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# Access to Isotopic and Elemental Composition and Their Distribution in Solid Materials by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry

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**Abstract:** Laser ablation-inductively coupled plasma-mass spectrometry is becoming a powerful analytical technique for *in situ* trace element determination and isotope ratio determination in solids.

A number of fundamental studies using a 193 nm ArF excimer and a 266 nm Nd:YAG laser ablation system were carried out to study the wavelength-dependent ablation behaviour of different materials. New optical arrangements used for the laser beam delivery onto the sample surface and increased fluency at 266 nm show tremendously improved ablation characteristics of this wavelength, especially for highly transparent samples. The investigations indicate that sample removal is wavelength- and material-dependent.

Fast signal acquisition using a new generation ICP-MS with 'Time-Of-Flight' mass analyser, permits more information to be obtained per sample run in respect to traditional scanning instrumentation. Especially when dealing with samples of small amount and large isotope menus, the capabilities of an ICP-TOFMS result in greatly improved time resolution.

The complex matrix introduction in laser ablation leads to a number of interferences, which were studied using the recently introduced dynamic reaction cell technology in ICP-MS. Gas reactions using hydrogen allow argides to be removed, while maintaining the multi-element capabilities of ICP-MS. A comparison of standard mode and DRC indicates excellent agreement between both modes of operation and demonstrates the potential of this technique for trace element analysis.

**Keywords:** Dynamic reaction cell · ICP-MS · ICP-TOFMS · Laser ablation

## Introduction

The use of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS, Fig. 1) for trace and ultra-trace element analysis in a wide variety of solid samples and liquids has steadily increased in recent years. Improved ablation characteristics offered by new ablation systems allow the controlled ablation of a wide variety of materials and the quantitative determination of more than

70 elements [1–3]. However, the ablation of highly transparent samples strongly depends on the energy density and wavelength applied to the sample and is therefore not always successful using the laser ablation systems commercially available today. The spatial resolution of the available laser systems ranges from 4 to 300  $\mu\text{m}$  and a depth resolution in the range of 60 nm per laser pulse (on sapphires) can be obtained using homogenised laser beam profiles. However, the lack of reference materials and the related non-matrix matched calibration procedures have led to studies on different laser wavelengths to improve the ablation characteristics [4][5]. For example, 193 nm excimer laser ablation systems allow controlled ablation of opaque and transparent samples and they are well

suited for non-matrix matched calibration, accurate quantification and show fewer matrix-dependent ablation characteristics [6]. Frequency-quadrupled 266 nm Nd:YAG lasers, in contrast, show significantly higher non-stoichiometric ablation (so-called elemental fractionation), which is mostly considered to be dependent on the sample material and the associated ablation behaviour. Newly developed 213 nm laser ablation systems indicate improvements in the ablation characteristics, which are assigned to improved absorption behaviour. Reduced elemental fractionation effects have also been reported [7]. To investigate the source of elemental fractionation for the 266 nm Nd:YAG laser based ablation systems an extensive investigation was carried out aimed at a better understanding of the ab-

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lation process and modification of these systems in order to improve their applicability for non matrix-matched calibrations.

The ablation process leads to analytical signals with large variations in time. The signal structure obtained for repeated laser pulses carries information about the changes of concentration in the aerosol. The amount of sample necessary to obtain qualitative, quantitative or isotopic information of a sample depends mainly on the acquisition speed and the dispersion of the aerosol during the transport into the ionisation source. These parameters were studied using an ICP-TOFMS (Fig. 2), which provides the advantage of nearly simultaneously sampling of ions and a fast sequential detection system [8]. Using this technique allows to study the aerosol, generated from single laser pulses, in its temporal behaviour with high reproducibility.

Laser ablation-ICP-MS is used as a rapid elemental analysis technique, because samples require no chemical preparation for separation of trace and matrix elements. This approach, on the other hand, may increase the problem of spectral interferences, since the entire matrix is introduced into the ion source. As a result, various interferences can occur, which limit the access to individual elements. High resolution sector field instruments or cool plasma operation conditions can help to overcome these interferences. The latter approach in fact leads to other problems, such as reduced acquisition speed or reduced ionisation efficiency for multi-element analysis. In addition, the spectral resolution provided by currently available instrumentation is not always sufficient to resolve the occurring interferences. Recently introduced dynamic reaction cell technology for ICP-MS, which allows the selective reduction of interferences by stimulated ion-molecule reactions, was used to study the effect of argide interferences resulting from ablation of transition element matrices [9].

