

NUCLEAR FORENSICS INTERNATIONAL TECHNICAL WORKING GROUP

ITWG GUIDELINE ON SECONDARY ION MASS SPECTROMETRY (SIMS)



EXECUTIVE SUMMARY

Secondary Ion Mass Spectrometry (SIMS) is used for elemental and isotopic analysis of solid samples. SIMS is a destructive technique, although the amount of sample consumed during analysis is usually quite small. The greatest strength of SIMS is the ability to analyze very small areas (as small as 50 nm using the NanoSIMS, for example) and to generate high-spatial resolution maps of the distribution of elements and isotopes in the sample. SIMS may also be applied for the analysis of individual micrometer sized particles. SIMS is a surface sensitive technique, since the secondary ions at any point in the analysis derive from the top 3-5 monolayers of material. However, repetitive analyses can be performed over longer periods as the primary ion beam sputters away the sample (to a depth of several microns in some instances) in a technique known as "depth profiling". The measurement of the isotopic composition of the sample is usually straightforward, only requiring the analysis of the sample and that of an isotopic reference material for determination of the mass bias of the instrument. Quantification of elements, however, involves the analysis of matrix matched standards for the determination of the relative sensitivity factor (a function of both the element to be analyzed and the matrix). SIMS can be used in nuclear forensics for exploring the heterogeneity of the material on fine spatial scale. It can also be used to characterize small "dust" particles, deriving from the sample itself or from the environment where the sample has been processed or stored.

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1. INTRODUCTION

In Secondary Ion Mass Spectrometry (SIMS), an energetic, focused primary ion beam sputters a solid sample surface. The sputtering process creates positively and negatively charged ions (secondary ions), as well as neutrals, from the top 3-5 monolayers of material (see Figure 1). These secondary ions can either be atomic ions or polyatomic ions formed from atomic constituents of the sample. The choice of primary ion beam depends on the nature of the analysis. In general, an O_2^+ or O^- beam is used for the analysis of positive secondary ions, generated from electropositive elements, and Cs⁺ is used for the analysis of negative secondary ions, generated from electronegative elements. By applying a positive potential to the sample surface, positive secondary ions are accelerated into the mass spectrometer for analysis. Similarly, by holding the sample surface at a negative potential, negative secondary ions are accelerated into the mass spectrometer for analysis. SIMS can be used to measure the concentration of any element from H to Pu, over a dynamic range of more than nine orders of magnitude.



Fig. 1. Schematic of the sputtering process in SIMS.

* Note that this guideline covers only dynamic secondary ion mass spectrometry, in which the primary ion dose exceeds 10¹²/cm² and most, if not all, molecular information has been destroyed by the ion bombardment. At low primary ion dose (<10¹² ions/ cm²), the polyatomic ions may be characteristic of intact molecules or fragments of molecules.

Different commercial SIMS instruments use different mass analyzers, including double-focusing, quadrupole, and time-of-flight mass analyzers. For example, the ims-series of SIMS instruments (ims-3f, ims-4f, ims-5f, ims-6f, and ims-7f) use a doublefocusing mass spectrometer, consisting of a 90° spherical electrostatic sector and a 90° stigmatically focusing magnetic sector to separate the secondary ions according to their mass-to-charge ratio, while compensating for differences in angle of motion and ion energy (see Figure 2). Since most ions are singly charged, the mass spectrometer separates the secondary ions effectively according to their mass. Double focusing gives these instruments the capability for moderately high mass resolving power (ability to separate closely spaced masses). The mass resolving power $(M/\Delta M)$ for the imsseries of instruments, for example, is variable from approximately 300 to 20,000, depending on the instrument settings.

In addition, many SIMS instruments are stigmatically focusing, in which the spatial position of ions as they leave the sample surface is maintained and magnified through the instrument. Stigmatic focusing allows the real-time visualization of mass-resolved images through the use of a position-sensitive detector, such as a phosphor screen or resistive anode encoder. This mode of imaging is called "direct" or "microscope" ion imaging. Mass-resolved images can also be reconstructed on an electron multiplier detector from the secondary ion intensity information acquired while rastering a finely focused primary ion beam over the surface of the sample. This mode of imaging is called "microprobe" or "rastered" ion imaging.

The intensity of the mass-resolved ion beam is measured either with a Faraday cup, ion multiplier, or position-sensitive detector. The Faraday cup captures the ion beam, allowing the direct measurement of the resulting current. The ion multiplier converts ion impacts into electrical pulses, which are then counted for a specific period of time to yield a count rate (ions per unit time). The





position-sensitive detector simultaneously counts ion impacts and measures their position of impact on the detector surface.

