

**ADVANCED ANALYTICAL INSTRUMENT FACILITY FOR ANALYSIS OF RETURN SAMPLES FROM NASA SPACE EXPLORATION MISSIONS.** I. V. Veryovkin, W. F. Calaway, C. E. Tripa and M. J. Pellin, Materials Science Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, U. S. A., e-mail: verigo@anl.gov

**Introduction:** Chemical analyses of samples returned to Earth by space exploration missions, such as Genesis and Stardust, have one common feature even if they are conducted with very different analytical techniques: the samples are unique and irreplaceable. They belong to the class of *atom-limited samples* because the amount of sample material available for analysis is finite. Isotopic analyses of these samples are particularly challenging because they either alter or consume/destroy the precious samples. Under these conditions, minimized sample consumption by the analysis is extremely important. A key figure of merit of the analytical technique to be implemented in such cases is useful yield, the number of atoms consumed by the analysis divided by the total number of atoms available in the sample.

Resonance Ionization Mass Spectrometry (RIMS), a variant of Laser Post-Ionization (LPI) Mass Spectrometry (MS), became the technique of choice for many elemental and isotopic analyses because of its unique selectivity and high efficiency. To conduct analyses of samples delivered by NASA's Genesis mission, a new instrumental facility based on this method has been constructed at Argonne National Laboratory. A newly developed LPI MS instrument forms the core of the facility, which also includes a variety of advanced lasers for post-ionization.

**Experimental:** The new instrument inherited its name from a decommissioned instrument, SARISA, (Surface Analysis by Resonant Ionization of Sputtered Atoms), to emphasize our continued commitment to developing analytical methods based on the synergy of mass spectrometry with laser post-ionization. The new generation SARISA [1] was specifically designed to minimize sample consumption during laser post-ionization analyses. This design has been perfected by advanced three-dimensional computer modeling. First, a "virtual reality" computer model of the instrument ion optics was developed with SIMION 3D software and thoroughly tested and optimized. When estimated analytical capabilities of the instrument met the requirements, another computer model, this time with Computer Aided Design software, AutoCAD 3D, was developed and optimized for the actual hardware that included all ion optics and all vacuum and mechanical components. In 2005, the construction of the new SARISA with all planned components was completed,

the instrument became fully operational, and analyses of Genesis samples began [2].

Here we briefly describe the features of SARISA that make it uniquely suitable for *analyses of the atom-limited samples*.

Neutrals are the predominant species in ion sputtering and laser desorption, two most efficient microprobe methods that convert sample surface material into analyzable gas phase atoms and molecules. LPI efficiently converts these ion sputtered or laser desorbed neutrals into ions. SARISA combines this capability with very efficient extraction of photoions from large photoionization volumes ( $\sim 30 \text{ mm}^3$ ) and their delivery to the ion detector through a time-of-flight (TOF) reflectron-type mass spectrometer (mode #1 in Fig.1). The overall transmission of ion optics in this regime is about 95%. This results in a remarkably high useful yield for the SARISA instrument, exceeding 20% in many cases, which permits analyses of samples containing very small numbers of atoms of interest [1].

SARISA can use both Single Photon Ionization (SPI) and Resonantly Enhanced Multi-Photon Ionization (REMPI) of secondary neutrals. Each method has certain advantages, and the availability of them both widens the range of analytical applications. SPI can be performed using excimer (ArF at 193 nm) or F<sub>2</sub> (157 nm) laser light, which allows simultaneous detection of most elements in a sample. REMPI can be performed using a set of tunable Ti-sapphire solid-state lasers, which allows selective detection of one element of interest while greatly reducing isobaric interferences. In the REMPI mode, trace analysis at the part per trillion levels is possible with SARISA.

