

A miniature laser-ablation time-of-flight mass spectrometer for sub-ppm analysis of planetary surfaces

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Abstract

The performance of a laser ablation mass spectrometer (LMS) developed in our group for planetary research will be demonstrated. From the measurements of elemental and isotopic composition of the NIST reference samples the detection limit of ~100 ppb was determined. LMS can be considered quasi-quantitative for the measurements for most elements [2] using relative sensitivity coefficients (RSCs) for each species that have been established in prior calibrations. The quantitative detection of the lighter elements (e.g., C, P, S) is less accurate since the RSCs are larger. The isotopic fractionation effects are found to be negligible and the error in their determination is generally smaller than 1 %. In studies of minerals and meteoritic materials, the elemental composition of major, minor and trace elements can be obtained together with their isotopic pattern proving that this approach can be powerful in the investigation of the composition of airless surfaces of asteroids, planets, and their moons on in situ and sample return missions [4].

1. Introduction

Time-of-flight mass spectrometers (TOF MS), based on pulsed laser ion sources are of considerable interest for landed missions to Mars, asteroids, comets, and planetary moons. The mass spectrometric analysis can provide both elemental and molecular composition of the material including the grain-scale and bulk major, minor, and trace composition with minimal sample manipulation and preparation. These informations are of particular interest because they can be used to investigate the origin and evolution of solar system objects.

2. The LMS Instrument

The LMS instrument is a small size reflectron-type time-of-flight mass spectrometer specifically developed for the application to space research [1]. The total dimension of the instrument is 120 mm x

60 mm (length x diameter). A flight instrument would be somewhat longer since the laser electronics will be accommodated in a compartment above the ion mirror. The anticipated weight of the flight unit would be about 500 g including all electronics [1]. LMS has been carefully designed by taking into account the results achieved from detailed simulation of ion trajectories. In present setup the mass analyser is coupled with 1064 nm output of Nd:YAG laser, which is used for the ablation and ionisation of NIST standard materials and natural samples. Other wavelengths and laser systems are under investigation.

The mass spectrometric measurements can be prepared with a high resolution exceeding $m/\Delta m = 800$ (see Figure 1 for lead isotopes). Sample charging effects during the laser ablation process and other effects (e.g., space charge) are found to be negligible at the applied experimental conditions and measurements are highly reproducible.

The LMS instrument was optimised for high sensitivity to detect trace elements at the level of ppm and below. This sensitivity is achieved without special sample treatment, allowing for easy application of the LMS instrument on a space platform. Figure 2 shows two examples of element detection: at low masses the elements boron at 5 ppm (⁹B and ¹⁰B) and carbon (¹²C and ¹³C) at 0.39%, elements which usual-



Figure 1: Pb isotope series measured in the NIST 664 stainless steel sample.

ly are difficult to detect, and at intermediate masses the titanium isotopes, with 49 Ti detected at the level of 300 ppb.

Detailed comparisons of measured abundances by LMS with the NIST values were performed for two stainless steel samples (SRM 661 and SRM 664). With these measurements, shown in Figure 3, a dynamic range in excess of 6 decades is achieved for the LMS instrument. For the quantitative abundance measurements calibration factors for each element were established and typically are in the range of 0.5 to 2 for most elements, and with factors of the order of 10 for elements with high first ionisation potential [2]. The latter is a result of the long laser wavelength ($\lambda = 1064$ nm) used in this study.

Based on detection limits of ~100 ppb the *in situ* age determination via 207 Pb/ 206 Pb system, albeit with limited accuracy, becomes possible with such an instrument for minerals where Pb is in the ppm range. For example, Figure 1 shows a measurement of the



Figure 2: Low-mass section of mass spectrum from NIST SRM 661 sample, and, bottom panel, Ti, Cr, and V isotopes in the NIST SRM 665 sample.

lead isotopes at 67 ppm lead in the NIST SRM 664 sample, where even ²⁰⁴Pb at 1.4% of the Pb (corresponding to 0.94 ppm total) can be identified in the measurement. Even though laboratory measurements are of higher accuracy, such *in situ* age determinations are nevertheless is of great value in planetary science [3].



Figure 3: Comparison of the elemental abundances measured with the LMS instrument with the abundances given by NIST for two stainless steel samples SRM 661 and SRM 664.

References

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