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Anthony D. Appelhans
John E. Olson
Michael B. Ward
David A. Dahl

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Seven Channel Multi-collector Isotope Ratio Mass Spectrometer

Anthony D. Appelhans*, John E. Olson, Michael B. Ward, David. A. Dahl[a]
Idaho National Laboratory
P.O.B. 1625 Idaho Falls, ID, USA

Abstract

A new magnetic sector mass spectrometer that utilizes seven full-sized discrete dynode electron multipliers operating simultaneously has been designed, constructed and is in preliminary testing. The instrument utilizes a newly developed ion dispersion lens that enables the mass dispersed individual isotope beams to be separated sufficiently (35 mm) to allow a full-sized discrete dynode pulse counting multiplier to be used for each beam. The ion dispersion lens is a two element electrostatic 90 degree sector device that causes the beam-to-beam dispersion to increase faster than the intra-beam dispersion. Each multiplier is contained in an isolated case with a deflector/condenser lens at the entrance. A 9-sample filament cartridge is mounted on a micro-manipulator two-axis stage that enables adjustment of the filament position with 10 micron resolution within the ion lens. Results of initial testing with actinides will be presented.

Introduction

The measurement of isotope ratios of actinides at trace levels in environmental samples presents a significant challenge to mass spectrometry. Historically such measurements were made via thermal ionization with multi-sector instruments incorporating a single pulse counting detector system using either a discrete dynode electron multiplier or a Daly detector[1]. Peak stepping was employed to cover the range of isotopes required with some form of mass-fractionation correction. The development of multi-collector magnetic sector instruments offered a means for increasing the sensitivity, accuracy and precision of these measurements by avoiding the dead time associated with peak stepping and the need for mass fractionation corrections (when the total evaporation method was employed). Wieser and Schwieters[2] provide a comprehensive description of the development of multiple collector isotope ratio mass spectrometry. In the commercial multi-collector instruments available today various types of electron multipliers coupled to pulse counters are used to detect extremely low level signals. However, the space constraints at the focal plane of the instruments has limited the number or type of electron multipliers that can be used. Nu instruments[3] employ discrete dynode multipliers, but are limited to 3; IsotopX[4] (formerly GV) and Thermo-Scientific[5] utilize miniaturized channel electron multipliers. With the goal of further improving the limit of detection of multi-collector instruments we have developed an ion-optical configuration that enables simultaneous measurement of up to 7 isotopes using full-sized discrete dynode electron multipliers. In this paper we present the status of the development of this instrument, describe the ion optical design of the instrument configured for measurement of Pu isotopes, and present the results of initial tests.

Ion Optical Design

The instrument is based on a traditional single magnetic sector design utilizing off-normal entrance and exit poles to extend the focal length, increase the dispersion and provide Z focusing. A unique ion lens, which we call an electrostatic dispersion lens[6,7] (EDL), is used to provide the additional separation of the ion beams needed to accommodate the full sized discrete dynode detectors. The

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thermal ionization ion source and acceleration lens is based on a previous design[8] with high transmission efficiency. The instrument was designed using the SIMION[9] 3D ion optics modeling software. Figure 1 shows the ion optics model and a set of ion trajectories for U.

