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IMPROVED ANALYTICAL SENSITIVITY FOR URANIUM AND PLUTONIUM IN ENVIRONMENTAL SAMPLES: CAVITY ION SOURCE THERMAL IONIZATION MASS SPECTROMETRY

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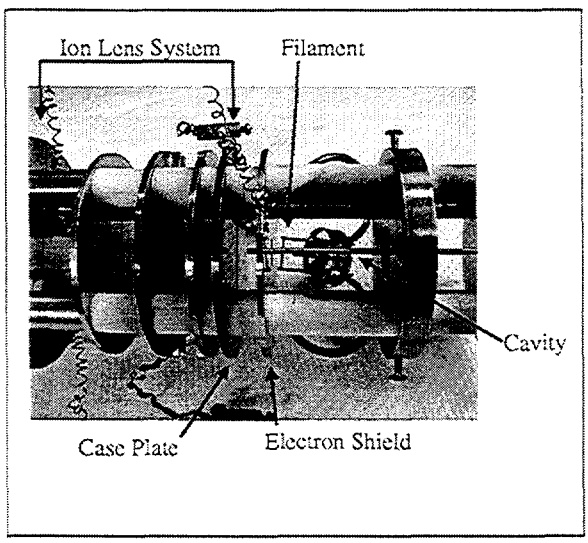
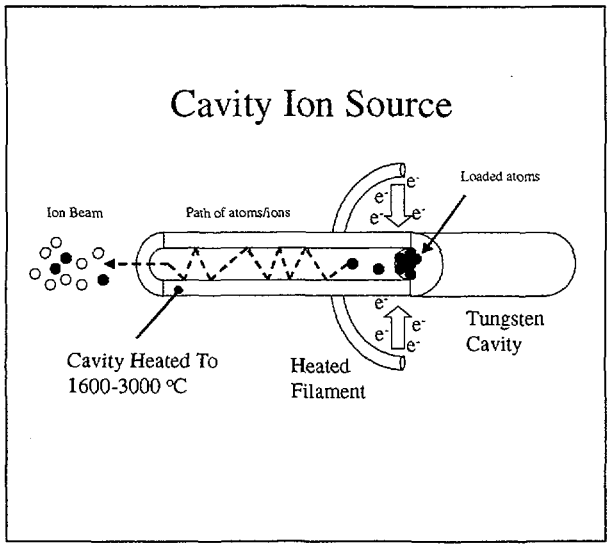
Following successful field trials, environmental sampling has played a central role as a routine part of safeguards inspections since early 1996[1] to verify declared and to detect undeclared activity. The environmental sampling program has brought a new series of analytical challenges, and driven a need for advances in verification technology. Environmental swipe samples are often extremely low in concentration of analyte (ng level or lower), yet the need to analyze these samples accurately and precisely is vital, particularly for the detection of undeclared nuclear activities. Thermal ionization mass spectrometry (TIMS) is the standard method of determining isotope ratios of uranium and plutonium in the environmental sampling program. TIMS analysis typically employs 1-3 filaments to vaporize and ionize the sample, and the ions are mass separated and analyzed using magnetic sector instruments due to their high mass resolution and high ion transmission. However, the ionization efficiency (the ratio of material present to material actually detected) of uranium using a standard TIMS instrument is low (0.2%), even under the best conditions. Increasing ionization efficiency by even a small amount would have a dramatic impact for safeguards applications, allowing both improvements in analytical precision and a significant decrease in the amount of uranium and plutonium required for analysis, increasing the sensitivity of environmental sampling.

A new thermal ionization source, designed originally for isotope separators[2] and then modified by by Olivares and coworkers at LANL to operate with a quadrupole mass spectrometer[3], has shown 10x higher ionization efficiency than conventional TIMS filaments for several elements. Thus, this new source produces 10 times greater signal from the same amount of analyte. If this source could be coupled with a magnetic sector mass spectrometer capable of high precision measurements of isotope ratios, the implication for safeguards measures is obvious – it would provide the ability to obtain isotope ratio data from samples previously too low for detection.



To support the IAEA and its role in non-proliferation and nuclear safeguards, we have developed a high efficiency ion source and coupled it to a magnetic sector mass spectrometer. This new source is called a thermal ionization cavity (TIC) ion source because it consists of a tungsten rod with a deep, narrow cavity bored into one end. The sample is loaded into the cavity and then the rod is heated by electron bombardment. Figure 1 is a photo of the TIC source used in the Oak Ridge National Laboratory instrument.

The cavity ion source is able to achieve greater ionization efficiency for two reasons. First, the Saha-Langmuir equation predicts that ionization efficiency increases at higher temperatures and the cavity source is able to operate at much higher temperatures compared to conventional filaments (~3000 °C as compared to ~2000°C). Second, the confined volume of the cavity allows a greater number of surface interactions compared to the filament source. Figure 2 illustrates the interaction of atoms with the cavity.



As mentioned previously, we have coupled a high efficiency cavity source to one of our sector instruments at ORNL[4]. The initial design was able to heat the cavity to ionizing temperatures and to produce a stable signal (5% rsd over 1 hour). Using an NBS uranium sample, U350, the cavity source demonstrated its ability to deliver highly precise isotope ratio measurements. A relative standard deviation of 0.079% was obtained for the U^{235}/U^{238} ratio. Precision of < 0.1% is obtainable for a single nanogram of U010 on a routine basis. Although the development of the source is still in its infancy, tests of ionization efficiency indicate that the cavity source offers significant improvements compared to the filament source. However, ionization efficiencies on the order reported by Olivares[5] have yet to be realized.

The prototype ORNL source provides the basis for designing a cavity ion source for the commercial mass spectrometers at the IAEA Safeguards Analytical Laboratory. Results of the design and testing of this source, scheduled for Spring of 2001, will be reported.

While the cavity ion source is slightly more complex than the conventional filament design, it offers the potential of an order of magnitude increase in signal for the same amount of sample during routine analysis. This will result in the lowering of detection limits, while maintaining the same level of precision in results. These results are achievable, not by extensive chemical techniques or new instrumentation, but by relatively slight modifications to the source of a proven instrument.

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