Capabilities of Hybrid SIMS-SSAMS System for Nuclear Forensics Applications

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Abstract. Mass spectrometry of particulate samples by Secondary Ion Mass Spectrometry (SIMS) is a very useful nuclear forensics tool. However, there are limitations caused by interferences from molecular species, such as $^{238}U^{1}H$ while measuring ^{239}Pu. These interferences ($> 10^4$ M/ΔM) can exceed the resolving power of SIMS. Accelerator Mass Spectrometry (AMS) is capable of eliminating such molecular ion interferences, but lacks spatial information and generally requires use of negative ions. This requirement limits its sensitivity, since actinide and lanthanide elements preferentially generate positive atomic ions ($\sim 10^4 : 1$). The US Naval Research Laboratory (NRL) has installed a hybrid SIMS-AMS system, using a Single Stage AMS (SSAMS) as a replacement for the normal Cameca IMS 4f SIMS electron multiplier detector. The NRL design enables analysis of either positive or negative ions. Thus, this system offers the potential to provide SIMS-like particle analysis without the forest of signals from molecular species, and is capable of measuring important positive atomic ions. This should improve measurement sensitivity and precision to determine isotopic distributions of actinides, lanthanides, and transition metals; and elemental abundances of trace species in particles or small features. Initial measurements and instrument capabilities are described.

1. Introduction

Secondary Ion Mass Spectrometry (SIMS) is a well-developed microanalysis tool, and is employed for particulate analysis in nuclear forensic examinations. However, interferences from molecular species with nominally the same mass as an isotope of interest cause sensitivity limitations. For masses beyond 90 u, the resolution required to reject interferences can exceed 10^4 M/ΔM, which is a challenge for SIMS. Examples of the resolution required at a given isotopic mass to reject binary molecules containing H, C, or O are shown in Fig. 1. Ternary molecules can create even greater challenges.

On the other hand, Accelerator Mass Spectrometry (AMS) is a well-developed tool for precise isotopic analysis of bulk material. By accelerating analyzed ions to high energy, they can transit a gas cell to destroy all molecules, thereby removing interferences. In the case of ^{14}C, residual molecules of ^{13}C-H and ^{12}C-H_2 can be rejected to levels below 10^{-15} of the ^{12}C intensity. However, conventional AMS instruments employ negative ions for analysis; so suffer from diminished sensitivity for electropositive species, such as actinides, lanthanides, many transition metals, and alkali and alkali-earth elements. While molecular ions, such as oxides, are used to improve sensitivity, this approach adds complexity to the analysis and cannot always be used. Additionally, AMS is a bulk analysis technique; so individual particles are not measureable.

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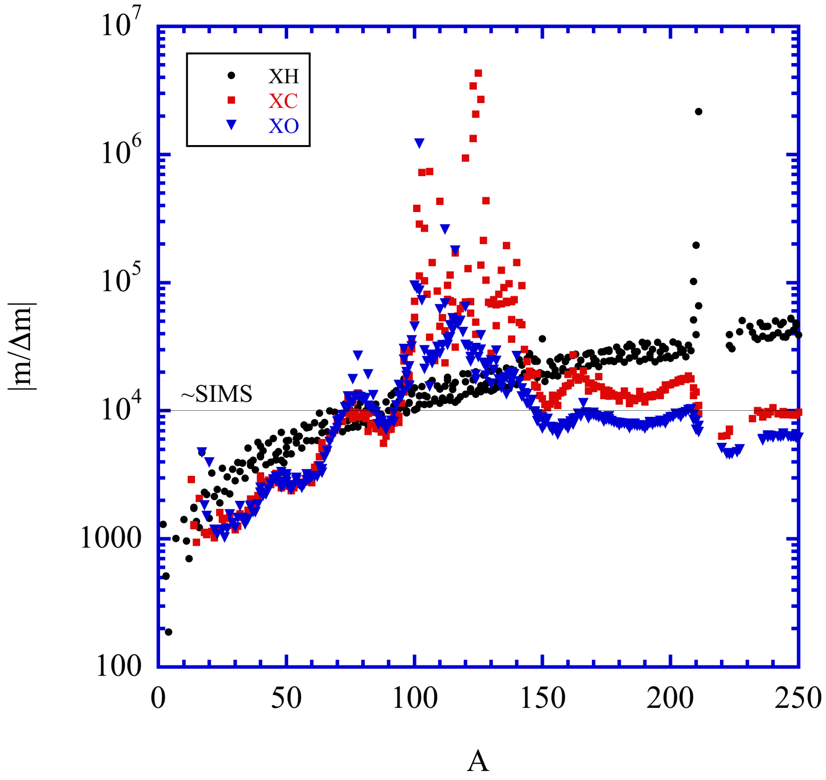

FIG. 1. Mass resolution needed to separate atomic species of interest from binary molecules containing H, C, or O. Above atomic mass of 90, SIMS is strongly challenged by these molecules. This includes the second and third row transition metals, lanthanides, and actinides.

