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Research note

Emission spectroscopic monitoring of particle composition, size and transport in laser ablation inductively coupled plasma spectrometry

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Abstract

The spectroscopic line emissions of copper and zinc from atomized particles generated by orthogonal pre-pulse laser ablation of brass and transported from the ablation cell through tubes into an ICP have been simultaneously measured end-on with fast photomultipliers. It was shown that simultaneous line monitoring of major elements provides not only information on the aerosol transport in laser ablation ICP-spectrometry, but also on the ratios of small to single larger particles and their respective elemental compositions and, therefore, on possible elemental fractionation problems. Furthermore, the spectroscopic information can be easily exploited for proper adjustment of the laser fluence in order to minimize the production of large particles, to improve the transport efficiency and to reduce the noise of analytical signals in laser ablation ICP-spectrometry. The present particular experiment on orthogonal pre-pulse laser ablation of brass confirms the recent finding that such kind of double-pulse arrangement produces predominantly ultra-fine particles. Individual brass particles with diameters $\gtrsim$250 nm could be analyzed. They showed large Zn depletions as expected. Finally, strong accumulations of aerosol particles were found in the ablation cell used even at low laser pulse frequencies.

Keywords: Particle characterization; Particle transport; Double-pulse laser ablation; Inductively coupled plasma spectrometry; Emission spectrometry

1. Introduction

Laser ablation (LA) is certainly one of the most attractive sample introduction techniques in ICP spectrometry [1]. It is a fast technique since it does not require extensive sample preparation. Moreover, it provides the potentiality of rapid micro-analysis or depth-profiling if the pulsed laser beam is tightly focused or modified to a flat-top profile by adequate optics, respectively. LA-ICP spectrometry is always a powerful quantitative analytical technique if standard reference samples of similar composition and morphology are available. However, accurate analyses can be difficult if matrix-matched standards are lacking.

There are different reasons why systematic errors may arise in LA-ICP spectrometry if such standard reference material is not available. The main sources of error may arise in the following processes: the ablation process itself, the formation of particles, the transport of the aerosol, and the atomization in the ICP [2–4]. Fractional element evaporation may occur in the crater region and change the element composition, in particular, if the elements have very different volatilities. In this case, care should be taken if there is a good deal of re-solidified melt in the crater after ablation. The particles which are formed in the cooling laser induced plasma should have a size distribution appropriate for loss-free transport from the ablation cell to the ICP. Such particles have diameters between ~10 nm and ~10 μm. Smaller and larger tend to get lost by diffusion and gravitational settling/inertial deposition, respectively [5]. Losses have influence on the analysis since the elemental compositions of laser produced particles depend on their size [6,7]. Finally, the aerosol should be completely atomized during their trajectory through the center of the ICP, implying that the particles are enough small-sized taking into account their volatility.

This paper reports on a simple experimental arrangement which provides direct and quantitative information on particle

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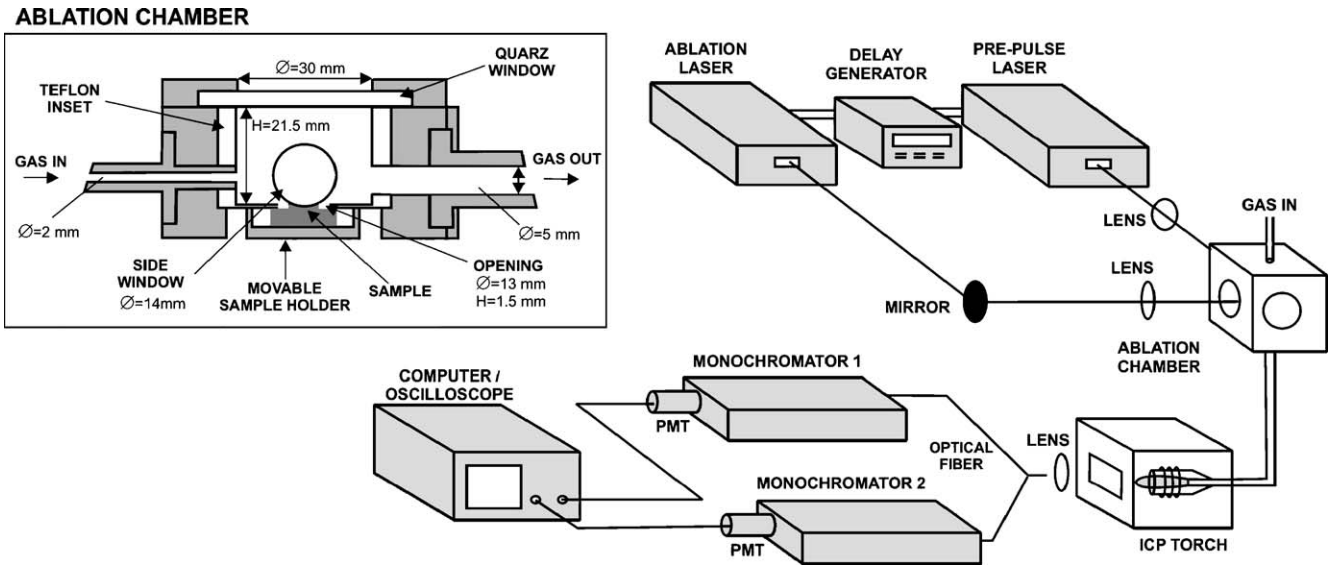

