



Ultrasonic nebulization atmospheric pressure glow discharge – Preliminary study



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ARTICLE INFO

Article history:

Received 9 March 2016

Received in revised form 20 April 2016

Accepted 28 April 2016

Available online 7 May 2016

Keywords:

Ultrasonic nebulization atmospheric pressure glow discharge

Elemental analysis

Optical emission spectrometry

Solution cathode glow discharge

ABSTRACT

Atmospheric pressure glow microdischarge (μ APGD) generated between a small-sized He nozzle jet anode and a flowing liquid cathode was coupled with ultrasonic nebulization (USN) for analytical optical emission spectrometry (OES). The spatial distributions of the emitted spectra from the novel coupled USN- μ APGD system and the conventional μ APGD system were compared. In the μ APGD, the maxima of the intensity distribution profiles of the atomic emission lines Ca, Cd, In, K, Li, Mg, Mn, Na and Sr were observed in the near cathode region, whereas, in the case of the USN- μ APGD, they were shifted towards the anode. In the novel system, the intensities of the analytical lines of the studied metals were boosted from several to 35 times. As compared to the conventional μ APGD-OES with the introduction of analytes through the sputtering and/or the electrospray-like nebulization of the flowing liquid cathode solution, the proposed method with the USN introduction of analytes in the form of a dry aerosol provides improved detectability of the studied metals. The detection limits of metals achieved with the USN- μ APGD-OES method were in the range from $0.08 \mu\text{g L}^{-1}$ for Li to $52 \mu\text{g L}^{-1}$ for Mn.

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1. Introduction

The atmospheric pressure glow discharge (APGD) is a kind of excitation source, which has been extensively explored in the analytical optical emission spectrometry (OES) since 1993/94 [1,2]. It is also known in literature as the electrolyte cathode atmospheric glow discharge (ELCAD) [2,3] and the solution cathode glow discharge (SCGD) [4]. One of the most notable advantages of the μ APGD is that no nebulizer or spray chamber is required for the sample solutions' introduction and the transport of the analytes into this excitation source. Analyzed sample solutions are integral components of the discharge, i.e., a liquid cathode that is bombarded by high energy ions. Subsequently, the droplets of the sample solutions are transferred to the negative glow zone of the discharge, where excitation processes occur [5]. The mechanism of the analytes transport is not entirely clear. Some studies suggest that the electrospray-like nebulization process plays a key role in this process [6], however, the sputtering is also considered [5]. The use of this phenomenon made it possible to manufacture simplified and miniaturized analytical systems that found applications in trace element analysis by analytical OES and atomic absorption spectrometry (AAS) [7]. However, one problem encountered in these systems is that the transport efficiency of the analytes to the phases of the discharge remains still relatively low.

Cserfalvi et al. [5] studied the intensities of the emission lines of several metals in an ICP-OES system, in which a conventional pneumatic

nebulizer, commonly used for the analytes transport to the plasma, was replaced by an APGD close-chamber device that converted the analyzed sample solutions into a respective mist. Unfortunately, in comparison to the IC-OES system with the pneumatic nebulizer, the acquired intensities of the emission lines of the studied metals were lower from 3 to even 30 times. In a similar experiment, Zhu et al. [8] examined the transport efficiency of As, Pb, Se and Sn. Although the liquid cathode solutions introduced to the APGD contained these elements at a level of 10 mg L^{-1} , no measurable signals of As, Pb, Se and Sn were recorded by ICP-OES. In our previous paper [9], it was found that the transport efficiency of As and Sb into the μ APGD operated with a small-sized He jet, assessed by determining the residual concentrations of these elements in the liquid cathode solution treated by the microdischarge, did not exceed 1% (As) and 8% (Sb). Simultaneously, the mass loss of the sample solution introduced as the liquid cathode of the discharge system via the sputtering and evaporation of water was up to 18%.

Despite the low transport efficiency of different APGD systems, the detectability of elements competitive with those offered by ICP-OES can still be achieved. The detection limits of alkali metals are usually below $1 \mu\text{g L}^{-1}$, and for many other elements, e.g., Ag, Cd, Cu, Hg, In, Mg, Mn, Tl and Zn, they do not exceed $10 \mu\text{g L}^{-1}$ [3,10–16]. Bearing all this in mind, it can be expected that the improvement of the transport efficiency of the analytes to the discharge would make the APGD a powerful excitation source for analytical OES.