While a SIMS instrument has been combined with a conventional AMS previously [1, 2, 3, 4, 5], these devices were only able to measure negative ions from the SIMS. With recent developments in AMS technology, specifically, Single Stage AMS (SSAMS) instruments [6], it is now possible to perform AMS on positive ions as well [7]. This offers an opportunity to build a cornerstone instrument, combining the advantages of SIMS and AMS for particulate analysis of electropositive elements. As illustrated in Fig. 2, bulk measurements with few molecular ions is provided by Inductively Coupled Plasma Mass Spectrometry (ICPMS) for positive ions, and free of molecular ions by AMS for negative ions. SIMS generates either positive or negative ions and provides spatial resolution, but suffers from molecule interferences. By using a SIMS instrument to generate desired positive (or negative) ions from particulates, and a bipolar SSAMS instrument to destroy molecular ions and measure the residual atomic isotopes, one can construct such a cornerstone instrument (see dark grey blocks in Fig. 2); and that is what the Naval Research Laboratory (NRL) has done.

2. Atomic ion SIMS (ai-SIMS) instrument at NRL

The ai-SIMS instrument at NRL is comprised of a Cameca IMS 4f SIMS instrument generating 4.5 keV positive ions, but where the conventional electron multiplier detector has been replaced by a larger than normal National Electrostatics Corp. SSAMS system operating at up to ±300 kV. It is larger to accommodate a magnet to analyze 75 MeV·u ions, or 246 u ions @ 300 kV. The two systems are joined by an Einzel lens and steering elements. The main elements of the SSAMS system are shown in Fig. 3. They include an injection magnet,

