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A high efficiency cavity ion source using TIMS for nuclear forensic analysis

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Abstract

Using a high efficiency cavity interfaced to a ThermoFinnigan 'Triton' multi-collector TIMS, a total efficiency (atoms loaded to ions detected) of up to 10% for plutonium, strontium, and neodymium loaded on resin beads introduced into a rhenium cavity are feasible. A quantification limit well below 100 attograms of plutonium (10^4 atoms $^{239-242+244}$Pu) can be reported. Furthermore, the achieved accuracy and precision are suitable to gain crucial geolocation information at sub-nanogram concentration for elements like strontium. The use of a high efficiency cavity in combination with a multi-collector TIMS appears to be a promising analytical tool to gain crucial (nuclear) forensic information.

Keywords: High efficiency cavity; Thermal ionization mass spectrometry; Nuclear forensic; Nuclear safeguard

1. Introduction

The analysis of the isotopic compositions of various elements can reveal substantial information about the intended purpose, the origin, age, and chemical processing and manufacturing of a nuclear, radiological or conventional material. For example, actinides, in particular plutonium and uranium isotopes, provide information about the source of the material and its nuclear fuel cycle history [1,2], whereas elements like strontium, neodymium, oxygen or other stable isotopes encode details about the geographical origin and provenance [3–6]. Also referred to as an 'isotope fingerprint', it has emerged as a powerful tool to gain crucial (nuclear) forensic intelligence and can be applied to various fields like nuclear safeguards, investigation of nuclear accidents or illicit trafficking of nuclear materials, non-proliferation control, bioassay, and low-level environmental monitoring, criminalistics, food authentication or wildlife forensic [1–7].

Mass spectrometric methods are predominantly used for low-level isotope ratio measurements. Inductively coupled plasma mass spectrometry (ICP-MS), multi-collector ICP-MS, thermal ionization mass spectrometry (TIMS), and secondary ion mass spectrometry (SIMS) are routinely used for bulk or particle analysis, e.g. for plutonium, with detection limits at the picogram to femtogram level [8–10]. Resonance ionization mass spectrometry (RIMS) demonstrates detection limits on sub-femtogram levels for isotope resolved analysis of plutonium [11,12], but no RIMS system is yet commercially available. Accelerator mass spectrometry (AMS) has a detection limit of attograms of plutonium [13], with extremely high isotopic selectivity, but the experimental equipment is rather complicated and costly, and sample utilization is generally inefficient.

The efficiency and thus detection limit of a TIMS system can be enhanced by replacing the conventional flat ribbon filament with a high efficiency cavity (HEC) ion source [14]. Previous studies for uranium and plutonium at Oak Ridge National Laboratory and the IAEA's Safeguard Analytical Laboratory, Austria, showed promise for high efficiency when utilizing this ion source coupled to a single-collector TIMS [15]. With higher operating temperatures, larger ratio of surface area to volume, and confined geometry, higher ionization efficiencies are potentially feasible. We present here results using a HEC coupled to a state-of-the-art

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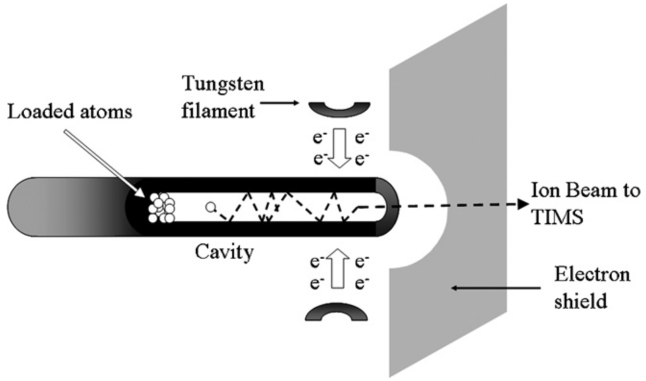

Fig. 1. The high efficiency cavity ion source system is shown (not to scale) with the three parts: cavity (Re, W, or Ta), heating filaments (tungsten), and electron shield. The sample is loaded at the base of the cavity, the cavity heated via electron bombardment from the tungsten filaments, and consequentially evaporated, ionized and transferred to the mass spectrometer.

multi-collector TIMS system for low-level analysis of isotope fingerprints of Pu, Sr, and Nd.