Therefore, in the present paper, an original μ APGD system, operating between a small-sized He nozzle jet as the anode and a flowing liquid cathode solution, was coupled with an ultrasonic nebulizer (USN) to

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enhance the transport efficiency of the analytes and the performance of the μ APGD. The resultant analytes—containing dry aerosol was introduced to the discharge through the He nozzle jet anode. The spatial distributions of the atomic emission lines of the selected metals were studied for the coupled USN- μ APGD system and the μ APGD system with the introduction of analytes from the liquid cathode sample solution. Furthermore, the effect of the He gas flow rate and the addition of the non-ionic surfactant to the liquid cathode solution were investigated. Although the results concerning the USN- μ APGD are of a preliminary nature, they let us prove the validity of such a combination. It should also be mentioned that the concept of the introduction of the dry aerosol into the μ APGD seems to be quite rational. Previously, Manard et al. [17] introduced to the liquid sampling (LS)-APGD the sample particles produced by laser ablation (LA) prior to the determination of Ca and Sr by the analytical OES and mass spectrometry (MS).

2. Experimental

2.1. Instrumentation

The μ APGD was operated between a small-sized He jet and a flowing liquid cathode solution in an open-to-air discharge chamber (see Fig. 1). The distance between electrodes (i.e., discharge gap) was 5 mm. Using a peristaltic pump (Masterflex L/S, Cole-Parmer, UK), the liquid cathode solution (acidified with 0.1 mol L^{-1} HCl) was delivered to the discharge chamber at 3.0 mL min^{-1} through a quartz tube (ID = 2.0 mm) that was inserted into a graphite tube (ID = 4.0 mm); the edge of the graphite tube was 2 mm above the edge of the quartz tube. As compared to our previous work [18], in the present system, the ID of a stainless-steel nozzle, used for introducing the He jet-supporting gas, was larger, i.e., $750 \mu\text{m}$. For the conventional μ APGD, the He jet-supporting gas flow rate was within the range of $50\text{--}300 \text{ mL min}^{-1}$ and was regulated using a flow controller and a digital flow meter. The flow rate of 75 mL min^{-1} was found to provide the best performance in reference to stabilizing the surface of the liquid cathode solution and the discharge column, and was applied throughout the work, unless otherwise stated. In the case of the coupled USN- μ APGD system, a higher flow rate of the He jet-supporting gas was required ($300\text{--}1500 \text{ mL min}^{-1}$) because it was also used to carry the resultant dry aerosol from the USN device. For both μ APGD systems, a HV-dc power supply (Dora, Poland) was used and operated in a constant current mode. Stable microdischarges were maintained after supplying a voltage of 1300 V (a voltage drop across the ballast resistor was subtracted) to the stainless-steel nozzle through a $5 \text{ k}\Omega$ ballast resistor. The liquid cathode solution was grounded

through a Pt wire attached to the graphite tube. The resultant discharge current was 40 mA. Both microdischarges were ignited by inserting an isolated stainless steel wire into the gap between the electrodes. In the case of the conventional μ APGD system, analytes were introduced to the discharge through the electro-spray-like nebulization and/or the sputtering of the flowing liquid cathode sample solutions. For the coupled USN- μ APGD, an additional peristaltic pump was applied to introduce the sample solutions at 3.0 mL min^{-1} to the ultrasonic nebulizer (U-5000AT+, CETAC Technologies Inc., USA). Nebulization took place in a glass chamber on a transducer unit. Subsequently, the obtained mist was swept out from the chamber by the He jet-supporting gas (at 700 mL min^{-1} , unless otherwise stated), carried to a heated U-tube, vaporized at $140 \text{ }^\circ\text{C}$ and introduced to a condenser ($3 \text{ }^\circ\text{C}$). The total length of the glassware module, consisting of the chamber, the U-tube dryer and the condenser, was about 1.5 m. Finally, the resultant dry aerosol was introduced to the μ APGD through a transferring tube attached to the stainless-steel nozzle, acting as the anode.