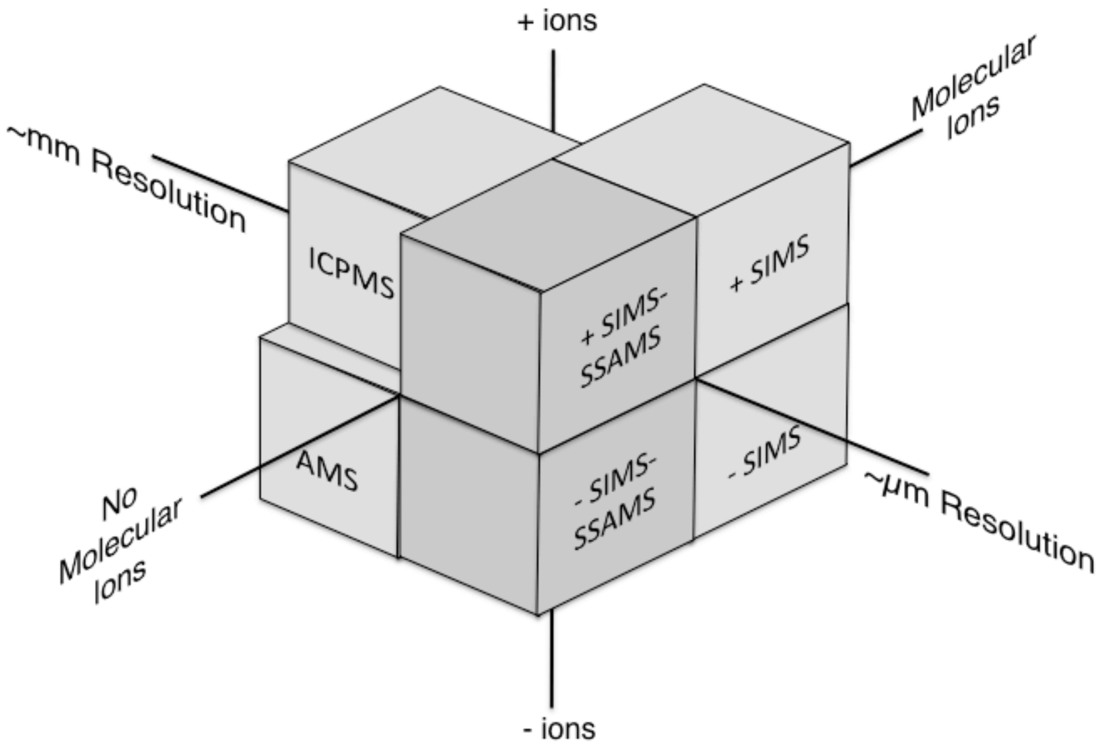

FIG. 2. Attributes of different mass spectrometric techniques: ICPMS, AMS, SIMS, and hybrid SIMS/SSAMS. The preferred quadrant for actinides, lanthanides, and other electropositive elements in particulate samples is the corner occupied by the hybrid technique.

acceleration tube, molecule destruction chamber, analyzing magnet, electrostatic analyzer, and electron multiplier detector. Power to operate components on the high voltage deck is provided by a pair of motor-generator sets, although only one set is depicted in Fig. 3.

Because both magnets in the SSAMS system are large, the response time to change the field is long. To expedite switching between masses, the SSAMS is provided with beam-energy "bouncing" through both magnets. This alters the ion beam energy for its transit through a magnet, so the mass-energy product required by the magnetic field can remain constant, but a different mass can be selected. For the analyzing magnet, the energy can be bounced ± 20 keV, or ±6.5% at 304.5 keV, meaning the mass can be bounced ±6.5% at 304.5 keV. Larger changes require either lowering the accelerating voltage so the bouncing voltage is a larger percentage, or changing the magnetic field. For isotopic distributions or nearby elements, this would not be necessary.

From previous efforts at NRL to combine SIMS with a tandem accelerator for trace element analysis [8], we learned that charge state (q) +1 ions are preferred for this type of analysis. At a higher q, molecule fragments can create ambiguities with atomic ions. These occur when a fragment's fraction of the original molecule mass (equal to the mass under examination) is nominally equal to the ratio of its q to that of the atomic species investigated. For example, if ^{236}U is selected for analysis at a q of +2 at energy E, then a molecule of $^{118}Sn_2$ at energy E could fragment and produce a $^{118}Sn^{+1}$ ion, at an energy of 0.5 E, since the two molecule fragments equally share the initial energy. Since electrostatic analysis selects ions based on E/q, it would not differentiate between $^{236}U^{+2}$ and $^{118}Sn^{+1}$-fragment ions. Similarly, since a

