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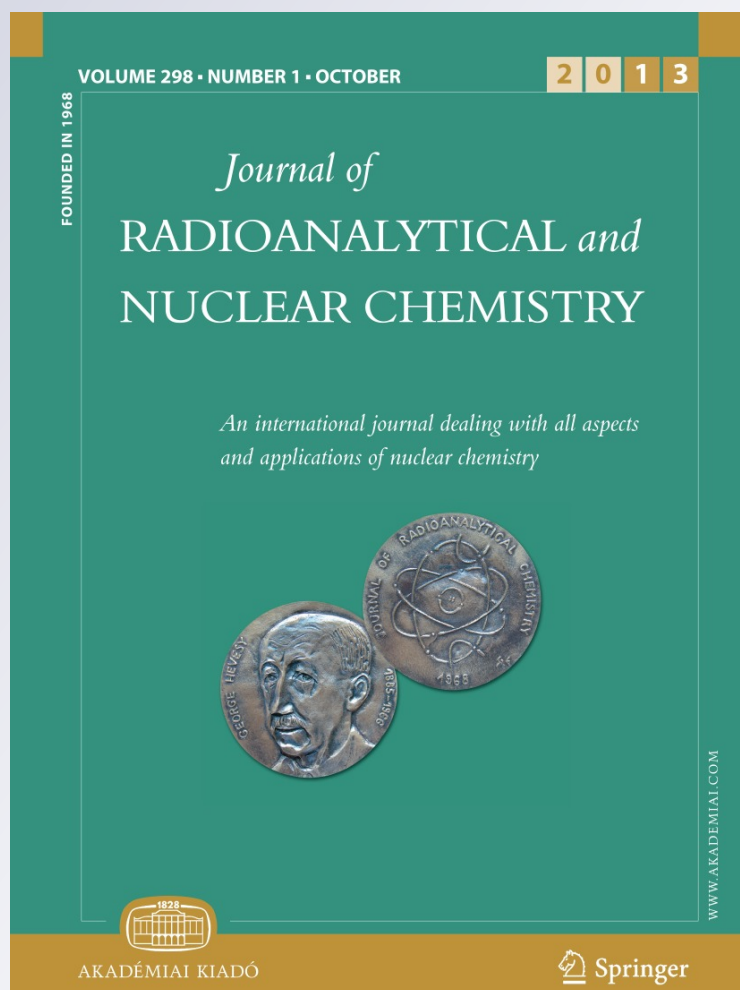
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VOLUME 298 · NUMBER 1 · OCTOBER

2013

FOUNDED IN 1968

# Journal of
## RADIOANALYTICAL and
## NUCLEAR CHEMISTRY

*An international journal dealing with all aspects and applications of nuclear chemistry*

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# New methodology for uranium analysis in swipe samples for nuclear safeguards purposes

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**Abstract** Environmental swipe sampling for safeguards purpose has been used by International Atomic Energy Agency since 1997, being a powerful tool to detect undeclared materials and activities. This work describes a new methodology for swipe samples analysis based on ultrasound-assisted acid leaching and compares it with traditional total digestion bulk analysis. The proposed method requires few preparation steps, decreasing the risk of contamination, reduced amounts of reagents and a good option to extract uranium from swipe sample. In a real case study, the swipe samples were collected in a conversion plant at IPEN/CNEN, Brazil. The measurements were carried out by ICP-MS and the results showed relative error lower than 0.96 % for uranium isotopic ratios for the certified reference material (NBS U200). The uncertainties were estimated by following the ISO GUM, with a confidence level of 95 %. The uncertainties percentage for $n(^{235}U)/n(^{238}U)$ ratio of the samples ranged from 2.5 to 4.3 %. The values of uranium isotopic ratio obtained for each method demonstrate the viability of using the methodology proposed in this work.

**Keywords** Nuclear safeguards · Swipe sample · Bulk analysis · Uranium leaching · Ultrasound · ICP-MS

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## Introduction

Nuclear safeguards are measures aimed to protect and control nuclear material existing in any plant or facility in the nuclear fuel cycle. They certify that signatory states are in agreement with the non-proliferation treaty (NPT); in other words, they are actions to ensure the peaceful use of nuclear material [1, 2].

Aiming to strengthen the effectiveness of the nuclear safeguards systems, the Governors board of International Atomic Energy Agency (IAEA) approved, in 1997, the additional protocol (INFCIRC/540 (corrected)) which provides the legal base for environmental sampling for safeguards purpose. This procedure has been one of the most powerful verification techniques used by safeguards inspectors for the detection of illicit nuclear activities in wide-areas (inside and/or outside the facilities) in states under international nuclear safeguards. In this context, one of the procedures to collect environmental samples on surfaces by smears is known as swipe sample (SS) [3–5].

