



Anion-exchange polymer filament coating for ultra-trace isotopic analysis of plutonium by thermal ionization mass spectrometry

Joseph M. Mannion^{a,*}, Charles R. Shick Jr^b, Glenn A. Fugate^{b,1}, Brian A. Powell^c,
Scott M. Husson^a

^a Department of Chemical and Biomolecular Engineering, Clemson University, 127 Earle Hall, Clemson, SC 29634, USA

^b Savannah River National Laboratory, National Security Directorate, Aiken, SC 29808, USA

^c Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA

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ABSTRACT

A new sample loading procedure was developed for isotope measurements of ultra-trace amounts of Pu with thermal ionization mass spectrometry (TIMS) that is based on a polymer thin film architecture. The goals were to simplify single filament TIMS sample preparation for Pu, while preserving the sensitivity and accuracy of the resin bead loading method, and to eliminate sample losses experienced with the bead loading method. Rhenium filaments were degassed, dip-coated with a thin (~120 nm) hydrophobic base layer of poly(vinylbenzyl chloride) (PVBC), and spotted with an aqueous solution comprising triethylamine-quaternized PVBC and diazabicyclo[2.2.2]octane crosslinker. This procedure formed a toroidal, hydrophilic anion-exchange polymer spot surrounded by the hydrophobic base polymer. The thin film-coated filaments were direct loaded with 10 pg of New Brunswick Laboratory certified reference material (NBL CRM) 128 from a 9 M HCl matrix. Aqueous sample droplets adhered to the anion-exchange polymer spot, facilitating sample loading. Toroidal spots with a thickness of 20–30 μm generated the highest sample utilization, surpassing the sample utilization of the standard bead loading method by 175%. Measured isotopic ratios were in good agreement with the certified value of the ²³⁹Pu/²⁴²Pu ratio for NBL CRM 128. The use of dimpled filaments further aided sample loading by providing a well-shaped substrate to deposit the sample droplet. No sample losses were experienced with the thin film loading method over 65 sample analyses. Finally, polymer coatings suppressed filament aging under atmospheric conditions, enabling the bulk production of filaments with adequate shelf life for future analyses.

1. Introduction

Thermal ionization mass spectrometry (TIMS) with isotope dilution is recognized internationally as the gold standard for obtaining isotopic ratios and mass amounts of Pu [1]. Isotopic analysis of ultra-trace quantities of Pu is possible by TIMS [2,3], a technique that remains important in the fields of nuclear safeguards [4], nuclear forensics [5], and environmental monitoring [6]. While expensive and time consuming, TIMS is used for analyses requiring high levels of sensitivity and accuracy [7]. Sample loading techniques have a large influence on Pu detection limits by TIMS (direct loading ≈ 10¹¹ atoms; electroplating ≈ 10¹⁰ atoms; resin bead loading on Re filament ≈ 10⁷ atoms; resin bead loading in Re cavity ≈ 10⁴) [8,9] and, in some cases, contribute significantly to the time investment associated with these analyses [10].

Carbon-based filament additives have been used in sample preparation schemes for the thermal ionization of actinides since at least the 1960s, when carbon addition was identified as a means to suppress sample oxidation in early vacuum systems [11]. Decades of research has resulted in a variety of carbon incorporation methods, and carbonaceous additives are understood (or believed) to provide at least three additional benefits to sample utilization (defined as the quotient of sample atoms detected and sample atoms loaded):

- 1) Carbonaceous additives promote the formation of Pu-carbides [12]. The conversion of Pu to the carbide form is believed to stabilize the sample against thermal ionization, resulting in ionization at elevated temperatures [13]. As described by the Saha-Langmuir equation (Eq. (1)) [14], when the difference between the work function of a surface and the ionization energy of the deposited

* Correspondence to: Savannah River National Laboratory, National Security Directorate, Building 703-43A Room 18-7, Aiken, SC 29808, USA.

E-mail address: joseph.mannion@srs.gov (J.M. Mannion).