The intensity of the mass-resolved ion currents can be converted to elemental concentrations

In addition to conventional SIMS instruments, such as the ims-3f through ims-7f instruments, there are new generation SIMS instruments with special applications in nuclear forensics. Large geometry instruments, the use of which is sometimes termed "LG SIMS", afford increased transmission at higher mass resolving powers, allowing the reduction of interferences without a concomitant loss in sensitivity. These instruments can also be equipped with multiple detectors in order to measure up to seven masses simultaneously. The Cameca ims-1280 and the Sensitive High Resolution Ion Microprobe (SHRIMP, Australia Scientific Instruments) are examples of large geometry SIMS instruments. In addition, the NanoSIMS is a uniquely designed SIMS instrument that offers extremely high spatial resolution (50 nm), but also with excellent sensitivity.

through the use of relative sensitivity factors (RSFs). RSFs are determined through the analysis of standards similar in elemental composition to the sample of interest. RSFs can vary over 5-6 orders of magnitude, depending on the matrix and element of interest, so appropriate standards are necessary for accurate quantification.

Standards of two general types are used to determine RSFs for the matrix and element of interest: bulk standards and ion implanted standards. Bulk standards are homogeneous solid materials with concentrations of specific elements certified by other, usually multiple, analytical techniques. Bulk standards are available from national and international standards-making bodies. Ion implanted standards are fabricated through high-energy ion implantation of the element of interest into the matrix. Ion implanters can accurately measure the flux (ions per second) of the element of interest and the implantation time to determine the total implanted dose (ions). By depth profiling through the implanted region and integrating the resulting count rate, RSFs can be calculated. Ion implant standards can be fabricated to order by most ion implant laboratories. In the

absence of appropriate standards, one can use RSF systematics to estimate the RSF [1].

2. USE OF XRD FOR NUCLEAR FORENSICS

Bulk analyses assume that the material analyzed is homogeneous and can be represented by a single concentration or isotopic ratio without loss of information. SIMS can be used to measure isotopic and elemental abundances in bulk samples, but inductively coupled plasma mass spectrometry (ICP-MS) is usually more sensitive and accurate/precise for bulk measurements than SIMS. Even so, SIMS may still be appropriate for special cases. SIMS may also be the technique of choice for electro-negative elements (C, N, O, F, Cl, S) for which ICP-MS has poor sensitivity.

In many cases, however, the nuclear material will be heterogeneous. This heterogeneity may convey information about either the source of the material or the process used to make it. Because of the small size of the primary ion beam, SIMS can be used to measure isotopic and elemental abundances as a function of lateral (X & Y) position. The spot size of a SIMS primary ion beam is usually around 1 µm, but can be as small as 50 nm on the NanoSIMS. Plots of isotopic or elemental abundances versus lateral position are called "images" or "maps". SIMS can also be used for the analysis of individual micronsized particles, which corresponds to picograms of uranium oxide. Even so, SIMS offers the possibility for measuring the isotopic composition for both major and minor isotopes of such small particles with good precision.

SIMS can be used to measure isotopic and elemental abundances, as a function of time. If the sputter rate remains constant during the analysis, or varies in a known way, the variation of isotopic and elemental abundances as a function of depth can be calculated (special equipment such as a profilometer that measures the crater depth is required to convert the analysis time into sample depth). Plots of isotopic or elemental abundances versus depth are called depth profiles. SIMS may also be used in concert with other microanalytical techniques to enhance the amount of information derived from the sample. One commonly used combination is scanning electron microscopy (SEM) and SIMS, in which the SEM is used for feature location, identification, and elemental analysis (by X-ray spectroscopy), followed by feature relocation and analysis by mass spectrometry in the SIMS instrument.

3. SAMPLE REQUIREMENTS

SIMS can only be used to analyze dry, solid samples that are stable in the instrument's vacuum and do not degas. SIMS samples must either conform dimensionally to the instrument's sample holder or may be cut to fit. Small samples, such as particles, can be mounted or dispersed onto an appropriate substrate that fits into the instrument's sample holder (see Admon, 2009). The sample surface must be as smooth as possible because the quality of an analysis strongly depends on the surface roughness, especially for depth profiling. The sample must also be conductive. If not, sample metallization (coating) and/or a SIMS electron gun for charge neutralization are required.

