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Collection and separation of particles by size from laser ablated material

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Abstract

Inductively coupled plasma mass spectroscopy with electrothermal vaporization has been combined for the analysis of size-classified particles from laser ablated material. An Nd:YAG laser operating in the Q-switch mode with a wavelength of 355 nm (third harmonic) was used to produce particles from a brass sample. The particles were transported by argon as carrier gas into a 11-stage impactor (0.013–11.4-μm aerodynamic particle diameter) and collected on small graphite disks (7 mm in diameter) arranged in front of the jet nozzles of cascade stages. To determine the elemental composition of the particles, the graphite disks were inserted into a specially designed electrothermal vaporizer. ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{207}Pb, and ^{208}Pb were chosen for measurements. Calibration was carried out with elemental standard solutions. Relative standard deviation of the analytical signals were measured in the range from 7% (Zn) to 13% (Pb). The absolute limits of detection of these metals in solution were between 1 pg (Pb) and 10 pg (Zn). (Int J Mass Spectrom 219 (2002) 373–379)

Keywords: Brass; Laser ablation; Cascade impactor; ETV ICP-MS

1. Introduction

Laser ablation is an alternative sampling technique to the technique of sample dissolution. Sample preparation time is significantly reduced, thus minimizing the risk of contamination. Laser ablation combined with inductively coupled plasma mass spectrometry (LA ICP-MS) avoids many of the problems associated with solid analysis by conventional solution ICP-MS. For example, interferences inherent in solution nebulization such as ArO^+ are minimized and detection limits are improved for most matrices. Whilst LA ICP-MS is well established for trace element determination in micro samples, the application to bulk analysis is sparse in routine laboratories [1–6]. One of the main arguments mentioned against laser ablation is that the signal fluctuations are too high for practical analyses. The cause of extraordinary fluctuations may be due to ion intensity spikes interfering with analyte signals [7–9]. A possible explanation is that particles produced by the short laser pulse and transported by the carrier gas into the inductively coupled plasma have such a size that they are not decomposed and dissociated but only ionized. Then the ionized clusters are transferred into the mass analyzer and detected as ions, thus interfering with the analytical ion intensities

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according to their charge to mass ratio. It can be supposed that particles are broken off by the shock of the laser pulse or they are created by condensation and agglomeration in the shock wave during the cooling phase of the laser plasma [11]. Experimental conditions of the laser process can influence the creation of intensity spikes. For example, it was found for the sample material SiC that intensity spikes do not appear when the Q-switched mode was replaced by the free running mode of an Nd:YAG laser [9].

In laser ablation ICP-MS, samples are transported as particles by an argon stream into the plasma. Since the ablated plume consist of major fraction of the ablated species in the ground state, mass spectrometry is powerful technique for characterizing these ablated species. The reliability of analytical results can be impaired if the elemental concentrations of the material introduced into the plasma differs significantly from the concentrations in the sample. Therefore, the processes forming particles such as nucleation, condensation, and agglomeration are factors determining the analytical performance of the LA ICP-MS as well as the particle loss by sedimentation or the ablation process itself [12–14]. To date, the influence of particle forming processes on analytical qualities such as reproducibility and accuracy is little known. The measurement of the size distribution and elemental composition of the ablated particles may be useful to optimize laser parameters such as wavelength, pulse energy, and pulse duration [15–18]. In this paper, we will identify the ablated species ejected from brass sample and determine their concentrations. The aim of this work was to develop a technique for the quantitative analysis of size-classified particles produced by laser ablation. To demonstrate the capability of the technique, the major elements of brass, i.e., Cu, Zn, and Pb, in samples of brass were chosen for measurements.

2. Experimental

2.1. Particle production

The ablation duration for particle production were chosen to 10 s (100 shots), 50 s (500 shots), and 250 s (2500 shots) for each spot. The Nd:YAG laser (Model 320 Perkin–Elmer/Sciex Instruments Thornhill, Canada) was used for laser ablation. The 355-nm laser beam was provided by the third harmonic of a Q-switched laser system with a pulse duration of 9 ns, 240-μs pulse duration, the laser beam energy 0.27 mJ, and a repetition rate of 10 Hz [18–20]. The laser beam was introduced into the sample chamber through a silica window and focused onto the brass surface with an incident angle of 90°. A piece of brass alloy (length = 30 mm, width = 20 mm, and height = 4 mm) was cleaned with acetone using a supersonic wave cleaner before the laser irradiation. The sample was mounted on a small, moveable sample stage in the ablation cell (volume = 63 cm^3). High purity argon gas (99.99%) was introduced into the chamber with a gas flow of 1 L min^{-1}.

