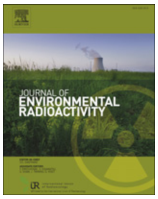
Journal of Environmental Radioactivity 113 (2012) 8–15

Contents lists available at SciVerse ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad



Direct uranium isotope ratio analysis of single micrometer-sized glass particles

Stefanie Kappel[a], Sergei F. Boulyga[b], Thomas Prohaska[a,*]

[a] University of Natural Resources and Life Sciences Vienna, Department of Chemistry, Division of Analytical Chemistry, VIRIS-Laboratory, Konrad-Lorenz-Strasse 24, 3430 Tulln, Austria
[b] Safeguards Analytical Services, Department of Safeguards, International Atomic Energy Agency, Wagramer Strasse 5, 1400 Vienna, Austria

ARTICLE INFO

Article history:
Received 6 October 2011
Received in revised form
30 March 2012
Accepted 30 March 2012
Available online

Keywords:
Laser ablation
Multi collector ICP-MS
Uranium isotope ratio analysis
Particle analysis
Nuclear forensics
Nuclear safeguards

ABSTRACT

We present the application of nanosecond laser ablation (LA) coupled to a 'Nu Plasma HR' multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) for the direct analysis of U isotope ratios in single, 10–20 μm-sized, U-doped glass particles. Method development included studies with respect to (1) external correction of the measured U isotope ratios in glass particles, (2) the applied laser ablation carrier gas (i.e. Ar versus He) and (3) the accurate determination of lower abundant $^{236}U/^{238}U$ isotope ratios (i.e. 10^{-5}). In addition, a data processing procedure was developed for evaluation of transient signals, which is of potential use for routine application of the developed method. We demonstrate that the developed method is reliable and well suited for determining U isotope ratios of individual particles. Analyses of twenty-eight S1 glass particles, measured under optimized conditions, yielded average biases of less than 0.6% from the certified values for $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios. Experimental results obtained for $^{236}U/^{238}U$ isotope ratios deviated by less than −2.5% from the certified values. Expanded relative total combined standard uncertainties U_c ($k = 2$) of 2.6%, 1.4% and 5.8% were calculated for $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$, respectively.

1. Introduction

The isotopic fingerprints of uranium (U) and plutonium (Pu) are of particular interest for international safeguards (Axelsson et al., 2009) and nuclear forensics (Mayer et al., 2007) as the knowledge of these signatures enables to link nuclear material to its respective nuclear processes and activities (Donohue, 2002). U and/or Pu isotopic signatures are stored in micrometer-sized particles (Donohue, 1998) that can be emitted during nuclear processes. The absolute amount of nuclear material in such particles usually ranges from picograms to nanograms (Axelsson et al., 2009). Sampling of such material is performed in nuclear facilities (e.g. enrichment facilities, hot cells, etc.) and the nearby environment by means of swipes (Donohue, 1998, 2002). Analyzing individual particles has the advantage that possible signatures of unknown isotopic compositions can be detected, even if they are masked by dust particles or other matrices that have declared or natural isotopic signatures. In comparison, bulk analysis, which comprises the analysis of the entire swipe, would only yield an average value of different isotopic signatures present on the swipe (Donohue, 1998).

Fission track-thermal ionization mass spectrometry (FT-TIMS) (Esaka et al., 2004; Lee et al., 2007) and secondary ionization mass spectrometry (SIMS) (Betti et al., 1999; Ranebo et al., 2009; Tamborini, 2004) are usually applied for the isotopic characterization of single, micrometer-sized particles from safeguards samples (Donohue, 1998). The performance of TIMS in terms of accuracy and precision of isotope ratio measurements is unquestioned (Heumann et al., 1998); however, the need for a nuclear reactor for irradiation (Lee et al., 2007) of the FT detector with thermal neutrons is the main drawback of FT-TIMS. SIMS offers the advantage of combining the localization of particles collected by means of swipes and the determination of the isotopic information in one instrument (Betti et al., 1999). Moreover, scanning electron microscopy combined with energy-dispersive X-ray spectrometry (SEM-EDX) is applied for the localization of particles and the determination of the elemental composition (Ciurapinski et al., 2002; Donohue et al., 2008), as well as morphological characterization of the particles (Kips et al., 2007; Ranebo et al., 2007).

