Feasibility of Using Graphite Powder to Enhance Uranium Ion Intensity in Thermal Ionization Mass Spectrometry (TIMS)

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Abstract: This study explored the feasibility of using a carburization technique to enhance the ion intensity of isotopic analysis of ultra-trace levels of uranium using thermal ionization mass spectrometry (TIMS). Prior to fixing uranium samples on TIMS filaments, graphite powder suspended in nitric acid was deposited on rhenium filaments. We observed an enhancement of $^{238}\text{U}^+$ intensity by a factor of two when carburization was used, and were able to roughly optimize the amount of graphite powder necessary for carburization. The positive shift in heating current when evaporating filaments upon carburization implies that uranium was chemically altered by carburization, when compared to normal fixation processes. The good agreement between our method and known standards down to an ultra-trace level shows that the proposed technique can be applied to isotopic uranium analysis down to abundances of $\sim$10 pg.

Keywords: carburization, thermal ionization mass spectrometry (TIMS), uranium, nuclear safeguards

Introduction

The determination of isotope ratios in uranium (U) with high accuracy and precision is important in order to monitor activities in nuclear facilities towards nuclear safeguards, as well as to track the history and origins of nuclear materials.\textsuperscript{1-2} Inductively coupled plasma mass spectrometry (ICP-MS), secondary ion mass spectrometry (SIMS), and thermal ionization mass spectrometry (TIMS) are widely used for isotopic measurements for these purposes, although their typical applications differ.

ICP-MS is typically used for bulk analysis to determine the amount and isotope ratios of nuclear materials (such as uranium and plutonium (Pu)) in environmental samples.\textsuperscript{3} The main advantages of ICP-MS are its ease, the promptness with which samples can be introduced, and its high performance according to the metrics of sensitivity, accuracy, precision, and repeatability.\textsuperscript{4} Despite these advantages, the technique has low abundance sensitivity, a high mass bias, and vulnerability to matrix effects and isobaric interferences.\textsuperscript{3-4} SIMS is used to measure the isotope ratios of U and/or Pu within individual particles from environmental samples.\textsuperscript{5-6} SIMS is especially good for high spatial selectivity, which enables us to focus the analysis on a specific location with microscopic spatial resolution. However, isobaric interferences - mainly from hydrides and oxides - and a relatively low sensitivity when compared to ICP-MS are the main demerits of SIMS. A recently developed SIMS method, which uses a large-geometry equipped with a multi-collector system, has improved its sensitivity, accuracy, and precision.\textsuperscript{7}

Among the aforementioned types of mass spectrometry, the TIMS method gives the most accurate and precise isotopic measurement of U and Pu down to ultra-trace concentrations. This method also offers negligible mass biases, matrix effects, and isobaric interferences, which enables the determination of near-absolute isotopic ratio values.\textsuperscript{8-9} TIMS combined with fission track (FT) technique for particle screening is the most powerful analytical method for particle analysis, and has been adopted by many laboratories within the Network of Analytical Laboratories of the International Atomic Energy Agency (NWAL).\textsuperscript{10-11}

Despite its accuracy, the TIMS method has a much lower
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sensitivity than ICP-MS. For example, the ionization efficiency of TIMS (which is closely related to sensitivity), was determined to be ~0.1% for uranium. This efficiency is typically greater than 90% for ICP-MS. Thus, the analytical performance of TIMS is mainly dependent on ionization efficiency when analyzing ultra-trace concentrations, as is the case in analysis for nuclear safeguards and forensics.

The TIMS ionization efficiency is theoretically described by the Langmuir-Saha equation. According to this equation, the simplest way to enhance ionization efficiency is to increase ionization temperature. However, temperatures that exceed 2500 K result in the melting of filaments and breakage. Another possible method is to manipulate the electron work function of the filament materials. For example, a metal-carbon solid solution formed by dissolving carbon into rhenium was reported to enhance the electron work function, resulting in enhanced ionization efficiency.