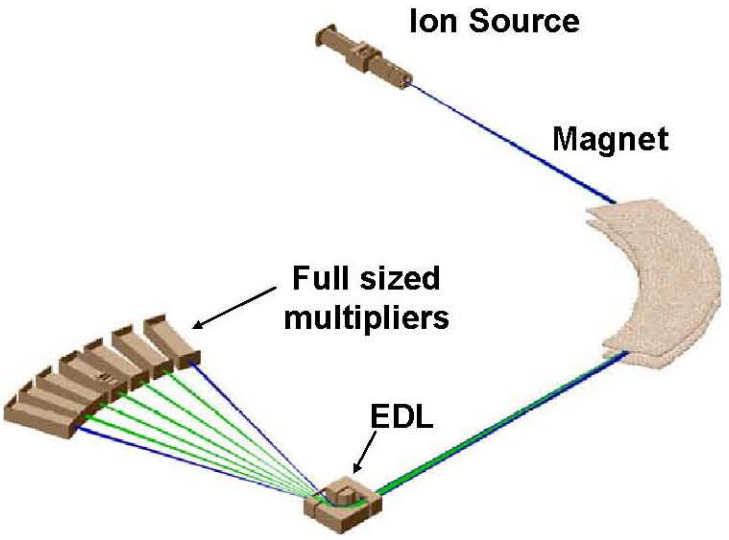

Figure 1 Isometric view of the SIMION ion optical model of the instrument.

The EDL is a relatively simple 2-element lens operating at nearly the same voltage as the ion source. The field within the lens causes the mass-separated beams to disperse without sacrificing resolution. Figure 2 presents a potential energy surface view of the EDL with a set of ion trajectories. Ions entering on the low mass side are accelerated as they enter the lens while ions entering on the high mass side are decelerated. Thus within the lens each isotope beam has a slightly different energy and thus is deflected through a different angle. At the exit all of the beams return to their initial energy. The EDL is physically located such that the focal point of the magnet is approximately at the center of the EDL; this produces the minimum broadening of each beam. The amplified dispersion with minimal broadening results in the beams being separated by ~4 cm 35 cm from the EDL exit, enough room to fit in full sized discrete dynode detectors at each beam position. The EDL was sized to accommodate 7 beams in the 230-250 amu mass range; the size could be changed to accommodate more or fewer beams.

Mechanical Design

The overall layout of the instrument as constructed and a photograph is shown in Figures 3 and 4. Sample filaments are mounted in a 9-position cartridge that sits on an X-Z (side to side and up-down) micro-adjustable stage. The stage, powered by UHV compatible ceramic motors, can be moved in 10 μm increments horizontally and vertically, allowing the sample to be optimally positioned in the ion lens. Figure 5 shows photographs of the sample cartridge mounted in the vacuum chamber and the sample cartridge. A two-color pyrometer mounted on a viewport with a line of sight to the backside of the filament is used to monitor filament temperature. Two sets of two-axis deflectors are located between the ion lens and the magnet along with a retractable Faraday cup. The magnet is mounted on a platform that allows the height, tilt, and angular orientation to be adjusted relative to the flight tube. The flight tube contains a series of angled baffles on the inner and outer radius to reduce transmission of scatter ions. A retractable slit is located just in front of the EDL; this can be used to operate the instrument in a single mass mode by setting the EDL voltages to zero so that the beam passes through the grid (Figure 2) to a detector mounted on the EDL (Figure 3).

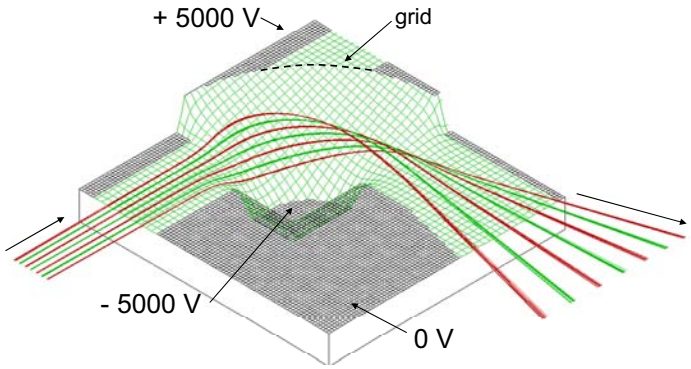

Figure 2 Potential energy surface view of the electrostatic dispersion lens and photograph. The mass separated beams enter on the left. The grid on the back electrode allows the ion beams to pass through the lens to a detector (not shown) when the electrodes are grounded.