2.2. Particle collection

The ablated material was transported by an argon gas flow in 1 L min^{-1} range which was drawn by a pump into an 11-stage cascade impactor (Berner-Impactor). The cascade impactor has a nominal flow rate of 24.9 L min^{-1}. To reduce the flow rate of the argon stream through the ablation cell a by pass was installed. Each impact stage represents a certain range of aerodynamic diameter. The ranges of particle diameter are different for each impact stage. With increasing stage the range of particles diameter increased. The values of aerodynamic diameter of collected particles varies from 0.013 to 11.4 μm. The impact plates were covered with separate graphite impact targets in such a way that each target is placed in front of a nozzle. The graphite targets, disks of 7-mm diameter and 2-mm thickness, were made from a rod of pure graphite [10]. Particles which cannot follow the gas stream do impact on the graphite disks and hold on the rough surface.

2.3. Particle analysis

After loading with particles each graphite disk is transferred into a specially designed graphite tube.

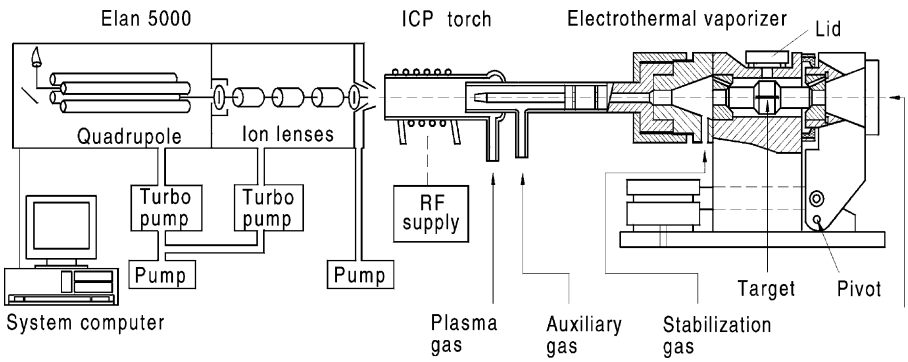

Fig. 1. Electrothermal vaporizer with an inductively coupled plasma mass spectrometer.

The two parts of the graphite tube are put together, then the tube is inserted into a electrothermal vaporizer which is connected with an ICP-MS instrument. Fig. 1 shows the vaporizer coupling with the ELAN 5000 instrument (Perkin–Elmer/Sciex) used in our investigations. The graphite tube is connected with two graphite cones as electrodes. The vaporizer is immediately coupled with the injector tube of the inductive coupled plasma without using any valve. Operating conditions are listed in Table 1.

2.4. Calibration

The calibration was carried out with referenced standard solutions (Merck Eurolab GmbH) in 0.5–200 ppb range. For each measurement, 10 μL of the elements containing solutions were introduced with a micropipette into the cleaned tube on graphite disk [10]. The calibration graphs are linear within the concentration range of interest for all measured elements.

The accuracy of the calibration was checked by the analysis of brass. At first, some parts of the sample (each about 0.2 g) were dissolved in 4 mL supra pure acid (HCl/HNO_3 3:1; Merck) and filled up to 20 mL with sub-boiling distilled water. This solutions diluted 1:1000 (Cu, Zn, and Pb) were analyzed both by ETV ICP-MS and solution ICP-MS. Instead of particles from laser ablation, filings of brass were analyzed by direct vaporizing. The results and the detection limits for ETV ICP-MS are given in Tables 2 and 3. The

Table 1
Working conditions for ETV ICP-MS

ETV	Temperature (°C)	Hold time (s)	Transport gas (L min^{-1})	Stabilization gas (L min^{-1})
Drying	60	4	0	1.2
	500	10	1	1.2
Vaporization	2750	4	10	0
	2500	1	10	0
Cooling	1000	4	10	0
ICP		MS		
RF power	1000 W	Dwell time	20 ms	
Plasma gas	15.0 L min^{-1}	Replicates	120	
Auxiliary gas	0.8 L min^{-1}	Scanning mode	Peak hop	
Transport gas	1.0 L min^{-1}	Application	Graphics	
Isotopes	^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{207}Pb, ^{208}Pb			