Changing the chemical form of analytes can also improve ionization efficiency. Recently, Kraiem et al. suggested mechanisms by which uranium is ionized in TIMS when in the presence of carbon using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and modified Knudsen cell mass spectrometry (KCMS). Graphite, collodion, and carbon-containing gases (for example, benzene), have all been used as a carbon source in this method. They revealed that such carbon sources transform uranyl nitrate into uranium carbide species, which are first evaporated upon heating (mainly as U and UC2), and ionized as U+ with high efficiency.

This study investigated the feasibility of using carburization for uranium samples, using a suspension of graphite powder to enhance ion intensity within TIMS analysis. An ultra-trace level of uranium was used to investigate the effect of graphite carburization. This includes behaviour upon evaporation, the ionization of uranium during measurement, and the dependence of such phenomena on the amount of graphite coating used. A preliminary verification of the proposed carburization technique for the isotopic analysis of uranium within an environmental sample was performed using a certified reference material for TIMS measurement. Our analysis is the first step towards further experimental studies outlining the additional benefits and drawbacks of carburization using graphite powder.

Experimental

To avoid sample contamination, all analytical processes were performed in a clean facility controlled to ISO 5 and ISO 6 levels.

Within this method, the analyte consisted of a nitric acid solution containing a uranium certified reference material (U030, National Bureau of Standards, USA). After this, approximately 10 pg of uranium from the U030 solution was transferred onto a background minimized, zone-refined rhenium filament (ZRF), and dried using a 0.6 A current.

Three suspensions of graphite powder were prepared: 0.0014 g (G1), 0.0029 g (G2), and 0.0051 g (G3) of graphite powder were mixed with 0.5 mL of 2 M nitric acid. The suspensions were vigorously mixed prior to transfer to ensure macroscopic homogeneity.

Suspensions (~2 µL) were added to filaments where the uranium solution was also loaded, and allowed to dry. A current of 1.8A was then applied for 30 seconds to fix the uranium and graphite on the filament. Carburized ionization filaments were prepared by loading the same volume of G2 suspension on blank ZRF’s, followed by fixation. A double-filament system, which pairs a sample loaded filament and an ionization filament (IF), was adopted to measure isotopes using TIMS. Thus, the filament combinations were: 1) sample and normal IF, 2) sample and carburized IF, and 3) carburized sample and normal IF.

A thermal ionization mass spectrometer (TRITON Plus, Thermo Fisher Scientific, Bremen, Germany) was used to monitor 238U intensity under continuous heating. The maximum intensity (in mV) within each measurement was recorded to compare between carburization conditions. Due to the lack of reproducibility in TIMS ion intensity, multiple measurements of the same samples were performed. Additionally, to remove any bias introduced by measurement time, measurements for each filament combination were performed alternatively.

The isotopic ratios of (n(234)U)/n(238)U, (n(235)U)/n(238)U, and (n(236)U)/n(238)U were measured simultaneously using an advanced multi-ion counter (MIC) system equipped with a spectrometer. The continuous heating method was also applied during this measurement; the heating current was increased at 200 mA/min, which was lower than for 238U monitoring (400 mA/min), to minimize data skew.

Results and Discussion

Surface morphology of carburized filament

Figure 1 shows scanning electron microscopy (SEM) images detailing the surface of a sample-loaded rhenium filament before and after carburization (using the G2 solution). These images show that the graphite powder had an average size of ~10 µm, and was not monodispersed. The graphite powder completely covers the surface; however, we could not determine the powder coating thickness. We did not observe differences between filament surfaces carburized either by G1 or G3.

As shown in Figure 1(c), only carbon and rhenium elements were observed by energy dispersive X-ray spectroscopy (EDS) equipped with SEM. Any change in chemical form of the loaded uranium was not identified in
either SEM images or EDS, but such changes were possible.

**Carburization of ionization filaments**

The maximum $^{238}\text{U}^+$ ion intensity produced by TIMS measurements of filament combinations 1 and 2 were compared to investigate the effect of carburization. Mean intensities (calculated from triplicate measurements) were 3.5 mV (combination 1) and 4.2 mV (combination 2). Considering their standard deviation (SD), which were 0.3 mV and 0.7 mV, clear effect of carburization of ionization filaments (Combination 2) were not observed. This implies that the electron work function did not change, where a solid solution of rhenium-carbon was not formed upon carburization of rhenium filaments within the graphite powder suspension.