Even though both TIMS and SIMS are state-of-the-art techniques, the International Atomic Energy Agency (IAEA) is pursuing improvements and new method developments in order to obtain a complete picture of a particle's history and to help verifying the absence of undeclared activities. Recently, laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied for

---

[*] Corresponding author. Tel.: +43 1 47654 6092; fax: +43 1 47654 6059.
E-mail addresses: stefanie.kappel@boku.ac.at (S. Kappel), s.bulyha@iaea.org (S.F. Boulyga), thomas.prohaska@boku.ac.at (T. Prohaska).

0265-931X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jenvrad.2012.03.017

direct actinide isotope analysis of single particles (Boulyga and Prohaska, 2008; Lloyd et al., 2009; Varga, 2008). Varga analyzed U isotope ratios of U_3O_8 powder particles (i.e. depleted, natural, low-enriched and highly enriched U) – having lateral dimensions of 10–30 μm – by employing a high resolution double-focusing ICP sector-field mass spectrometer equipped with a single collector. The U amount in a 10 μm particle was estimated to approximately 0.46 ng, assuming a spherical particle (Varga, 2008). Depleted uranium oxide particles (i.e. larger than 20 μm), embedded in dust and surface soil, were directly analyzed by Lloyd et al. (Lloyd et al., 2009) by employing LA-multi collector (MC)-ICP-MS for the determination of $^{235}U/^{238}U$ and $^{236}U/^{238}U$. The sampling volume corresponded to approximately 4 ng U (Lloyd et al., 2009). The applicability of LA-MC-ICP-MS for isotope ratio analyses of U and fission products of micro-samples (i.e. dimensions ranging from 100 μm to 1 mm) collected in the vicinity of Chernobyl was demonstrated by Boulyga and Prohaska (Boulyga and Prohaska, 2008).

The present work describes the application of ns laser ablation coupled to MC-ICP-MS for the direct determination of $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratios in single, U-doped, 10–20 μm-sized glass particle reference material (Raptis et al., 2002). The purpose of the glass particles applied in this study is the simulation of environmental samples (e.g. soil, sediment or dust) that contain hot particles (Raptis et al., 2002), which is of interest considering a future application of the presented method for such samples. Hence, method development and the merits of this analytical technique are demonstrated by means of this reference material, in which absolute U amounts are in the picogram range. To the authors' knowledge it is the first time that a certified reference material is used for the validation of LA-MC-ICP-MS for U isotope ratio analyses in single particles. The full evaluation and validation of the presented method is described. In addition, a novel approach for operator-independent data processing, including non-laborious external correction of the isotope ratios of interest is presented in this work.

2. Materials and methods

2.1. Reagents, standards and certified reference materials

Analytical reagent grade nitric acid (65% (m/m), Merck KGaA, Darmstadt, Germany) underwent sub-boiling distillation twice (Milestone-MLS GmbH, Leutkirch, Germany) prior to use. 1% (m/m) HNO_3 was prepared by diluting purified 65% (m/m) HNO_3 with reagent grade type I water (18.2 MΩ cm at 25 °C, Ultra Clear Basic Reinstwassersystem, SG Wasseraufbereitung und Regenerierstation GmbH, Barsbüttel, Germany) that was also purified by sub-boiling distillation (Milestone-MLS GmbH, Leutkirch, Germany) prior to use. Certified isotope reference materials – CRM U500 (New Brunswick Laboratory, U.S. Department of Energy, Washington, DC, U.S.) and IRMM-187 (European Commission-JRC, Institute for Reference Materials and Measurements, Geel, Belgium) – were applied for external correction and the determination of the secondary electron multiplier yields. An in-house prepared mixture, having a $^{236}U/^{238}U$ isotope ratio of 8.96×10^{-7}, of IRMM-184 (European Commission-JRC, Institute for Reference Materials and Measurements, Geel, Belgium) and U500, was used for optimizing the deceleration filter. This mixture was obtained by diluting and gravimetrical mixing of both IRMM-184 and U500 in order to obtain a solution with a $^{236}U/^{238}U$ isotope ratio that is approximately twice as high as the $^{236}U/^{238}U$ abundance sensitivity that was determined without applying the deceleration filter. Determination of the abundance sensitivity for uranium isotopes at the mass m-2 u was employed with a ^{233}U isotopic spike solution ((99.4911 atom percent of ^{233}U; CRM 111-A (New Brunswick Laboratory, U.S. Department of Energy, Washington, DC, U.S.)). A natural U solution (IRMM-184) was used for the determination of the UH^+/U^+ hydride ratio when introducing liquid standards. Dilution of the standards was accomplished with 1% (m/m) HNO_3 in order to get solutions exhibiting concentrations in the low ng g^{-1} range (i.e. smaller than 10 ng g^{-1}). The isotope amount ratios of the certified reference materials used in this study are given in Table 1.