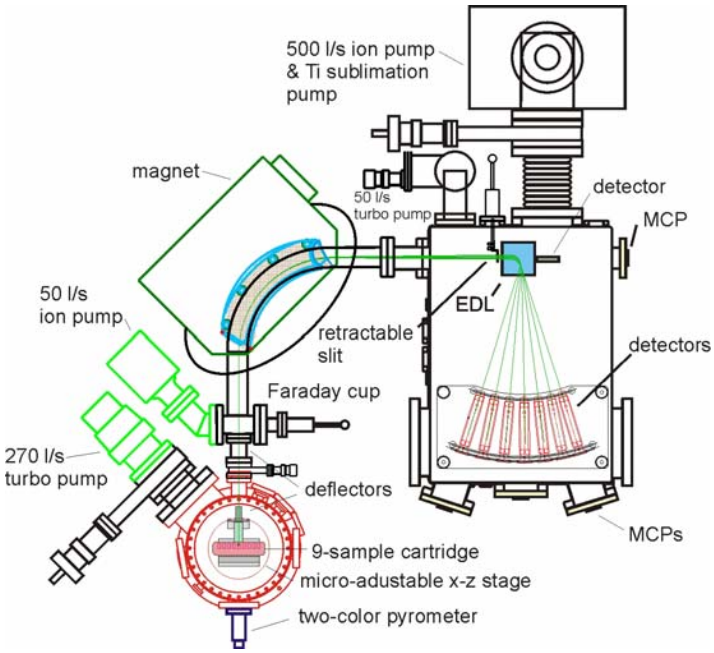

Figure 3 Physical layout of the instrument; footprint is 1.5 m x 1.5 m.

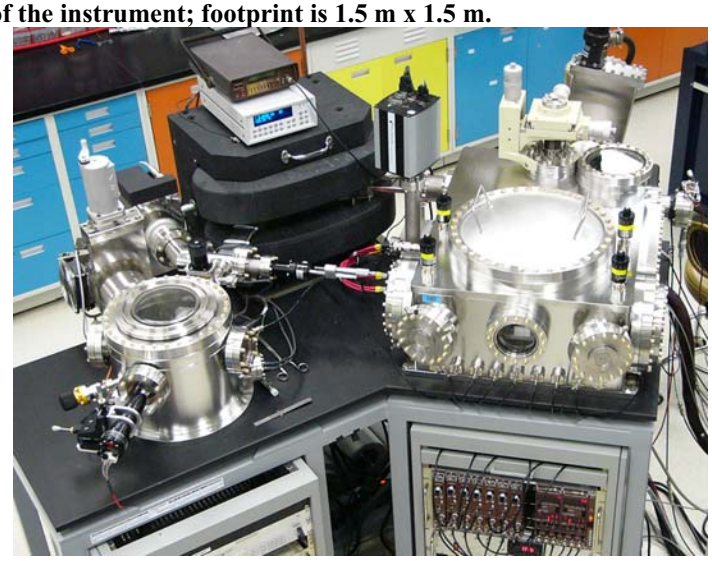

Figure 4 Photograph of the instrument, source chamber on the left, detector chamber on the right.

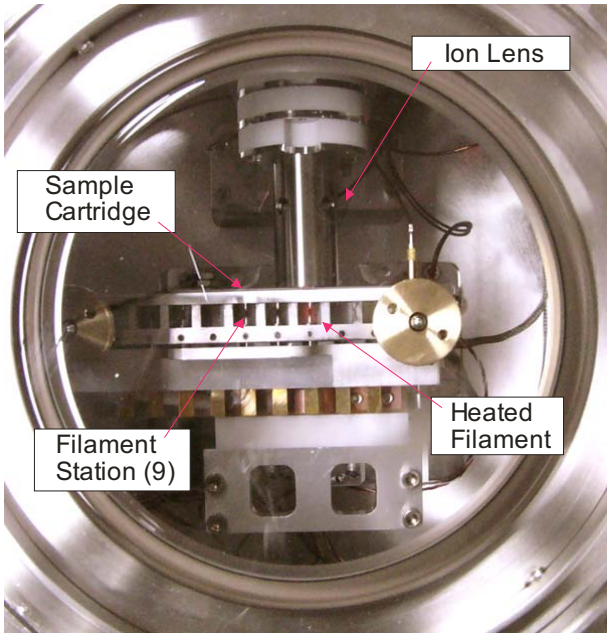

Figure 5 View through the top port of the source chamber (left) and the sample cartridge.