**Amount of graphite deposited**

The effect of sample carburization at different levels of graphite deposition was also investigated. We investigated this by measuring the averaged maximum ion intensities of $^{238}\text{U}^+$ produced by TIMS measurements for three U030 sample replicates carburized by G1, G2, and G3. The maximum intensities were 6.0 mV (G1), 6.7 mV (G2), and 4.3 mV (G3). Although the effect of carburization was not obvious, carburization by G2 enhanced the ion intensity of $^{238}\text{U}^+$ the most. However, only little increase in the intensity was observed in the carburization by G3, where over-carburization (through the use of surplus graphite powder) can interrupt efficient evaporation or ionization of uranium.

**Enhancement of $^{238}\text{U}^+$ intensity by carburization**

Figure 2 shows $^{238}\text{U}^+$ signal profiles (with and without carburization using G2) during TIMS measurements of U030 samples (~10 pg) as a function of the heating current applied to the evaporation filament (EF). The ion signal first appeared at a threshold current, increasing until it peaked, and then decreased as current increased.

The ion intensity was enhanced by factor of ~2 when carburization by G2 was applied. As mentioned above, depositing graphite powder on ionization filaments has little effect on the electron work function of rhenium. Therefore, the enhancement of $^{238}\text{U}^+$ intensity seems to be derived from other mechanisms.

**Preliminary isotopic analysis of uranium**

We determined the uranium isotopic ratios for two U030 samples (~10 pg) carburized by G2, with the results summarized in Table 1. We also noted that the graphite powder used in carburization was likely to contain impurities (including uranium) that could affect the resultant isotopic ratios. However, the good agreement between isotopic ratios determined through our method...
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Table 1. Uranium isotopic ratios in U030 samples carburized using G2

<table>
<thead>
<tr>
<th>Isotopic Ratio</th>
<th>Certified Value</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n(^{234}U)/n(^{238}U)$ ($\times 10^4$)</td>
<td>1.961 $[\pm 0.010]$</td>
<td>1.99 $[\pm 0.13]$</td>
<td>1.94 $[\pm 0.19]$</td>
</tr>
<tr>
<td>$n(^{235}U)/n(^{238}U)$ ($\times 10^7$)</td>
<td>3.1430 $[\pm 0.0030]$</td>
<td>3.152 $[\pm 0.017]$</td>
<td>3.154 $[\pm 0.028]$</td>
</tr>
<tr>
<td>$n(^{238}U)/n(^{232}U)$ ($\times 10^4$)</td>
<td>2.105 $[\pm 0.010]$</td>
<td>2.16 $[\pm 0.16]$</td>
<td>2.18 $[\pm 0.17]$</td>
</tr>
</tbody>
</table>

*Numbers in parentheses indicate expanded uncertainty, $U_e = k u_c$, where $u_c$ is the combined uncertainty for $k = 2$ at a ~95% confidence level.

with the certified values (shown in Table 1), implied that such impurities are negligible for determining isotopic ratios down to ~10 pg.

Opportunities for future study

Further analytical data must be accumulated to undertake more intensive statistical analysis regarding the enhancement of uranium ion intensity by carburization. Although the contribution of uranium impurities in graphite powder was confirmed to be negligible in this study, isotopic analysis of uranium samples with less than ~10 pg of uranium must be performed to determine whether such impurities are problematic at lower abundances. In addition, further spectroscopic investigation (such as X-ray photoelectron spectroscopy), is required to identify the chemical forms of uranium transformed by carburization.

Conclusions

We present a feasibility study on the carburization of uranium samples to enhance TIMS sensitivity. Graphite powder in a suspension form was deposited onto rhenium filaments at a high temperature. The uranium ion ($^{238}U$) intensity of TIMS was monitored to investigate the effect of carburization using graphite powder, as well as the evaporation behaviour and ionization of uranium under carburized conditions, and the dependence of such behaviour on graphite deposition concentrations. Preliminary isotopic analysis of uranium at ultra-trace concentrations agreed with certified values, demonstrating the feasibility of our proposed technique. Further experimental study is required to investigate carburization using graphite powder.

Acknowledgments

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References