

Preliminary Results of Uranium and Plutonium Efficiency Measurements Using a High Efficiency Cavity Ion Source Interfaced with a Finnigan MAT 262 Mass Spectrometer

K.B. Ingeneri, L.R. Riciputi
Oak Ridge National Laboratory
P.O. Box 2008; MS-6375
Oak Ridge, TN, 37831-6375

P.M.L. Hedberg
International Atomic Energy Agency
Safeguards Analytical Laboratory
Seibersdorf, Austria

Abstract

Evolving goals of safeguards environmental sampling of uranium and plutonium demand decreased sample sizes. Thermal ionization mass spectrometry (TIMS), with samples loaded on metallic filaments for vaporization and ionization before mass analysis, has been the mainstay analytical technique for precise isotope ratio measurement and, using isotope dilution, abundance determination. However, the ionization efficiency (ratio of element ionized to element available) of TIMS is poor for uranium and plutonium. Thus, improved ionization efficiency would increase analytical sensitivity and reduce sample size requirements, enhancing environmental sampling safeguards methods. We have developed a High Efficiency Cavity Source (HECS) that is interfaced with a commercial TIMS instrument (MAT 262) at the IAEA Safeguards Analytical Laboratory. The sample is loaded in a cavity bored into a metal (tungsten, W or rhenium, Re) rod, which is heated by electron impact. The source's confined geometry and ability to operate at much higher temperatures provide the potential for enhanced ionization efficiency compared to traditional TIMS sources.

Preliminary tests yielded total efficiencies of 0.4% to 1.2 % for plutonium and 0.1 to 0.6% for uranium. Following enhancements in the optics of the HECS source the total efficiencies have increased to an average of more than 2 % total efficiency for both uranium and plutonium.

1. Introduction

1.1 Need for a High Efficiency Ion Source

In the wake of terrorist activities on September 11th, 2001 and with knowledge of the heightened tensions between nuclear powers such as Pakistan and India, the entire world is much more aware of the potential for a devastating nuclear event. Environmental sampling and nuclear forensics are powerful tools in discovering undeclared nuclear activities, or verifying declared activities. Both these methods require very precise and accurate analyses of both elemental abundance and isotopic composition. However the abundance of uranium and plutonium in

environmental samples is often low, at the very limits of detection for conventional thermal ionization mass spectrometry (TIMS). This is due to inefficient conversion of atoms to ions (which can be analyzed) in a conventional TIMS source. To support the IAEA in its environmental safeguards sampling mandate Oak Ridge National Laboratory (ORNL) has entered a US support program task to develop a high efficiency cavity source (HECS). The goal of the HECS project is to enhance sample utilization efficiencies (ions detected/atoms loaded) to 1% for uranium and 2% for plutonium, significantly improving the precision, accuracy, and detection limits in environmental samples.

1.2 The High Efficiency Cavity Ion Source

The high efficiency cavity source consists of 3 parts, the cavity, the heating filament, and the electron shield. The cavity is a solid metal rod of high purity tungsten or rhenium 1mm in diameter. A hole $\sim 0.5\text{mm}$ in diameter and 5-8 mm deep is milled into one end of the rod. The result is a small, narrow cavity in which the sample to be analyzed is placed. The heating filament consists of a thin rhenium ribbon, identical to the filaments used during TIMS analysis. When heated, the filament produces electrons, which bombard the cavity. The cavity can be heated past the melting point of rhenium ($\sim 3300^\circ\text{C}$) in this manner. The third element of the HEC source is the electron shield. The electron shield is a charged plate that protects the ion lenses from being bombarded by high-energy electrons. Figure 1 depicts the general layout of the micro-cavity source and identifies the three main components. In addition, two important terms are illustrated. The Trap Current is the current flow of the electrons bombarding the cavity and is highly correlated to the temperature. In order to direct the electrons formed at the filament to impact with the cavity, a voltage difference, the Trap Voltage, is maintained between the two.