The detectors (ETP model AF150H) are each contained in an enclosure that mounts on a positioning dock. The positioning docks are mounted on a platform whose vertical position is adjustable from outside the vacuum system. The positioning docks can be moved on the platform to establish the required spacing between detectors and the detector enclosures can be removed from the positioning dock for detector replacement. This allows the detectors to be replaced without requiring realignment. Figure 6 is a photograph of 6 detector assemblies mounted on the platform.
The instrument control and data acquisition software was written in LabVIEW (www.ni.com/labview) and runs on a PC connected via IEEE-488, RS-232, and USB.

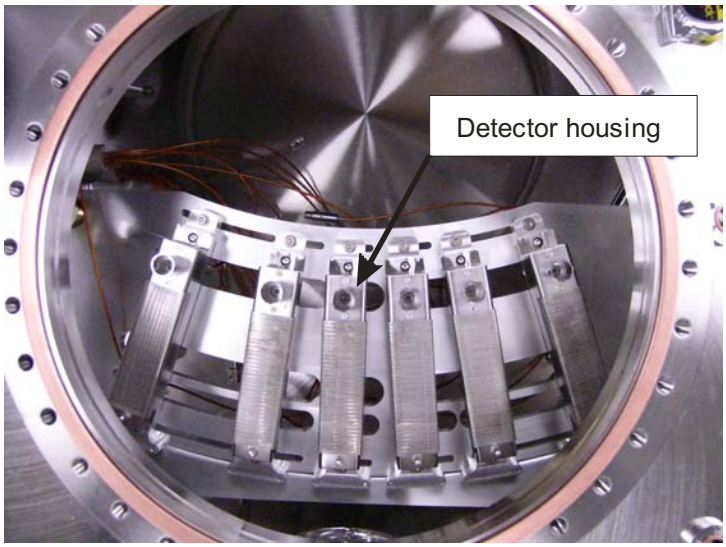

Figure 6 Photograph of six detectors mounted on the adjustable platform in detector chamber (left) and (right) a detector mounted in its housing with the top screen removed.

Results

The results presented in this paper are preliminary in that we are reporting data generated during the initial setup and testing of the instrument. Further refinement of the operating protocols and fine tuning of the integrated system are ongoing and thus the ultimate performance is yet to be determined.

Figure 7 illustrates the mass resolution of the instrument measured simultaneously on two of the detectors. The sample was U-500, an approximately equal mixture of ^{235}U and ^{238}U. The theoretical resolution for the magnet is 540 and the measured resolution (m/Dm at 1% of the peak height) was very close to this value. The resolution varies with detector position because the beam width after passing through the EDL is not constant across the mass range. There are no slits in front of the detectors and thus in a scan the beam traverses the entire detector dynode. Since the beam width is on the order of the detector opening the peaks do not have flat tops. Modifications to reduce the beam width are being implemented which will improve both the resolution and the resolving power. The resolving power at m/z 235, defined as the mass divided by the mass difference between 5% and 95% of the peak height is ~1400.

