

TRACE ELEMENT LASER ABLATION ICP-MS IN $\text{Li}_2\text{B}_4\text{O}_7$ FUSED GEOSTANDARDS CALIBRATED WITHOUT MATRIX-MATCHED STANDARDS

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ABSTRACT

Laser ablation ICP-MS has been used as a complementary technique to electron microprobe and XRF. The determined values are compared with different reference values, measured using XRF and solution nebulization ICP-MS. Eight lithiumtetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) fused geostandards were analysed using LA-ICP-MS. The deviation of the measured concentration in comparison to certified or recommended values demonstrate the potential of laser ablation-ICP-MS for trace element determinations. Limits of detection, reproducibility, deviation from reference values, as well as possible error sources are presented.

INTRODUCTION

Routine analysis of major, minor, and few trace elements in rocks and minerals are mainly carried out by XRF [1] and solution nebulization ICP-MS. The sample digestion procedures for solution nebulization ICP-MS of geological materials (rocks, minerals and soils) are particularly problematic, time-expensive and often inaccurate. For this reason, alternative and precise instrumental procedures for routine trace element (e.g. rare earth elements) analysis are of paramount interest. LA-ICP-MS has turned out to be an accurate determination of elements [2-3] with barium as the internal standard and matrix-matched calibration. An excimer laser ablation ICP-MS system has been used to investigate the ablation behaviour of Li-tetraborate glasses in comparison to reference glass standards (SRM 612 and SRM 610 from NIST) for non-matrix matched calibration capabilities for quantitative multi-element analysis.

EXPERIMENTAL

Preparation of $\text{Li}_2\text{B}_4\text{O}_7$ fused bead technique used for XRF and Laser Ablation ICP-MS analysis in geological samples

Bead fusion has been established as a valuable preparational method for eliminating the problems of particle size variation and mineralogical effects, which play a major role in X-ray fluorescence matrix effects. Automation of casting glassy beads contributes notably to the achievable accuracy, by minimizing the potential human errors inherent in manual methods. In addition, the preparation of $\text{Li}_2\text{B}_4\text{O}_7$ fused beads (1:5 ignited sample to $\text{Li}_2\text{B}_4\text{O}_7$; 4 cm in diameter and approximately 2 mm thick glassy discs) provides a high degree of reproducibility and speed; in addition, the beads are suitable for wider application in quantitative analysis of major and trace elements. $\text{Li}_2\text{B}_4\text{O}_7$ beads are time-stable, which make them very useful for recalibration procedures. This has been shown in our laboratory, which has worked with $\text{Li}_2\text{B}_4\text{O}_7$ beads for over 25 years [1]. However, surface polishing with diamond paste is required before each recalibration.

The excimer laser ablation-inductively coupled plasma-mass spectrometry system

The prototype laser system at ETH Zürich is shown in Figure 1. It is commercially available from GeoLas, MicroLas (Göttingen, Germany), and is coupled to a modified ICP-MS (Elan 6000, Perkin Elmer Inc., Norwalk, Connecticut, USA). This system was originally designed for bulk analysis, depth profiles, and fluid inclusion analysis in minerals [4]. The operating conditions of this study for the $\text{Li}_2\text{B}_4\text{O}_7$ beads are summarized in Table 1. Signals were recorded in transient mode as indicated in Figure 2. This detection mode allows a direct observation of the ablation process and contains valuable information about the sample homogeneity. For data reduction the procedure of [5] has been used. The total time of analysis was 2 minutes per single analysis and 3-5 replicates were carried out on each sample to determine the reproducibility. Silicon and/or calcium were used as internal standards for the quantification of major, minor, and trace elements.

