

A MINIATURIZED LASER ABLATION MASS SPECTROMETER FOR SPACE RESEARCH.

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Introduction:

The Laser Ablation Time-Of-Flight Mass Spectrometry (LA-TOF MS) is a well accepted method for the acquisition of chemical composition of solid materials. Miniaturized LA-TOF MS's have recently been developed for space research and are considered to be an important part of the instrumentation dedicated to study planetary surfaces[1-4]. They offer rapid analysis of the entire elemental and isotopic composition of well spatially resolved (10-50 μm) sections of the surface without needing further sample preparation. High spatial resolution (i.e. lateral and vertical) can be achieved providing opportunities for in-depth profiling and microanalysis (e.g. identification of individual mineral grains by means of elemental composition). Additionally, the detection of trace elements, namely rare earth element fractionation patterns, can provide further information on the nature of planetary formation and differentiation. Knowledge of the isotopic composition, including the use of age determination methodology, offers also great opportunities in planetary search for life. Biologically related isotopic fractionation effects have been well investigated in various terrestrial environments. The detection of such fractionation effects on surfaces of other planetary bodies can provide important information for potential life activities. These data are of particular interest in the investigation of the origin and evolution of the Solar System.

Instrument and Results:

Here we describe and present initial results on the current performance of a Laser Ablation TOF Mass Spectrometer (LMS) developed in our group. The instrument is a small size reflectron-type time-of-flight mass spectrometer specifically developed for the application to space research (Figure 1) [3]. It has been carefully designed by taking into account the results achieved from detailed simulation of ion trajectories. [3]. The current dimensions of the instrument are 120 mm length \times 60 mm \varnothing . The flight instrument will be slightly larger and will combine laser and electronics. Nevertheless, the weight will not be larger than 1.5 kg.

To determine the capabilities of our instrument including mass resolution, sensitivity and the ability for quantitative analyses, mass spectrometric measurements were performed using NIST Standard Reference Materials (SRM) for iron (SRM 661, 664, and 665), minerals and meteorite samples. The primary purpose for the use of the NIST standard reference materials was to investigate the detection sensitivity and quantitative capabilities of our analyzer.

The ablation of the material surface to be analysed was performed by either a IR (1064 nm) or UV (266 nm) laser beams focused to spots of 15-20 μm and performed over irradiances in the range of 0.1 to 1 GW/cm^2 . At these experimental conditions high temporal stability of ion formation and a low sample consumption was achieved and highly averaged mass spectra (up to 64'000 waveforms/spectra) could be measured with typical mass resolution of $m/\Delta m \sim 600\text{-}800$. The extended dynamic range of the spectrum spanning 10^7 is achieved by recording a high gain (HG) and low gain (LG) mass spectrum. A LG spectrum covers mass peaks of major and minor elements and HG spectrum -of minor and trace elements.

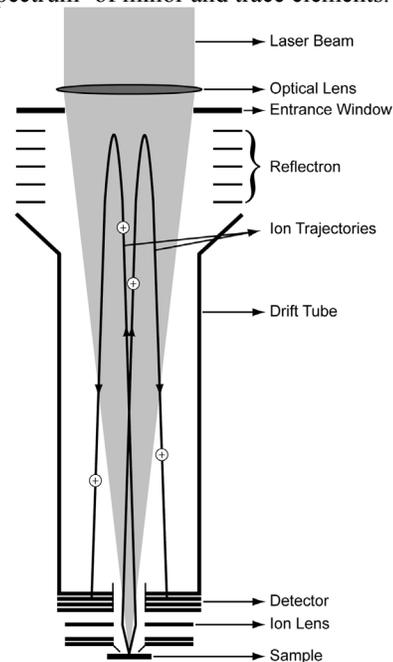


Figure 1: Schematic representation of the laser ablation mass analyzer. Laser beam is introduced through the window placed on the top of the reflector and focused on the sample by an optical lens. The ions generated in the ablation process are collimated by an ion lens, separated according to their mass to charge ratio in the mass analyzer, and finally detected by a Multichannel Plate (MCP) detector.