Fig. 1. Experimental arrangement used. Inset: details of the ablation cell.

size and composition, transport properties, and atomization in the ICP. The experimental arrangement is based on the simultaneous acquisition of selected emission lines of different elements applying end-on observation of an ICP coupled with a laser ablation cell.[1] It will be demonstrated that, with such arrangement, a fast survey of particle transport and wash-out time of the ablation cell can be obtained. This is particularly important in single pulse ablation studies such as, for example, micro-analysis or depth-profiling, since the signal dispersion determines the sensitivity and the pulse frequency. Furthermore, the arrangement provides the possibility to measure relative ratios of major elements in individual particles with diameters larger than ~250 nm and can give hints on possible fractionation effects and, therefore, on the expected accuracy of the analyses. The direct observation of large particles can also be used to optimize the laser fluence for particular samples, since it is known that too high laser fluences can produce significant number of large particles as a result of splashing of the crater melt. As mentioned above, such particles can then be lost on their way to the ICP.

The advantages of emission spectroscopic monitoring will be demonstrated by simultaneous detection of zinc and copper in particles generated by ns-laser ablation of brass with an orthogonal pre-pulse breakdown above the ablation spot. Recently, such double-pulse arrangement is becoming very popular in laser-induced breakdown spectrometry (LIBS) since it enhances the spectral line emission and the detection power (see [8] and references therein). As recently shown in our laboratory by particle sorting applying a low-pressure impactor, a double-pulse configuration with orthogonal pre-pulse breakdown is producing predominantly ultra-fine aerosols (diameter below 200 nm) while the fraction of bigger particles with diameters >200 nm is much larger in single pulse ablation [9].

2. Experiment

The experimental arrangement is displayed in Fig. 1. The pulsed nanosecond lasers, their beam configurations, the focusing conditions, the ablation cell, cell gas and gas flow were the same as reported in the recent publication on the measurement of ultra-fine particles generated by laser sampling of brass with orthogonal pre-pulse laser breakdown in argon [9]. The sample was brass as in [9], but the Cu/Zn ratio (1.39) was slightly lower than in the sample used in [9] (Cu/Zn = 1.54). Therefore, this part of the arrangement will only be described here very briefly.

Two Nd:YAG lasers operating at their fundamental wavelengths (1064 nm) with pulse lengths of about 8 ns were used in orthogonal beam configuration for laser ablation. The tightly focused radiation of the first laser (Spectron SL 801) produced a plasma breakdown in the ablation cell gas (argon, pressure: 1 atm) 1.5–2.5 mm above the sample. The second laser (Spectron SL 401) was focused by an $f = 10$ cm lens onto to the sample for ablation. The position of the beam focus was slightly below the surface so that the beam diameter on the surface was about 85 μm. Constant pulse energies (91 mJ and 10 mJ) were applied throughout the experiment for the pre-pulse and the ablation laser, respectively.

The delay between both lasers was set to 20 μs by a delay-generator (DG535 by Stanford Research Systems, Inc.). The repetition rate of the double pulse was varied between 0.05 Hz and 10 Hz.

An argon gas flow at atmospheric pressure was applied to transport the generated particles from the chamber into the ICP. The diameter of the gas inlet tube was 2 mm, while the outlet

[1] A similar arrangement has been discussed in a talk presented by G. Horlick (University of Alberta) at Pittcon 2004 in Chicago. We thank the editor for bringing the abstract of the talk to our attention.