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Measurement of trace uranium isotopes using a porous ion emitter

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ABSTRACT

The extent to which thermal ionization mass spectrometry (TIMS) can measure trace quantities of ^{233}U and ^{236}U in the presence of a huge excess of natural uranium is evaluated. This is an important nuclear non-proliferation measurement. Four ion production methods were evaluated with three mass spectrometer combinations. The most favorable combinations are not limited by abundance sensitivity; rather, the limitations are the ability to generate a uranium ion beam of sufficient intensity to obtain the required number of counts on the minor isotopes in relationship to detector background. The most favorable situations can measure isotope ratios in the range of 1×10^{-10} if sufficient sample intensity is available. These are the triple sector mass spectrometer with porous ion emitters (PIE) and the single sector mass spectrometer with energy filtering.

1. Introduction

There are three uranium isotopes in nature that are readily detectable: ^{238}U (99.27%), ^{235}U(0.72%), and ^{234}U (0.0055%)[1]. In addition, there are ultra trace quantities of ^{236}U resulting from thermal neutron capture in the crust by ^{235}U that are beyond the limits for detection by thermal ionization mass spectrometry (TIMS) techniques but within the detection limits of an accelerator mass spectrometer (AMS) [2]. In a nuclear reactor, neutron capture produces ^{236}U from ^{235}U by a (n, gamma) reaction [3]. If ^{232}Th is present in the fuel, the (n, gamma) reaction results in ^{233}U formation. ^{233}U is also produced from the alpha decay of ^{237}Np to ^{233}Pa followed by beta decay to ^{233}U. Detection of either ^{233}U or ^{236}U provides evidence that some portion of the uranium has been in a neutron flux, even if it is diluted with natural or enriched uranium by many orders of magnitude [4–10]. Differing possibilities for ^{233}U production leads to different ^{233}U/^{236}U ratios, depending on the history of the material [4,11,12]. Hence, detection of ^{233}U and/or ^{236}U is a signature both for reprocessing and for the type of fuel cycle.

Tumey et al. at Lawrence Livermore National Laboratory have evaluated the utility of AMS for analysis of ^{233}U and ^{236}U [10]. TIMS is also capable of conducting measurements of ^{233}U and ^{236}U, although not at as wide of ratio as AMS. TIMS also lacks the AMS ability to destroy molecular interference during the analysis, a feature that requires verification that the spectrum is free of hydride and/or hydrocarbons. There are few facilities capable of conducting measurements by AMS, while there are many TIMS instruments available. Understanding the capability of TIMS instruments would better define when TIMS could be used, and when an AMS is required.

Detection of a clandestine reprocessing operation from a sample collected downwind/downstream from a suspected facility is expected to be in the presence of a huge excess of natural uranium [7,10]. This is due to trace amounts of natural uranium in the environment mixing with miniscule quantities released from the facility. Three factors determine the ability to conduct this measurement: abundance sensitivity of the mass spectrometer, sample availability, and efficiency of the mass spectrometer. (Efficiency includes ionization efficiency, transmission efficiency and background). Abundance sensitivity determines the ability to make measurements at mass 233 and 236 in the presence of natural uranium [13,14]. The high-mass tail from ^{235}U must be considered at 236 in addition to the low-mass tail from ^{238}U. In addition, when measuring mass 236, hydride generation will need to be considered as a possible contributor [5]. Spectral interferences from hydrocarbons also must be ruled out, although this is easier to monitor than hydride formation since when hydrocarbons are present they tend to be at every mass. If there is no plutonium in the sample, as expected from an environmental release that has undergone rigorous uranium separation and purification, verifying that there is not a peak at 239 indicates that neither hydride or hydrocarbons are present in the spectrum. Tailing from ^{234}U and ^{235}U could influence the baseline signal at 233, interfering with the ^{233}U measurement. Measurement of the abundance sensitivities one and two Dalton up and down from the ^{238}U isotope provides the information required to determine the baseline contributions. In addition, the ability to generate an ion beam of intensity sufficient to provide an ade-

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quate number of counts on these minor isotopes in relationship to the background counts on the detector is required. The signal to noise and signal intensity issues turn out to be the ultimate limitation for the instrumental conditions giving the highest abundance sensitivity.