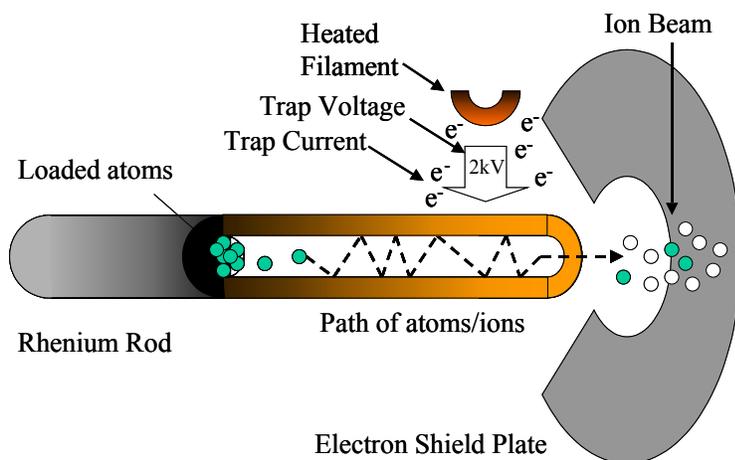


Figure 1. Illustration of the High Efficiency Cavity (HEC) Ion Source.

2. Experimental

2.1 Cavity Ion Source Design

The main purpose of the HECS is to enhance the ability to analyze small environmental samples of uranium and, in particular, plutonium. The ion source needs to be applicable to commercial instruments to be of practical use for the IAEA Safeguards efforts. To this end, we have

constructed a HEC source that operates on a Finnigan MAT 262 magnetic sector thermal ionization mass spectrometer.

Typical analyses of environmental samples on the MAT 262 at the IAEA's Safeguards Analytical Laboratory are single filament measurements. Up to 13 samples can be loaded onto a sample turret, which holds the filaments and a shield plate. The shield plate protects the ion lenses from excessive bombardment by rhenium atoms and ions formed when the filaments are heated. In designing the HECS, a sample turret was modified so that a cavity could be mounted into place without altering the filament contacts. Likewise, the filament shield also acts as an electron shield effectively protecting the ion lenses with minimal modification. A photograph of the ion source mounted on the sample turret can be seen in figure 2.

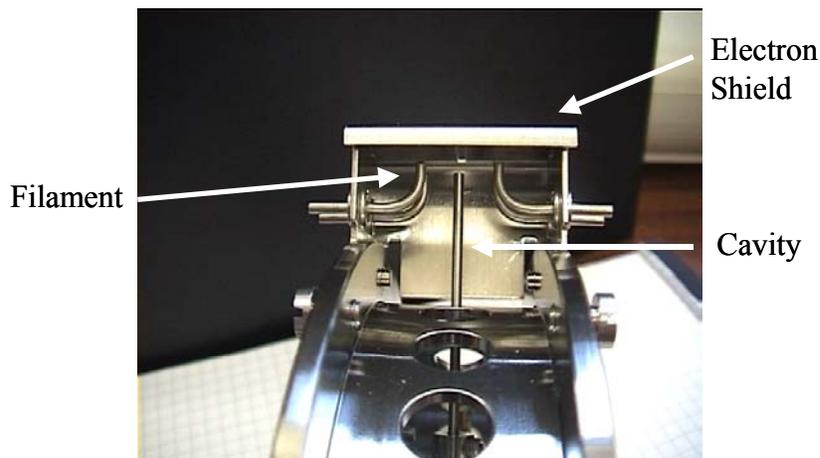


Figure 2. Digital Image of the HECS on a Finnigan MAT 262 mass spectrometer.