In a conversion plant, for instance, one of the main information to be monitored is the uranium isotope ratio. Uranium-containing particles originated from a conversion plant can be transported as aerosols and deposited on surfaces. The uranium isotope ratios in these particles have to be related to declared activities performed in the facility [6]. Therefore, any change in the isotopic ratio declared can bring evidence of undeclared activities and requires a more detailed investigation.

The analysis performed in the SS can be subdivided into individual particles analysis and bulk analysis (BA). Individual particles analysis is normally performed directly on the SS using secondary ions mass spectrometry, (SIMS) [5, 7], laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS [8], fission track thermal ionization

mass spectrometry, FT-TIMS [9], techniques. Bulk analysis involves total digestion and chemical separation of actinides [4, 10–16] providing information about the average isotopic composition of uranium in the whole sample, which has been analysed by TIMS or ICP-MS.

This work aims to present a new method of SS analysis based on ultrasound-assisted acid leaching (UAL) as a tool for uranium extraction procedure to determine uranium isotopic ratios for nuclear safeguards purposes, using an ICP-MS and comparing it with BA with total digestion.

## Experimental

### Instrumentation

Uranium isotopic ratios $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were performed by ICP-MS (Agilent 7500ce with an octapole reaction system, Hachioji-shi, Tokyo, Japan) using micromist nebulizer and spray chamber operated at 4 °C. The measurements were performed by using the conditions shown in Table 1. Muffle furnace (Quimis Q-318M24, 3720 W, Diadema, SP, Brazil) was used to dry ashing the SS. Ultrasound system utilized was Thornton T14 (Inpec Eletrônica LTDA, Vinhedo, SP, Brazil).

### Materials

Ultra-pure reagents and Milli-Q®-purified water (Millipore, France), with resistivity 18.2 MΩ cm at 25 °C, were used in the assays. All containment vessels were cleaned with 1.45 mol kg$^{-1}$ nitric acid and Milli-Q water before use.

**Table 1** Optimized operating condition and data acquisition parameters of ICP-MS analysis

| Instrument and data acquisition settings for the ICP-MS | |
| --- | --- |
| Sample and skimmer cone | Nickel |
| RF-power (W) | 1,500 |
| X, Y, Z torch position | Daily |
| Nebulizer gas flow rate (L/mim) | 0.95 |
| Plasma gas flow rate (L/mim) | 15 |
| Auxiliary gas flow rate (L/mim) | 0.8 |
| Octopole RF (V) | 170 |
| Octopole bias voltage (V) | −6 |
| Number of repeats | 6 |
| Stabilization time (s) | 25 |
| Integration time $^{234}U$, $^{235}U$ and $^{236}U$ (s) | 3 |
| Integration time $^{238}U$ (s) | 0.3 |
| Dwell time (μs) | 10 |

The uranium separation was performed by using a BioRad® poly-prep columns (2 mL of chromatography support medium and 10 mL of eluent or sample) filled in with anion exchange resin Dowex® AG 1 × 8, 100–200 mesh (Sigma-Aldrich, USA).

The ICP-MS operation parameters were optimized and the mass discrimination factor (Fmd) calculated with certified reference material (CRM) from NIST, (former National Bureau of Standards) NBS U200.

### Swipe sampling area: case study

The Nuclear and Energy Research Institute (IPEN/CNEN), São Paulo, Brazil, operates a MTR research reactor, IEA-R1, which uses uranium enriched up to 20 % of $^{235}U$ as nuclear fuel. This material is produced at the Nuclear Fuel Center department (CCN, IPEN/CNEN) [17, 18].

A practical exercise using the proposed method was performed by collecting SS at the CCN/IPEN in selected points of the facility (Table 2), by using a circular filter paper (provided by Montair Serviços e Cortes Ltda, São Bernardo do Campo, São Paulo, Brazil) with low uranium content, and placed inside double mini-grip bags to avoid contamination.

### Sample preparation procedure

In order to compare UAL and BA methods, the samples were cut in half and to each piece was applied a different procedure and analysed by ICP-MS.

### Bulk Analysis (BA)

The methodology is based on dry ashing and chromatography separation of uranium by using an anion exchange resin in hydrochloric media, following the procedure proposed by Williams et al. [16]. Initially, the SS was ashed in a muffle furnace at 450 and 600 °C for 2 h each.