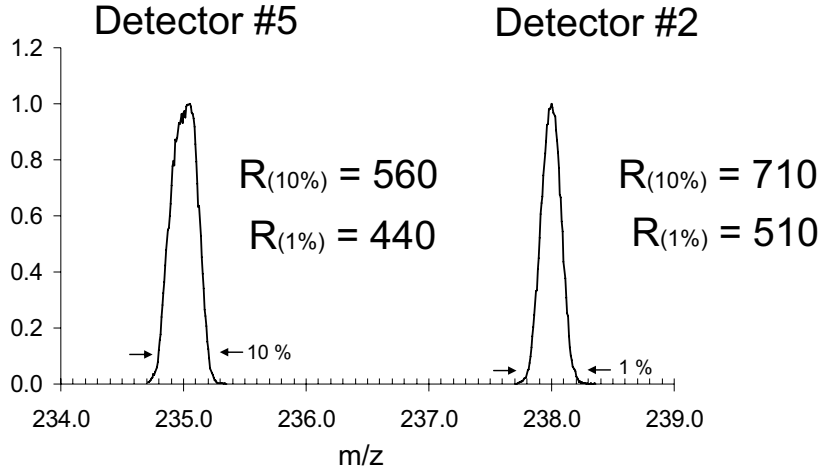

Figure 7 ^{235}U and ^{238}U peaks recorded on detectors 5 and 2; intensity normalized to unity. Resolution (R) measured at 1% and 10% of the peak height.

The abundance sensitivity of a single magnetic sector is generally considered limited to about 1 ppm (10^6); the measured abundance sensitivity of this instrument at mass 133 was 3 ppm with a pressure in the analyzer and detector chamber of 5 x 10^{-8} Torr. We have not yet analyzed Pu samples with major isotope signals high enough to determine the ultimate abundance sensitivity in this mass range.

Sensitivity has been measured using two protocols. In one the filament temperature was ramped to an intermediate temperature and held constant producing a near-constant signal of the major isotope. The sensitivity was then determined from the ratio of signal count rate to background count rate for different sample loadings. In the second protocol, the equivalent of the total evaporation method, the filament temperature was rapidly ramped to the maximum temperature and held constant resulting in a fast rise in signal followed by a slower decay and the signal was integrated over the entire period. In the second case the background can be determined by either using the signal at a nearby m/z position at which one expects no signal (m/z 243 in this case), or using the dark noise count rate measured prior to or after the temperature ramp. The advantage of the second method is that for very low level samples the integrated signal provides a better statistical measure than an instantaneous count rate.

Figure 8 shows the measured signals for a Pu spike solution containing a known isotopic composition for 244, 242 and 240 run with protocol 1 (constant signal). The samples were prepared by absorption of a known concentration on a resin bead which was then placed on the Re filament and carburized at 1400 C in benzene vapor prior being loaded into the mass spectrometer. To determine a background during these measurements the beam valve was closed for a brief period during each measurement (boxed areas). Combining measurements of the major and minor isotopes a sensitivity curve for this protocol was determined, shown in Figure 9. For this protocol the limit of detection was ~80 attograms with a S/N ~2.

Measurements were also made using protocol 2, the total evaporation method. Figure 10 shows the measured integrated signals for a 12 fg sample of 244 spike on a resin bead. The sample temperature was taken to ~1800 C for ~100 seconds then at ~315 seconds was ramped to 2250 C. Figure 11 shows the same data in the count/rate format. The 243 signal, for which there is no known Pu isotope in this spike, can be used as a conservative estimate of the scattered background noise; alternately, the actual counts in the respective mass channels after the signal has decayed away can be used as an estimate of the dark-count random noise. Using the 243 signal as the background estimate the S/N for the 240 isotope is 4.7; using the dark-count at 240 as background the S/N is 38. Using this protocol the limit of detection was 80 attograms with an S/N of ~4.

