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Design analysis of a laser ablation cell for inductively coupled plasma mass spectrometry by numerical simulation ☆

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Abstract

A laser ablation setup including outer chamber, sample tube, sample holder and transport tubing was modelled and optimized using advanced computational fluid dynamics techniques. The different components of the setup were coupled and the whole device was modelled at once. The mass transport efficiency and transit times of near infrared femtosecond (fs) laser generated brass aerosols in pure argon and helium–argon mixtures were calculated at experimentally optimized conditions and a transient signal was constructed. The use of helium or argon did not influence the mass transport efficiency, but the signal structure changed. The signal fine structure was retrieved and experimentally validated. Bimodal peak structures were observed that seemed to originate from turbulent effects in the tubing connecting a Y-connector and the injector.

Keywords: Laser ablation; Aerosol transport; Numerical simulation; Inductively coupled plasma mass spectrometry

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1. Introduction

1.1. Background

Direct solid microanalysis using laser ablation (LA) in combination with inductively coupled plasma mass spectrometry (ICP-MS) is nowadays one of the most frequently used techniques for a fast and powerful multi-element determination of solid samples at the trace and ultra-trace concentration levels of a wide variety of sample types [1–11].

The growing interest in LA as a sample introduction technique stems from the ability to sample diverse materials ranging from conducting to non-conducting inorganic and organic compounds as solids or powders. Besides bulk analysis, the focussing characteristics of lasers permit sampling in small areas, so that localized microanalysis and spatially resolved studies are feasible.

The first application of the use of LA for sample introduction into ICP-MS was reported by Gray [12], who used a ruby laser to vaporize portions of solid samples prior to transport to the plasma for ionization. His work is distinct from Laser Microprobe Mass Spectrometry (LMMS), in which the laser beam is used both to extract sample atoms from a solid and to ionize them. The essential differences are that in LA-ICP-MS the sample remains at atmospheric pressure instead at vacuum conditions and ionization is performed separately from LA in a second step in the ICP, thus permitting separate optimization of two successive processes.

In order to combine LA with ICP excitation or ionization, the sample is setup in a chamber. Material is ablated from the sample and particles are formed. These particles are then transported to the plasma for atomization and ionization. An aerosol carrier gas is passed through the cell at a constant flow rate and directed through the plumbing system to the injector tube in the plasma torch.

During the LA-ICP-MS measurement, the ablation chamber geometry and the connective transport tubing play an important role. They affect the overall transport efficiency and the measured signal profile. The whole setup should be constructed in

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such a way that the aerosol loss is minimized and should allow rapid transport from the ablation site to the ICP source.

In the 80's, Moenke–Blankenburg and coworkers [13,14] performed some interesting experiments on the effect of setup geometry on the inductively coupled plasma optical emission spectroscopy (ICP-OES) signal profile. They demonstrated the influence of the volume of the ablation cell and the influence of the tube length/diameter on the signal dispersion. Based on their experimental findings a theoretical analytical model was developed. Moreover they implemented a single bead string reactor (SBSR) in their tubing, in order to minimize signal dispersion. This concept, adapted from flow-injection analysis [15], leads to sharper signals as compared with the free tube transport condition.

Leach and Hieftje [16] investigated experimentally the effects on transient signal profiles by varying the ablation cell volume, the diameter and the length of the transfer tube and the composition and flow rate of the ablation cell sweep gases. They observed that minimization of the cell volume and the length and diameter of the transfer tube dramatically decreased the peak width of the transient signals. Furthermore, they reported that the use of helium carrier gas also drastically decreased the peak width of transient signals.

Bleiner and Günther [17,18] studied experimentally the effect of setup geometry on single shot characteristics in combination with ICP-MS. Moreover, they developed a theoretical analytical description for the effect of setup geometry on the signal characteristics. Their theoretical relation was based on a product of a cell-related elution function and a tube-filling function [6–8], assuming laminar flow in the transfer line and ideal mixing in the ablation cell. The study showed that the ablation cell volume and shape influenced the signal structure most notably. Moreover they reported that the mass transport efficiency for cells up to 100 cm^3 could be maintained under different transport conditions.

Plotnikov [19], however, noted that the form of their function deviated from the experimental data. He suggested a new response curve without detailed consideration of the physical meaning of all the parameters of the function.

Recently, some other analytical transport models were proposed for the LA-ICP-MS temporal intensity distribution. Gäckle and Mertens [20,21] modelled the temporal intensity distribution in LA-ICP-MS by means of single shot, scanning and drilling mode.

Koch et al. [22] suggested the use of computational fluid dynamics (CFD) in order to describe the transport characteristics of ablation cells in a quantitative way.

In 2006, Bleiner and Bogaerts [23] presented the first systematic numerical investigations on the effect of laser ablation setup on the ns-LA-ICP-MS profile by means of CFD. The performance of several sample chambers was studied later on [24]. Compared to previous models, they considered the particle size as a variable in their calculations and investigated its effects on the transport efficiency and signal characteristics. It was demonstrated that the use of junction or barriers such as the SBSR in the tubing could perturb and deteriorate the transport efficiency. Moreover it appeared that a strict laminar condition in the tubing as stated in [20,21] was not valid; the threshold velocity for turbulence onset in their model was as low as 2% of the speed of sound. Finally they completed the findings of [19] by an in-depth physical study of the signal profile and demonstrated the lack of mass conservation in the previous models.

The models summarized above, described the temporal intensity distribution based on analytical expressions. The attractive aspect of this approach is the fact that similar calculations can be repeated in a fast and straightforward way. Besides they were helpful in retrieving the characteristics of ablation setups.

From a theoretical point of view, however, this approach is not suitable for predicting the signal fine structure, nor the correct signal profile since it is based on mean flow properties and since it disregards the highly non-linear physical processes that influence the overall signal intensity.

In order to improve and design ablation setups and in order to reconstruct an ICP-MS signal theoretically, it is expedient to use pure numerical approaches. Nevertheless, one should realize that no model will ever be able to predict the exact temporal intensity, due to the simple fact that every model has its limitations.

1.2. Aim of the study

The aim of this work is to investigate an ablation setup as has been used in [25] by means of CFD simulations. The mass transport efficiency and transit times of near infrared femtosecond (fs) laser generated brass aerosols in pure argon and helium–argon mixtures will be calculated and a transient signal will be constructed. Based on the modelled flow and signal patterns, the weaknesses of the ablation setup will be detected. Accordingly, future theoretical work would then focus on the further optimization of the present design by removing the detected drawbacks, changing the flow rates and ablation cell dimensions and finally lead to a fully optimized cell.

1.3. Why using CFD?

Computational fluid dynamics constitutes a new third approach in the philosophical study and development of the whole discipline of fluid dynamics. In the 17th century the foundations of experimental fluid dynamics were laid, the 18th and 19th century saw gradually the development of theoretical fluid dynamics. The advent of high-speed computers combined with the development of accurate numerical algorithms for solving physical problems has revolutionized the way we study and practice fluid dynamics today.

Although many of the key ideas for numerical solution methods for partial differential equations were established more than a century ago, they were of little use before computers appeared. While the first computers built in the 1950's performed only a few hundred operations per second, machines are now being designed to produce teraflops i.e., 10^{12}-floating operations per second.

It requires little imagination to see that computers might make the study of fluid flow easier and more effective. Once the power of computers has been recognized, interest in numerical