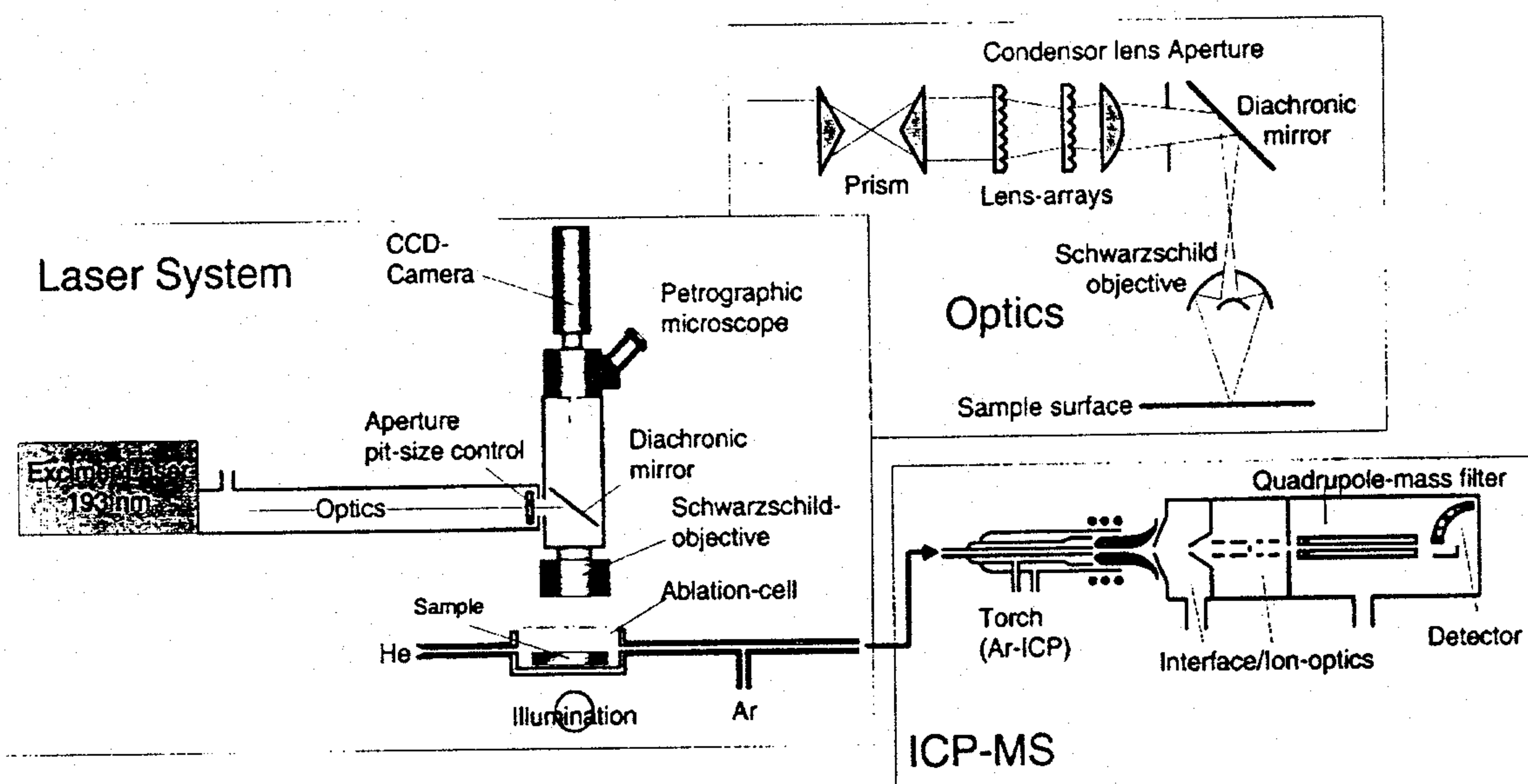


FIG. 1: Scheme of the excimer laser ablation-inductively coupled plasma-mass spectrometry system (ETH Zürich, [4]).

TABLE 1: ICP-MS working parameters.

ICP-MS	ELAN 6000 (Perkin Elmer Corp., Norwalk, USA)
Power	1.1-1.6 kW
Vacuum	$1.35 \cdot 10^{-5}$ Torr (0.75 mm cone orifice, Al-cone)
Carrier gas flow (helium)	1.2 l/min
Auxiliary gas flow	1.2 l/min
Cool gas flow	16 l/min
Quadrupole settling time	3 ms
Detector Mode	Pulse counting and Analog (Dual)
Dwell time/isotope	10 ms
Points/isotope	1
Isotopes	(max. 40 per run)