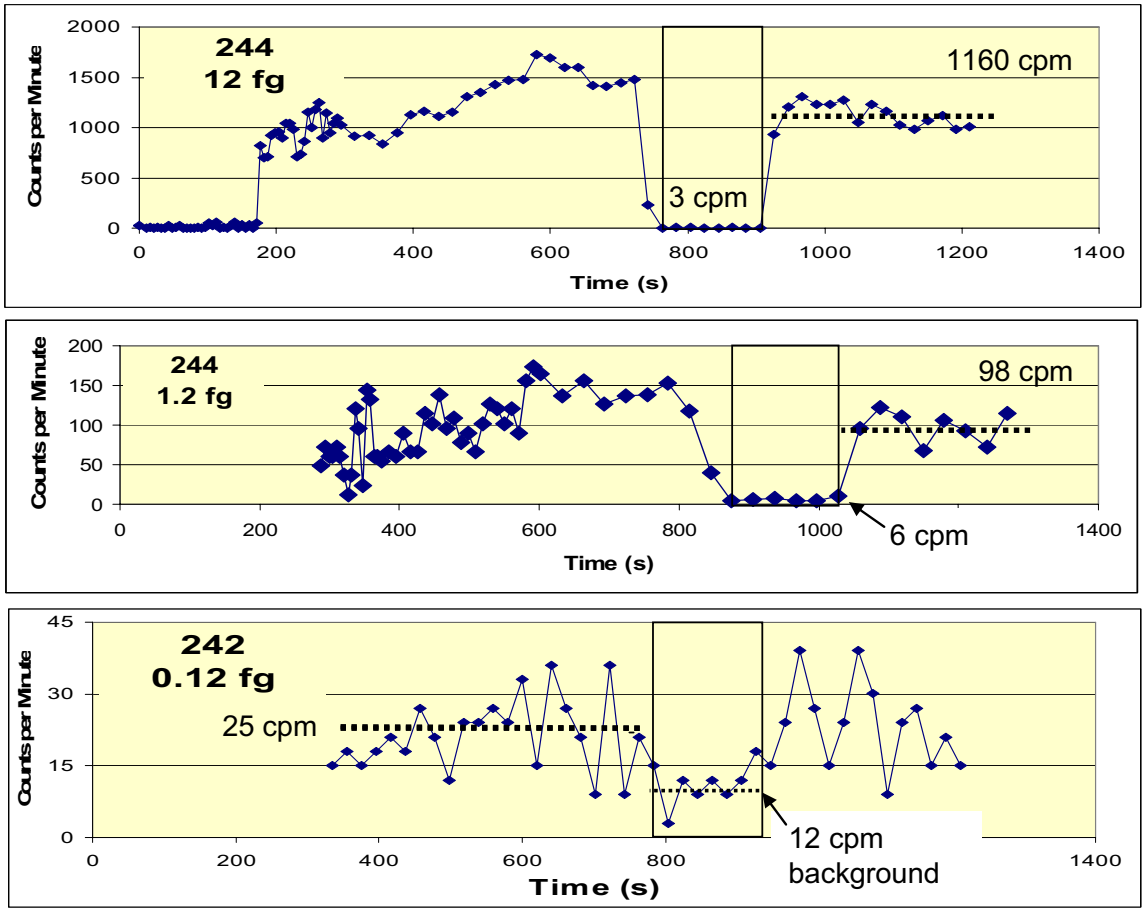

Figure 8 Measured count rates for ^{244}Pu and ^{242}Pu from 12 and 1.2 fg samples (244) and the count rate for the minor isotope ^{242}Pu from the 1.2 fg sample. The boxed areas are regions where the beam valve was closed to measure the detector dark noise.