The studies of SRM samples by IR-laser ablation yielded semi-quantitative results. The analysis of the elemental composition showed considerable differences between the abundances reported by NIST and the experimental values were noticed. [5]. Although the detection of several trace elements present in SRM

samples can be achieved at the \sim ppm level (e.g., Hf, Pr, Hf in SRM 661), the abundances of light elements and elements characterized by high ionization potential (IP) were sometimes hundred times lower than their quoted values. The measurements of the isotopic composition can be, in general, reproduced with \sim 1% accuracy. Significant improvements of the instrumental performance have been achieved using an UV-laser beam. Our initial studies of NIST standards (SRM 661, 664 and 665) show improvements of the quantitative performance and better detection efficiencies of light elements (e.g., C, Si and S). The measurements show also that by the application of UV-laser ablation a considerable reduction of clusters can be achieved. The clusters of major elements were readily formed when IR-laser beam was used.[5]

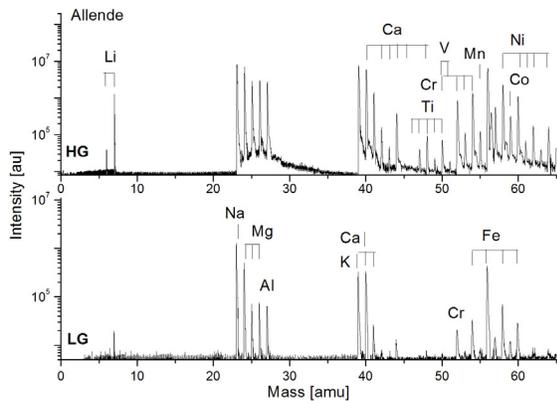


Figure 2: Portions of mass spectra of a matrix component of Allende meteorite. The effective dynamic range of the mass spectrum is 10^6 after combining the spectra recorded in high gain and low gain channels.

The studies of minerals (e.g., galena) and meteoritic samples (e.g., Allende) were conducted on raw unprepared samples. The measurements could be conducted at similar experimental conditions as for SRM samples and similar dynamic range of the spectra and mass resolution were achieved. The analyses of mass spectra yield a major, minor and trace elements concentrations. [5] Although only semi-quantitative analysis could be conducted using IR laser, improvements to the quantitative analysis are expected by using UV laser. These studies are currently under way in our laboratory and we will present the results at the meeting.

Figure 2 shows a section of the mass spectrum of a matrix of carbonaceous chondrite meteorite, Allende, ablated by IR-laser beam. Table 1 compares the relative elemental abundance of metallic elements determined from the measured mass spectrum with the results obtained by other methods [5, 6]. The differences between measured and reported values are likely

due to the semi-quantitative performance of the mass analyzer. A small abundance of vanadium, which has not been reported in the literature for the Allende meteorite, could also be measured.[6] This and other meteoritic materials are currently being re-investigated using the UV-laser.

Table 1: Relative abundances of metallic elements determined in studies of Allende meteorite. The results are compared with literature reports .[5, 6]

Element	cat % [6]	Quoted El/Fe [6]	Exp El/Fe ($\pm \sigma$)
Ti	0.045	0.0044	0.0013 (0.0005)
V	—	—	0.0003(0.0001)
Cr	0.16	0.016	0.0542(0.008)
Mn	0.061	0.0059	0.0052(0.0007)
Fe	10.25	1.0	1,0(0.040)
Ni	0.57	0.056	0.1817(0.03)
Co	0.025	0.0025	0.0015(0.0008)

The performance studies of a miniaturized laser ablation reflectron-type time of flight mass spectrometer (LMS) show its high sensitivity in the detection of elements (\sim ppm). An increase of the dynamic range of recorded signals (\sim ppb) seems still to be possible by taking into account developments in detection technology (more sensitive detectors, multichannel detection). The investigations can be performed for any kind of solid state materials. A semi-quantitative performance is achieved using IR-laser beam, but current studies applying UV-laser are more encouraging and demonstrate improvements in the detection efficiency for low-mass elements and almost total absence of the interfering molecular clusters in the measured mass spectra. The investigations of silicate and other minerals are currently in progress in our laboratory.

The test results prove that LMS can be a powerful instrument in the investigation of the composition of airless surfaces of asteroids, planets, and their moons by both *in situ* and sample return-missions. Simplicity of operation, low power consumption and robust design make them advantageous over other analytical instruments considered for planetary exploration.

References:

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