2. Factors affecting abundance sensitivity

Tailing from a peak is caused by energy spread in the ion beam and by scattering of ions in the mass spectrometer, providing resolution is adequate [13,14]. Scatter occurs from ions colliding with neutral gas molecules and from instrument misalignment causing the beam to wipe the side of the vacuum housing and other components. This is mitigated by keeping the vacuum system clean and the instrument well aligned.

Keeping the vacuum system clean is also necessary in order to prevent hydrocarbon interferences and prevent hydride formation due to water vapor. Modern vacuum systems have made this much simpler than with older instruments. Both instruments used in this study do not use any oil in the pumping systems and have liquid nitrogen cold traps.

Energy spread in the ion beam is important since a magnetic sector is a momentum spectrometer and relies upon having a narrow energy spread to provide mass resolution. Current TIMS ion sources are heated with DC current. Depending upon various parameters, such as filament material and temperature, the voltage drop across a filament can range up to several volts [15]. Thus the energy of ions produced at one end of the filament can differ by more than 1 eV from those produced on the other end. This is significantly higher than the thermally induced energy that is in the range of 0.1–0.2 eV for temperatures used for uranium analyses.

The influence of energy spread was illustrated by a study in which thermal-ion imaging was conducted both from a filament and a tube [15]. The filament was heated with a DC current. The tube was heated indirectly, resulting in the ion-emitting surface being at a common voltage. Resolution of the image was a factor of 100 higher from the tube. This is projected to be a factor in the improved abundance sensitivity of the porous ion emitter (PIE) when there is no energy filtering.

The triple-filament source produces ions along the entire length and width of the center filament. This maximizes energy spread. The resin-bead and PIE ion sources have much smaller areas of ion emission that limit energy spread as discussed in the results.

3. Experimental

The extent to which TIMS can be applied to analysis of ^{233}U and ^{236}U in the presence of a large excess of natural uranium has been explored using four different ion source configurations. These methods are: a triple-filament ion source, a resin-bead single-filament ion source, and a PIE single-filament source mounted on both a rhenium and a tantalum base filament. Sample utilization efficiencies for these types of sources are 0.001%, 0.6% and 1.7% respectively [16,23]. After finding that performance was well within experimental error for the PIE's on rhenium and tantalum, the tantalum technique was dropped. These sample-loading techniques were analyzed on a single magnetic sector instrument with and without an energy filter and on a triple-sector instrument (with one electrostatic and two magnetic sectors). Peak shape was evaluated by comparing the flat top width of the signal peaks to the width at the base (width taken at 5% of peak height).

3.1. Sample preparation and analysis

All filaments were zone-refined rhenium with the exception of the few tantalum filaments. These were spot welded onto standard VG54 posts. All were degassed in vacuum at ~3 A for 30 min.

In experiments using the triple-filament configuration, the sample is loaded on one side filament and volatilized onto the hot center filament. A solution of uranium in nitric acid was added one drop at a time to a side filament using a micro pipette. Each drop was dried with a current of ~1 A applied to the filament. When all of the solution was applied and dried (1 ug of uranium total), the current was slowly raised until there was a dull red glow. The current was then held for 10 s. The loaded filament is mounted in the holder with a bare rhenium center and second side filament. Single rhenium filaments folded into a v-trough were used for the resin-bead samples. Methods for preparing resin-bead samples have been widely reported in the literature [17–22].

The PIE has been described previously [23]. Briefly, the PIE is a 50/50 mix, by mass, of rhenium and platinum powder that is sintered to itself and to the filament by heating to the melting point of platinum resulting in a rhenium and platinum metal structure that is 0.1–0.2 mm in diameter. A cationic exchanger is then added, one drop at a time, to load approximately 10 ng of exchange polymer diluted in water to 3–4% by mass. Uranium is loaded as a solution onto the PIE by wicking the solution into the porous structure avoiding contact with the base rhenium filament. This is benzene treated as described previously [24].

A VG54 (circa 1990) with an energy filter (referred to commercially as a warp filter) was used for the single-sector experiments. Analysis started when the pressure was less than 2×10^{-8} torr. Normally, the energy filter is engaged on the VG54. For runs without the energy filter, all elements were disconnected from the power supply and grounded. The triple-sector instrument is a modified VG54 as described elsewhere [25]. The first two sectors are magnets, while the third is an electrostatic sector (38 cm radius of deflection and a deflection angle of 81.5°). Prior to the analysis, the three sectors are scanned in sequence to ensure that they are appropriately calibrated. During an analysis, the two magnets are scanned in tandem, and the electrostatic sector is held constant.