¹ Present Address: Oak Ridge National Laboratory, Nuclear Security & Isotope Technology Division, Oak Ridge, TN 37831, USA.

sample is negative (rhenium work function ≈ 4.7 eV [15]; Pu first ionization energy = 6.06 eV [16]), thermal ionization efficiency is positively related to the temperature of ionization. Therefore, ion production occurring at elevated temperatures vis-à-vis Pu carbide formation results in increased ionization efficiency.

$$\frac{n_+}{n_0} = \frac{g_+}{g_0} e^{\frac{W-I}{kT}} \quad (1)$$

n_+/n_0 is ionization efficiency, g_+/g_0 is the ratio of statistical weights of the ionic and atomic states, W is the work function of the ionization surface, I is the ionization energy of the sample, T is the temperature of ionization, and k is the Boltzmann constant.

- 2) “Carburization” or “carbonation” of rhenium filaments provides a more favorable surface for sample ionization to occur [17]. In thermal ionization processes, the work function of an ionization surface is related to ionization efficiency exponentially (Eq. (1)). Therefore, high work function materials are desired in the construction of TIMS ionization filaments (for the production of positive ions). Rhenium is a preferred filament material for TIMS analyses of Pu, in part due to its high work function [18], which can be increased further through carbon dissolution at high temperatures (> 1500 °C) [19]. Modern carburization processes often involve exposing rhenium filaments to volatile organic compounds under vacuum while resistively heating the filaments [17,20]. This process is estimated to increase the average work function of polycrystalline rhenium by ~ 0.4 eV [21]. Localized filament carburization also may occur with methods such as “bead loading”, where small (40–300 μm) polymer beads are affixed directly upon rhenium ionization filaments [22]. Other carbonaceous additives, such as collodion, aquadag, and graphite, which are applied directly to the filament before analysis, have been tested for use in Pu analysis by TIMS [17] and contribute to filament carburization when heated [23].
- 3) Extractive polymeric materials, such as anion-exchange resin beads, are capable of concentrating the sample into a geometrically small region on the ionization surface, producing a narrower ion beam [22]. This aids in ion-beam focusing, resulting in increased ion transmission into the mass spectrometer [7]. Bead loading, involving concentration of Pu on resin beads [24], has shown improved sample utilization compared to more dispersed means of sample loading, such as electrodeposition and simple direct loading [8]. Anion-exchange resins often are used in the cases of Pu sample loading, as Pu readily forms an anionic complex in concentrated nitric [25] and hydrochloric acid [26].

Ion source geometries other than flat ribbon filaments have been studied in efforts to increase ionization efficiency and focus ions emitted from the ion source. Modified filament designs have aimed to increase contact, or the number of interactions, between the sample atoms and the ionization surface. In TIMS analysis of Pu, the majority of the loaded sample is emitted from the filament as neutral gas atoms (ionization efficiency: direct loading ≈ 0.01 – 0.1% ; resin bead loading ≈ 0.1 – 1.0%) [9]. By loading the sample in a concave ionization source, neutral gas atoms emitted from the initial point of loading have opportunities to interact with the ionization surface multiple times. In one design, the cavity source, high ionization efficiencies ($\sim 10\%$) relative to other methods were achieved by loading the Pu sample into the back of a capped rhenium tube heated by an electron gun [27]. It is theorized that neutral gas atoms produced at the closed end of the tube will scatter along the inside of the tube, thus having multiple opportunities to collide with the tube surface and become ionized. Porous ion emitter designs have emulated this concept by creating micro-porous rhenium structures on electrically heated filaments [7]. Other ion source geometries include the “boat” or V-shaped filament, where rhenium ribbon is crimped into a trough shape. V-shaped filaments have been shown to increase ion focusing [28] and aid in sample

loading [17].

