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Draft INFL Guideline on SIMS

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Nuclear Forensic International
Technical Working Group

Guidelines Task Group
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INFL GUIDELINE ON SECONDARY ION MASS SPECTROMETRY (SIMS)

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EXECUTIVE SUMMARY

Secondary Ion Mass Spectrometry (SIMS) is used for elemental and isotopic analysis of solid samples. The greatest strength of SIMS is the ability to analyze very small areas (as small as 50 nm using the CAMECA NanoSIMS, for example) and to generate high-spatial resolution maps of the distribution of elements and isotopes within the sample. The measurement of the isotopic composition of 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 is commonly used in nuclear forensics for exploring the heterogeneity of the material on fine spatial scale.

1. INTRODUCTION

In Secondary Ion Mass Spectrometry (SIMS), an energetic, focused primary ion beam sputters the sample surface. The sputtering process creates positively and negatively charged ions (secondary ions) in addition to neutrals. Secondary ions can either be atomic ions or polyatomic ions formed from atomic constituents of the sample. At low primary ion doses, the polyatomic ions may be characteristic intact molecules or fragments of molecules. 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 ions, generated from electropositive elements, and Cs^+ is used for the analysis of negative 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.

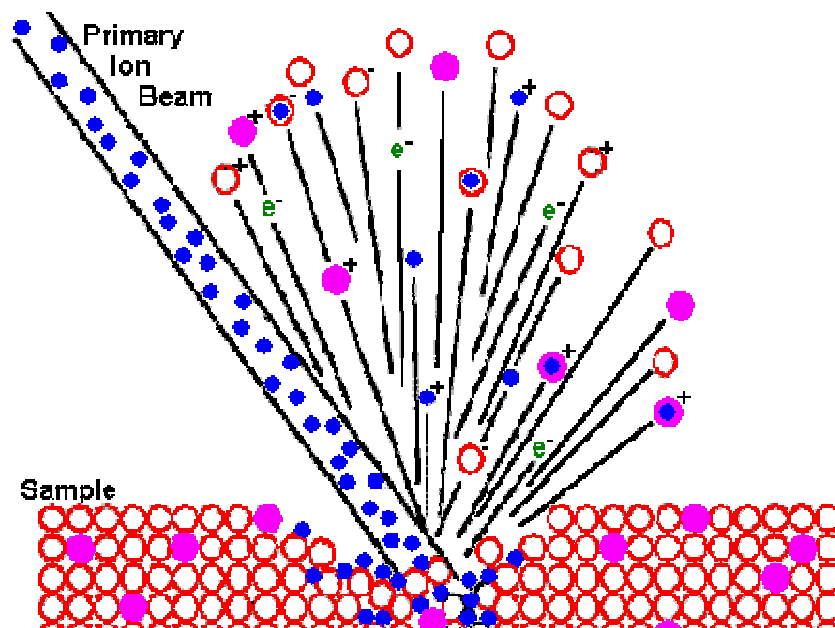


Figure 1. Schematic of the sputtering process in SIMS.

Different commercial SIMS instruments use different mass analyzers, including double-focusing, quadrupole, and time-of-flight mass analyzers. The CAMECA ims-series SIMS instruments, for example, use a double-focusing 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. 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 ($M/\Delta M$) on a CAMECA 3f-7f instruments, for example, is variable from approximately 300 to 20,000, depending on the instrument settings.

