



Analytical evaluation of a quadruple-mode micro-flow ultrasonic nebulizer for sample introduction in microwave induced plasma spectrometry

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ABSTRACT

The analytical potential of a coupled continuous-micro-flow ultrasonic nebulizer quadruple-mode micro-capillary system (μ -USN-QCS)-argon-helium microwave induced plasma-optical emission spectrometry (MIP-OES) has been evaluated for the purpose of determination of inorganic elements (Ba, Ca, Cd, Cu, Fe, Mg, Mn, Pb, Sr, Zn). The nebulizer incorporates four solution capillaries with independent liquid feeding and a common gas inlet. Four different spray chambers were evaluated and the geometry of the best performing one was optimized. A univariate approach and the simplex optimization procedure were used to achieve optimized conditions and derive analytical figures of merit. Analytical performance of the ultrasonic nebulization system was characterized by a determination of the limits of detection (LODs) and precision (RSDs) with the μ -USN-QCS-MIP-OES observed at a $40 \mu\text{L min}^{-1}$ flow rate. The experimental concentration detection limits for simultaneous determination, calculated as the concentration giving a signal equal to three times of the standard deviation of the blank (LOD, $3\sigma_{\text{blank}}$ Criterion, peak height) were in the range from 2.8 ng mL^{-1} for Cu to 30 ng mL^{-1} for Ba. The method offers relatively good precision (RSD ranged from 6% to 8%) for micro-sampling analysis. The methodology was validated through determination of elements in certified reference materials (NRCC DOLT-2, NRC GBW 07302, NIST 2710 and NIST 1643e) and by the aqueous standard calibration technique. The measured contents of elements in the reference materials were in satisfactory agreement with the certified values.

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1. Introduction

The microwave induced plasma-optical emission spectrometry (MIP-OES), besides different spectrometric techniques as such inductively coupled plasma-optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS) techniques has been designed for elements determination in various samples [1]. The argon or helium microwave induced plasma (Ar-MIP or He-MIP) offers some attractive characteristics, such as its unique features of high excitation efficiency for metal and non-metal elements, capability of working with various gases, capabilities for simultaneous determination of elements, low cost for instrumentation and maintenance, and convenience of operation [2]. However, microwave induced plasmas have been less used even though they show a considerable potential as spectral excitation source. This is mostly due to difficult sample introduction and lack of stability of such plasmas against liquid samples or aerosols. This major disadvantage of MIPs compared with other plasma techniques arises from the low power, and hence the low plasma energy, with which the discharge is maintaining. Despite

this, MIP-OES is subject to continuous research, aiming to improve its analytical and operational characteristics. One of the most important fields of this research deals with the liquid sample introduction systems [3–5]. One of the factors limiting sensitivity in plasma emission spectrometry (MIP, ICP, DCP) is sample transport [6]. The liquid sample introduction by means of pneumatic nebulization is most common in ICP and MIP spectrometry's, but the sample transport has been one of the key factors limiting sensitivity in those techniques. The conventional liquid sample introduction systems, using a pneumatic nebulizer and a spray chamber, are generally only about 1%–5% efficient.

An alternative way of increasing the sample introduction efficiency in plasma spectrometric techniques is to use ultrasonic nebulizers (USN) [7]. USNs have been shown to be more efficient at aerosol formation and can produce aerosols with smaller and more uniform droplet size. Generating a finer primary aerosol with a very small mean drop size (ideally $\leq 5 \mu\text{m}$) is an alternative to direct injection to the plasma, as such fine aerosol drops should pass to the plasma with high efficiency. This results in more efficient atomization, higher sensitivity, and reduced matrix effects. It has been reported that ultrasonic nebulizers are capable of operating at flow rates down to $20 \mu\text{L min}^{-1}$, without the need for any makeup solvent, and to provide very high transport efficiency [8,9]. The ability to provide very high transport efficiency at

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flow rates in the range of 2–20 μL suggest good potential for ultrasonic micronebulizers use with microwave induced plasma spectrometry. Ultrasonic nebulizers are popular with inductively coupled plasma (ICP) optical emission (OES) and mass spectrometry (MS). However, over the past decades, only a few ultrasonic nebulizer designs have been developed for use with MIP-OES [2,8–20].

In another attempt to improve the nebulization efficiency, Kovachev et al. introduced a multiple nebulizer for ICP-OES [21]. The prototype described possesses four nebulization nozzles system, with independent liquid feeding and a common gas inlet, incorporated in a single spray chamber. The higher quantity of primary aerosol reached the plasma was reported. However, the different individual nozzles performance was observed in this prototype and relatively low transport efficiency.

The aim of this study was to evaluate, for the first time, the performance of specially designed continuous micro-flow ultrasonic nebulizer quadruple-mode micro capillary system ($\mu\text{-USN-QCS}$) to operate stably with liquid flows as low as ca. 40 $\mu\text{L min}^{-1}$ for elemental determination in MIP-OES. Having multiple independent nebulizing capillaries permits the simultaneous introduction in the spray chamber of aerosols from different solutions (sample, solvent, standard element solutions, internal standard solutions) which could be applicable e.g., to the hydride generation technique. The elements are nebulized in situ and determined by argon-helium microwave induced plasma spectrometry. The optimization of variables affecting the process was carried out by using univariate and simplex optimization approach. The validation of proposed method was carried out by analyzing four different certified reference materials. The $\mu\text{-USN-QCS}$ was made an integrated part of the microwave plasma emission spectrometer, and the results obtained were shown to be satisfactory.