Aggarwal et al. recently reported a membrane-based method of sample loading utilizing phosphate-bearing extractant polymers [29]. Two methods of membrane loading are reported by Aggarwal et al.: 1) membrane sections were submerged in sample bearing solution before washing and being placed onto filaments; and 2) membrane sections were loaded in solution, washed, then held in contact with the filament by hand while slowly heating the filament, melting and depositing the sample bearing polymer onto the filament. Although novel, these loading methods result in a more dispersed ion production region than in the case of bead loading. Additionally, membrane sections must be manipulated by hand after exposure to radioisotopes, a challenge shared with the bead loading method.

The goals for this work were to simplify sample loading for TIMS analysis of Pu while retaining the sensitivity afforded by the established bead loading method, and to eliminate sample losses often experienced with the bead loading method (up to 25% in some cases [7]). The objective was to develop a Pu extractive filament pre-coating that retains the ion focusing afforded by the resin bead method while also making direct loading by pipette possible, thereby eliminating the need to handle and position radioisotope-bearing anion-exchange material. This objective was attained using a bi-layer coating design composed of a nanothin hydrophobic underlayer with a toroidal, quaternary amine-bearing polymer microspot deposited on top. The coating methods were designed to enable the bulk production of analysis-ready filaments with a long shelf life. Standard and dimpled filaments were evaluated, as it was hypothesized that sample deposition into the concave well of the dimpled rhenium filament would promote ion formation and aid in direct loading by pipette.

2. Experimental section

2.1. Chemicals and materials

The following materials were used as received from Sigma-Aldrich: chloroform (Reagent Plus[®] $\geq 99.8\%$ with 0.5–1.0% ethanol as stabilizer, CAS# 67-66-3); 1,4-diazabicyclo[2.2.2]octane (DABCO) (Reagent Plus[®] $\geq 99\%$, CAS# 280-57-9); hydrogen peroxide solution containing inhibitor (30 wt% in water, CAS# 7722-84-1); poly(vinylbenzyl chloride) (PVBC), (60/40 mixture of 3- and 4- isomers CAS# 121961-20-4); and sulfuric acid (95–98%, ACS reagent grade, CAS# 7664-93-9).

Hydrochloric acid (Optima[™] grade for ultra-trace elemental analysis, CAS# 7647-01-0, 7732-18-5), methanol (Optima[™] LC/MS grade, CAS# 67-56-1), nitric acid (Optima[™] grade for ultra-trace elemental analysis, CAS# 7697-37-2, 7732-18-5) and triethylamine (TEA, 99%, reagent grade, CAS# 121-44-8) were used as received from Fisher Scientific.

Silicon substrates were acquired from Nova Electronic Materials as 4” N/Ph $< 100 > 1$ – $10 \Omega\text{-cm}$ 500–550 μm thick SSP prime grade Si wafers diced to 1 cm \times 3 cm pieces. Anion-exchange resin beads were obtained from Bio-Rad (AG[®] 1-X2 Anion-exchange Resin, analytical grade, 50–100 mesh, chloride form). Collodion solution (flexible, CAS# for solution constituents: 60-29-7, 9004-70-0, 8001-79-4, 76-22-2, 64-17-5) was acquired from J.T. Baker. Rhenium ribbons (0.76 mm W \times 0.03 mm H) and wafers (1 cm \times 3 cm \times 0.1 cm) were made of zone-refined rhenium (minimum of 4-pass zone refined; 99.999% Re) from H. Cross Company.

Pu solutions for TIMS measurements were prepared from a dilution of a primary standard containing New Brunswick Laboratory (NBL) certified reference material (CRM) 128 with a certified $^{239}\text{Pu}/^{242}\text{Pu}$ atom ratio of 0.99937 ± 0.00026 (determined October 1, 1984) at Savannah River National Laboratory (SRNL). Based on the half-lives of ^{239}Pu and ^{242}Pu , the approximated $^{239}\text{Pu}/^{242}\text{Pu}$ ratio would be 0.9985 on October 1, 2017. The decay corrected $^{239}\text{Pu}/^{242}\text{Pu}$ ratio (October 1, 2017) was used for calculating the deviation of measured ratios from

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