Spectrochimica Acta Part B 93 (2014) 52–60

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Measurement of the isotopic composition of uranium micrometer-size particles by femtosecond laser ablation-inductively coupled plasma mass spectrometry

Amélie Hubert [a,*], Fanny Claverie [b,c], Christophe Pécheyran [b], Fabien Pointurier [a,1]

[a] CEA, DAM, DIF, F-91297 Arpajon, France
[b] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, UMR 5254, Hélioparc Pau-Pyrénées, 2 Avenue du Président Angot, 64053 Pau, France
[c] Novalase SA, ZI de la Briqueterie, 6 Impasse du Bois de la Grange, 33610 Canejan, France

ARTICLE INFO

Article history:
Received 31 August 2012
Accepted 16 December 2013
Available online 24 December 2013

Keywords:
Femtosecond laser ablation
Uranium particles
ICP-MS
Fission tracks

ABSTRACT

In this paper, we will describe and indicate the performance of a new method based on the use of femtosecond laser ablation (fs-LA) coupled to a quadrupole-based inductively coupled plasma mass spectrometer (ICP-QMS) for analyzing the isotopic composition of micrometer-size uranium particles. The fs-LA device was equipped with a high frequency source (till 10 kHz). We applied this method to 1–2 μm diameter-uranium particles of known isotopic composition and we compared this technique with the two techniques currently used for uranium particle analysis: Secondary Ionization Mass Spectrometry (SIMS) and Fission Track Thermal Ionization Mass Spectrometry (FT-TIMS). By optimizing the experimental conditions, we achieved typical accuracy and reproducibility below 4% on $^{235}U/^{238}U$ for short transient signals of only 15 s related to 10 to 200 pg of uranium. The detection limit (at the 3 sigma level) was ~350 ag for the ^{235}U isotope, meaning that $^{235}U/^{238}U$ isotope ratios in natural uranium particles of ~220 nm diameter can be measured. We also showed that the local contamination resulting from the side deposition of ablation debris at ~100 μm from the ablation crater represented only a small percentage of the initial uranium signal of the ablated particle. Despite the use of single collector ICP-MS, we were able to demonstrate that fs-LA-ICP-MS is a promising alternative technique for determining uranium isotopic composition in particle analysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

It has become increasingly important for safeguards and environmental monitoring purposes to develop and apply analytical techniques to particulate matter collected at established nuclear facilities in order to check the consistency of the declarations by facility operators [1]. Sampling consists in collecting dust material by wiping surfaces with cotton cloths inside nuclear facilities. This dust contains U particles that have been produced in the processes implemented in the facility. These highly mobile particles are found in many locations in the facility and their isotopic, elemental and structural compositions provide specific information about the activities carried out in the installation [2].

Uranium has three naturally occurring isotopes (^{234}U, ^{235}U and ^{238}U). ^{235}U is the only U isotope that is fissile with thermal neutrons. The $^{235}U/^{238}U$ uranium isotopic ratio shows only minor variations in nature (around 7.25×10^{-3}), but due to anthropogenic enrichment, it fluctuates from slightly enriched for civilian applications (in nuclear power plants) to highly enriched for research or military applications. Depleted uranium (lower ^{235}U content than NU—natural uranium) is also produced as a by-product of uranium enrichment processing. Consequently, uranium isotopic measurements allow a discrimination of the different origins (natural, enriched, etc.) and purposes of nuclear material detected in the samples (civilian, military). However, as the amount of material contained in each of the micrometer-size particles usually encountered in the sample is very low (in the picogram range), a very sensitive analytical technique is required.

So far, the analysis of such environmental samples has been investigated using two different methodologies [2]: bulk analysis [3] which consists in measuring the uranium and plutonium isotopic signatures of the entire sample, and particle analysis which consists in separating particles in order to determine their individual isotopic signature. Individual particle analysis has the advantage of being selective and detecting different isotopic compositions (i.e. origins) in one location, whereas bulk analysis gives only the average uranium isotopic composition. Therefore, single particle analysis is a very powerful approach for determining the presence of undeclared nuclear activities. Currently, two analytical techniques are used for particle analysis, each with their advantages and drawbacks: Fission Track-Thermal Ionization Mass Spectrometry (FT-TIMS) [4,5] and Secondary Ionization Mass Spectrometry (SIMS) [6–9].