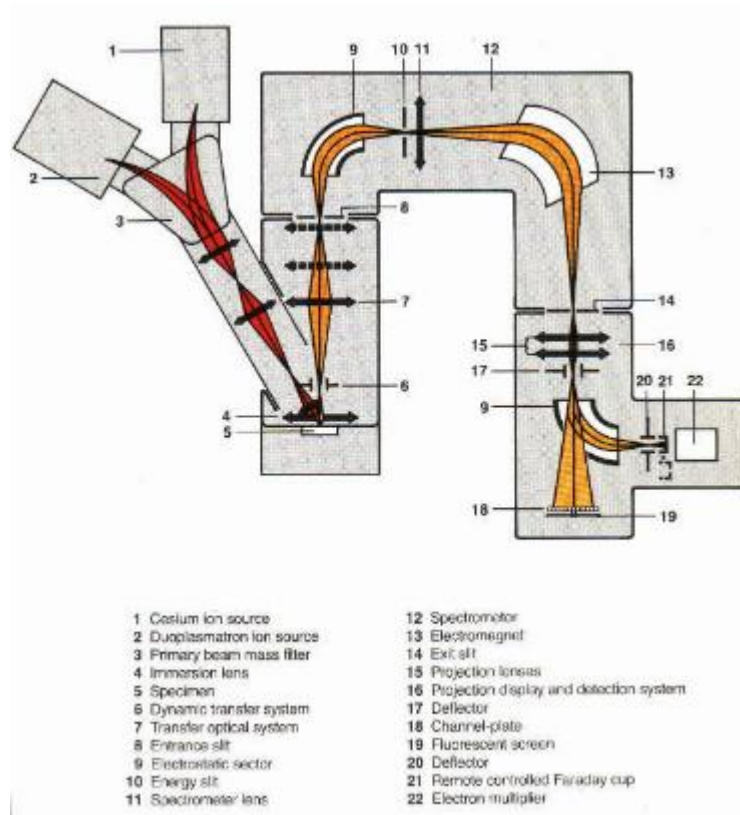


Figure 2. Schematic diagram of a CAMECA ims-4f SIMS instrument.

In addition, most of the CAMECA 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 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 through the use of relative sensitivity factors (RSF's). RSF's are determined through the analysis of standards similar in elemental composition to the sample of interest. The RSF's for a given element can vary over 5-6 orders of magnitude, so appropriate standards are necessary for accurate quantification.

Standards of two general types are used to determine RSF's 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 analysis by other, usually multiple, 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, RSF's 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 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, e.g., the analysis of Si when HF has been used during the sample dissolution process. SIMS may also be the technique of choice for electro-negative elements (C, N, O, F, Cl, S) for which ICPMS 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 for the CAMECA NanoSIMS 50. Plots of isotopic or elemental abundances versus lateral position are called "images" or "maps."

In addition, 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 (Z) can be calculated. Plots of isotopic or elemental abundances versus depth are called "depth profiles."

3. SAMPLE REQUIREMENTS

SIMS can only be used to analyze solid samples. 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 onto an appropriate substrate that fits into the instrument's sample holder.

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., $^{40}\text{K}^+$ and $^{40}\text{Ar}^+$ in the measurement of $^{40}\text{Ca}^+$, the analysis can also suffer from interferences from molecular ions of the same nominal mass, e.g., $^{28}\text{Si}^{16}\text{O}^+$ and $^{12}\text{C}_3\text{H}_8^+$ in the measurement of $^{44}\text{Ca}^+$. 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 mass filtering of the primary ion beam and improved sample chamber vacuum.

5. FAQ

- Cost: SIMS instruments typically cost several million US\$ and require at least one fully trained operator. There are companies that provide commercial SIMS services, although many of these will not analyze nuclear material. The typical cost for a SIMS analysis from one of these companies will be in the range of a 300-500 US\$
- SIMS is an extremely sensitive analytical technique, so sample-handling practices that avoid sample contamination or cross-contamination are essential.
- 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 RSF's. 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 non-uniform substrate will cause time variation in the ion signal. Since deadtime correction schemes assume a relatively constant ion signal over the time of measurement, 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 the CAMECA 3F instruments, 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 artefacts, 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

[1] R. G. Wilson, F. A. Stevie, and C. A. Magee, "Secondary Ion Mass Spectrometry: A Practical Handbook for Depth Profiling and Bulk Impurity Analysis," John Wiley & Sons, New York, 1989.

[2] A. Benninghoven, F. G. Rüdener, and H. W. Werner, "Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications, and Trends", John Wiley & Sons, New York, 1987.