

LASER SETUP MULTI-ELEMENT RIMS ANALYSIS OF GENESIS RETURN SAMPLES.

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Resonance Ionization Mass Spectrometry (RIMS), being the combination of Resonance Multi-Photon Ionization (RMPI) and Mass Spectrometry (MS), is a well-known and widely used method in trace analysis of materials [1]. It has excellent sensitivity and atomic selectivity (or specificity) and is one of the methods of GENESIS mission sample analysis. However the experimental arrangement of RIMS imposes technical limitations on the number of elements being analyzed simultaneously in single experiment. The problem is that the resonance ionization process requires at least two independent photons of different wavelengths for each element. Taking into account that the tunable light sources commonly used in RIMS technique are Ti:sapphire or dye lasers, and that they also require pumping lasers, the complexity (and the cost) of the laser system dramatically increases with the number of elements that need to be detected in given experiment. Therefore, it is a common experimental situation that only one element is detected/analyzed in each RIMS experiment. This limitation does not pose a problem when the amount of species for the analysis is not limited or when there is only one element to be detected. The opposite situation arises in case of strong indigence of supplied samples because in RIMS analysis the samples are consumed during experiment and, despite this amount can be very small it may create a problem. This situation is typical for space exploration where the samples returned to Earth are non-renewable. Thus, the development of new versatile RIMS methods which increase the number of studied elements in each experiment without a significant cost increase and complexity of the instrument is one of our goals. In this abstract we demonstrate the experimental setup for multi-element (Mg, Ca, and Cr) analysis of implanted Solar Wind in GENESIS collector materials and discuss the possibility of using this approach to measure other sets of elements, as well as potential problems.

It is well known that a RMPI process consists of at least two steps: the first is the resonance photo-excitation of atom to the excited state ($A \xrightarrow{h\omega_1} A^*$), and the second is the ionization ($A^* \xrightarrow{h\omega_2} A^+$). To get the best ionization efficiency, both ω_1 and ω_2 have to be finely tuned and, therefore, at least two separate tunable lasers are required for each element. However, it is possible to sacrifice the ionization efficiency and to use a photon energy different from optimal one on the second step.

It is a rather common approach which allows experimentalists to reduce the number of lasers. This idea was implemented in our SARISA instrument [2] to get RIMS analysis of three elements (Mg, Ca and Cr) in single experimental round. The laser beam configuration is shown in Fig.1. Two DPSS lasers (Photonics DM40) were used to pump four independent Ti:sapphire laser cavities. Each cavity has a Q-switch which is individually triggered to synchronize the excitation and the ionization laser pulses in time. The output radiation of the Ti:sapphire lasers was frequency doubled (or tripled) to obtain the required photon energies for the atomic transitions. All four laser beams directed at the analysis (photo-ionization) volume above the sample can be collinearly overlapped, by using beam splitting (dichroic) mirrors, and focused by a fused silica lens right above the target to optimize the power density. To increase the ionization efficiency, the laser beams were reflected back to the ionization volume by using a prism retroreflector (double-pass configuration). The high-power density beam cross-section at the target is approximately round, with a diameter of ~ 0.9 mm.

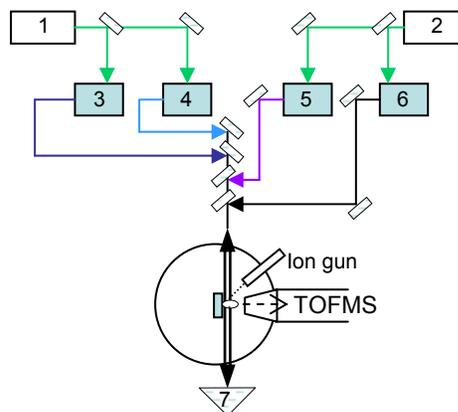
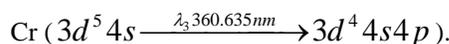
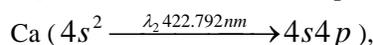
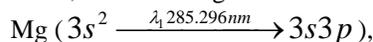


Fig.1. Optical scheme of multi-element RIMS: 1,2 – pumping DPSS lasers, 3-6 Ti:sapphire lasers, 7 – Porro prism retroreflector.