S1 and S3 glass particles that are doped with U of certified isotopic composition (European Commission-JRC, Institute for Reference Materials and Measurements, Geel, Belgium) were used for method development, optimization, validation and proof of principle. The particles were produced by the IRMM for the IRMM support programme to the International Atomic Energy Agency (IAEA) and for the IRMM external NUSIMEP quality control programme (Nuclear Signatures Interlaboratory Measurement Evaluation Programme). Matrix glass, consisting of 70% SiO_2, 15% B_2O_3, 10% Na_2O, 4% CaO and 1% Al_2O_3 (i.e. borosilicate glass), was mixed with U_3O_8, in order to produce U-containing glass particles. The U-doped glass was blended with matrix glass in order to simulate environmental samples (e.g. soil, sediment or dust) that contain hot particles. A detailed description of the preparation of the used glass particles is given in Raptis et al. (2002). The analysis of the matrix glass enabled to exclude interferences occurring from matrix elements (e.g. Al, Pb, Si, etc.). The size of the glass particles was between 10 and 20 μm (Raptis et al., 2002). Certified isotope amount ratios of the utilized particles are given in Table 1. The estimated U amount per 10 μm-sized glass particle was less than 100 pg when assuming (1) a spherical shape, (2) a borosilicate glass density of 2.5 g cm^{-3} and (3) an U_3O_8 amount of 5% (m/m) (Raptis et al., 2002). About 1.1 mg of each glass particle standard were distributed on a cellulose acetate membrane filter (OE 67, Whatman GmbH, Dassel, Germany) and treated in a closed glass Petri dish with acetone vapor for about 30 min. The transparent membranes were then affixed, using customary glue, to a glass object plate. Both the membrane and the glass object plate were screened for their U blank.

2.2. Instrumentation

All isotope ratio measurements were accomplished with a double-focusing high resolution sector-field MC-ICP-MS (Nu Plasma HR, Nu Instruments Limited, Wrexham, U.K.) A solid state nanosecond laser ablation system (UP 193, ESI-NWR Division, Electro Scientific Industries, Inc., Portland, CA, U.S.) was coupled to the MC-ICP-MS in order to perform direct analyses of the glass particles of interest. Both Ar and He were employed as carrier gas. A membrane desolvation system (DSN-100, Nu Instruments Limited, Wrexham, U.K.) was connected in parallel to the LA-MC-ICP-MS setup. This setup enables liquid sample introduction without the necessity of de-coupling the laser system for the measurement of the liquid U reference material. No liquid solution was aspirated

Table 1
Isotope amount ratios of certified reference materials used in this study.

	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
S1 (U in glass)	0.000 055 7(11)	0.007 304 5(36)	0.000 010 08(11)
S3 (U in glass)	0.000 279 6(17)	0.043 343(22)	0.000 424 8(10)
IRMM-184	0.000 053 138(32)	0.007 262 3(22)	0.000 000 124 46(17)
IRMM-187	0.000 387 00(16)	0.047 325(14)	0.000 071 965(39)
CRM U500[a]	0.010 422(19)	0.999 6(14)	0.001 518 8(62)

[a] The given isotope amount ratios and uncertainties ($k = 2$) were calculated from the certified atom percents of ^{234}U, ^{235}U, ^{236}U and ^{238}U, and respective uncertainties stated in the certificate.