2. Experimental procedures

2.1. Instrumentation

A Carl Zeiss Echelle spectrometer (Model PLASMAQUANT 100) using fiber-optical light-guides and photomultiplier tubes (PMT) and TE_{101} microwave plasma cavity assembly was used for the evaluation of the $\mu\text{-USN-QCS}$, and it was essentially the same as previously described [22]. It was considered important to heat the transfer line from the spray chamber to the microwave plasma to completely reduce water vapor (aerosols) and to avoid broad peaks, plasma instability and memory effects. Therefore, between the cyclonic spray chamber and the microwave plasma cavity, the plasma torch was electrically heated with a constantan heating wire (the torch was covered with a 60 cm wrapped heating wire). The input power for the heating wire was supplied from a Variac transformer (operated at 14 V). The transducer quartz plate was cooled with a closed circuit water cooling system. Instrument settings and operational parameters used for the experimental $\mu\text{-USN-QCS-MIP-OES}$ system are summarized in Table 1. A schematic diagram of the entire experimental set-up (i.e., sample introduction system-MIP-OES) is shown in Fig. 1.

2.2. Quadruple capillary mode sample introduction system

Solution introduction was accomplished in the continuous mode micro-flow ultrasonic nebulizer, which incorporate four nebulization capillaries with independent liquid inlets and a common gas inlet.

The nebulizer is the modified triple-mode micro capillary ultrasonic nebulizer of much smaller size and having four separate solution capillaries [23]. Those capillaries were used for delivery of the standard element solution. The integrated internal water-cooled ultrasonic nebulizer was operated at 1.65 MHz with a forward power of 80 W. The ultrasonic nebulizer used consisted mainly of an electronic unit and a nebulization unit. The electronic portion of the humidifier consists of a power supply, a fan motor, a transformer, an electronic control

Table 1
Operating conditions for $\mu\text{-USN-QCS-MIP-OES}$ system.

<i>MIP-OES parameters</i>	
Mounting	Czerny-Turner in tetrahedral set-up
Focal length/mm	500
Spectral range/nm	193–852
Order lines	28th–123rd
Microwave frequency/MHz	2450
Microwave power/W	165 (100–180, variable)
Microwave cavity	TE_{101} rectangular, water cooled
Microwave generator	700 W, MPC-01 (Plazmatronika Ltd., Wrocław, Poland)
Plasma viewing mode	Axial
Plasma torch, axial position	Quartz tube, 3.0 mm i.d., air cooled
<i>OES data acquisition</i>	
Plasma form	Annular
Read	On-peak
Integration time/s	0.1
Background correction	Fixed point
Determination	Simultaneous
Wavelength/nm (line type)	Ba 455.403 (II), Ca 393.366 (II), Cd 226.502 (II), Cu 324.754 (I), Fe 238.204 (II), Mg 285.213 (I), Mn 257.611 (II), Pb 405.783 (I), Sr 407.771 (II), Zn 213.857 (I)
Plasma supporting gas (He) flow rate/ mL min^{-1}	250 (100–300, variable)
<i>Quadruple-mode capillary ultrasonic nebulization parameters</i>	
Instrument	Quadruple-mode ultrasonic nebulizer
Solution flow mode	Continuous
Transducer frequency/MHz	1.65
Acoustic power/W	80
Transducer type	Piezo-electric quartz plate, water cooled
Spray chamber	Mini-cyclonic
Sample solution flow rate/ $\mu\text{L min}^{-1}$	40 (10–80, variable)
Nebulizer gas (Ar) flow/ mL min^{-1}	800 (300–1000, variable)

board, a float switch for monitoring water level in the cooling water tank and a transducer to produce a 1.65 MHz ultrasonic wave. Fig. 2 shows the main components of the continuous-type $\mu\text{-USN/QCS}$. Nebulization was achieved by placing four identical solution injection capillaries (narrow PFA tubes with 0.5 mm orifices) in contact with the nebulizer surface (the vibrating plate). The capillaries were cut straight and placed close to each other in almost direct contact with the quartz surface of the ultrasonic transducer. The four capillaries were provisionally numbered (capillary I–IV). In this manner four independent solutions might be pumped simultaneously to the quartz piezoelectric transducer (1.65 MHz resonant frequency) at a flow rate in the range 10–80 $\mu\text{L min}^{-1}$ using a peristaltic pump, where they were effectively mixed and dispersed into droplets of ca. 2.0–2.5 μm in mean droplet diameter (0.1–4.5 μm size distribution) [24].

The ultrasonic nebulizer was directly connected to one of the glass spray chambers tested: two cyclonic (with internal volumes of 15 and 50 mL) and two “on axis” (single pass and double pass with internal volumes of 8 mL). Spray chambers tested with main dimensions are shown in Fig. 3. The cyclonic spray chamber made it possible to introduce argon in a pseudo concentric manner, thereby minimizing turbulence. The system was used without desolvation, unlike most higher flow ultrasonic nebulization systems. A spray chamber was held in the PTFE nut, a tight connection being provided by a rubber sealing ring. The transducer quartz plate was cooled with a closed circuit water cooling system. To prevent the analyte (aerosol) from depositing on the plasma quartz torch, the outlet of the spray chambers was electrically heated (the torch was covered with a 60 cm wrapped heating wire).

The liquid samples were introduced through the ultrasonic nebulizer by means of a four channel peristaltic pump (model Perimax12, SPETEC, Erding, Germany). Each channel of the pump supplied one capillary of the nebulizer. The gas flow rate was controlled by means of a

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