Spectrochimica Acta Part B 92 (2014) 51–59

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Effect of operation conditions of the drop-on-demand aerosol generator on aerosol characteristics: Pseudo-cinematographic and plasma mass spectrometric studies

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ARTICLE INFO

Article history:
Received 30 April 2013
Accepted 2 December 2013
Available online 12 December 2013

Keywords:
Drop-on-demand
Thermal inkjet
Droplet size distributions
Optical aerosol characterization
ICP-MS

ABSTRACT

The recently presented drop-on-demand (DOD) aerosol generator overcomes some of the drawbacks of pneumatic nebulization, as its aerosol is no longer generated by gas–liquid interaction. In the current study, an advanced imaging technique is presented, based on a CCD camera equipped with magnifying telecentric optics to allow for fast, automated and precise aerosol characterization as well as fundamental studies on the droplet generation processes by means of pseudo-cinematography.

The DOD aerosol generator is thoroughly characterized regarding its droplet size distribution, which shows few distinct populations rather than a continuous distribution. Other important figures, such as the Sauter diameter ($D_{3,2}$) of 22 μm and the span of 0.4 were also determined. Additionally, the influence of the electrical operation conditions of the dosing device on the aerosol generation process is described. The number and volume of the generated droplets were found to be very reproducible and user-variable, e.g. from 17 to 27 μm ($D_{3,2}$), within a span of 0.07–0.89. The performances of different setups of the DOD as liquid sample introduction system in ICP-MS are correlated to the respective achievable aerosol characteristics and are also compared to the performance of a state-of-the-art μ-flow nebulizer (EnyaMist). The DOD system allowed for improved sensitivity, but slightly elevated signal noise and overall comparable limits of detection. The results are critically discussed and future directions are outlined.

1. Introduction

In the field of atomic spectrometry, conventional concentric nebulizers with liquid flow rates in the mL min^{-1} range are used for the vast majority of applications in routine analysis [1], although their performance is often not ideal. In fact, those systems are considered as the Achilles' heel of the analytical chain. Consequently, numerous studies were published, suggesting miniaturized liquid sample introduction systems with liquid flow rates in the μL min^{-1} range, for their improved sample utilization, and thus, sensitivity [2].

The ideal liquid sample introduction system for ICP spectrometry has to fulfill numerous and – to a certain extent – contrary needs. The produced aerosols should be uniform, regarding size, velocity and droplet transport time [3–5]. Conventional pneumatic nebulizers, used at liquid flow rates in the mL min^{-1} range, generate aerosols which are not ideal [2,6–9], hence achievable sensitivity and signal noise are not ideal, neither [8,10–13]. Those aerosols have to pass a suitable spray chamber to improve their aerosol characteristic and to meet the prerequisites for sample introduction e.g. into the ICP source [6,7]. However, this process takes places at the expense of transport efficiency. In contrast, miniaturized liquid sample introduction systems can be operated at liquid flow rates below the saturation limit of water vapor in Argon, thus providing extensive solvent evaporation of the produced aerosol before it enters the plasma [8].

Key parameters to describe and compare aerosols used for sample introduction in atomic spectrometry are primarily the droplet size distribution and the mean diameter. As two aerosols with calculative identical mean diameters may differ extremely, other important parameters like the span of the distribution, the axial and radial velocities as well as the droplet number density can be given [9].

The before mentioned figures affect the performance of any liquid sample introduction system in ICP spectrometry [3–5,9]. Ideally, the aerosol should consist of only small droplets, as too large droplets act as local heat-sink, suppressing e.g. excitation and/or the ionization of the analyte in its surrounding [11–16]. But, lowering the mean diameter of an aerosol produced from a given liquid volume will lead to a higher droplet frequency, thus higher droplet number density. Droplet collision and coagulation become more important, as the probability of such processes is related to the square of the droplet number density and losses within the spray chamber might be increased [2,6–8]. Accordingly, the liquid flow rate should be reduced to avoid such issues. Below a flow rate of 10 μL min^{-1}, the droplet number density is minimized significantly,

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http://dx.doi.org/10.1016/j.sab.2013.12.002

and thus droplet collision/coagulation will become negligible [17]. The reduction of the solvent intake will additionally improve the ionization capability of the ICP [18]. However, miniaturized pneumatic nebulizers for such liquid flow rates often come with reduced nozzle diameters which lead to pronounced clogging and high back pressure [8,19]. The EnyaMist provides an inner diameter of the sample transport capillary of 60 μm, while a nozzle exit diameter of 23–34 μm was found for the DOD [20,21]. Both are considered to be small within this context. Therefore, the EnyaMist is operated with an inline filter to prevent particles from entering the nebulizer body. However, clogging of the DOD was not observed during the performed studies [22,23].

The uniformity of an aerosol in terms of droplet size, velocity and direction of motion is not only important for transport effects within spray chambers, but also of importance for reasons of the ion extraction efficiency at the ICP-MS interface. The extraction region has a fixed cylindrical shape of approx. 0.8 by 2.0 mm and thus only ions within this region will contribute to the observed ICP-MS signal [24]. But droplets of different sizes will lead to ion clouds at different locations within the plasma [25]. Not only are larger droplets processed more downstream with respect to the load coil as the processes of vaporization and atomization take more time. Furthermore, the respective ion cloud will be of larger lateral dimension since the longer duration in vapor and atom state leads to more significant thermal diffusion of the respective cloud [26]. Therefore, two-dimensional imaging of the ion-distribution within the ICP can be an important diagnostic tool which is used in the presented study. The inhomogeneities of the droplets' size and velocity were already found to additionally contribute to signal noise [9,11,14]. To summarize, a minimum span of both, size and velocity of the generated droplets is therefore highly desired for aerosols to be introduced in atomic spectrometric excitation/ionization sources.