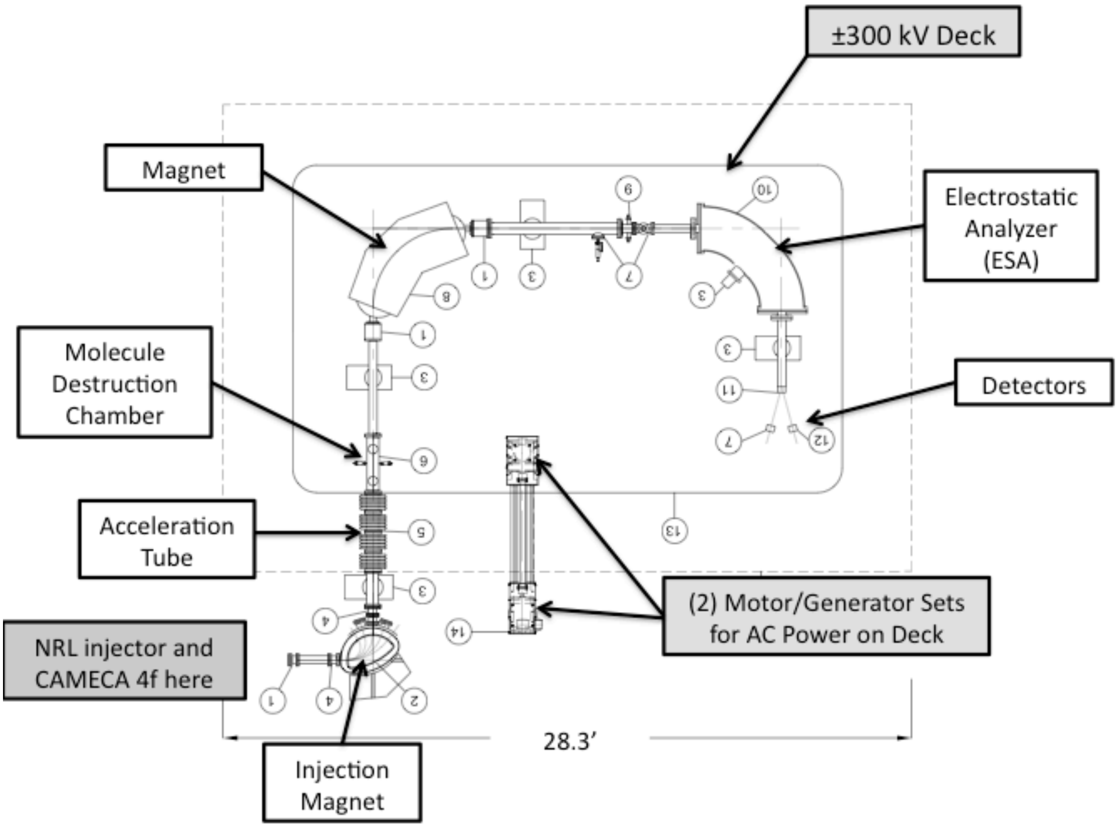

FIG. 3. SSAMS components shown are coupled to Cameca IMS 4f output to replace its normal electron multiplier. Connecting components include an electrostatic lens and steering element to optically match the two instruments. The SSAMS system accelerates ions 300 keV to enable molecule destruction in a gas cell, then performs mass spectrometry. Energy bouncing with a constant magnetic field enables fast switching of nearby masses (±6.5%)

magnet selects ions based on (M/q)·(E/q), where M is atomic mass, it would not discriminate between these two ions either. By choosing to analyze +1 ions, since this is the lowest q possible for analysis, no molecule fragments exist in a lower charge state to generate an ambiguity.

While SSAMS has been well tested and qualified for its primary application of radiocarbon analysis, there has been little work to date for applications at higher masses. Nevertheless, there is sufficient data to suggest viability of the concept for nuclear forensics applications. To fully implement this concept, some baseline performance characteristics need to be determined. These include a determination of the gas pressure required (for each gas, ion, and energy used) to obtain an equilibrium charge state distribution, and identification of the optimal gas and ion energy to produce the largest fraction of charge state 1+ ions. Vockenhuber et al. [9] showed (see Fig. 4) that while He gas is well suited for producing U^{+2} ions at energies down to 80 keV, other gases such as Ar, Kr and H might be better suited for producing U^{+1} ions. These gases and perhaps others will need to be evaluated for the best production of +1 ions. Additional factors that need to be ascertained are the ability of various gases to sufficiently destroy molecules at different ion energies; the magnitude of atomic beam attenuation that occurs at each of those conditions; and the stability, precision, and detection efficiency obtainable from the instrument.

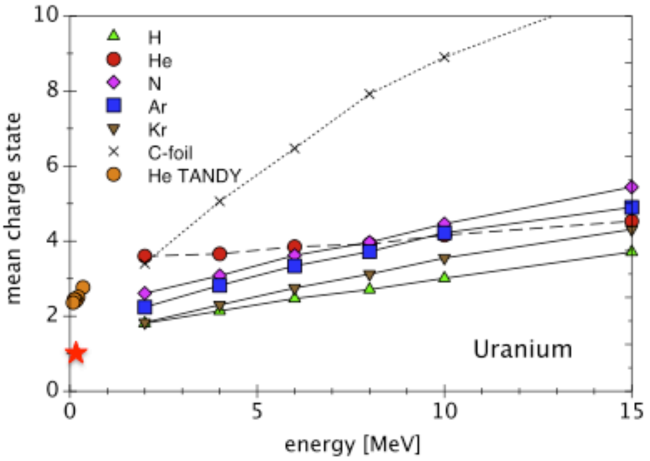

FIG. 4. While Fig. 1 from Volkenhuber et al. [9] shows He gas is well suited for producing U^{+2} ions at low energies, the trend with energy suggests other gases such as H, Ar, or Kr may be better suited for producing U^{+1} ions at low energy, approaching the location of the star (reprinted with permission from Elsevier).

3. Initial measurements

While only enabled for preliminary measurements in April 2014, the NRL ai-SIMS facility has already demonstrated viability of the proposed concept. Preliminary data was collected from samples of Ti, In, Cu, and HfH_2 for atomic and molecular positive ions while operating at 300 kV, using Ar gas for molecule destruction.

