

Practical Comparisons Between RF-GD-OES and SIMS

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Keywords: method comparison

Secondary ion mass spectrometry (SIMS) has been a very valuable tool for the analysis of bulk materials, particularly in the cases where very high sensitivity is required (e.g. precious metals, catalysts and semiconductor materials). SIMS relies on high energy (2-5 keV) bombardment (sputtering) of the sample using an ion beam (gun) in high vacuum ($< 10^{-7}$ Torr) as its means of removing material from the solid surface and mass analysis of those species which are ejected as charged species (ions).

Radio frequency glow discharge atomic emission spectrometry (RF-GD-OES) is similar to SIMS in that sputtering is the means of removing material from the sample surface. In contrast, though, the glow discharge is a reduced-pressure (10 Torr) plasma that generates the sputtering ions in situ from a low flow of argon. These ions are attracted to the sample (cathode), arriving with kinetic energies of ~ 100 eV. The respective ion currents, in the microampere range for SIMS and ~ 1 ampere for the RF-GD-OES, result in much greater ablation rates for the latter, mm/min vs. nm/min. On the other hand, the analyte detection efficiency for SIMS is orders of magnitude higher than for the photon production/collection in RF-GD-OES. Thus, very high absolute sensitivities may be achieved with SIMS. The combination of slow erosion and high detection efficiency results in SIMS limits of detection (LOD) that are usually expressed in units of atoms/cm³ or monolayers, while the RF-GD-OES LODs are expressed in terms of ppm. On a weight percent basis, SIMS detection limits are on the order of ppb-ppm, across the periodic table, while the RF-GD-OES has more limited elemental coverage (depending on the instrumentation and elemental sensitivities).

Other than the fundamental differences between SIMS and RF-GD-OES, there are more important practical differences which will deter-

mine the appropriateness of the two methods. These differences are described below.

1 Analysis time

Because of the need for extremely low pressures for SIMS analysis, extensive pump down times are required. For many analyses, pump down times of more than 1 hour are common. It is important to realize that the presence of residual gases (N or O) on the sample surface greatly effect the performance of the SIMS experiment, both in terms of absolute sensitivity and in the relative sensitivity between the elements. For this reason, sample carousels containing many samples are usually loaded in the source volume at a single time. On the other hand, even in the case of gaseous element analysis, the RF-GD-OES pump down time is more on the order of 1 minute. The actual ion beam sputtering time for SIMS analysis is typically 15 minutes to 1 hour, depending on the desired sensitivity. With a simultaneous spectrometer, RF-GD-OES analysis times are typically less than 5 minutes.

2 Complexity of instrumentation

The need for very high vacuum integrity and the great number of contamination/matrix effects require a great deal of operator sophistication. Most SIMS instruments are operated by professional scientists, not technicians. Conversely, the RF-GD-OES instrument can be operated by a skilled technician.

3 Elemental coverage

A SIMS analysis produces ions from all of the elements present, with the mass analyzer being able to detect all masses (isotopes). In this way, SIMS offers complete elemental coverage in any

analysis. Alternatively, RF-GD-OES must employ a scanning monochromator which can access a wide wavelength range (VUV-NIR) to cover the most sensitive transitions for each element. Of course, if a polychromator is employed, there must be a PMT positioned for each element to be determined.

4 Quantification

In SIMS analysis, the elemental sensitivities vary by many orders of magnitude, and are sensitive to matrix identity and experimental conditions. For this reason, very strict matrix matching is required for quantification. Calibration curves are not used in SIMS, relative sensitivity factors (RSFs) are generated from standards. On the other hand, RF-GD-OES can use similar matrix standards to generate calibration curves which may, or may not, need to be run very often. The quality of quantification in RF-GD-OES is less sensitive to contaminants than SIMS.

5 Sensitivity

When talking about sensitivity in SIMS and RF-GD-OES, the key point is knowing whether elemental (bulk) concentration is the frame of reference or if elemental coverage is important. The difference is that SIMS removes a very small amount of material from a small region (mm^2) whereas RF-GD-OES is truly a bulk sampling method. With SIMS, the operator gets very good information about a specific point, which may be the primary interest as this is a microscopic method, but inhomogeneities in bulk materials will be greatly amplified. For common transition metals, the bulk sensitivity is not much different.

6 Cost

As with any analytical method, the initial capital costs depend on the level of sophistication built into a particular system (e.g., a polychromator is more complex than a monochromator). In general, the most basic SIMS instrument will be much more expensive (>2X) than the analogous OES system. It is usually the case, though, that the SIMS instrumentation will be part of a larger apparatus which also involves scanning electron microscopy (SEM), Auger electron spectroscopy (AES), and the like. A 'stand-alone' SIMS instrument is seldom what a person buys. Therefore, the key to the justification of the cost of a RF-GD-OES system is that its unique capabilities can be shown to justify the expense of an additional analytical system.



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