2. Experimental

In this study, a high efficiency cavity interfaced to a ThermoFinnigan 'Triton' multi-collector TIMS additionally equipped with seven multi-ion counters (MIC) was used. The HEC system consists of three parts (Fig. 1): the cavity, two heating filaments (tungsten), and an electron shield [15]. For a cavity, a Re, W or Ta rod with a narrow cavity (approx. 1 mm diameter × 10 mm depth) bored into the end is used. A total of up to 21 cavities can be loaded into the TIMS on one sample wheel. The analyte (Pu, Sr, or Nd) was loaded on resin beads (anion Bio-Rad AG 1 for Pu, cation Bio-Rad AG 50 for Sr, and cation Dowex 1 × 8 for Nd) and the sample is loaded at the base of the cavity and covered with a sub-millimeter thin layer of carbon (AquaDAG, i.e., dissolved inorganic carbon in ethanol). The certified reference materials NBL 126 and 137 were used for the Pu measurements, NBS 987 for Sr and a conventional certified AAS standard for Nd. The resin bead acts as a 'point' source, improving the focus and thus additionally enhancing the efficiency. A voltage of −1500 V is applied between the cavity and the electron shield (approximately 2–3 mm distance between tip of cavity and electron shield), thus ensuring that electrons are focused towards the cavity and the positive ions towards the electron shield, and further transmitted into the mass spectrometer by the source lens and the nominal 'Triton' accelerator voltage of 10 kV. The cavity is heated via electron bombardment, emitted from the tungsten filaments by applying a current of up to 4 A. The sample inside the cavity consequentially evaporates and further ionizes. The actual contribution to the formation of the ions by thermal ionization (enhanced by multiple wall collisions inside the cavity), electron bombardment, and field ionization is yet unknown. Shielded tungsten filaments are used to protect the insulators of the filaments from the heated cavity (>2000 °C) and preventing the early failure of the heating filaments. The HEC source is completely interchangeable with the normal filament source (switched within a few minutes). Additional shielding of the 10 kV insulators inside the ion source region was installed to protect the high voltage insulators from Re, Ta or W spray emitted from the cavity during operation at high temperatures.

3. Results and discussion

The total efficiency (atoms loaded to ions detected) was determined for plutonium using (a) cavities with liquid load (which allows for relatively straightforward sample loading and handling), (b) resin beads loaded [15] into a cavity and (c) resin beads loaded into a small sub-centimeter cone-shaped depression (called dimple) on a single flat ribbon filament. All are compared to normal single flat ribbon filaments (Fig. 2(a)). The median total efficiency for Pu is ≈ 0.05% for normal Re filament load, ≈ 0.15% for Re cavity with liquid load (without AquaDAG), and ≈ 0.75% for resin bead load on dimpled Re filaments. Isotope ratio measurements were performed down to sub-femtogram levels using Re cavities or resin bead load on dimpled Re ribbon filaments (Fig. 2(b)). The isotope ratio ^{241}Pu/^{239}Pu was used to perform an 'age-dating' of the NBL 126 and 137 using the decay of ^{241}Pu ($T_{1/2} = 14.35$ years). At ^{241}Pu = 0.03, 4.4, and 13.5 fg per sample (Fig. 2 (b)), an age of (1.2 ± 5.1), (1.9 ± 1.6), and (1.7 ± 0.7) years was found, respectively, compared to the reference age of 1.8 years. All Pu measurements were performed with a single discrete dynode secondary electron multiplier (SEM) and isotope ratios were acquired by peak jumping. The relative standard deviation (RSD) using the SEM and peak jumping is limited due to the counting statistics for low amounts, and is usually not better than 0.1% for Pu. A detection limit of $(0.1-1)$ fg of plutonium $= (10^5-10^6)$ atoms ($^{239-242+244}$Pu) using Re cavity with liquid load and well below 100 attogram (10^4 atoms $^{239-242+244}$Pu) for resin bead load on dimpled Re ribbon filaments can be reported. No bias in the isotope ratio measurements was observed (within precision). Combining both approaches, Re cavity and resin bead load, an even higher average efficiency