Table 2
Comparison of results obtained by ETV ICP-MS and solution ICP-MS

	ICP-MS (mg g^{-1})	ETV ICP-MS (mg g^{-1})	
	Nebulization	Analysis after digestion	Vaporization of filings
Cu	585 ± 9	589 ± 6	616 ± 17
Zn	396 ± 7	392 ± 6	365 ± 21
Pb	18.7 ± 0.3	18.4 ± 0.6	19.5 ± 4.0

Table 3
Reproducibility and detection limits for ETV ICP-MS

	Concentration range (pg)	Linear regression coefficient	Relative standard deviation (%)	Limit of detection (pg)[a]
Cu	25–2000	0.9904	11	5
Zn	25–2000	0.9993	7	12
Pb	5–2000	0.9974	13	1

[a] Limits of detection (LOD, 3σ blank, $n = 12$).

agreement of the concentrations is acceptable for the purpose of this study.

3. Results

3.1. Analysis of size fractionated particles

The analysis of the particles disposed on the disks from the different impactor stages permits to calculate the collected mass and concentration of the investigated elements. Fig. 2 shows the collected mass per nozzle for the elements Cu, Zn, and Pb as a function of the particle size expressed as aerodynamic diameter. The distribution curves indicate correlation between the elements investigated despite the curves differ with different ablation times. With increasing pulse number the ablated masses increase. The collection efficiency of ablated particles from brass is good enough for more then 500 shots without an auto focus system. The maximum of the distribution curves is for all elements between 0.2 and 0.4 μm of particles aerodynamic diameter range. As for the measurement with 100 and 500 shots (Fig. 2a and b), we observe a second maximum with 5.8-μm diameter, which is

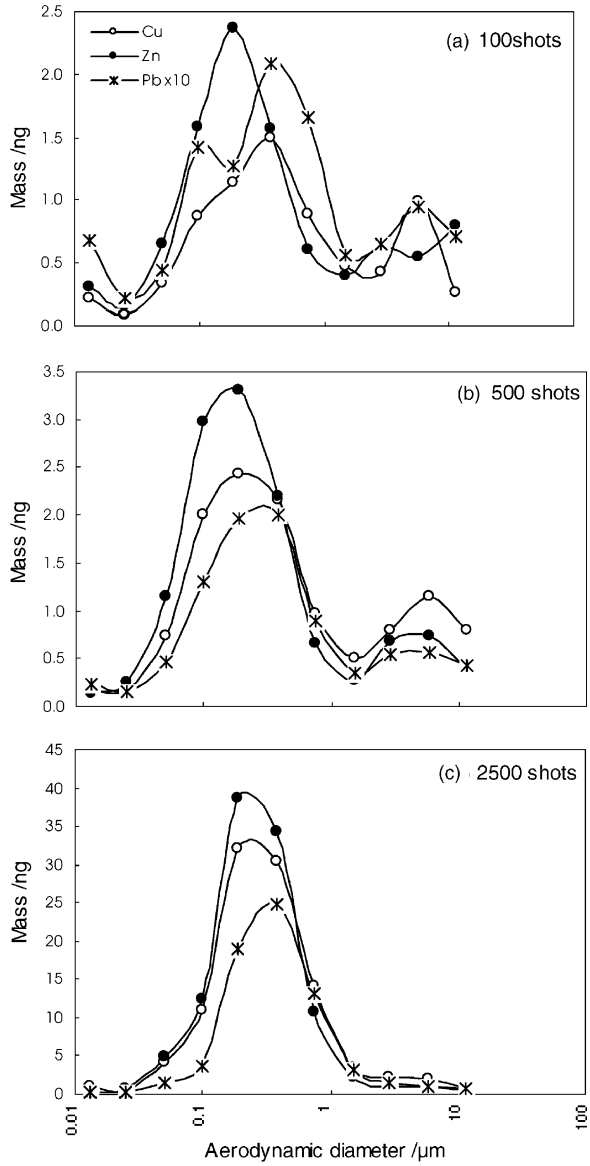

Fig. 2. Distribution of the collected mass per nozzle for Cu, Zn, and Pb, ablated with (a) 100, (b) 500, and (c) 2500 laser shots.

three times smaller. In the case of 2500 shots (Fig. 2c), this dependence is less visible, and the second peak is quite shallow. The particle mass is strongly dependent on aerodynamic diameter. The ablated mass of the Cu and Zn particles with 0.1–0.4-μm diameter is about

