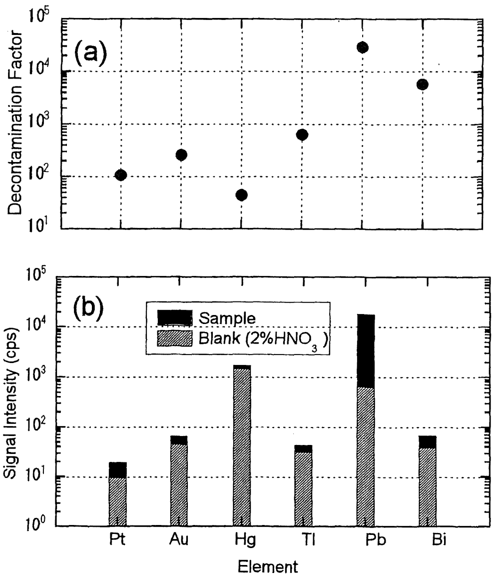

Fig. 3 DF and signal intensity of elements in uranium sample

Figure 3(a) shows the decontamination factor for the elements heavier than Pt after the anion-exchange process. These elements producing polyatomic ion were sufficiently removed because of the large decontamination factor without Hg.

Figure 3(b) shows the comparison of signal intensity of the element heavier than Pt in uranium measurement sample. The total signal intensity (sample+ blank) of these elements including the signal of blank (2% HNO_3) were less than $1x10^5$ cps. Since the contribution rate of Pt for uranium by producing polyatomic ion is to about $1x10^{-5}$,8) the effects of these elements on the measurement of 1 cps (0.0005ppt) uranium are negligible small.

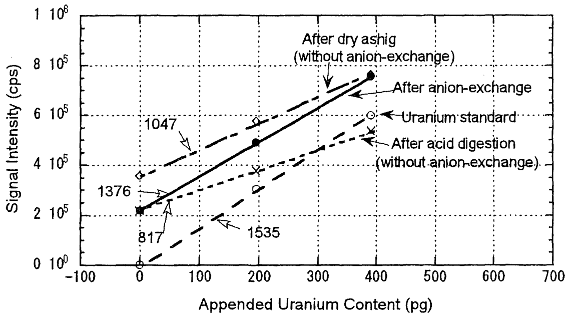

Fig. 4 Comparison of inclination of uranium concentration curve

Figure 4 shows the comparison of inclination of uranium concentration calibration curve given by SAM for the sample solutions before and after anion-exchange process. The inclination of each calibration curve given as numbers in **Fig. 4** indicates in unit of cps/pg-U. The matrix effect was negligibly small for the solution sample after anion-exchange, as the inclination of sample calibration curve was almost consistent with that of standard calibration curve. On the other hand, the matrix effect was detected in two solution samples before anion-exchange.

3. Uranium contamination

Since the uranium concentrations in each acid were less than detection limits, the contribution from acid in the ream of treatment process were calculated by the product of the concentration and treatment volume given in **Table 1.**

Figure 5 shows the comparison of uranium content attributed by each component relating to the sample. The uranium contamination from vessel had the largest contribution in the ream of process in spite that the Teflon vessel with alkaline and hot acid washing was used, as 3 to 7 pg/treatment of uranium contamination was detected. This contamination mainly occurs in acid heating process of the sample to dry up. On the treatment of pico-gram per sample for uranium, the Teflon vessels should be further cleaned by other mean.

The contaminations from reagent and atmosphere in the clean facility were relatively low. The symbol of downward bow in **Fig. 5** indicates the maximum value. The chloric-acid used in the anion-exchange process is largest contribution among the reagents because of the relatively high impurity level and large preparation volume as about 30ml.