## Results and Discussion

### Laser Ablation

Based on the beam quality of a 193 nm ArF excimer laser ablation system equipped with homogeniser optics [10], a 266 nm Nd:YAG system was designed and its ablation behaviour was tested for different matrices. Fig. 3 shows the system, which consists of a Nd:YAG laser with an output energy of 100 mJ at 266 nm,

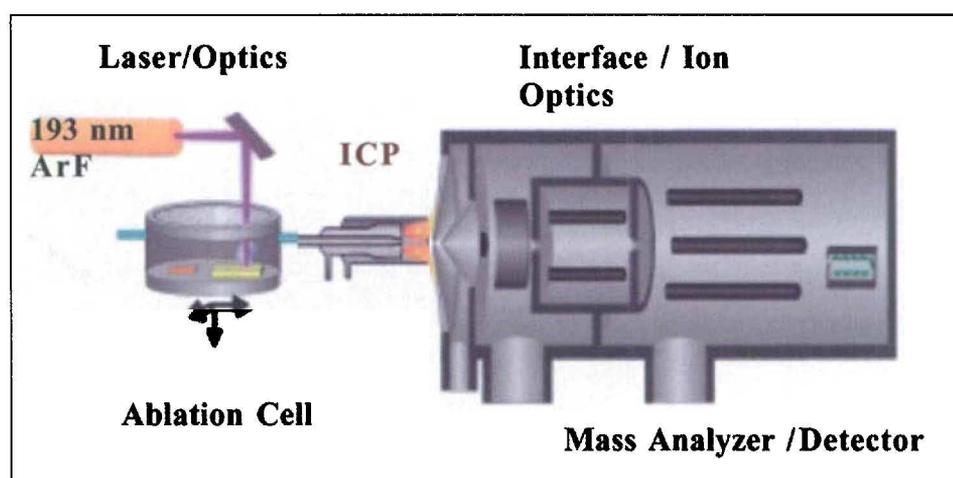


Fig. 1. Schematic set-up of a Laser Ablation-ICP-MS system with quadrupole mass filter

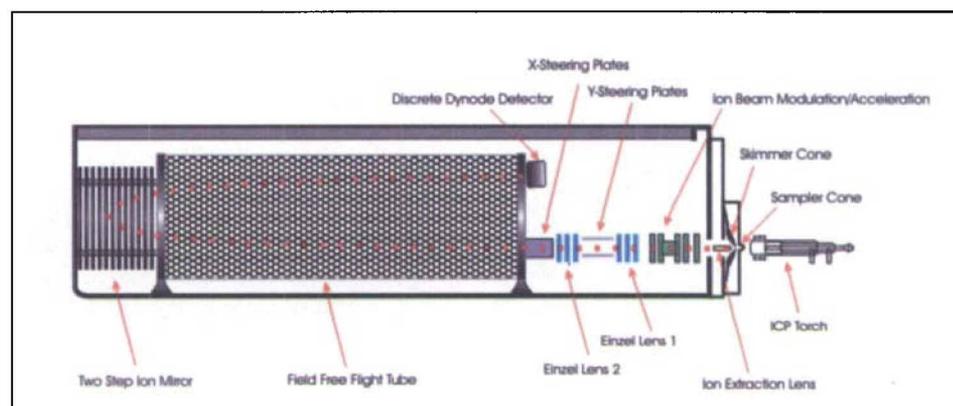


Fig. 2. Schematic view of the on-axis ICP-TOFMS (LECO Corp., St. Joseph, MI, USA). The acquisition of 20000 full mass spectra per second improves isotope precision by virtually elimination of the flicker noise of the ion source. In addition, composition of individual particles entering the ionisation source can be determined.