3.1 Molecule breakup

The selected samples were used to produce abundant +1 ions of TiO, InO, Cu_2, and HfH. The intensity of each was measured as the pressure of Ar was incrementally changed. As expected, the intensity diminished exponentially with increasing Ar pressure. Data for the $^{63}Cu_2$ molecule is shown in Fig. 5. In this case, the decay is diminished at low intensities, as would be the case if an impurity of ~ 10 ppm of ^{126}Te was present in the Cu sample. Note that over the range of Ar pressures applied, the molecule intensity decreased by over seven orders of magnitude.

3.2 Atomic ion attenuation

Atomic +1 ions of Ti, In, Cu, and Hf were measured to evaluate attenuation of their intensity caused by the use of Ar gas. Data for the attenuation of ^{63}Cu is shown in Fig. 6. Again the expected exponential decay is observed, but in this case, a reduction of only 70% is observed upon using the same highest pressure as used for the $^{63}Cu_2$ breakup measurement.

3.3 Cross sections

The observed exponential decay in intensity is related to the cross section for an Ar atom to either destroy the incident molecule; or to scatter the incident atomic ion out of the required trajectory to be measured. The decrease in ion intensity with increasing gas thickness is described by

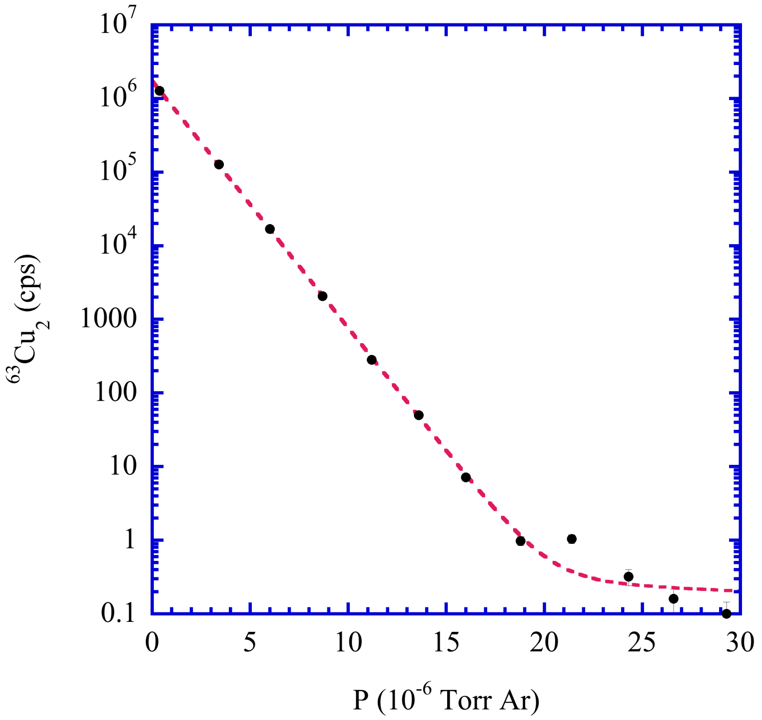

FIG. 5. Intensity decrease of $^{63}Cu_2$ molecule with increasing Ar gas pressure. Two exponentially decaying terms were fit to the data, with the slower decay consistent with a presence of ~10 ppm ^{126}Te.