Samples analyzed on single filaments were heated to 2.1 A over 5 min, followed by 0.1 A current increases until the major uranium signal reaches ~100 counts per second. The ion lens and turret position were then adjusted to maximize intensity on the collector, followed by focusing the lens a minimum of three times. The temperature was then adjusted to produce the ion intensity needed for analysis. For samples analyzed by the triple-filament method, 4 A were applied to the center filament, and 1 A to the side filament. The signal was optimized by adjustment of the turret to maximize signal intensity, followed by focusing the lens a minimum of three times. The temperature was then adjusted to produce the ion intensity needed for analysis.

Depleted uranium was used for all experiments; hence ^{238}U was approximately 300 times more intense than ^{235}U. Depleted uranium was chosen because tailing from all the uranium isotopes will be proportional to those measured for ^{238}U and the lack of other major isotopes simplified measurement interpretations. Filament alignment and focusing conditions were optimized, and the sample was scanned over a mass range of 232.5 u–237.5 u and 238.5 u–239.5 u in 0.05 u steps. Since clean baseline was measured at the 1.5 u for the more favorable configurations, this demonstrates that the 2 u position is also free from tailing from the major peak. Each mass spectrum was recorded and saved. After a scan, the current was raised to increase the signal, and the sample rescanned until the sample was exhausted. Runs were alternated between the high and low mass sides of 238. The 238 intensity was measured with an off-axis Faraday cup and care was taken to ensure that the

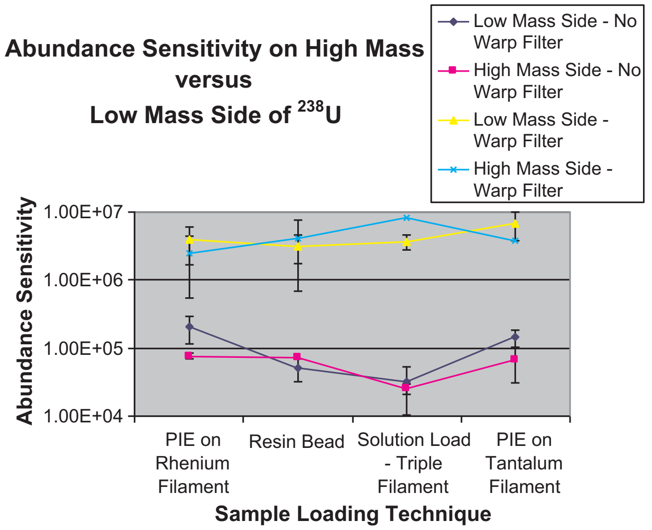

Fig. 1. High mass versus low mass abundance sensitivity on single sector instrument with and without energy filtering (1 standard deviation uncertainty shown).

238 beam was never on the ion counting system as the high intensity would have damaged the system. All other data was from ion counting by electron multiplier for the triple sector instrument and a Daly detector for the single sector VG 54.

A few analyses were conducted with PIEs mounted on tantalum filaments. Tantalum can be heated to temperatures suitable for uranium ionization but, due to a lower work function, is less efficient as an ionizer. These analyses were performed in order to answer two questions. First, is ion production exclusively from the PIE or does some or all ionization originate from the base filament? Second, if some ionization comes from the base filament, will that increase the energy spread in the ion beam that causes the beam to broaden?

4. Results and discussion

Fig. 1 compares the high and low mass-abundance sensitivities with and without the energy filter for the single-sector instrument. There is little difference between the high and low mass sides for a given set of circumstances. Instruments with poor vacuum conditions and/or poor alignment have much poorer abundance sensitivity on the low mass side than on the high mass side due to energy loss from collisions. The fact that this was not observed during these experiments demonstrates that the vacuum and alignment conditions were appropriate.

Fig. 2 displays the abundance sensitivity data at 1 u mass difference from 238 u for all samples under all conditions. There was no contribution 1.5 u away from mass 238 other than for one circumstance. This circumstance was the triple-filament ion source without the energy filter on the single-sector instrument. Since this configuration is not well suited for these measurements, the following data analysis ignores this configuration. If there is no contribution at 1.5 u there obviously will be no contribution at 2 u. Therefore, for the 1 ug of uranium loaded and signals achieved (up to 2×10^8 cps) from resin beads and PIE's abundance sensitivity does not have an effect 2 u away from mass 238. Only detector background will contribute 2 u away at a measured value of 0.1 cps.