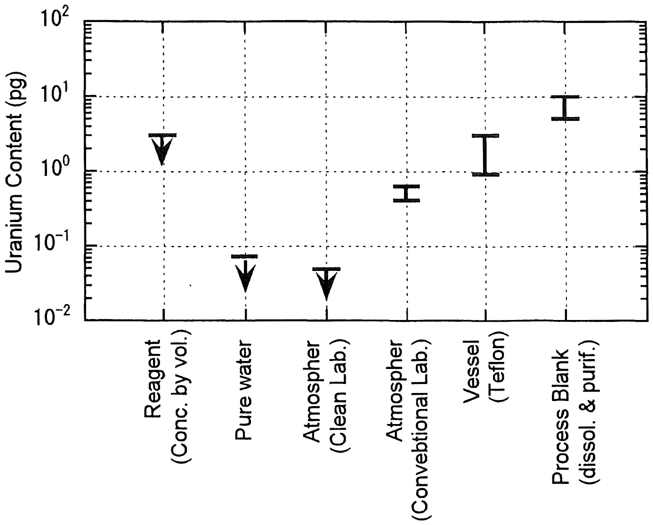

Fig. 5 Uranium contamination during sample treatment

The cross contamination in dry ashing process as a first step of sample preparation, which is the uranium content ratio between blank and uranium sample, was less than 2x10^{-6}. It indicates that samples containing from pico-gram to micro-gram uranium, that is screening limit by radiation measurement, can be treated at the same time with negligible cross contamination.

IV. Conclusions

The uranium contaminations during sample treatment and the chemical treatment method of swipe samples were estimated. The contamination was below 10 pg uranium per sample treatment, and it is possible to treat the sample of pico-gram order of uranium by using clear facility and removing the contribution from Teflon vessels. The sample dissolution was achieved by dry ashing and repetition treatment of acid digestion, and also concomitant elements were sufficiently removed by anion-exchange process. On the precise uranium isotope ratio measurement for swipe sample, the removal method for non-spectroscopic and spectroscopic interference was clarified. We demonstrated the applicability of the treatment process for uranium isotope measurement up to 100 pico-grams.

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References

1) H. Nishimura, M. Magara, T. Oda, S. Usuda, K. Watanabe, T. Adachi, H. Noguchi, “Environmental sample analysis program in Japan”, *IAEA-SM-*351/98, *Vienna* 1997.
2) M. Magara, Y. Hanzawa, F. Esaka, et al., “Development of analytical techniques for ultra trace amounts of nuclear materials in environmental samples using ICP-MS for safeguards”, *Applied Radiation and Isotopes (Pro. Low-Level Radioactivity Measurement Techniques, SCK-CEN, Mol, Belgium,* 18-22 *Oct.* 1999), 53, p.87-90 (2000).
3) Matheson M. Fraser, Diane Beauchemin, “Effect of concominant elements on the distribution of ions in inductivity coupled plasma-mass spectroscopy”, *Spectrochimica Acta Part* B 55, 1705-1731 (2000).
4) J.A. Olivares, R.S. Houk, “Suppression of analyte signal by various concominant salt in inductivity coupled plasma mass spectrometry”, *Anal. Chem.* **58**, 20-25(1986).
5) S. Sakurai, S. Usuda, K. Watanabe, et al., “Present Status of JAERI’s R&D on Ultra- Trace-Analytical Technology for Safeguards Environmental Samples”, *Proceedings of 42^{nd} INMM* (15-19) *July* 2001, *Indian Wells, California, USA..*
6) D. L. Donohue, “Strengthening IAEA safeguards through environmental sampling and analysis” *J. Alloy and Compounds* **271-273**, 11-18(1998).
7) H. Natsume, H. Umezawa, S. Okazaki, T. Suzuki, T. Sonobe, S. Usuda, “Squencial Ion-Exchange Separation of Heavy Elements and Selected Fission Products for Burnup Measurement”, *J. Nucl. Sci. Technol.,*9[12] (1972).
8) M. Magara, T. Sakakibara, S. Kurosawa, M. Takahashi, S. Sakurai, et al., “Isotope ratio measurement of uranium in safeguards environmental samples by ICP-MS”, *International Symposium on Isotope Effects in Physics, Chemistry and Engineering,* (22-23) *August*2001, *Nagoya, Japan (to be published).*