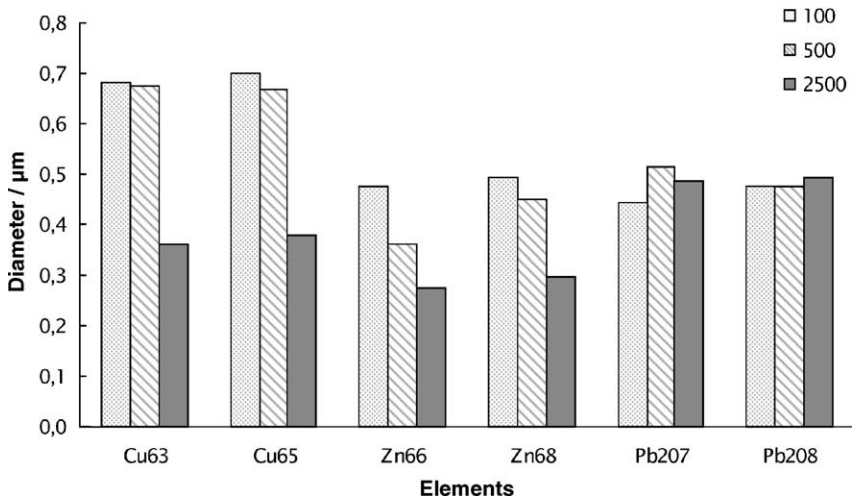

Fig. 3. Diagram of mean aerodynamic diameters for all elements studied.

10 times higher than the Pb particles, in all cases studied.

Fig. 3 shows a diagram for the mean aerodynamic diameter for 100, 500, and 2500 laser pulses. For Cu and Zn isotopes the mean aerodynamic diameter decrease with increasing the laser pulses. For Cu the mean particles size decreases from 0.7 to 0.36 μm, and for Zn it drops from 0.49 to 0.28 μm. The ablated particles are smaller with increasing number of laser shots. The ablation process on the brass alloy generated bigger particles in the beginning than in the last phase, especially, when many laser pulses ablate material from the sample without any further auto focusing of the laser beam. Only for Pb isotopes the dependence of mean particle size on the number of laser pulses is not clearly visible. The mean aerodynamic particle diameter is almost constant in the range between 0.44 and 0.5 μm.

The correlation coefficient between the same isotopes is sufficiently good only for the main elements of brass alloy, i.e., Cu—0.997, Zn—0.915, and Pb—0.213.

Because the total concentration of Cu, Zn, and Pb is 99% in the brass, we can determine with acceptable accuracy the concentrations of these elements in the particles depending on the size (aerodynamic diameter). The mass of each element was divided by the entire mass which was calculated by addition of the masses of Cu, Zn, and Pb collected on the target.

The results for the concentrations at the several impact stages are given in Fig. 4. For three ablation times the distribution of elemental composition is comparable, and on average the concentrations are the same within the confidence interval of 95% as the one for bulk analysis with solution ICP-MS. But we obtained different concentrations depending on the particle size. The elements Cu and Pb were well correlated with 500 and 2500 laser shots and had the highest concentrations in particles with an aerodynamic diameter in the range between 0.7 and 5.8 μm. The distribution curve for Zn was different. The highest concentrations were in the aerodynamic diameter range from 0.05 to 0.38 μm. During the laser ablation process the concentration of the main component of brass alloy ejected particles is constant. But the isotopes of Cu particles are bigger than those of Zn particles. Therefore, the concentration distribution for Cu and Zn is different as well as the location of the maxima.

