Spectrochimica Acta Part B 125 (2016) 52–60

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Online monitoring of nanoparticles formed during nanosecond laser ablation

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ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 20 September 2016
Accepted 20 September 2016
Available online 21 September 2016

Keywords:
Laser ablation
Inductively coupled plasma mass spectrometry
Fast mobility particle sizer
Particle size distribution

ABSTRACT

The particle size distribution of dry aerosol originating from laser ablation of glass material was monitored simultaneously with Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analysis and two aerosol spectrometers – Fast Mobility Particle Sizer (FMPS) and Aerodynamic Particle Sizer (APS). The unique combination of LA-ICP-MS and FMPS offers the possibility of measuring the particle size distribution every 1 s of the ablation process in the size range of 5.6–560 nm. APS extends the information about particle concentration in the size range 0.54–17 μm. Online monitoring of the dry aerosol was performed for two ablation modes (spot and line with a duration of 80 s) with a 193 nm excimer laser system, using the glass reference material NIST 610 as a sample. Different sizes of laser spot for spot ablation and different scan speeds for line ablation were tested. It was found that the FMPS device is capable of detecting changes in particle size distribution at the first pulses of spot laser ablation and is suitable for laser ablation control simultaneously with LA-ICP-MS analysis. The studied parameters of laser ablation have an influence on the resulting particle size distribution. The line mode of laser ablation produces larger particles during the whole ablation process, while spot ablation produces larger particles only at the beginning, during the ablation of the intact layer of the ablated material. Moreover, spot ablation produces more primary nano-particles (in ultrafine mode size range <100 nm) than line ablation. This effect is most probably caused by a reduced amount of large particles released from the spot ablation crater. The larger particles scavenge the ultrafine particles during the line ablation mode.

1. Introduction

Laser ablation (LA) sampling, together with inductively coupled plasma mass spectrometry (ICP-MS) as a detection system, has become a routine method for the direct analysis of various solid samples. The product of laser ablation contains a mixture of vapour, droplets and solid particles. All components are finally transported to a plasma by a carrier gas as a dry aerosol including mainly agglomerates of nanoparticles. In general, the characterisation of aerosols by their particle size distribution (PSD) represents an indispensable tool for fundamental studies of the interaction of laser radiation with materials. Many works have studied PSD of dry aerosol for different samples [1–3] and different ablation conditions such as wavelength [1,3–5], pulse duration [3,6–8], repetition rate [9], pulse energy [6] or carrier gas type [10] and flow rate [9]. Another field of research is the influence of particle size on the ICP-MS signal and elemental fractionation [11–19].

Dry aerosol can be studied by different offline or online techniques. Offline methods include particle collection on special filters, grids or discs and their subsequent analysis. The sample collection can be improved by enhancing the collection efficiency either by using an electrostatic sampler [7] or by separating and depositing particles on substrates according to their size, based on their aerodynamic diameter, e.g. a cascade impactor [20,21]. The offline methods enable not only the visual determination of the particle shapes and size through various microscopic methods (Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Electron Microprobe Analysis (EMPA), etc.) but also the study of particle composition by a subsequent chemical analysis (ICP-MS, Particle-induced X-ray Emission (PIXE), etc.) of collected samples [2,7,20,22–24]. The stoichiometry of the ablation can be checked by bulk analyses of all particles using a dissolution method. Furthermore, Energy Dispersive X-ray spectroscopy (EDX) allows the acquisition of the composition of specific particles on the filter, which is very useful for clarification of the fractionation processes [7,23–27]. Nevertheless, the main disadvantage of the offline methods are the lack of time resolution. All the gathered samples include the mass collected during the whole sampling period. In other words, it

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http://dx.doi.org/10.1016/j.sab.2016.09.017
0584-8547/

means that the offline methods do not bring any information about particle dynamics (the evolution of particle sizes and concentration over time). If such information is required, the use of online sampling methods becomes necessary.

The online monitoring of the particle size distribution can be performed by different types of aerosol analysers. Several different techniques using different physical principles are used to detect the airborne particle concentration (number or mass) – such as Condensation Particle Counters (CPC), photometers such as Optical Particle Sizer (OPS) or Optical Particle Counter (OPC) or electrometers. With regard to particle size, two main principles are used – sizing particles according to their mobility in an electrostatic field (Differential Mobility Analyser (DMA)) and sizing particles according to their aerodynamic behaviour in an accelerated flow (Aerodynamic Particle Sizer (APS)). By combining the particle counters and sizers, a complex aerosol spectrometer can be obtained. The most frequently used for laser-generated aerosol analysis is the Scanning Mobility Particle Sizer (SMPS) system in the submicrometre size range of particle diameters (units of nanometres to 1 μm) [28–30] and APS systems measuring in the size range of 0.5–20 μm. For the processes which involve quick changes in particle concentration, the Fast Mobility Particle Sizer (FMPS) is a very efficient solution, combining principles of the sizing of particle diameters according to their mobility in an electrostatic field along with the detection of their concentration by a set of electrometers. Furthermore, the FMPS system has not been used in combination with the LA-ICP-MS method before.