a beam expander, three mirrors to separate the contribution of the 532 nm radiation, two homogeniser arrays, a condenser lens and a field lens. The original, heterogeneous energy distribution of the gaussian beam is converted into a homogeneous illuminated field and imaged onto the sample surface. The beam size on the sample surface is adjusted by apertures, and the energy density at the image point is constant for every spot size that can be applied (Fig. 4). The energy density on the sample surface can be varied for each crater diameter between 2–40 J/cm<sup>2</sup> by changing objectives (5x and 10x demagnification), the homogeniser array distance or by insertion of a beam splitter. At this energy density it was possible to ablate even highly transparent samples, such as fluorite and quartz. The crater profile has been characterised by profilometry and shows a flat bottom structure, indicating a very uniform removal

of sample material over the entire crater (Fig. 5). This is a direct result of the homogeneous energy distribution in the laser beam and a proof for the successful homogenisation of the beam.

Ablation rates for metals were determined to be in the range of 0.1 μm/pulse, which is very similar to those obtained using 193 nm laser ablation with similar energy density. Silicate materials on the other hand were ablated at a rate of up to 2 μm/pulse, which is an order of magnitude higher than for the comparable 193 nm ArF excimer ablation system. [11].

The resulting transient signals from the 266 nm are similar to transient signals produced using the 193 nm ArF excimer system. However, the ablation rate for transparent samples differs significantly between the two wavelengths. Therefore, the critical depth to diameter ratio [12] is reached much faster. The calculation of the fractionation index [13] shows that

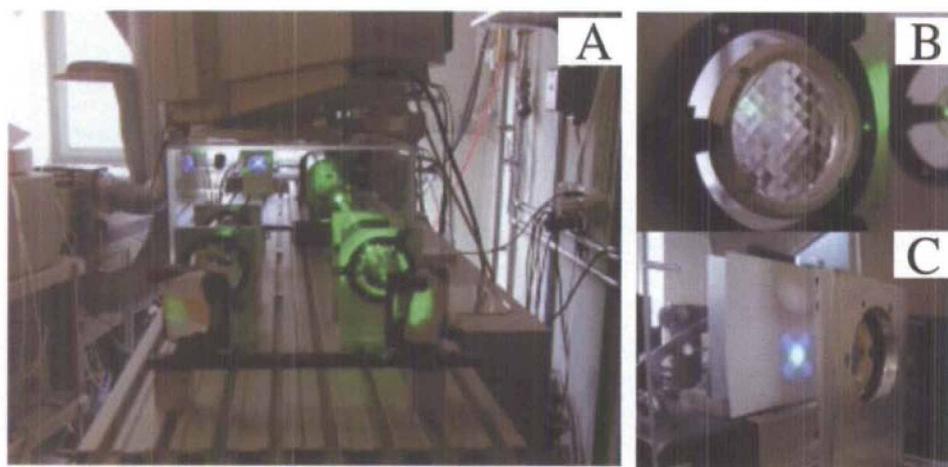


Fig. 3. Photograph of the newly designed high power homogenized 266 nm Nd:YAG laser ablation system. A) Shows the 266 nm laser with remaining 532 nm, B) A single homogeniser array C) An image of the homogenized beam profile before the aperture.



Fig. 4. Cascade ablation using four different apertures from 120 up to 40  $\mu\text{m}$  at 20  $\text{J}/\text{cm}^2$  into a glass matrix.