The point that stands out for the single-sector instrument when the energy filter was engaged is that the abundance sensitivity from different sample loading techniques is nearly constant (Fig. 2). When the energy filter was not engaged, the abundance sensitivity was much lower overall and varied significantly for the ion sources. The triple-filament source without the energy filter is by far the poorest, demonstrating the effect of increased energy spread in the ion beam. Data trends for the triple-sector instrument are similar to data trends from the single-sector data without the energy filter, but with the abundance sensitivity improved by two orders of magnitude. The conclusion from comparing these results is that the second magnet and the electrostatic sector analysis (ESA) are highly effective for removing scattered ions since they are focusing sectors, but the energy filter is superior to the ESA for producing a very narrow energy spread. In order for the ESA to be as effective as an energy filter, the ESA slits would have to be reduced such that the reduction would impact both the peak shape and the ion transmission. The downside of the energy filter is that it decreases ion transmission. Since ion transmission changes with the voltage of the energy filter it is necessary to re-calibrate the Faraday-cup/pulse-counter sensitivity ratio anytime these settings are changed.

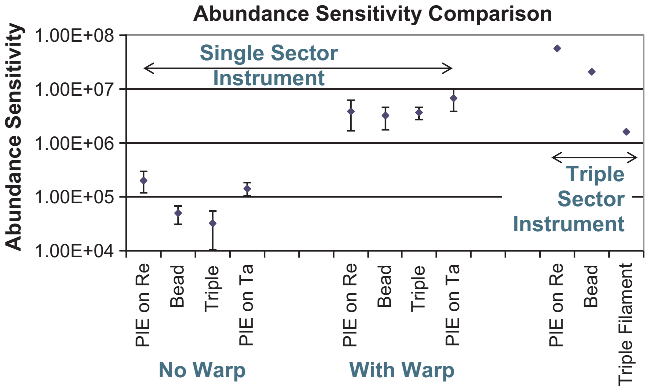

Fig. 2. Abundance sensitivity data for samples loaded on PIEs, on beads and on triple filaments analyzed on the different instrument configurations (1 standard deviation shown).

The smaller the area of ion emission, the larger the ratio of peak top width to base width should be for peak shape and comparable filament geometries and focusing, although this is not expected to be a large effect. These ratios of top to base for each source are displayed in Fig. 3 for the single sector instrument. The results do not show a big difference in the peak shape due to the sample source for the three single-filament sources. These small differences are easily ascribed to minor differences in filament positioning and focusing. The triple-filament source had a decrease in the ratio that is attributed to the larger ion emission area that results in a larger spread in the ion energy.

The possibility of hydride formation and hydrocarbon contamination was examined. These are important for the ^{236}U determination since a ^{235}U hydride and any hydrocarbon contam-

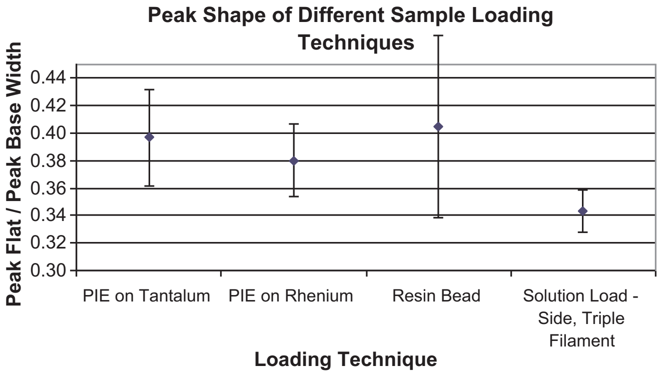

Fig. 3. Peak shape from four different sample loading techniques (1 standard deviation shown).

ination would interfere with the measurement. While there was measurable tailing at the 239 mass, no discernable peak on this tail was ever observed. Hydride formation is not a problem even for these extreme ratios, with the stipulation that vacuum conditions are maintained at a suitable level so that water vapor is kept to a minimum. Hydrocarbon contamination would be a problem for both ^{233}U and ^{236}U, but since neither instrument has ever had an oil sealed pump this was not an issue. It was important to conduct this measurement at the 239 mass since there are measurable traces of ^{236}U in commercially available depleted or enriched uranium.

