Isotopic fractionation studies of uranium and plutonium using porous ion emitters as thermal ionization mass spectrometry sources

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ABSTRACT

Investigations of the isotope fractionation behaviors of plutonium and uranium reference standards were conducted employing platinum and rhenium (Pt/Re) porous ion emitter (PIE) sources, a relatively new thermal ionization mass spectrometry (TIMS) ion source strategy. The suitability of commonly employed, empirically developed mass bias correction laws (*i.e.*, the Linear, Power, and Russell's laws) for correcting such isotope ratio data was also determined. Corrected plutonium isotope ratio data, regardless of mass bias correction strategy, were statistically identical to that of the certificate, however, the process of isotope fractionation behavior of plutonium using the adopted experimental conditions was determined to be best described by the Power law. The fractionation behavior of uranium, using the analytical conditions described herein, is also most suitably modeled using the Power law, though Russell's and the Linear law for mass bias correction rendered results that were identical, within uncertainty, to the certificate value.

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1. Introduction

Instrumental bias represents a significant source of error in isotope ratio mass spectrometry (IRMS); the ability to make precise and accurate isotopic ratio measurements is critical for nuclear forensic efforts. In the context of mass spectrometry, the term *bias* is used to describe a combination of effects, that occur in a mass spectrometer, leading to a difference between the measured and true isotope ratio(s) present in a sample. Such effects may occur during the formation, transmission, and detection of ions. In thermal ionization mass spectrometry (TIMS), mass fractionation occurs as the sample is heated by the metal filament. The rate at which each isotope evaporates from the hot metal filament is mass dependent; lighter isotopes are preferentially evaporated relative to heavier isotopes in the thermal ion source. This is a result of the higher translational velocities of lighter isotopes, for a given kinetic energy, and the tendency of heavier isotope to form stronger chemical bonds [1]. The consequence is a time-dependent variation in measured isotope ratios; the sample reservoir (*i.e.*, the sample remaining on the filament at a given time) tends to become relatively enriched in heavier isotopes as the analysis proceeds. Another significant factor influencing mass bias is the size of the sample. As sample size increases, competition between analyte atoms for filament surface area also increases [2,3]. This effect is magnified in traditional single filament analysis where analyte atoms are evaporated and ionized by the same filament. The result is a substantial loss of analyte as evaporated neutral atoms, biased in favor of lighter isotopes, at relatively low filament temperatures where ionization is less likely to occur. This time-dependent behavior of measured isotope ratios hinders the accurate determination of the true isotope ratio of a sample through direct measurement because the effects of mass bias cannot be totally controlled and reproduced. In TIMS, multiple filament materials and/or geometries may be employed depending on application; fractionation effects will vary on a run-to-run and method-to-method basis. Typical mass bias for single filament TIMS analyses is on the order of a few tenths of a percent per atomic mass unit (% amu^{-1}) for high mass elements (i.e., $\gtrsim$180 amu), whereas mass bias associated with multicollector-inductively coupled mass spectrometry (MC-ICP MS) can be expected to be approximately an order of magnitude larger for the same mass range [4,5]. However, correcting for instrumental mass fractionation can be accomplished by normalizing the measured ratio of interest to a known or accepted reference ratio. Measured isotope ratios are commonly corrected for fractionation by applying one of the well known mass bias correction laws that appear in the literature. These include the Linear law [6,7],

the Power law [6–8], Russell's law [6–9], and Rayleigh's distillation law [7–10]. Several studies of isotopic fractionation behavior during TIMS analysis have centered around creating models for correcting mass bias that are specific to the ion source (e.g., PIE, resin bead, thermal ion cavity) [11–14]. Andreasen and Sharma have concluded that isotope ratios corrected for mass fractionation using the Russell's law are fully satisfactory given the current level of precision obtainable in TIMS analyses [14]. As precision of isotope ratio measurements continues to improve, it may become advantageous to apply fractionation models that are source specific.

All fractionation laws assume that evaporation and ionization of a sample occurs in a single, homogeneous domain atop a filament. In reality, this assumption is not well justified as a sample loaded atop a filament is not a point source. A temperature gradient exists across the filament; mass fractionation behavior is temperature dependent. Recently introduced PIE techniques have been shown to address such issues. Watrous et al. have demonstrated that PIEs are very effective at containing a sample within the porous structure and do not permit sample migration across the filament [15]. The small footprint of the PIE serves to localize the analyte loading area at the center of the filament such that the instrument optics will behave as if each sample were a point source. Localized loading leads to a reduced ion energy spread as a function of voltage drop and temperature gradient across the filament surface leading greater ion transmission through the ion optics and enhanced abundance sensitivity when compared other techniques [15]. The PIE's ability to more accurately represent a point source suggests that they may potentially reduce the effects of mass bias associated with the thermal gradient across the filament when compared to other single filament techniques. The objective of this investigation is to evaluate the fractionation effects arising from the use of PIEs as TIMS sources in the measurement of uranium and plutonium isotopic systems. Fractionation effects were evaluated according to each of the mass bias correction strategies, the Linear, Power, and Russell's laws, introduced above and distinctions in applicability are discussed.