SIMS is a destructive analysis technique, although the amount of material removed during most analyses is quite small.

4. PRO'S AND CON'S OF THE TECHNIQUE

One of the key advantages of SIMS is the ability to measure both elements and isotopes with high sensitivity. Detection limits vary with the element of interest and the matrix, but typically range from 1 ppba to 1 ppma. Under optimum conditions, elemental concentrations from SIMS data can be obtained with +/- 2 % precision and +/- 10 % accuracy. The precision of isotopic ratios from SIMS data is often limited by counting statistics and can approach 0.1 % or better. With proper calibration of the mass bias of the instrument, the accuracy of isotopic ratios from SIMS data is comparable to the precision. SIMS analysis can be affected by isobaric interferences, that is, ionic species so close in mass to the species of interest that the mass spectrometer cannot separate them. In addition to interferences from atomic ions of the same mass, e.g., ⁴⁰K⁺ and ⁴⁰Ar⁺ in the measurement of ⁴⁰Ca⁺, the analysis can also suffer from interferences from molecular ions of the same nominal mass. e.g., ${}^{28}Si^{16}O^+$ and ${}^{12}C_{2}H_{2}^+$ in the measurement of ⁴⁴Ca⁺. These molecular ions can be formed from constituents in the sample itself (usually matrix level constituents), the sample vacuum, and the primary ion beam. Interferences can be reduced to some extent by instrumental improvements, such as increasing the mass resolving power or energy filtering, mass filtering of the primary ion beam, and improved sample chamber vacuum. However, increasing the mass resolving power or energy filtering decreases the sensitivity.

SIMS also suffers from hydride formation (²³⁵UH+ for example) which needs to be taken into account when measuring the minor isotopes (²³⁶U+ in the example).

5. FAQ

- Cost: SIMS instruments typically cost several million US\$ and require at least one fully trained operator.
- SIMS is an extremely sensitive analytical technique, so sample-handling practices that avoid sample contamination or crosscontamination are essential. (Availability of a clean room or a laminar flow box has proven to be useful.)
- Quantification of elemental concentration requires a relative sensitivity factor (RSF) for the element of interest in the material to be analyzed. Therefore, matrix-matched standards are crucial for accurate quantification.
- In general, the measurement of isotopic ratios by SIMS does not require RSFs. However, it does require all of the standard considerations

for good isotopic analysis, including accurate measurement of counting system deadtime, measurement of mass bias, stable isotopic signals or a good scheme for drift correction, etc.

- Rastering the primary ion beam over a nonuniform substrate will cause time and space variation in the ion signal. Since deadtime correction schemes assume a relatively constant ion signal over the time of measurement and the rastered area, it is usually preferable to measure isotopic ratios using a static (non-rastered) primary ion beam.
- Methods of handling isobaric interferences:
- In the case of elemental quantification, isobaric interferences can sometimes be avoided through selection of an alternative isotope for measurement. This approach presumes accurate knowledge of the isotopic composition of the element of interest.
- The interference can be reduced through energy filtering. The energy distribution of atomic ions is usually much broader than the distributions of molecular ions. By applying an energy offset, most of the molecular ions can be eliminated, while still allowing a reasonable fraction of the atomic ions to be measured.
- Interferences can also be reduced by increased mass resolving power. Increased mass resolving power allows the instrument to detect the species of interest, while eliminating the interfering ions. However, the mass resolving power of traditional SIMS instruments, such as the ims-3F through -7f, although moderately high, is nonetheless limited. Therefore, some interferences are too close in mass to the species of interest for the instrument to separate them.
- In cases where an interference cannot be avoided or eliminated, the resulting analysis merely determines an upper limit for the isotope or element of interest.

- Depth profiling can potentially suffer from several types of artifacts, including crater edge effects, knock-on effects, charge-driven diffusion. Please read Reference 1 for a more detailed discussion.
- The user must carefully choose the characteristics of the primary ion beam:
 - The type of primary ion beam (O_2^+, O^-, Cs^+) affects the sensitivity of the analysis.
 - Increasing primary ion beam energy usually improves ion current and beam focusing, but decreases depth resolution through increased ion beam mixing.
 - Angle of incidence of the primary ion beam affects the sputter yield and depth resolution of the analysis.
 - The spot size of the primary ion beam determines the analytical area in the case of a static beam and the quality of the crater in the case of a rastered beam.

6. USEFUL REFERENCES

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