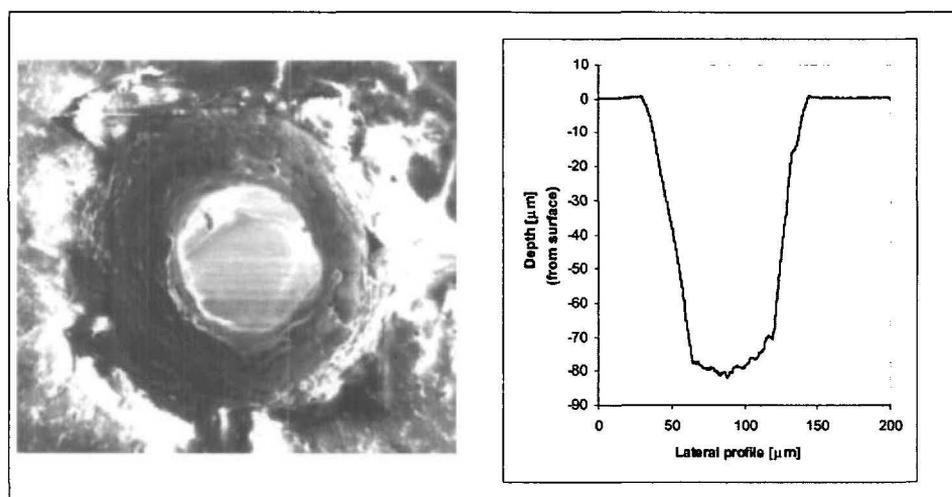


Fig. 5. Ablation crater (80  $\mu\text{m}$  i.d.) of a  $\text{CaF}_2$  sample using the 266 nm Nd:YAG system (20  $\text{J}/\text{cm}^2$ , 10 Hz, left). Crater profile measured using a profilometer (right).

the new ablation system reduces the elemental fractionation in comparison to values reported earlier for 266 nm systems.

However, the source of elemental fractionation, which can be induced by variation of the aerosol composition during the ablation process, selective transport of particles of different size or by matrix effects during ionisation, is still not fully understood. Comparing the 193 nm ArF excimer laser system and the 266 nm Nd:YAG has indicated a significant difference in the formation of particles and their transport [6]. First experiments using filter material inside the transport tube from the ablation cell to the ICP indicate that the removal of larger particles leads to more stoichiometric ionisation in the ICP (Fig. 6). Therefore it must be assumed that the elemental fractionation also occurs during the ionisation event in the ICP. More robust plasma conditions or other gas combinations are required to increase the energy transfer into the plasma to digest all particles entering the plasma have to be developed.

#### LA-ICP-TOFMS

Simultaneous sampling of ions is one of the major requests in direct solid sampling. Therefore, various sampling strategies were tested to analyse micro inclusions in a wide variety of matrices. Fig. 7 shows the transient signal of the ablation of a fluid inclusion in a NaCl matrix. Multi element analysis (50 isotopes) together with Sr-isotope ratio analysis was carried out. The figure shows good correlation between the Sr-isotopes (RSD for  $^{86}\text{Sr}/^{87}\text{Sr}$  in the range of 1–3 % for individual inclusions) during the acquisition period. The inclusion was released from the halite crystal using a laser repetition rate of 20 Hz at 193 nm to improve the signal-to-noise ratio.

#### LA-ICP-DRCMS

The formation of polyatomic argide ions of matrix elements is one of the major limitations for trace element analysis. Examples are matrices of Ti, Cr, Ni, and Fe where polyatomic argide ions obstruct the direct determination of monoisotopic trace elements such as Nb or the platinum group elements [14]. Due to the formation of  $\text{ArTi}^+$ ,  $\text{ArCr}^+$ ,  $\text{ArNi}^+$ , and  $\text{ArFe}^+$ , most isotopes in the  $m/z$  range between 88 and 100 are not measurable at trace element levels. Many of these interferences cannot be separated even by ICP-MS instrumentation that provides