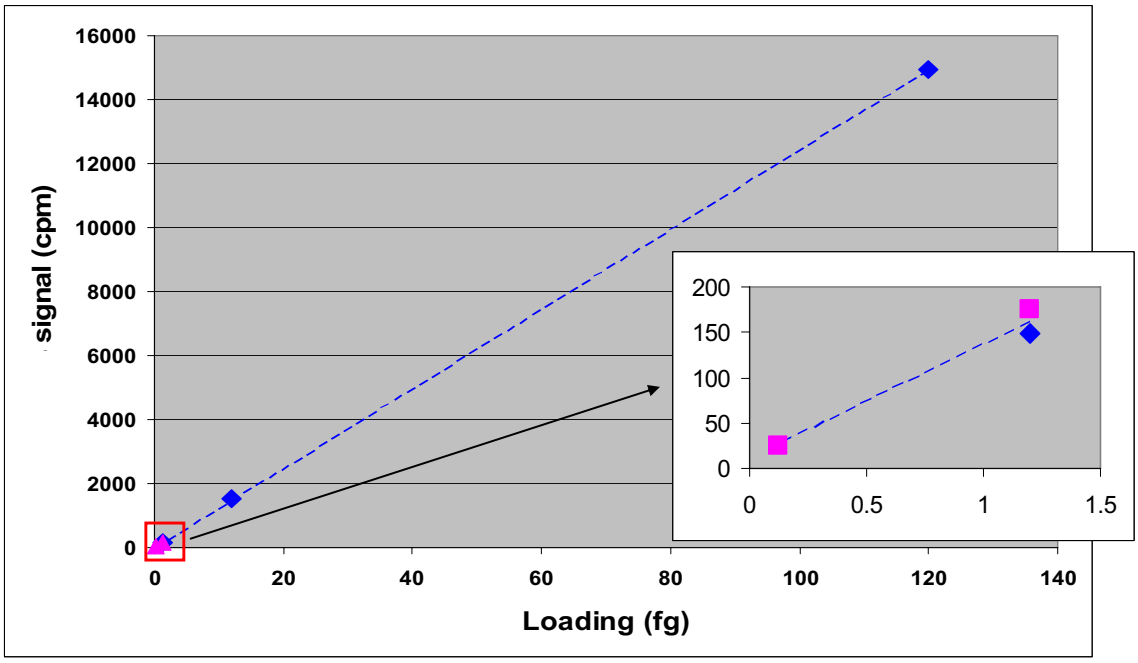

Figure 9 Measured sensitivity using protocol 1 for the ^{244}Pu spike and minor isotopes. The diamonds correspond to the 244 major isotope, the triangles and squares to the 242 and 240 minor isotopes; dashed line is the linear fit to the data.

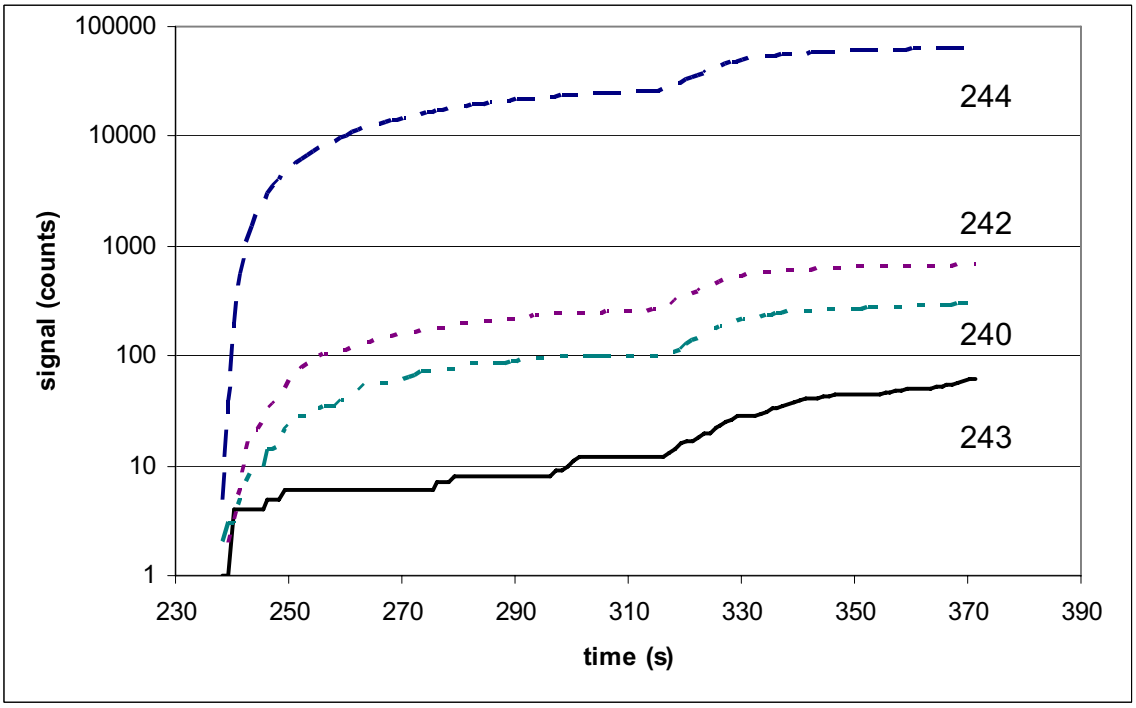

Figure 10 Integrated counts of the 244, 242, and 240 isotopes from a 12 fg ^{244}Pu sample and for m/z 243 (no Pu isotopes at this mass) collected using protocol 2. Temperature was ramped to 1800 C at 240 s then to 2250 C at 315 s.