2. Experimental methods and equipment

2.1. Isotopic standards and reagents

Samples were prepared from New Brunswick Laboratory certified reference material (NBL CRM) 144 plutonium isotopic standard (NBL: Argonne, IL; USA) and Institute for Reference Materials and Measurements isotopic reference materials (IRMM IRM) 199 uranium isotopic reference standard (IRMM: Joint Research Centre; Geel, Belgium). Platinum (325-mesh) and rhenium (325-mesh) metal powders as well as the water soluble poly(4-styrene-sulfonic acid) polymer ion exchange solution (M_w = 75,000, 8 wt.% in H_2O) were procured from Sigma–Aldrich (St. Louis, MO). High-purity, zone-refined rhenium filament ribbons were acquired form H. Cross Co. (Moonachie, NJ; USA). Optima^{TM} grade nitric acid was purchased from Fisher Scientific (Pittsburgh, PA; USA). A typical craft variety hot melt adhesive (not well characterized) was purchased from a local hardware store.

2.2. Rhenium filament preparation

Filament assemblies were fabricated by spot welding strips of rhenium (0.76 × 0.03 mm) to standard filament support posts; prior to welding, filament posts and rhenium strips were cleaned via sonication in acetone and dried in a laboratory oven. The filament assemblies were then loaded into GV Instruments Ltd. (now Isotopx: Middlewich, Cheshire; UK) filament bake-out unit which was then sealed and evacuated to approximately ~10^{-7} mbar

(~10^{-5} Pa). Degassing was performed by incrementally heating the filaments to 4.5 A at a rate of approximately 0.25 A min^{-1}; filaments were held at 4.5 A for 15 min.

2.3. PIE stock material and filament preparation

PIE stock material was prepared by incorporating equal parts, by mass, of platinum powder, rhenium powder, and hot-melt adhesive atop a quartz glass microscope slide heated atop a laboratory hot plate to ~120°C, the melting point of the hot glue. Once thoroughly integrated, the stock mixture was loaded into a specially designed extruder, heated, and expelled as a small diameter, ~550 μm, rope onto a quartz glass plate. Details of extruder design and operation can be found in Ref. [16]. After cooling, sections approximately 100 μm in height were cut from the stock material rope, as needed, and affixed at the center of standard, high-purity zone-refined rhenium single TIMS filament assemblies via gentle heating at 1 A for approximately 5 s. The PIE stock was sintered to the filament using a GV Instruments Ltd. (now Isotopix: Middlewich) filament bake-out unit evacuated to ~10^{-7} mbar (~10^{-5}Pa). The filament temperature was slowly increased, 0.25 A min^{-1}, to 1700°C; filaments were held at this temperature for approximately 20 min. Filaments were allowed to cool overnight prior to sample loading. A detailed description of PIE filament fabrication has been presented by Watrous et al. [15].

2.3.1. Sample loading

Two drops, each approximately 1 μL, of poly(4-styrenesulfonic acid) water soluble cation exchange resin, diluted to a concentration of ~3% by mass using 18 MΩ deionized (DI) water, were added to each PIE. The ion exchange resin was dried by heating at 1 A for 15 s. The ion exchange resin was added to promote sample incorporation into the PIE structure. Samples were loaded directly onto each PIE in nitrate form using a 2.5 μL capacity pipette and dried via gentile heating at 1 A for approximately 15 s.

2.4. TIMS instrumentation

Mass spectrometric analyses were carried out using a GV Instruments Ltd. (now Isotopx: Middlewich, Cheshire; UK) IsoProbe T^{TM} multi-collector TIMS at Los Alamos National Laboratory (LANL). This mass spectrometer is equipped with a 20-position sample turret, a single-focusing magnetic sector fitted with a 54 cm magnet, nine fully adjustable Faraday cup collectors, a Daly detector ion-counting system, and a wide aperture retarding potential (WARP) filter positioned between the main collector array and rear ion counting Daly detector. Programming and performance of the mass spectrometer was controlled via the GV Instruments IonVantage software package installed on a Dell Optiplex PC (Round Rock, TX; USA). Amplifier gains cross-calibrations are conducted on a weekly basis and automated corrections are built into the software. To ensure maximum measurement precision, the instrument was warmed under electronic conditions similar to those employed during sample analysis for at least an hour. Preliminary instrument tuning was conducted each day, prior to sample analyses, using the $^{187}Re^+$ beam from a bare rhenium filament. Fine tuning of the mass spectrometer was carried out using a low intensity beam of the major isotope present in each sample immediately preceding analysis. The liquid nitrogen cold trap was filled, as needed, to improve vacuum in the ion source housing maximizing ion transmission and reducing abundance sensitivity.

2.4.1. Mass spectrometric analysis

Uranium and plutonium isotope ratio measurements were conducted using a total evaporation (TE) technique similar to the method described by Callis and Abernathey [17] and Fiedler