Using a quartz lens ($f = 60$), the radiation emitted by the μ APGD was imaged (1:1) on the entrance slit ($10 \mu\text{m}$) of an imaging spectrograph (Shamrock 500i, Andor, UK) equipped with two holographic gratings (1200 and $1800 \text{ lines mm}^{-1}$) and a UV-Vis CCD camera (Newton DU-920P-OE, 1024×255 pixels, Andor, UK). The acquisition time was 10 s. The intensities of the studied molecular bands as well as the atomic emission lines of the analytes were background-corrected.

2.2. Reagents and sample preparation

Compressed He (99.999%) was supplied by Air Products (Poland). Re-distilled water was used throughout. Non-ionic surfactant Triton X-705 and single-element stock (1000 mg L^{-1}) standard solutions of Ca, Cd, In, K, Li, Mg, Mn, Na and Sr were supplied by Sigma-Aldrich (Germany). The analyzed sample solutions containing the studied metals were introduced as the flowing liquid cathode in the case of the μ APGD or through the ultrasonic nebulizer in the case of the coupled USN- μ APGD system. All these solutions were acidified with ACS grade concentrated HCl (Avantor Performance Materials, Poland) to a final concentration of 0.1 mol L^{-1} . For the USN- μ APGD, the flowing liquid cathode was just a 0.1 mol L^{-1} HCl solution, used to support the discharge.

3. Results and discussion

3.1. The spatial distribution of the emission

The spatial distribution of the intensities of the atomic emission lines of the analytes (Ca, Cd, In, K, Li, Mg, Mn, Na, Sr), within the 5.0 mm discharge gap, was investigated for the μ APGD and the novel coupled USN- μ APGD system. When metals were delivered as the components of the liquid cathode solution, the intensities of their atomic emission lines remained relatively low, likely because the positive metal ions transported from the liquid cathode solution, before recombining to the neutral atoms in the cathode dark space and diffusing into the negative glow region, can be re-attracted to the negatively charged cathode [19]. This process is determined by the pressure in the discharge column, the cathode fall and the average energy of the electrons in the near-cathode region [20]. The distribution profiles of the atomic emission lines of metals reached the maximum in the near cathode region of the discharge, i.e., within the distance of 1–2 mm from the cathode surface (see Fig. 2). These results are consistent with those obtained for other APGD systems operated at higher discharge currents ($70\text{--}80 \text{ mA}$) but with narrower discharge gaps ($\sim 3 \text{ mm}$) and using metallic rods as anodes instead of the gaseous nozzle jet [7,21,22].

For the USN- μ APGD, where positively charged metal ions were delivered to the discharge in the stream of the He jet-supporting gas as the dry aerosol and through the nozzle anode, the intensities of the atomic emission lines of the studied metals were evidently boosted,

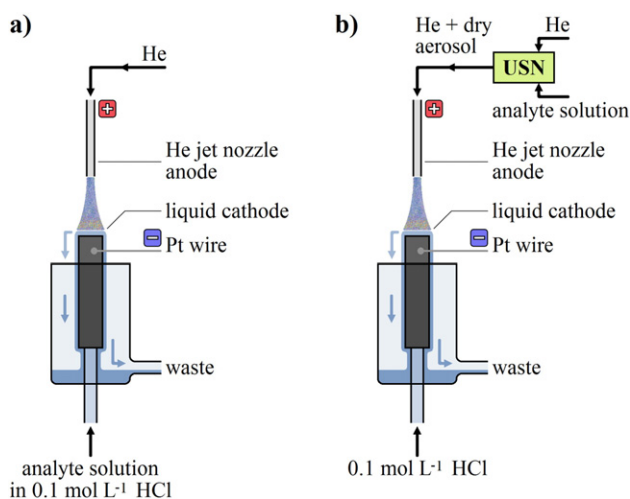


Fig. 1. The experimental set-up of the μ APGD systems operated between a small-sized He jet and a flowing liquid cathode solution: a) — the conventional system, b) — the system combined with the USN device.

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