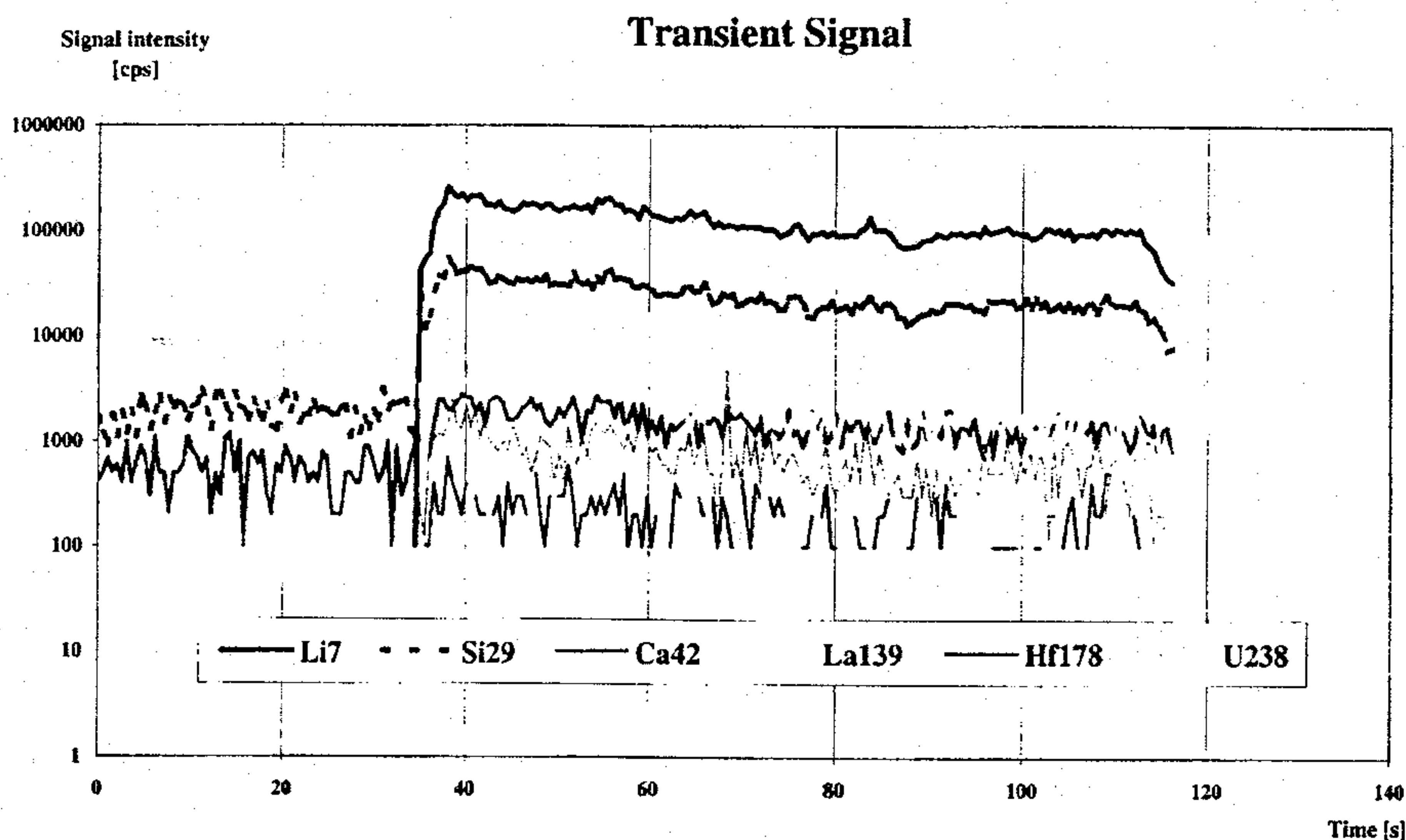


FIG. 2: Example of a LA-ICP-MS signal in time-resolved acquisition mode (AGV-1).

RESULTS AND DISCUSSION

Laser ablation ICP-MS has been used as a complementary technique to electron microprobe and XRF, and the potential of the 193 nm excimer laser has been previously described [4]. However, matrix-matched standards are often required to perform accurate analyses. Different $\text{Li}_2\text{B}_4\text{O}_7$ fused USGS (US Geological Survey) and NIM (National Institute of Metallurgy, South Africa) geostandards (basalt BHVO-1, andesite AGV-1, rhyolite RGM-1, pyroxenite NIM-P, syenite NIM-S, syenite STM-1, dolerite DNC-1, basalt BCR-1) have been analysed using LA-ICP-MS. NIST 612 (National Institute of Standards and Technology, USA) has been used as the external calibration standard and SiO_2 has been used as the internal standard for correction of the different masses ablated.

Forty isotopes, including a few major and minor elements, have been measured. The reproducibility as an expression of the quality of the fused beads was determined to greater than 5 % for most of the major and minor elements ($n = 8$, across the whole sample), and to greater than 10% for most of the trace elements above. Even concentrations of as low as 240 ng/g have been determined with reproducibilities better than 16%. An example for the achievable accuracy is shown in Figure 3 (AGV-1).

The determined values are compared with different reference values, which were measured using XRF and solution nebulization ICP-MS. The deviation of the measured concentration in comparison with certified or recommended values [7] demonstrates the potential of laser ablation ICP-MS as a complementary technique for trace element determinations. The limits of detection depend on the amount of sample introduced into the ICP-MS. The crater diameter of approx. 80 μm within the glass beads caused by the laser beam was found to be sufficient to determine concentrations as low as 100 ng/g.