Considering the limitations of these techniques (TIMS has a low sample throughput and lacks sensitivity, measurement of minor isotopes

* Corresponding author. Tel.: +33 169 26 70 65; fax: +33 169 26 40 00.
E-mail address: amelie.hubert@cea.fr (A. Hubert).
[1] Tel.: +33 169 26 70 65; fax: +33 169 26 40 00.

0584-8547/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.sab.2013.12.007

by SIMS can be biased by molecular interferences [8,9]), the feasibility of using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) for uranium particle analysis was demonstrated by a few teams [10]. On the one hand, LA sampling allows bulk analysis as well as in-depth profiling, surface mapping and micro-analysis with good spatial resolution (at best a few μm). On the other hand, ICP-MS is considered to be a highly sensitive measurement technique and when coupled to LA it allows the direct analysis of solid samples. Particles can therefore be directly ablated individually for determining their corresponding isotopic composition. However, without a uranium particle localization technique, only relatively "large" uranium particles (at least 10 μm) can be analyzed [11–14]. Another group [15] presented direct analysis of U containing particle using ICP-MS after chemical purification of the particles. This method requires a perfect control of the blank level in all the reagents used. In a recent paper [16], we described the use of LA-ICP-MS in combination with precise uranium particle localization techniques (fission track and scanning electron microscope). After location, LA-ICP-MS particle analysis is fast (a few minutes per particle) and therefore a great number of particles can be analyzed per day. The sample preparation procedure allows particles to be fixed on the sample holder before localization and LA-ICP-MS measurements. Therefore, particles were not blown out by laser shots. Particles smaller than 1 μm were successfully analyzed using a commercially-available nanosecond-UV laser (Cetac LSX 213 nm) coupled to a quadrupole based-ICP-MS (ICP-QMS Thermo "X-Series II") on two particle-containing samples already analyzed in the same laboratory by FT-TIMS and SIMS. Their ^{235}U content was in the femtogram range. $^{235}U/^{238}U$ ratios were measured for all located particles. LA-ICP-MS results, although less precise and accurate (typically 10%) than the results obtained by FT-TIMS and SIMS due to short (20–40 s), transient and noisy signals, were in good agreement with the certified values or with the results obtained with other techniques. Thanks to a good measurement efficiency ($\sim 6 \times 10^{-4}$) and a high signal/noise ratio during the analysis, LA-ICP-MS can be considered a very promising technique for fast particle analysis.

The aim of this study is to test the use of a newly developed infra-red femtosecond laser ablation (fs-LA) system coupled with a quadrupole based ICP-MS in order to analyze NU micrometer size particles, and evaluate the reproducibility, accuracy and sensitivity of this method. A thorough study was conducted to optimize analytical conditions (wet/dry plasma, laser spot size, shot frequency, etc.) for uranium particle analysis. Statistical treatments were also applied on raw results to optimize the precision of $^{235}U/^{238}U$ ratio measurements. The isotope fractionation effect and the extent of deposition of ablation debris in the vicinity of the ablated area were also investigated. In addition to micrometer-size particles of known isotopic composition (NU), the fs-LA-ICP-QMS method was also applied to a real cotton cloth sample. Results were discussed and compared to those obtained with the FT-TIMS and SIMS techniques.