2.2 The MAT 262 Mass Spectrometer

The MAT 262 is a magnetic sector multi-collector mass spectrometer with a thermal ionization source. The mass analyzer is a 1 tesla magnet with a 23 cm radius at 90° . Because the source is nearer to the magnet than the detector, the system has a magnification of 1.4, with a resolution of greater than 500.¹

The multi-sample source magazine can fit 13 samples which can be single, double or triple filaments. In addition to the multiple Faraday cup array, a secondary electron multiplier (SEM) detector is present for the measurement of very low ion signals. Isotopic ratios with a high abundance sensitivity can be obtained using a Retarding Potential Quadrupole (RPQ) system mounted in front of the SEM detector. Standard abundance sensitivities for this instrument are 2 ppm at mass 237 for uranium.

The mass spectrometer is computer controlled using customized software based on National Instruments LabView platform. The flexibility of this program allowed new routines to be developed to incorporate the additional experimental parameters, such as the Trap Current and Trap Voltage. Due to the necessity of maintaining the Trap Voltage, a magnetic scan, rather than

the typical voltage scan, is used both for peak centering and obtaining mass spectra. Modules for ramping and maintaining cavity temperature have also been developed.

2.3 Sample Preparation

Standard uranium beads were prepared using AG 50W-X8 cation beads obtained from BIORAD Laboratories. 100-200 beads in their nitrate form were counted and delivered into a clean Teflon flask. 1-2 ml of U500 standard solution of the appropriate concentration was added to the flask. After agitation, the beads were allowed to sit for 48-72 hours. The solution was then filtered and 3 washes of 1ml 0.1M nitric acid were used to rinse the beads. Several beads were then dissolved and spiked so that they could be quantified using isotope dilution methods. The beads were found to contain 10 ng +/- 15% per bead. Pu beads (Dowex 1x2 anion resin) containing 30 pg of Pu were produced using a similar method.

A bead of either U or Pu was loaded into a cavity using a clean pair of manipulators and then gently pushed to the bottom of the cavity using a probe. The bead was then covered with just enough (0.1 to 0.5 microliters) of water suspended graphite to secure it in place. Once dry, the cavity is loaded onto the sample turret and mounted in the spectrometer. When the vacuum reaches a nominal pressure (about 1×10^7 mbarr), the sample is ready to be run. At a trap current of 5 mA, the cavity is hot enough to burst the bead, which is noted by a spike in the pressure (5×10^6 mbarr). After the bead has been burst, the cavity temperature can be ramped quickly to ionizing temperatures. Routinely, the signal is focused at a low temperature and then the total evaporation module of the software is run. Total efficiency measurements are calculated from the result of the total evaporation measurements as the ratio of ions detected vs the atoms loaded.

3. Results

3.1 Initial Results

To form a useful basis comparison, several 10 ng uranium beads were analyzed using a single filament TIMS analysis. The resulting efficiency measurements ranged from 0.0005% to 0.2 % with an average of 0.012% efficiency. A batch of tungsten cavities were then loaded with one 10 ng bead and analyzed. Results from the tungsten cavities ranged from 0.02 to 0.08%. The average of 8 replicate measurements was 0.047%, a factor of 4 improvement.

Rhenium has a higher work function than tungsten and therefore is expected to have a greater ionization efficiency. The same batch of 10 ng beads was loaded onto rhenium cavities and total evaporation measurements were recorded. The use of rhenium resulted in a marked improvement with results between 0.1 and 0.6%. Compared to single filament measurements, a rhenium cavity yielded between 20-40 x's better efficiency than single filaments.

While rhenium does produce higher efficiency numbers, it is more expensive and more difficult to machine than tungsten. An experiment was designed to test if significant improvement from the tungsten cavity could be obtained by coating the sample with rhenium powder before analysis. A 1 ml aliquot of fine rhenium powder in ethanol was injected into the cavity before the graphite over coat. Experiments yielded measurements between 0.1 and 0.2%. While there

was a significant improvement notice with the rhenium-carbon mixture in tungsten cavities, it is clear that Re cavities will result in the greatest ionization efficiency measurements.