It is necessary to point out that different methods for PSD estimation provide complementary data based on measuring different physical characteristics of particles. As an example, by comparing the offline impactor technique together with DMA (SMPS) and OPC, the different interpretations of the agglomerated nano-particles in the laser-generated aerosol are revealed. DMA yields physical diameters of particles (based on their mobility in an electrostatic field), which are larger than their volume-equivalent diameter in the case of porous particles and therefore, the mass of the particles cannot be determined accurately compared to the mass-correct impactor measurement. On the other hand, OPC provides particle diameter values, based on the optical equivalent particle diameter, which is strongly dependent on the optical properties of measured particles (scattering coefficient). If the optical properties of measured material are different from particles used during the calibration of the optical instrument (usually polystyrene latex spheres) then the results can significantly differ, usually strongly underestimating the diameter of particles compared to the real sizes [21].

The particle size distribution of laser generated particles is strongly dependent on the ablation conditions (laser parameters, atmosphere…) [10,31–33]. This knowledge is used not only for ICP spectrometry but also for nanoparticle formation [34–37] or pulsed laser deposition methods because different ablation conditions such as laser wavelength, pulse width and energy lead to different morphology, structure and composition of the deposited film [38].

This study deals with the 193 nm ns laser ablation of certified glass standard reference material (SRM) NIST 610. Some studies using SRM NIST 610 as a sample and 193 nm ablation systems were already published and all describe two the main processes used in particle formation. The first process involves condensation of nano-particles (in the 10 nm range) and their coagulation to clusters [5,7,39,40]. The second process includes direct ejection of melted material and the subsequent solidification to spherical particles. The SEM observation refers to spherical particles with a maximum diameter of 200 nm [39]. The characterisation of the clusters' size as non-spherical particles depends on the used particle determination technique and can vary by as much as one order of magnitude [21]. Therefore findings about cluster size differ (depending on the different particle size measuring techniques and different ablation conditions) in various works. Kuhn, Gunther [40] presents particle volume distribution up to 700 nm of particle diameter (spot size 40 μm, repetition rate of 10 Hz, fluence of 18 J cm^{-2}), Kroslakova, Gunther [5] refers to the connection between the spot size and the particle size distribution, 500 nm as a maximum particle size was observed for the 30 μm spot size and particles up to 1 μm occurred for 120 μm spot size (repetition rate 10 Hz, fluence of 28 J cm^{-2}). Guillong et al. [4] state that no particles larger than 400 nm were observed (spot size 60 μm, repetition 4 Hz, fluence of 4.2 J cm^{-2}).

In our study, FMPS and APS aerosol spectrometers were used together with LA-ICP-MS. The FMPS spectrometer offers the possibility of obtaining particle size distribution in quite a wide size range with high time resolution (about 1 s per scan) at the same time. This work is unique in terms of the instrumentation set-up; Laser ablation coupled with the FMPS spectrometer allows for online monitoring of particle physical properties during the ablation process with a high time resolution.

Quantitative LA-ICP-MS analysis traditionally requires parallel measurements of internal standard in order to account for the effects of particle properties on the response of the instrument. Thus, parallel use of FMPS data was also investigated as a potential supplement or alternative to internal standardisation.

2. Experimental

2.1. Sample

The study of the size and concentration of particles formed during laser ablation was carried out on the certified glass standard reference material (SRM) NIST 610. The sample surface was polished and cleaned with ethanol. This transparent glass is one of the most frequently used standards in laser ablation coupled with inductively coupled plasma mass spectrometry.

2.2. Experimental set-up

The particles produced by laser ablation of NIST 610 were analysed by ICP-MS and aerosol spectrometers FMPS and APS giving information about the physical properties of generated particulates.

2.2.1. LA-ICP-MS

The instrumentation consisted of an excimer laser ablation system Analyte G2 (Photo Machines Inc., Redmond, WA, USA) and ICP-MS with a quadrupole analyser Agilent 7500ce and a collision-reaction cell (Agilent, Japan). The laser operates at a wavelength of 193 nm with a pulse duration ≤4 ns. Using helium as a carrier gas with a flow rate of 0.65 l min^{-1}, the aerosol was washed out from the chamber (HelEx) and transported through a polyurethane tube (i.d. 4 mm) to the aerosol spectrometers and ICP-MS. Two ablation modes - spot and line scan - were performed. Spot ablation with different spot sizes and line scan ablation using 85 μm spot size and different scan speeds were compared. The experimental conditions are summarised in Table 1 together with the important parameters of ICP-MS. Selected isotopes were monitored with the total integration time of 1 s which was similar to the FMPS scanning rate.

2.2.2. Fast Mobility Particle Sizer (FMPS)

The FMPS spectrometer is an aerosol instrument measuring number size distribution in a fixed particle size range of 5.6–560 nm with a high time resolution (down to 1 s per sample). The FMPS sizes the particles according to their mobility in an electrostatic field and counts their number using a set of 22 electrometers.

After passing the two unipolar diffusion chargers, the aerosol particles gain a positive charge and continue to the DMA where they are sized according to their mobility in an electrostatic field. In this case, the central rod of the DMA is separated into 4 sections, each having constant positive voltage (0, 85, 470 and 1200 V) throughout the whole scan. The entering aerosol particles are repelled from the central rod, depending on their electrical mobility, and hit one of the electrometers positioned along the outer cylinder of the DMA. The current induced by