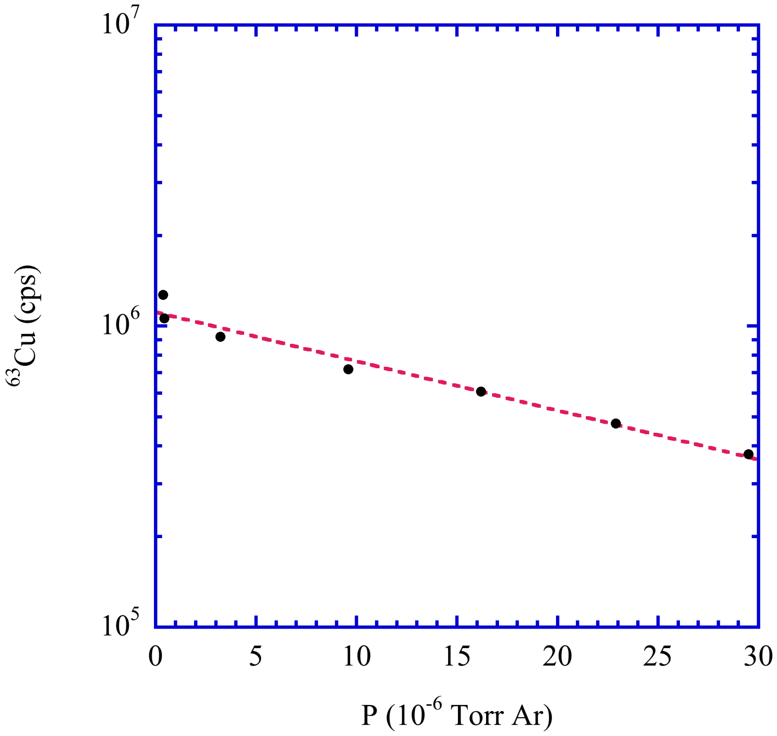

FIG. 6. Intensity decrease of ^{63}Cu atomic ion with increasing Ar gas pressure.

$$I = I_0 \exp(-\sigma \cdot N_{Ar} \cdot x_{Ar}) \tag{1}$$

where

I	is intensity measured with Ar present
I_0	is intensity measured with no Ar present
σ	is cross section per Ar atom (cm^2)
N_{Ar}	is density of Ar gas (cm^{-3})
x_{Ar}	is path length through Ar gas (cm)

The Ar density can be determined from its pressure and temperature through the ideal gas law, so the pressure reported in the data collected can be used along with the path length of the ions through the molecule destruction chamber to convert slopes on semi-logarithmic plots into the cross sections of interest. In this preliminary work, the Ar pressures were measured outside of the actual molecule destruction chamber, but were converted into an average pressure inside the chamber based on information provided by the SSAMS manufacturer.

Molecule destruction cross sections for the various ions measured is shown in Fig. 7a, while those for attenuation of atomic ions is shown in Fig. 7b. In both cases cross sections are similar amongst measured ions, despite differences in molecule type and binding energy, and in ion mass. This suggests a common mode of operation is feasible. Strikingly, there is a ~20 fold difference in cross section between molecule destruction and atomic ion attenuation. This result provides strong evidence the concept behind ai-SIMS is a valid and useful method.

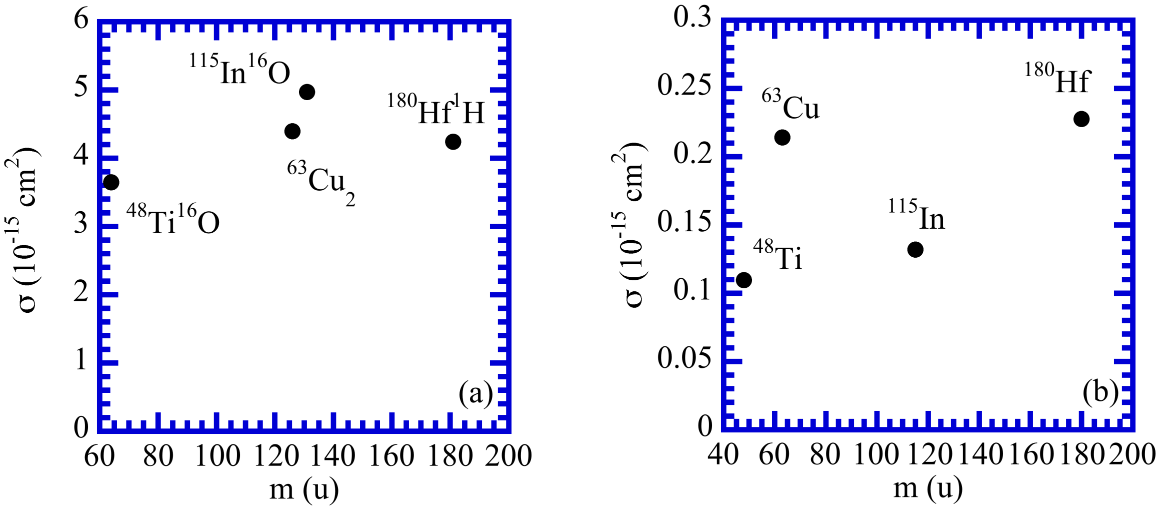

FIG. 7. Cross sections computed for a) molecule breakup of TiO, InO, Cu_2, and HfH, and b) attenuation of atomic ions of Ti, In, Cu, and Hf, with use of Ar gas and 300 keV ions. Note the factor of ~20 difference between molecule breakup and atomic attenuation values, and the commonality of values amongst the different masses and molecule types.