**Table 2** Description of SS collection points within the conversion plant

| Points/samples | Description |
| --- | --- |
| 1 | $UF_4$ recuperation room. Floor in front of extraction column |
| 2 | $UF_4$ production facility. Entrance floor |
| 3 | $UF_4$ production facility. Floor in front of hydrolysis reactor |
| 4 | $UF_4$ recuperation room. Air exhaust pipe over the workbench |
| 5 | $UF_4$ production facility. Floor in front of autoclave |

The residue was dissolved in 8 mol kg$^{-1}$ HNO$_3$. Uranium in the hexavalent state was purified and separated using a Dowex AG 1 × 8 in hydrochloric media. The solution was dried and dissolved in 0.29 mol kg$^{-1}$ HNO$_3$ for uranium isotopic analysis.

Ultrasound-assisted acid leaching (UAL)

The UAL method was based on Buchmann's et al. [19] work. Each sample was placed into clean polystyrene centrifuge tube containing 20 g of 0.29 mol kg$^{-1}$ HNO$_3$ and kept in ultra-sound bath for 15 min. Then the SS was removed from polystyrene tube and the remaining solution was centrifuged at 3,000 rpm for 3 min. The supernatant was transferred with a disposable pipette (capacity of 3 mL) to a clean polystyrene centrifuge tube and introduced directly in the ICP-MS for uranium isotopic ratio analysis.

Mass discrimination correction

In an ICP-MS the mass discrimination is related to the preferential transmission of heavier ions mainly due to space charge interactions occurring after the skimmer cone region, thus, a mathematical correction estimating the Fmd is necessary. The Fmd was determined from the values of the measured and certified isotopic ratio from an isotopic standard and used to correct the measured isotopic ratio in sample solutions with the aid of the following equation [20–23].

$$f_{md} = \frac{R_{certified}}{R_{measured}} \tag{1}$$

where $R$ certified is the value of certified isotopic ratio and $R$ measured is the value corresponding to the isotopic ratio obtained from the instrument.

$$CF = \frac{(f_{md} - 1)}{\Delta m} \tag{2}$$

where $CF$ is the mass discrimination and $\Delta m$ is the difference of nominal masses.

$$R_{corr} = R_m (1 + CF)^{\Delta m} \tag{3}$$

where $R_{corr}$ is the isotopic ratio corrected and $R_m$ is the measured isotopic ratio in sample.

The Fmd was determined for each isotopic ratio [$n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$] by measuring a 10 μg kg$^{-1}$ solution of a uranium isotopic standard, NBS U200.

Estimation of uncertainties

The uncertainty is a parameter, associated with the result, which characterizes the dispersion of values attributed to a measurand, based on the information used. Every measurement is subject to some degree of dispersion. This variability can originate from different sources such as the measuring instrument, the item being measured, etc. [20, 24]

The uncertainties were estimated based on the ISO GUM [20] following the equations considering all dominant components of the measurement and the combined uncertainty ($U_c$), Eq. 4.

$$u_c = \sqrt{\sum_{i=1}^{n} u(xi)^2} \tag{4}$$

where $u(xi)$ is the standard uncertainty of each component of uncertainty.

The level of confidence of 95 % was used. Thereby, the expanded uncertainty ($U$) was calculated by the following Eq. 5: where $Uc$ is the combined uncertainty, $k$ is the coverage factor.

$$U = u_c k \tag{5}$$

The results were expressed as the average of the measurements followed by its expanded uncertainty.

Results and discussion

Initially, the main operational parameters of the ICP-MS were optimized by using CRM NBS U200. The conditions and measurements are shown in Tables 1 and 3, respectively.

As it can be observed in the Table 3, the relative error for $n(^{234}\text{U})/n(^{238}\text{U})$, $n(^{235}\text{U})/n(238\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$

**Table 3** Relative error and uncertainty for the isotopic ratios of CRM NBS U200. Data for solution containing 10 μg/kg of uranium

| NBS U200 | | | | | |
|---|---|---|---|---|---|
| Atom ratio | Certified | This work | ±$U^a$ | Relative error (%) | Uncertainty (%) |
| $n(^{234}\text{U})/n(^{238}\text{U})$ | 0.001564 ± 0.000004 | 0.001579 | 0.000122 | 0.96 | 7.73 |
| $n(^{235}\text{U})/n(^{238}\text{U})$ | 0.251259 ± 0.000260 | 0.253163 | 0.002390 | 0.76 | 0.94 |
| $n(^{265}\text{U})/n(^{238}\text{U})$ | 0.002657 ± 0.000008 | 0.002667 | 0.000025 | 0.38 | 0.94 |