To convert sputtered ground-state atoms into excited states, the following transitions were used:



The laser pulse energies for each wavelength were: $E_{285}=45\mu\text{J}$, $E_{360}=275\mu\text{J}$, and $E_{422}=38\mu\text{J}$. The threshold

ionization wavelengths from the above excited states are: $\text{Mg}^* \rightarrow \text{Mg}^+$ ($\lambda < 375.24 \text{ nm}$), $\text{Ca}^* \rightarrow \text{Ca}^+$ ($\lambda < 390.8 \text{ nm}$), and $\text{Cr}^* \rightarrow \text{Cr}^+$ ($\lambda < 374 \text{ nm}$). It is clear that two colors (λ_1 and λ_3) can be utilized in the ionization step. It is well-known that, for atoms with one valence electron, the photoionization cross-section is a monotonic decay function, whereas for elements with a more complex electronic structure the cross-section function may have maxima and minima which may vary orders of magnitude [3]. Therefore, because none of the resonance wavelengths exactly matches the ionization thresholds, we could expect that the overall ionization efficiencies would not be optimal but still have acceptable values.

For the laser beam parameters mentioned above, the overall SARISA instrument useful yields for Mg, Ca and Cr were: $Y_{\text{Ca}} = 11\%$, $Y_{\text{Mg}} = 5.5\%$, and $Y_{\text{Cr}} = 1.1\%$, as determined on standard reference materials of certified Mg, Ca, and Cr concentrations. Taking into account that the previously reported maximum useful yield for the SARISA instrument was $\sim 20\%$, we can estimate the ionization efficiencies as 55%, 28%, and 5.5% for Ca, Mg, and Cr, respectively.

It needs to be pointed out that we did not saturate the RIMS signal for any of the elements, which means that any change in the laser power will result in a change in the ionization efficiency. Nevertheless, we performed successful depth profiling of Si implants as well as returned GENESIS samples. An example of simultaneous Ca, Mg and Cr depth profiles obtained in single RIMS experiment is shown in Fig.2. GENESIS returned samples analyzed this way are shown in an accompanying abstract [4].

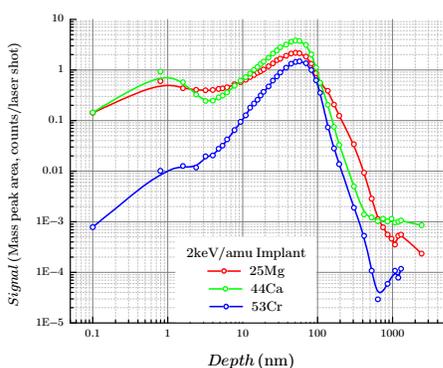
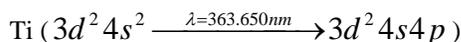
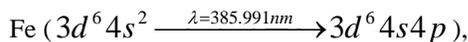
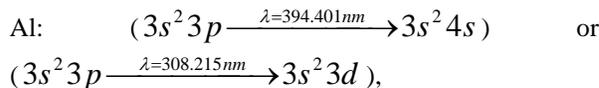


Fig.2. Three-element RIMS depth profiles of Mg, Ca, and Cr implanted in a Si matrix.

In the three element RIMS analysis presented here only three tunable lasers were employed. The fourth, available tunable laser could be used for the ionization

of an additional element. Below, we indicate possible elements and transitions:



The multi-element RIMS analysis has its own limitations. The use of two-color scheme sometimes requires laser radiation in the UV range for either the excitation or the ionization step (Mg is a typical example). The presence of UV photons results in unwanted ionization of other sputtered species which may interfere with the atoms of interest. For example, the silicon dimer ion Si_2^+ (56 amu) masks the iron main isotope ^{56}Fe , whereas the SiO^+ ion, that we also detected in our mass spectra, interferes with the ^{44}Ca isotope. It needs to be pointed out that for the carbon or sapphire substrates this problem does not exist. Thus the application of multi-element RIMS for the analysis of GENESIS or other space samples has undoubted advantages but requires the detailed analysis of experimental situation.

References: [1] Parks J. E. (1990) in: *Lasers and Mass Spectrometry*. Ed. By D.Lubman, N-Y. [2] Veryovkin I.V. et al. (2004) *Nucl. Instr. Methods Phys. Res. B*, 219-220, 473-479. [3] Letokhov V.S. (1987) *Laser Photoionization Spectroscopy*, N-Y. [4] Veryovkin I. V. et al. (2012) *LPS XVIII*, Abstract #2296.

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