Analysis of the plutonium beads in two tungsten cavities resulted in efficiencies of 0.08%. Total evaporation measurements of plutonium beads on rhenium cavities resulted in efficiencies between 0.4 and 1.2%. Although preliminary, these results match or exceed many of the best reported TIMS efficiencies.

Despite the fact that rhenium cavities provide ionization efficiencies much higher than typical single filament measurements, we suspected the ion source was not optimized for cavity measurements. Observation of the ion lenses during analyses indicated that they were far from optimized. Likewise, deposition on the first ion lens indicated that a significant amount of sample was lost due to poor ion transmission.

3.2 SIMION

After making the HECS source operational and these initial experiments were performed, another extensive SIMION modeling effort was undertaken using the geometry and lens voltages that were used. SIMION is a program developed by David Dahl, of the Idaho National Engineering and Environmental Laboratory, which is able to model electrostatic lenses. After careful measurements of the physical dimensions and operating voltages of the ion lens stack were made, a basic model of the ion source was developed. Simulations indicated that significant amounts of sample would be deposited on the first two ion lenses as well as the slit to the mass spectrometer, corresponding to our experimental observations. Figure 3 displays a simulation of uranium ions impacting the first ion lens. Several models were developed to characterize the behavior of the HECS. The effects of cavity position, lens voltage, and source geometry were all studied in detail to develop possible avenues to improve ion transmission through the source, without requiring significant modifications of the commercial instrument.

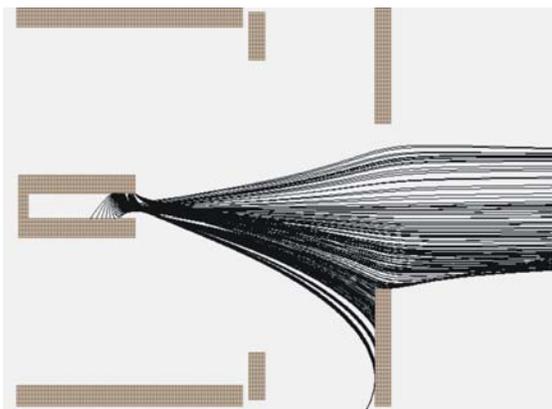


Figure 3. SIMION simulation indicating that a large number of sample ions hit the first ion lens and therefore are not detected.

3.3 High Efficiency Measurements

A number of altered front plates and electron shields were produced for testing the SIMION-based recommendations on the HECS equipped MAT 262. A second set of uranium and plutonium beads with 0.5ng and 0.18 ng loadings respectively were produced and quantified using the standard procedure. Initial testing using the uranium beads on a rhenium cavity with a rhenium-carbon overcoat produced measurements at the 0.5% level. The position of the cavity and the ion lens voltage were then optimized. After optimization, analyses of 20 uranium beads produced measurements with average efficiencies exceeding the 1% level. Analyses of a set of 15 plutonium beads resulted in average total efficiency measurements exceeding 2%.

3.4 Applications of the HEC Ion Source

The high efficiency cavity ion source has exceeded the original project goals of 1% average efficiency on uranium and 2% efficiency on plutonium. Single filament efficiency measurements produce 1 ion for every 2000-8000 atoms loaded. By comparison, the HEC source produces 1 ion for every 50-100 atoms loaded. These measurements are also higher than reported results from magnetic sector inductively-coupled plasma mass spectrometers (ICP-MS). These results suggest that, with implementation of the HEC source at SAL, the threshold for effective analysis of trace amounts of uranium and plutonium in environmental samples will be significantly reduced to a level not possible using traditional TIMS analysis. Due to the efficient utilization of the sample, precision and accuracy of isotope ratio measurements will also be improved. The HEC source may also prove a useful tool in other arenas where high sample utilization efficiency is critical.

References

1. MAT 262 Operating Manual (ISSUE 92, Rev.1)

Research sponsored by POTAS, U.S.D.O.E. under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle LLC.