[a] $U$ = expanded uncertainty with confidence level of 95 %

**Table 4** $n(^{234}U)/n(^{238}U)$. $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ isotopic ratios obtained for the samples submitted to different process and respective expanded uncertainties ($U$)

|        | $n(^{234}U)/n(^{238}U)$ | $\pm U$ | $n(^{235}U)/n(^{238}U)$ | $\pm U$ | $n(^{236}U)/n(^{238}U)$ | $\pm U$ |
|--------|---------|---------|---------|---------|---------|---------|
| 1 BA   | 0.00140 | 0.00025 | 0.140 | 0.005 | a | b |
| 1 UAL  | 0.00132 | 0.00025 | 0.130 | 0.005 | a | b |
| 2 BA   | 0.00101 | 0.00025 | 0.107 | 0.004 | 0.0009 | 0.0002 |
| 2 UAL  | 0.00092 | 0.00024 | 0.099 | 0.004 | 0.0008 | 0.0002 |
| 3 BA   | 0.00098 | 0.00025 | 0.108 | 0.005 | 0.0008 | 0.0002 |
| 3 UAL  | 0.00100 | 0.00024 | 0.122 | 0.004 | 0.0008 | 0.0002 |
| 4 BA   | 0.00174 | 0.00026 | 0.222 | 0.005 | 0.0013 | 0.0002 |
| 4 UAL  | 0.00176 | 0.00026 | 0.215 | 0.006 | 0.0013 | 0.0002 |
| 5 BA   | 0.00124 | 0.00029 | 0.162 | 0.019 | a | b |
| 5 UAL  | 0.00120 | 0.00025 | 0.158 | 0.005 | a | b |

[a] Not determined. Low counting of $^{236}U$ isotope

[b] $U$ = expanded uncertainty with confidence level of 95 %

and the uncertainties for $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ obtained from the CRM analysis were lower than 1 %. Due to the low statistical counts of the minor isotope ($^{234}U$), the uncertainty percent for $n(^{234}U)/n(^{238}U)$ isotopic ratio was higher than the previous ones. Thereby the Fmds were determined for uranium isotopic ratios and the values of the samples were corrected by Eqs. 1–3 and using the following values: Fmd $n(^{234}U)/n(^{238}U)$ = 0.9908; Fmd $n(^{235}U)/n(^{238}U)$ = 0.9925 and Fmd $n(^{236}U)/n(^{238}U)$ = 0.9962.

The sampling points were selected in a way to demonstrate the capability of the proposed methodology in detecting isotopic signatures at facility.

With regard to the safeguards purposes, the isotopic ratio $n(^{235}U)/n(^{238}U)$ and the isotope $^{236}U$ are the most important, because they carry the information about nuclear material enrichment and evidence of the use of reprocessed material, respectively.

Each half of the sample was submitted to a different process and the uranium isotope ratio results are shown in Table 4 with their respective expanded uncertainties ($U$). The results clearly demonstrated a good agreement within the uncertainties of measurements in almost every isotopic ratios analyzed.

It is important to notice that natural uranium is also manipulated in the facility, which can explain the

**Table 5** Comparison of the percent expanded uncertainties ($U\%$) obtained in three different studies analysing SS. The results are presented with their expanded uncertainty at 95 % confidence level

|                    | $U \%$  |
|--------------------|---------|
| Godoy [11]         | 0.2–1.9 |
| Szeles [14]        | 3.8–6.2 |
| This study—UAL     | 2.6–4.3 |
| This study—BA      | 2.5–4.3 |

enrichment values below 20 % in $^{235}U$ found in all analyses. The identification of $^{236}U$ isotope is evidence that the facility manipulates reprocessed uranium.

The Table 5 presents the uncertainties values of the measurements and compares them with others studies. The uncertainties reported by Godoy et al. [11] were achieved by the analysis of simulated SS from an inter-laboratory exercise program and Szeles et al. [14] utilized real-life SS, as well as this work.

## Conclusions

Nowadays, the safeguards system plays an important role in the nuclear security regime. Thus, many environmental samples are collected, requiring great efforts from the safeguards laboratories in developing new methodologies for their analysis.

The traditional BA of SS is a very time consuming method, involving total digestion. Besides, it carries a large amount of unnecessary contaminants, requiring laborious chemical separation procedures for the elements of interest.

The proposed method is simple, fast and efficient. The reduced time, $\sim 15$ min, necessary to extract uranium in SS is a great aid mainly in a large number of samples. The method provides a considerable decrease of the preparation steps, thereby reducing the risk of contamination.

As it was demonstrated, both methods provided similar results, and the data evaluation show that the findings were in good agreement with other studies. Therefore, it can be stated that the UAL method is capable of detecting changes in uranium isotopic ratio, with a high measurement quality, and might be considered an important strategy for the identification of nuclear activities.

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