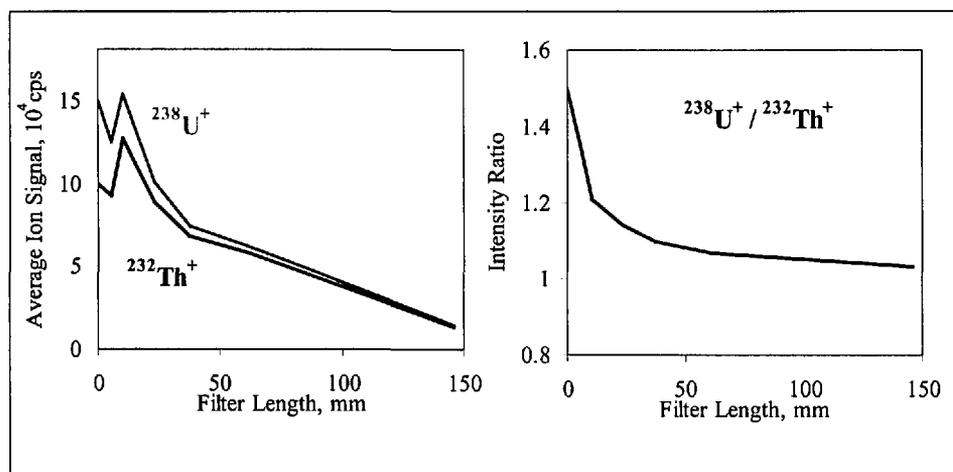


Fig. 6. Variation of average signals for <sup>238</sup>U and <sup>232</sup>Th (left) with variation of the amount of filter material inside the transport tube to ICP-MS (identical concentration and homogeneous distribution of Th and U in the sample). The right figure shows the variation of the element ratio in this experiment and indicates particle size dependent ionisation within the ICP

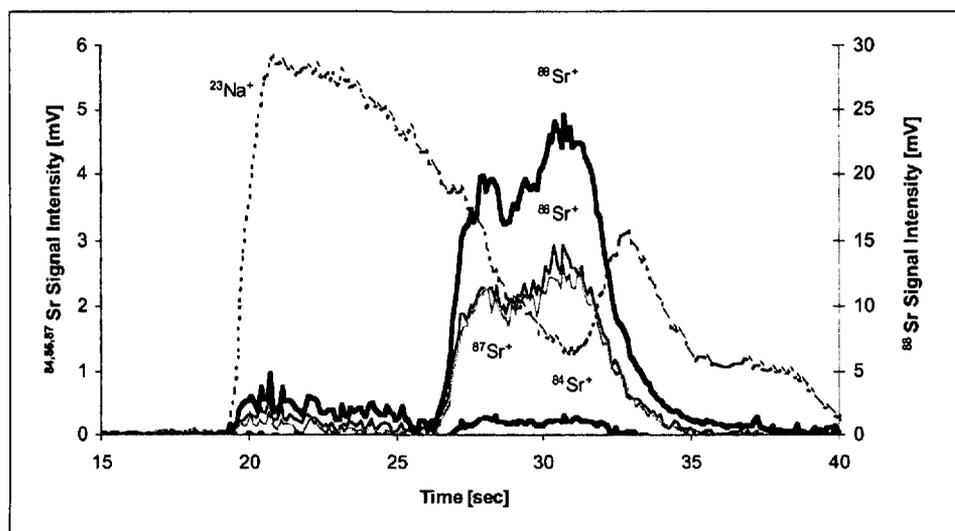


Fig. 7. Transient signal of the Sr-isotopes from a NaCl-crystal-hosted fluid inclusion sampled by LA-ICP-MS using a 60  $\mu$ m crater diameter and 20 Hz laser repetition rate.

high mass resolution. Various reaction gases were studied with the aim of reducing these interferences, while maintaining high sensitivity and the multi element capabilities. Hydrogen was found to be less reactive in comparison to other proposed gases ( $\text{NH}_3$ ,  $\text{CH}_4$ , etc.). Nevertheless it can be efficiently used to reduce the abundance of the  $\text{Ar}^+$ -ions (7–8 orders of magnitude) and associated polyatomic argide ions. The major advantage though, is that side reactions of analyte ions, which are problematic when using  $\text{NH}_3$ , were not observed with hydrogen. Fig. 8 shows that the signal intensity for  $\text{Ar}^+$  ions can be reduced to the instrumental background whilst still retaining the multi-element capabilities of the ICP-MS in general. This application allows the direct determination of <sup>40</sup>Ca with an improvement in detection capabilities by more than two orders of magnitude. Fig. 9 summarises the limits of determination (6

sigma criterion) for several elements in a quartz sample.

### Conclusion

The combination of laser ablation with different types of ICP-MS allows new insights into elemental composition of a wide variety of materials. Improved ablation characteristics using homogenised laser beam profiles at UV wavelength led to controlled sample uptake of nm layers at high lateral resolution. Calibrations using non-matrix matched standard materials can often be successfully applied for quantification, provided that the laser-induced particle size distribution is equivalently ionised in the ICP. Current research is aimed at the description of the laser-induced aerosol particle size distribution and composition in relation to laser wavelength and beam pro-