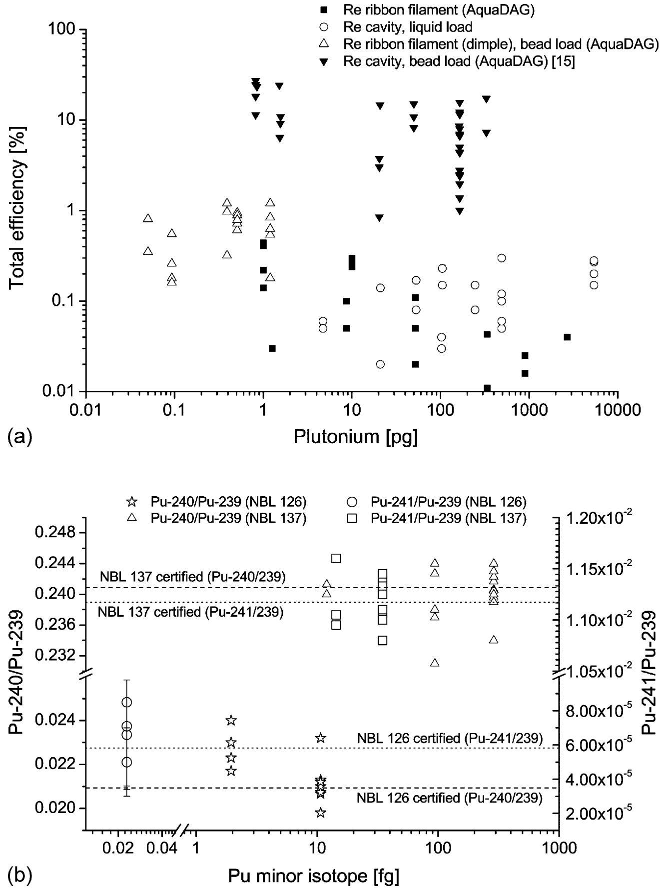

Fig. 2. (a) Total efficiency (atoms loaded to ions detected) for plutonium using different loading techniques (details see text), and (b) isotope ratio measurements using Re cavities or resin bead load on Re flat ribbon filaments with dimple.

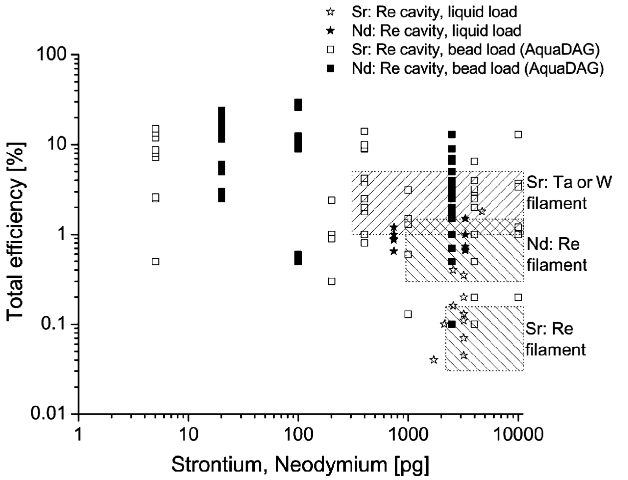

Fig. 3. Total efficiency (atoms loaded to ions detected) for Sr and Nd using different loading techniques (details see text). The shaded areas indicate efficiency values obtained using normal flat ribbon filaments.

can be expected for Pu using the ‘Triton’ multi-collector TIMS, as shown by Riciputi et al. [15] using an earlier generation single-collector TIMS. Besides the multi-collector faraday cups, our ‘Triton’ TIMS is additionally equipped with 7 multi-ion counters (MIC), potentially allowing the simultaneous analysis of multiple isotopes (no losses due to duty cycle) at ultra-low levels to improve counting statistics and precision, compared to peak jumping with a single SEM. This will result in a further improvement of the detection limit for plutonium. The HEC system can potentially be applied to uranium, too, as demonstrated by Riciputi et al. [15]. High purity Re cavity materials (e.g. zone refined Re) will be tested in future work to reduce the uranium blank originating from the Re material.

To further investigate the HEC-TIMS system, isotope ratio measurements using the ‘Triton’ multi-collector solid graphite faraday-cup detectors (low noise $10^{11}\,\Omega$ resistor) were performed on Sr and Nd samples loaded using both liquid and resin bead methods. A total efficiency of about 0.2% for Sr and about 1% for Nd was achieved using liquid loads with Re cavities comparable to flat ribbon Re filament liquid load with $\leq 0.1\%$ and $\leq 1\%$, respectively (Fig. 3). Variable but much higher efficiencies $(1-20\%)$ were achieved when the samples were loaded onto resin beads in a Re cavities (Fig. 3), significantly improving the sensitivity for isotope ratio analysis of Sr and Nd. The precision (RSD 0.01% or better) and accuracy for a resin bead load using a Re cavity and a slow heating profile is suitable to resolve crucial geographic signatures at ≤ 1 ng.

The cause of the dramatic difference in efficiencies using resin bead and liquid loading with Re cavities for Pu, Sr, and Nd is not currently understood. No AquaDAG was used for the liquid load experiments, which can change the work function and significantly suppress the formation of oxides, resulting in different ionization efficiencies. Further studies with different cavity materials (Re, W, Ta), cavity sizes, analyte elements, addition of Re powder, and loading techniques will be performed to enhance the efficiency and performance of the HEC-MC-TIMS system.

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