The PIEs used in this study were larger than the beads, so if everything else were equal, the bead should have had a narrower energy spread than the PIE. However, the data in Fig. 2 does not support this. The first possible explanation is that the sample spreads from the initial position of the bead across the filament, while the PIE does not readily permit migration across the filament. The second possible explanation is that the PIE sits on top of the filament and is heated indirectly by heat transfer from the filament, with no current passing through the PIE itself. If this were the case, the entire PIE would be at a uniform voltage and ions produced from the PIE would not have a reduced energy spread due to uniform voltage throughout the PIE.

As the sample is brought up to temperature it is possible that uranium migrates out from the bead, across the filament, to ionize from an area larger than the bead itself. Smith used SIMS to study this subject [20] with the conclusion that ionization occurred from the bead/filament interface and that carbon readily migrated into the rhenium filament. However, these uranium analyses were conducted after the analysis, not during. Additionally, it was shown that there was uranium across the filament. This was dismissed as being only a few monolayers, but this could be evidence of uranium migration since the mean time for volatilization might be very short. Measurements conducted during the analysis are more likely to be representative of the actual phenomenon.

To investigate the possibility of uranium migration away from the PIE, two experiments were performed. The platinum–rhenium PIE was sintered onto a tantalum filament instead of a rhenium filament, and uranium was added and analyzed. If appreciable ion formation were occurring on the base filament, the ion intensity from a PIE on a tantalum filament would have been reduced in comparison to the ion intensity for a PIE on a rhenium filament. Conversely, the abundance sensitivity would have been improved from the tantalum filament since ion emission from the base filament would have been suppressed and have been exclusively from the PIE. Ion intensities observed for both base filament metals were within experimental error. The abundance sensitivity results are presented in Fig. 4 and show no difference between the tantalum and rhenium base filament. This is evidence that the ionization is from the PIE and not the base filament.

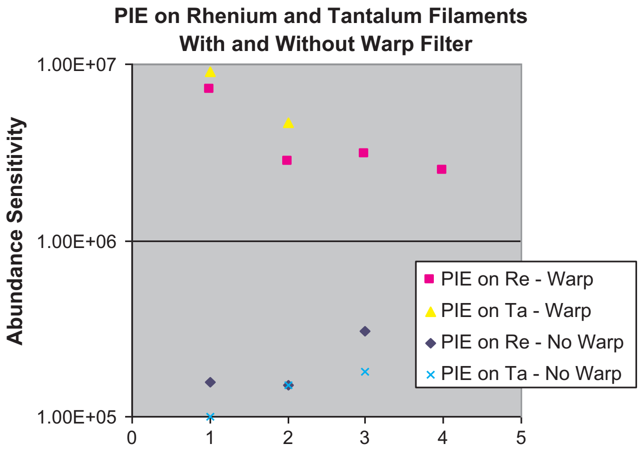

Fig. 4. Abundance sensitivity for PIEs on rhenium and tantalum filaments. The *x*-axis is filament number.

Second, a PIE containing praseodymium was imaged in a test stand equipped with a TIMS ion source and a commercially available micro-channel plate ion imaging detector. Praseodymium has a lower ionization potential than uranium, giving it higher ion-formation efficiency at a lower temperature than uranium, making it much simpler to obtain adequate brightness on the imaging screen. Also, the temperatures at which uranium ionizes would also ionize rhenium from the base filament, washing out any detail to a signal for uranium. The data from the imaging experiment is shown in Fig. 5. The imaging instrument is functionally equivalent to the one in an earlier publication [15].

Fig. 5 presents a side-by-side image of a PIE obtained on this imaging instrument and an optical image. The general shape of the PIE can be seen in the ion image, with more intense ion production in roughly a crescent shape. By adjustment of the focus of the stereo microscope to image the tallest portion of the PIE, this crescent shape became clear. The optical image viewed under the stereo microscope shows this crescent shape much more clearly than the photograph, although the photograph does give a limited view of the crescent shape. This indicates there is more ion production from the thickest part of the PIE. This evidence furthers the case that the analyte ions do not originate from outside of the original PIE structure.