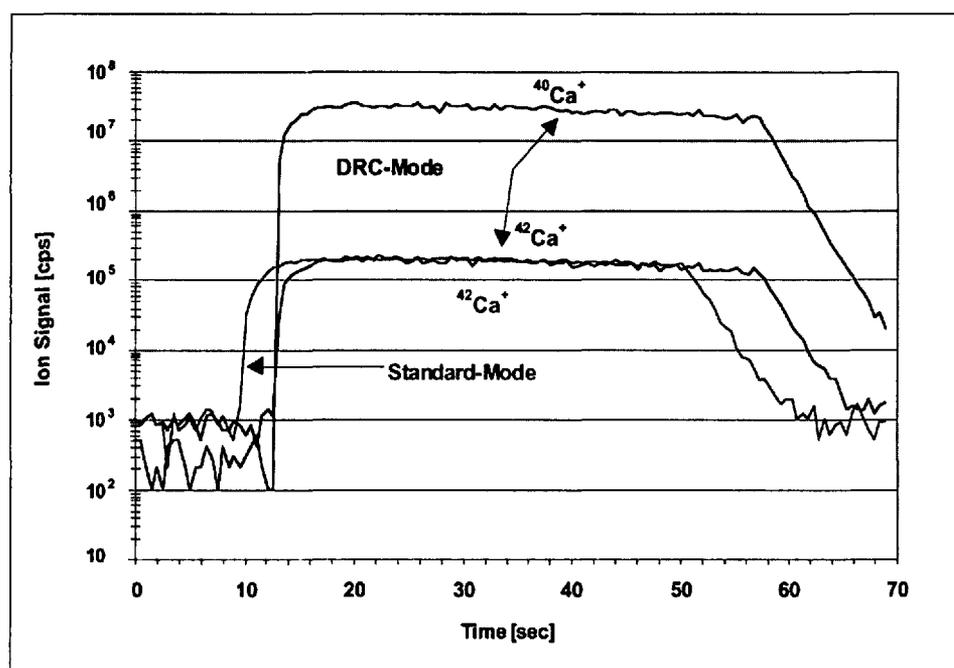


Fig. 8: Transient signal from ablation of NIST SRM 610 using 40  $\mu\text{m}$  spot size and 10 Hz laser frequency as obtained for standard mode ( $^{42}\text{Ca}^+$ ) or DRC-mode ( $^{42}\text{Ca}^+$ ,  $^{40}\text{Ca}^+$ ). Figure displays an overlay for two individual measurements for comparison.

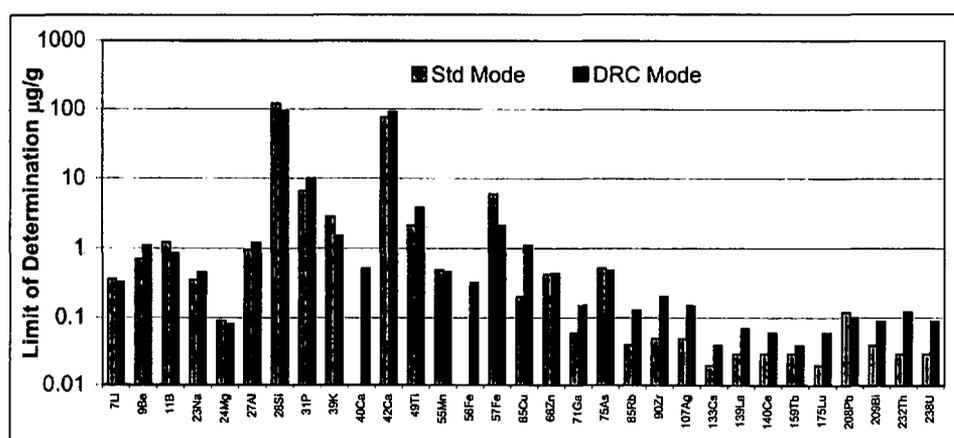


Fig. 9: Limits of determination determined in standard and DRC-mode using 40  $\mu\text{m}$  crater diameter and 10 Hz laser frequency (NIST 610 glass reference standard).

files. This, together with the interference reduction by ion molecule reactions, will further improve the understanding of laser-solid interactions and will expand the applicability of LA-ICP-MS for trace and ultra trace elemental analysis.

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