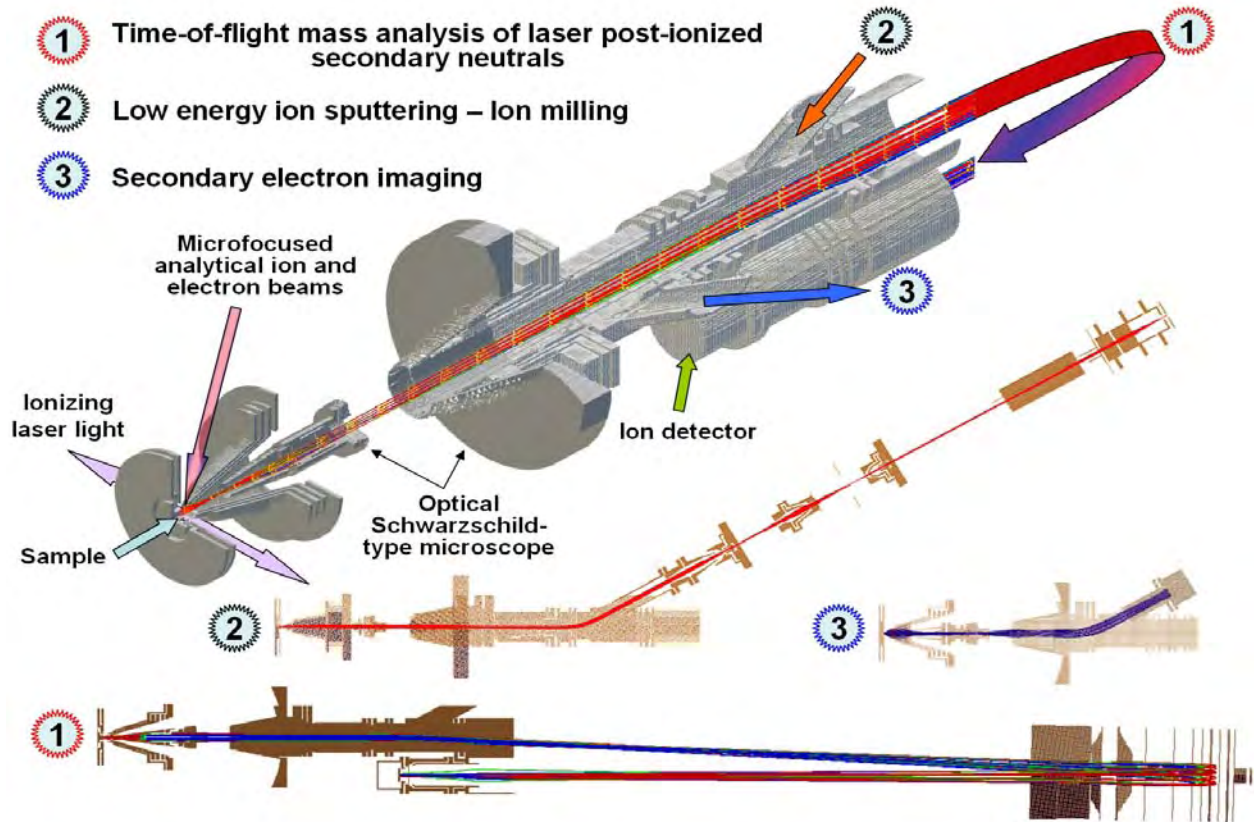
The analytical spot size of the *laser microprobe* of about 0.5  $\mu\text{m}$  has been achieved in SARISA by incorporating a high-resolution optical microscope of the Schwarzschild-type into the extraction ion optics (Fig.1). This in-vacuum optical microscope also enables real-time in-situ sample imaging during analyses.

Samples in SARISA are mounted on a unique positioning stage (XYZ-translations plus one rotation) that can maintain better than 50 nm closed loop precision for travels of up to 50 mm.

The analytical spot size for the *ion microprobes* in SARISA depends on the type of ion gun chosen for a particular analysis: currently, this parameter lies in the range of a few  $\mu\text{m}$  with the installed Atomika WF421

gas ion source, and it can be smaller than 50 nm with a liquid metal ion source. One such ion source will be soon installed on SARISA whose main vacuum chamber can simultaneously accommodate up to five analytical ion and electron guns pointed at the sample 60° from normal to its surface.

generally called *dual-beam analysis*, enables three-dimensional sample characterization with the highest spatial and depth resolutions possible. This is because each beam is independently optimized for its application. Zero incidence angle of the ion milling beam in SARISA permits attenuation of the ion impact energy



**Figure 1. Trajectories of photo-ions (1), low energy primary ions (2), and secondary electrons (3) in the SARISA instrument for three different operating modes.**

The second analytical gun currently installed on SARISA is a VG LEG1000 *electron microprobe*, whose small beam spot size (~100 nm) enables high resolution secondary electron (SE) imaging of the sample. This operating mode (#3 in Fig.1) is possible because an additional dedicated detector of secondary electrons is incorporated into the instrument ion optics. Once the liquid metal ion gun is installed, the spatial resolution of the SE imaging will be below 50 nm. One additional application envisioned for the microfocused electron gun in SARISA is electron-stimulated desorption (ESD) of neutral molecules and atoms.

In addition to these analytical guns, the SARISA instrument also incorporates a dedicated primary ion column for surface cleaning and ion milling by low energy ion sputtering at normal incidence angle. A Colutron ion source is used in this operating mode (#2 in Fig.1). The combination of the low energy sputtering with ion, electron or laser microprobes, which is

from 2000 eV all the way down to the sputtering threshold. Since for normal incidence ion bombardment there is virtually no increase in surface roughness, the resolution of one atomic layer is feasible for depth profile analyses in SARISA.

**Conclusion:** The ultimate goal of our development efforts was to be able to perform *quantitative* three-dimensional mass spectrometric analyses of *atom-limited samples*. SARISA currently provides the sensitivity and the spatial and depth resolutions needed for analyses of samples delivered by Genesis and Stardust spacecraft.

**Acknowledgements:** This work is supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38, and by NASA under Work Orders W-19,895 and W-10,091

**References:** [1] Veryovkin I.V. et al. (2005) *Nucl.Instr.Meth.B*, 241, 356. [2] Calaway W. F. et al. (2006) *LPS XXXIII*, Abstract #1814