All evidence points toward the conclusion that the PIE has a narrower energy spread than the bead which, in turn, has a narrower energy spread than the triple filament. One reason the PIE has this narrower energy spread is that the PIE does not allow migration away from the PIE prior to ionization while the bead does. It is also reasonable to assume that the PIE is at a

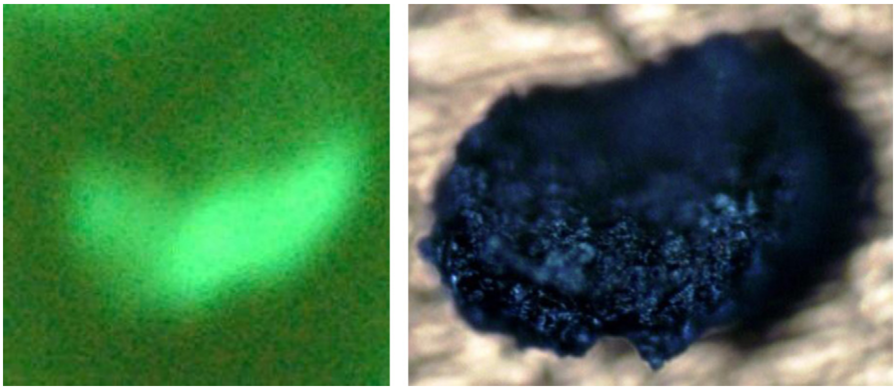

Fig. 5. Ion emission image next to optical image of PIE.

more uniform voltage than the base filament, although this is not proven.

Calculation of detectable levels of the ^{233}U and ^{236}U isotopes in the presence of a large excess of natural uranium is simplified by the fact that no tailing was observed 1.5 u away from the major peak at the ion intensity levels produced by these methods with the one exception, meaning that there also was none at 2 u. So ^{238}U will not contribute to ^{236}U levels, while ^{235}U will not contribute to ^{233}U. The level of ^{234}U in either natural or fully enriched uranium is sufficiently low that there will not be measurable tailing into the 233 mass. The limit on both the ^{233}U and the ^{236}U measurement thus comes down to the intensity level achievable to gain sufficient counts in comparison to the detector background. Thus, it is the combination of detector background versus count level that determines detection limits for ^{233}U and ^{236}U.

The abundance-sensitivity measurements 1 u from the major isotope range from a low of 5×10^4, for the triple filament on the single-sector instrument without energy filter, to 8×10^7 for the PIE on the triple-sector instrument. For the scenario with natural uranium and the best abundance sensitivity, the results again come down to ion intensity level versus detector background. Abundance sensitivity will not be a limitation for either the triple-sector or the single-sector instrument with the energy filter.

Assuming that abundance sensitivity is not an issue for these most favorable situations, the detection limits for the ^{233}U and ^{236}U isotopes will be determined by the signal-to-noise level. The background was measured at 0.1 cps for the single sector instrument. It is 0.1 cps for the triple sector instrument as well. For the purposes of this calculation, assume that a one microgram sample has been collected that produces a signal intensity of 10 pico amperes for ^{238}U for up to 5 min. This converts to 6.2×10^7 counts per second for the ^{238}U ion intensity. 1.1 counts per second would be a detectable signal over the background. This represents a signal of 1.8×10^{-19} A for each of the ^{236}U and ^{233}U isotopes, which translates to about 20 fg per isotope $[(1.8 \times 10^{-19}\ \text{A}/1 \times 10^{-11}\ \text{A}) \times 1 \times 10^{-6}\ \text{g}]$. Taking into account the abundance sensitivity of 8×10^7 for ^{235}U interfering with the 20 fg of ^{236}U would allow for the measurement at mass 236 without interference from ^{235}U for up to 1.6 μg. Using the natural abundance for uranium isotopes a calculated ^{236}U/^{238}U ratio of 1×10^{10} can be measured by TIMS using the PIE.

5. Conclusion

The ^{233}U and ^{236}U measurement for the triple-sector mass spectrometer and for the single-sector mass spectrometer with energy filtering is more likely to be limited by signal-to-noise ratios than by abundance sensitivity, unless there is a relatively large sample generating an ion beam in excess of single digit nano amperes for a prolonged period. When such a sample is analyzed, the triple-sector instrument with a PIE will produce the best data. A 1 μg sample is considered to be of the size most easily collected and, for this scenario, approximately 20 fg of each isotope can be detected.

Acknowledgements

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