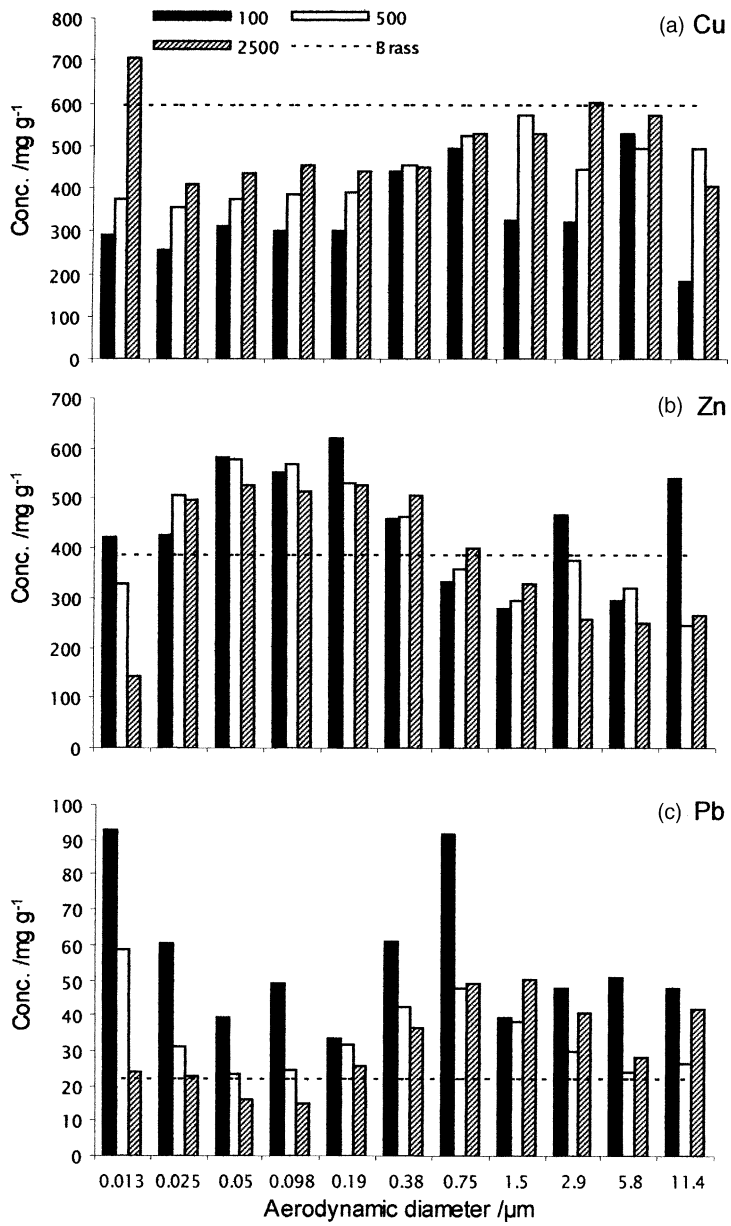

Fig. 4. Concentration of (a) Cu, (b) Zn, and (c) Pb in collected particles of a brass sample. The dotted line refers to concentrations as determined by solution ICP-MS. Laser ablation with 100, 500, and 2500 shots.

4. Conclusions

A technique has been developed for the analysis of size-classified particles produced by laser ablation using an 11-stage impactor with small graphite disks in front of the nozzles to collect the particles and determining the element contents of the collected samples by electrothermal vaporization ICP-MS. Elemental standard solutions can be used for calibration. The reliability of the calibration

was tested with samples of brass by solution ICP-MS.

As an example, the method has been applied to the determination of Cu, Zn, and Pb in particles produced by laser ablation of brass. The distribution of the mass deposed on the graphite disks hardly depends on the aerodynamic diameter. Two peaks were obtained, the main one between 0.1 and 0.4 μm and a smaller maximum at about 5.8-μm aerodynamic diameter. A possible explanation is that particles produced by laser ablation on brass surface have a main size about 0.2-μm aerodynamic diameter and a second, but bigger one, at about 5.8 μm. The clusters are loaded on the graphite disks in the adequate cascade impactor stage and then detected by ETV ICP-MS.

Additionally, it was found the concentration of Cu increased for particles with an aerodynamic diameter in the range between 0.1 and 1.5 μm. On the other hand, the content of Zn decreased in the same diameter range. Pb shows the same behavior as Cu. Although the elemental contents changed in dependence on the particle diameter, the element concentrations related to the whole particle mass transported by the carrier gas and collected on the graphite disks also agreed with the element concentrations in the brass sample.

The results of the present study indicate that the developed technique for particle analysis may be a useful tool for the solid sample analysis by laser ablation ICP-MS for major and trace elements. The fractionation of ablated material from solid sample surface by their aerodynamic diameter with a cascade impactor can be used to determine the physical properties of ablated particles. The fractionation process of laser ablated particles of brass is good enough for a laser ablation duration period of 50 s (500 shots with 10 Hz frequency). Its application, however, is limited because graphite is the target material for particle collection. Elements of special interest such as carbon or the refractory elements W, Mo or Si cannot be sensitively determined. The aim of further investigations is to solve this analytical problem.

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