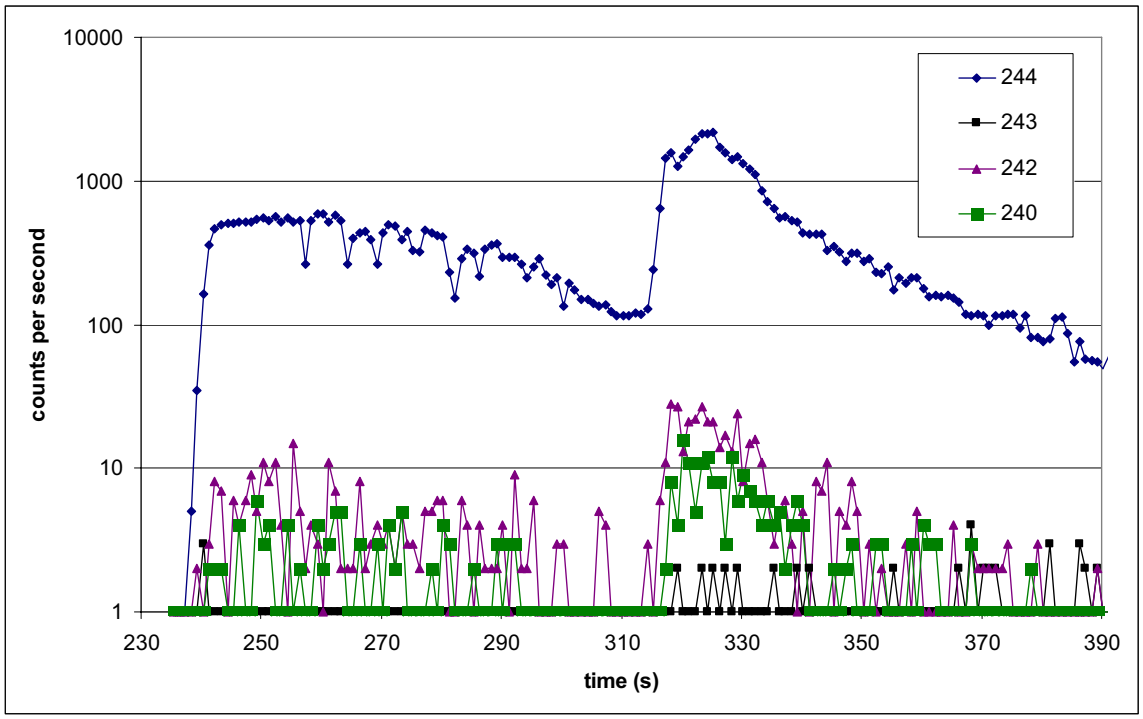

Figure 11 Count rate of the 244, 242, and 240 isotopes from a 12 fg ^{244}Pu sample and for m/z 243 (no Pu isotopes at this mass) using protocol 2. Temperature was ramped to 1800 C at 240 s then to 2250C at 315 s.

Discussion and Conclusions

The complexity of design, setup and operation and the issues of detector cross calibration and linearity offer significant challenges for multi-collector thermal ionization mass spectrometers, but the improvement in sensitivity and reduction in mass fractionation appears to outweigh the complexity issues. The design presented herein utilizing the electrostatic dispersion lens offers an alternate means for simultaneous detection, and the only one that can accommodate full sized discrete dynode detectors for each isotope channel. The accuracy and precision of the instrument has yet to be determined; the limit of detection of ~80 attograms is at present of the same order as commercially available multi-collector instruments.

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