3.4 Hydride interference for Hf isotopes

To demonstrate the relevance of ai-SIMS to nuclear forensics issues, Fig. 8 shows the effect of hydride molecules on the apparent isotopic distribution of Hf. As a greater amount of Ar gas is employed, the measured distribution more closely approaches that of the natural abundances expected. As this is preliminary data, the agreement is not exact, but the trend is clear. While this seems like an extreme example, since the sample was HfH_2, it demonstrates a real problem if one wants to measure a small amount of ^{239}Pu while a larger quantity of ^{238}U is present, and hydrides are able to form.

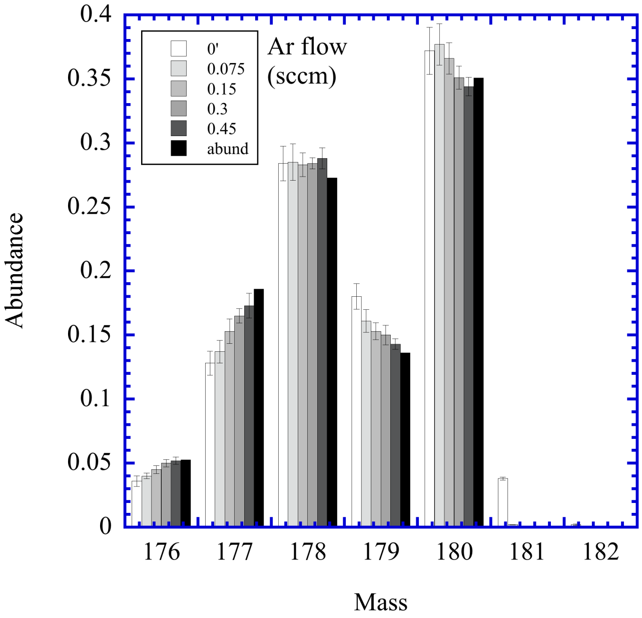

FIG. 8. Hydride molecules impact the apparent isotope distribution of Hf, when a HfH_2 compound is measured. The natural abundance is shown as black bar; with measured intensities approaching the natural abundance as Ar gas flow and molecule destruction increases. The data was normalized by summing the isotope contributions to 1.

4. Importance to nuclear forensics

Mono-hydride rejection by SIMS requires a mass resolution near 40,000 to measure isotopes of importance to nuclear forensics. With interfering molecules in parentheses, some isotopes of interest include ^{236}U (^{235}U·H) and ^{239}Pu (^{238}U·H) that reveal exposure to neutrons; ^{231}Pa (^{230}Th·H) and ^{210}Pb (^{209}Bi·H) that are indicators of age since chemical separation; ^{233}Pa/^{233}U (both ^{232}Th·H) that can indicate repurposing of ^{232}Th; ^{206}Pb (^{205}Tl·H) as a collateral fingerprint; and ^{210}Po (^{209}Bi·H) and ^{240}Pu (^{239}Pu·H) that can be a weapon component. By eliminating hydride molecules, ai-SIMS could provide greater precision and accuracy to measure these isotopes. Even for small particles where too few atoms of a trace isotope are expected to be observable, evidence of "spoofing" could be obtained due to non-uniformity in concentration leading to some particles having above average concentration that could be measured.

Besides the above-mentioned examples, greater sensitivity for trace elements and isotopic distributions may provide additional fingerprints for source material identification. Rare earth elements and transition metals are such candidates, as they are subject to molecule interferences that challenge the ability of SIMS alone to provide an assay of their content. The use of ai-SIMS may offer access to improved fingerprinting capabilities.

The existing ai-SIMS instrument at NRL is a prototype, hopefully able to contribute to important measurements, but also is intended to evaluate the performance characteristics of ai-SIMS and explore possible refinements to enhance its capabilities. For example, if the ion energy can be reduced, the SSAMS size could be reduced by a commensurate amount, potentially making the concept more widely available.

5. Conclusions

A novel concept known as atomic ion SIMS, or ai-SIMS, is under development at the Naval Research Laboratory to improve sensitivity and precision for microanalysis of particulates of interest to the nuclear forensics community. This approach will greatly reduce molecular ion intensities, so that trace quantities of isotopes and elements can be better quantified. Preliminary data has demonstrated that the concept is valid, and efforts to bring the hybrid instrument to full operation are underway.

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