2. Experimental

2.1. Instrumentation

The ablation system used in this study is a femtosecond LA device (Alfamet, Novalase SA, Amplitude Systèmes France) [17,18] fitted with a diode-pumped KGW-Yb crystal. The laser source delivers 360 fs pulses at an IR wavelength of 1030 nm and operates at high repetition rates (up to 10 kHz) and low energy (from 225 μJ at 100 Hz to 100 μJ at 10 kHz). The low energy level delivered by the laser source imposed the use of a narrow laser beam focused on the sample in order to keep the fluence above the ablation threshold. In the same way, the use of a high repetition rate laser source largely overcomes the lack of sensitivity which results from the low quantity of material ablated by low energy laser shots. A 50 mm focal length objective was fitted in the laser machine providing a 17 μm laser spot with maximum fluence varying from 39 J/cm^2 at 100 Hz to 15 J/cm^2 at 10 kHz). A fast 2D galvanometric scanner allows the laser beam to be rapidly moved with high repositioning precision (better than 5 μm at 280 mm·s^{-1}) in order to design complex trajectories in 2 dimensions. Then, when needed, the laser beam can be virtually enlarged by combining the high repetition rate to the fast movement of the laser beam as described below. Details of the LA device are described elsewhere [17,19–22]. These features are unusual compared to lower repetition rate and higher energy lasers commonly used for chemical analysis by commercially available nanosecond LA. The ablation cell used was cylindrical cell (15 cm^3, 4,5 cm diameter).

The ICP-MS used in this study was an "X Series II" (Thermo Fisher Scientific, Winsford, UK). Wet and dry plasma conditions were evaluated for this study. While dry plasma conditions were simply obtained introducing the laser produced aerosol using a conventional torch, wet plasma conditions were achieved by using a two inlet torch that mixes the dry aerosol together with a nebulized aerosol (HNO_3 2%). The optimization of the ICP-MS was performed with a 1 μg·l^{-1} uranium solution in wet plasma conditions, and by ablating a 100 μm wide line of the NIST612 glass standard material in dry plasma conditions. Each isotope was acquired with a dwell time of 20 ms.

In the case of the FT-TIMS technique, particles are extracted from the cotton and fixed on polycarbonate Lexan® disks with a polymer. These disks are then covered with a thinner Lexan® disk and irradiated in a nuclear reactor [16]. Fissions of fissile ^{235}U atoms induced by thermal neutrons result in fission fragments which impact on the polymer. After chemical etching, characteristic figures called fission tracks can be observed on the thinnest disk under an optical microscope. The position of the center of a cluster of fission tracks indicates the position of the corresponding uranium particle. Once located, the particles are removed and deposited on rhenium filaments (one particle per filament). These filaments are then introduced in the TIMS source, and each particle is analyzed individually. Particles are chosen according to the number of their fission tracks which depend on the quantity of ^{235}U present in the particle. A large number of fission tracks reveals either a large NU particle or a smaller particle made of highly enriched uranium (HEU—higher abundance of ^{235}U). This technique ensures the detection of a few HEU particles even if they are mixed with thousands of NU particles. However, the analysis time for this technique is quite long (at least several weeks). Decay of short-life activation radionuclides after irradiation of the sample prior to handling lasts one week. Sampling of individual particles is tricky and only 5 to 6 particles can be analyzed by TIMS per day. The analysis of a batch of 3 to 4 samples requires at least three weeks, and more often 2 months, provided the proper instruments and an irradiation facility are available.

When using the SIMS technique, particles are extracted from the cotton and deposited on a carbon disk. They can either be located using a Scanning Electron Microscope (SEM) or directly located with SIMS. Each single particle is then analyzed individually. This technique allows fast measurements as sample preparation and particle locations can be carried out in 2 to 3 days. About 30 particles can be analyzed per day. However, this technique is not selective for highly enriched uranium particles, and a large number of particles have to be analyzed in order to detect one particular minor isotopic composition among a large quantity of particles coming from the major isotopic compositions (for instance NU particles). Moreover, measurements of minor isotopes are hindered by polyatomic interferences [8,9]. Modern large geometry SIMS equipped with automated particle search algorithms has a much higher throughput than 30 particles per day and are currently under evaluation [23].

2.2. Samples

The evaluation of the LA-ICP-MS technique for particle analysis was based on the analysis of three different samples: IRMM541, IRMM184 and particles of NU. The IRMM541 (from Institute for Reference Materials and Measurements, Geel, Belgium) is a certified glass material with a

Download English Version:

https://daneshyari.com/en/article/1239541

Download Persian Version:

https://daneshyari.com/article/1239541

Daneshyari.com