It is important to note that sample preparation and the purity of the $\text{Li}_2\text{B}_4\text{O}_7$ powder used for the fusion can influence the reproducibility and the accuracy of the analysis, and need to be analysed prior to the laser analysis.

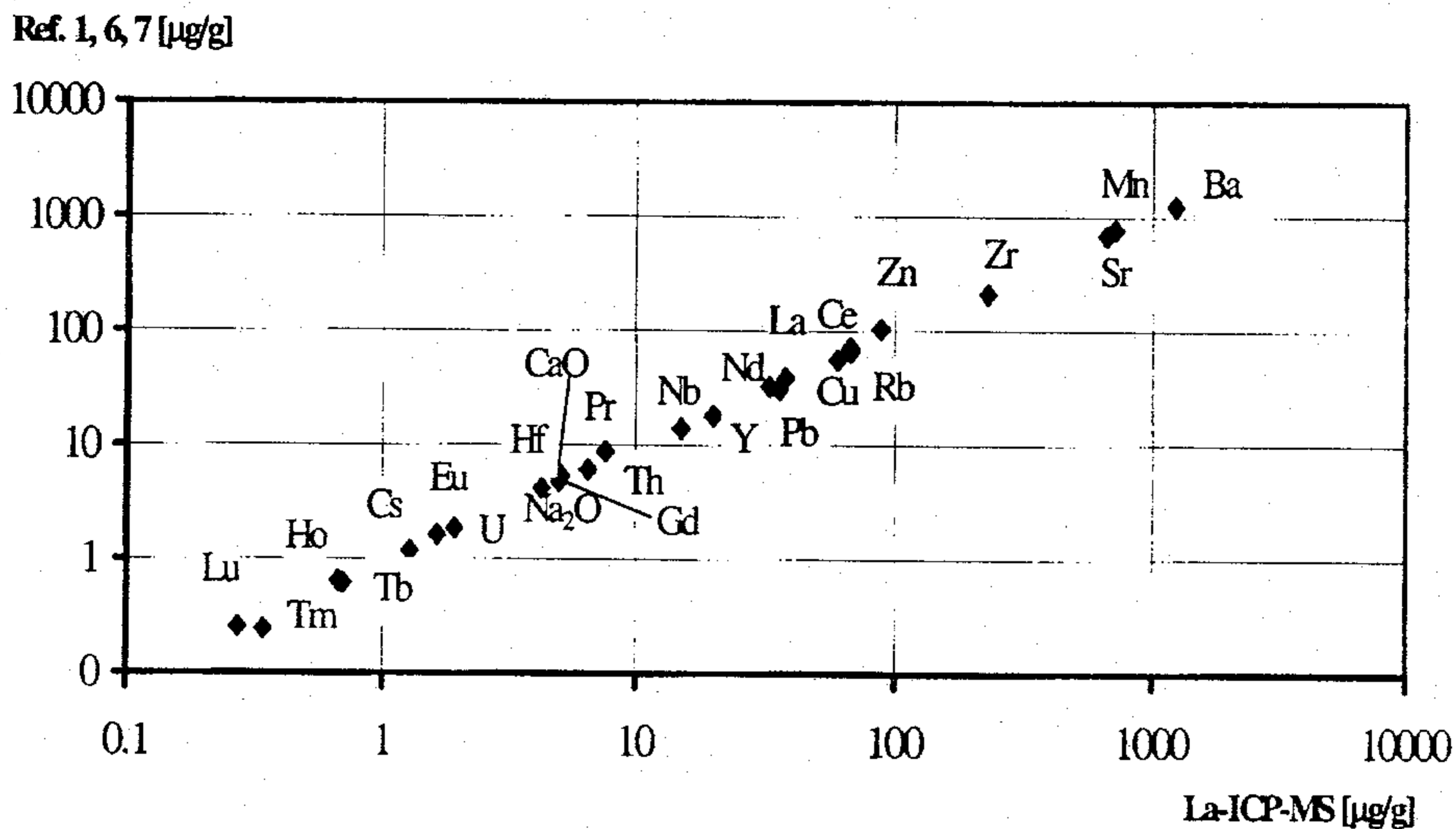


FIG. 3: Comparison of XRF data [1, 6, 7] vs data acquired with LA-ICP-MS in andesite AGV-1. CaO (4.94wt%) and Na₂O (4.26wt%).

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