There were several attempts presented in the past to improve the efficiency of liquid sample introduction. Besides conventional and miniaturized concentric nebulizers, different pneumatic designs like flow-focusing, flow-blurring or parallel path geometries were presented [8,19,27–31]. All of them are based on gas–liquid-interactions and therefore, the liquid and gas flow rate cannot be optimized independently without changing the aerosol characteristic and finally the transport efficiency. Changing the nebulizer geometry will affect the aerosol characteristics [19,29] but selecting suitable nebulizers which meet the different requirements of the respective application is too cumbersome. Another possibility for influencing the droplet generation process is to change the viscosity and/or surface tension of the sample solution [32,33]. In this case, the pronounced carbon intake into the plasma often requires the addition of oxygen to the carrier gas flow. However, any addition of liquids to the sample will lead to dilution along with the risk of sample contamination.

As alternative, discrete droplets can be introduced into the ion source, thus gas and liquid flow rates can be varied independently [23]. As such a sampling device, the MDMI was intensively used for diagnostic studies, although found to be not applicable to real sample analysis [9,25,34,35].

The recently presented drop-on-demand (DOD) aerosol generator overcomes some of the drawbacks of pneumatic nebulization, as its aerosol is no longer generated by gas–liquid interaction. Its superior sensitivity, the applicability to real samples and the possibility to apply alternative calibration techniques based on the dosing frequency of such device were recently outlined [22,23].

As this device is based on modified cartridges of former thermal-inkjet printers, the electrical operation conditions applied to the heating filament affect the droplet generation process through the nozzles. The aim of the presented manuscript is to further characterize such a DOD device, with special reference to the corresponding aerosol characteristics.

2. Experimental

Analytical figures of merit were determined using ICP-MS standard solutions (CertiPur, Merck KGaA, Germany and Sigma-Aldrich, Germany) containing 1.0 g L^{-1} of the element of interest. Dilutions were made with ultra-pure water (Millipore, Milli Q System, USA) acidified with conc. HNO_3 (p.a. grade, Sigma-Aldrich, Germany) to 1% (v/v). Optical studies and two-dimensional ion distributions within the ICP were performed using a 10 μg L^{-1} solution of In, unless otherwise quoted.

ICP-MS measurements were performed using a HP 4500 ICP quadrupole mass spectrometer with a shielded torch. Operation conditions regarding gas and liquid flow rates were optimized regarding maximum signal. The optimum parameters are shown in Table 1. Isotopes monitored in ICP-MS were chosen to the highest natural abundance. The ICP-MS signal was integrated for 0.3 s with ten repetitions unless otherwise quoted. Within this study, the original aerosol transport chamber [22] is directly compared to the more recent one, which was designed to host a dual-DOD system [23]. In the following, the chambers are named after the respective number of devices they can host: the single and the dual aerosol transport chamber.

For this study, the drop-on-demand generator was based on modified thermal-inkjet cartridges as presented before [22,23]. The employed cartridges (HP45) consist of 300 nozzles with a built-in thin-film resistor each. To drive the heating filament of the thermal-inkjet device, electrical pulses were applied, forcing the solvent to partly evaporate followed by the ejection of a certain number of droplets through the nozzle.

2.1. Advanced microcontroller

The developed and previously described DOD microcontroller [22] was further advanced to allow for most flexible pulse generation. The state-of-the-art system allows adjusting current and voltage, which are now variable for both source and drain supply of the DOD device. A short pulse, the so called *pre-pulse* can be added before each main dosing pulse. A schematic of such pulse pattern is shown in Fig. 1a.

2.2. Setup for optical aerosol characterization

The generated droplets were characterized via a setup shown in Fig. 2. It consists of a stroboscope (Xe arc lamp, Ministrob 2000N/S-ext, BBE, Arnsberg, Germany), two optical filters (550 nm short-pass reflection + IR absorbance, Edmund Optics, York, UK) and a CCD camera (Genie M-1280, Teledyne/DALSA, Ontario, Canada). The telecentric lenses (TZM 6 × 65, Sill Optics, Wendelstein, Germany) were chosen to avoid perspective errors in any distance/length measurement of the displayed objects, providing a larger depth-of-field (0.16 mm) compared to conventional optics. At the present setup, the transmitted light of an object is viewed.

The DOD devices as well as the camera were mounted on individual translation stages. The stroboscopic lighting was used in order to avoid motion blur during image acquisition. Due to the large magnification (6×) a very high optical resolution of 0.625 μm per pixel was achieved. As the diffraction limit may compromise the optical performance of such system, an optical filter system was used to block all wavelengths greater than 550 nm generated by the flash. To further reduce the effective exposure time, the decay of the flash was truncated by closing the camera's shutter just in time. A hardware trigger controller synchronizes all involved parts (cf. Fig. 1b). As earlier studies had shown [22], significant deviations in the droplet generation process can be found at dosing frequencies below 80 s^{-1}, but the maximum frame rate of 25 frames s^{-1} of the used camera is still too low. Therefore, a binary 12-stage frequency divider was implemented, to allow higher dosing frequencies while using only every 1/nth event for image acquisition (n = 2–4096).

The described setup allows for variable exposure time (0.4–4.0 μs) and variable delays between the dosing event and the flash (0–160 μs). Through this, different droplets can be displayed at various time intervals after ejection and thus different positions (see Fig. 1 of Electronic Supplementary material). The resulting images were then used to generate