



# Reduction of spectral interferences in atmospheric pressure glow discharge optical emission spectrometry



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## ABSTRACT

An atmospheric pressure glow microdischarge ( $\mu$ APGD) operated between a gaseous microjet and a flowing liquid cathode and sustained in various atmospheres (Ar, He, CO<sub>2</sub>) and in different discharge-systems (fully open-to-air, semi-closed) was investigated by optical emission spectrometry (OES). The morphology of the emission spectra of all the discharges was discussed. The effect of the microjet-supporting gas flow rate on the intensity of the interfering molecular bands, emission from analyte atomic lines and spectroscopic parameters was thoroughly studied. It was noticed that the appearance, the electron number density, optical temperatures and behavior of the CO<sub>2</sub>- $\mu$ APGD system completely differed from those assessed for the noble gas- $\mu$ APGD system. Regardless of the applied microjet-supporting gas, cutting off the air supply caused a reduction of the NO and N<sub>2</sub> molecular bands intensity, however, an apparent decrease in emission from analytical atomic lines was simultaneously noticed. Nevertheless, for  $\mu$ APGD operated in a semi-closed system, detectability of several metals (Cd, Co, Hg, Zn) evaluated with OES was improved twice. The obtained Limits of Detection (LODs) covered the range from hundreds  $\mu\text{g L}^{-1}$  (for metals characterized by low emission, i.e. Cr, Pb), through tens (Ca, Co, Cu, Hg, Mn, Sr, Zn) and several  $\mu\text{g L}^{-1}$  (Ag, Cd, Cs, In, Mg, Tl), to  $<1 \mu\text{g L}^{-1}$  for alkali metals (K, Li, Na, Rb). The measurement repeatability of  $\mu$ APGD-OES operated in the open-to-air system was below 1% and it was noticeably better than this received for the semi-closed system. The accuracy of  $\mu$ APGD-OES was confirmed by analysis of ground water samples (ERM-CA615 and ERM-CA616).

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## 1. Introduction

An atmospheric pressure glow discharge (APGD) generated in contact with flowing liquids is a new miniaturized emission source which has been successfully applied in optical emission spectrometry (OES) for several years [1,2]. It is also known in literature as a liquid sampling (LS) APGD [3,4], solution cathode glow discharge (SCGD) [5,6] and electrolyte cathode atmospheric glow discharge (ELCAD) [7–9]. One of the most important advantages of APGD is that it can be sustained in the ambient air atmosphere, providing low-cost operation and analysis. On the other hand, molecules containing nitrogen, i.e. NO, NH, N<sub>2</sub> and N<sub>2</sub><sup>+</sup> [10] are excited and their emission accompanies the spectra, which significantly reduces the APGD-OES detectability. Although the first attempts to use APGD in OES dates back to 1993 [11], little effort has been made so far to overcome spectral interferences originating from molecular nitrogen species.

Park et al. [12] investigated the effect of different discharge gases, i.e. air, Ar and He, on the emission spectra of APGD operated in a fully closed discharge cell. They did not pay too much attention to describe the behavior of the N<sub>2</sub> bands, however, it could be noticed that their intensities were the highest when Ar was applied as discharge gas. Moreover, they established that relative intensities of Cu I and Cd I analytical lines varied due to the discharge gas type in the following order: He < Ar < air.

Jenkins et al. [13] compared the detectability of Na in a miniaturized APGD-OES system sustained in air and Ar in a fully closed system. Even if the microdischarge was generated in Ar, some rotational structures of the molecular bands attributed to the N<sub>2</sub> rotational-vibrational systems were visible. What is more, they were even stronger than those observed when  $\mu$ APGD was operated in the air. As a result, despite better excitation of the Na atoms in Ar- $\mu$ APGD, the signal-to-noise ratio for Na I 589.0 nm line acquired for air- $\mu$ APGD was about 5–10 fold higher. The cited authors suggested that in this case the N<sub>2</sub> molecular bands were efficiently excited by the Ar metastable states and hence, if N<sub>2</sub> could not be totally excluded from the discharge, the operation in the air would be more desirable.

In one of our previous paper we found that an effective way to suppress the emission from nitrogen (NO, N<sub>2</sub>) and oxygen (OH) molecules and boost the emission from analytes atoms is the addition of non-ionic surfactants to the liquid cathode solution [14]. This modification allowed to significantly improve detectability of APGD-OES, that was later on revised by other researchers as well [15,16].

All papers cited above concerned traditional APGD operated with solid metal anodes. We cannot fail to notice that meanwhile arrangements in which a solid anode is replaced by a nozzle fed with miniature gas flow also have an interest [17,18]. In comparison to the conventional discharge arrangement with a pin-type electrode, APGD operated in

contact with a gaseous plasma microjet has some outstanding advantages. Just to mention that it is more stable, which results in lower standard deviations of background (SDB) and better repeatability [10]. Shirai et al. [19] generated APGD using a He microjet of a miniature flow that could be sustained in conditions with or without a glass tube cutting the ambient air supply. The use of such glass tube resulted in an almost complete absence of the emission from the  $N_2$  molecules. Unfortunately, they did not attempt to apply this modified discharge system to chemical spectroanalysis.

The aim of the present paper was to examine the effect of the modification in the discharge chamber construction and the impact of the discharge gas composition on the spectral interferences in  $\mu$ APGD-OES operated between a gaseous microjet and a flowing liquid cathode. The research hypothesis assumed that the  $\mu$ APGD operation in the  $CO_2$  atmosphere or in the semi-closed discharge chamber cutting off the air supply from the discharge core, would efficiently suppress the intensities of the nitrogen-containing molecular bands, and in consequence, improve detection power of  $\mu$ APGD-OES. At the beginning, the spectra morphology of the discharge sustained in various gases (Ar, He,  $CO_2$ ) and in different systems (open-to-air and semi-closed) were assessed and compared. Subsequently, the effect of the microjet-supporting gas flow rate on the selected spectroscopic parameters, i.e. optical temperatures, the electron number density, and the spectra morphology was investigated. Finally, the analytical performance of  $\mu$ APGD-OES operated using modified discharge systems was determined.

## 2. Experimental

### 2.1. Instrumentation and methods

APGD was generated in open-to-air and semi-closed systems. The first one has been described in our previous paper [10]. As compared to the mentioned work, in the present open-to-air system setup the inner diameter of the nozzle used was larger, i.e. 750  $\mu$ m. The second, semi-closed system is shown in Fig. 1. The cathode compartment consisted of a graphite tube (outer/inner diameter 6.0/4.0 mm) with an inserted quartz tube in such a way that its edge was 5 mm below the edge of the graphite tube. Microjet-supporting gases (Ar, He) were introduced through a stainless steel nozzle (length 35 mm, inner diameter 750  $\mu$ m) using a Tylan General (CA, USA) FC-2900 flow controller and a RO-28 digital flow meter to control their flow rates. The nozzle and the graphite-quartz tube were vertically oriented with a gap between them of 5 mm. Pt wires attached to the graphite tube and the nozzle were used to provide the electric contact to both electrodes. To prevent  $\mu$ APGD operated between a gaseous microjet and a flowing liquid cathode from penetration by the ambient air, the semi-closed quartz chamber was used, shielding the flowing liquid cathode compartment and the gaseous microjet nozzle. In such system, the gas came out from the chamber through an elliptical hole (diameters 8 and 5 mm), simultaneously acting as the observation window. Regardless of the discharge cell used, a liquid cathode solution (0.1 mol  $L^{-1}$  HCl) was delivered (at 3.0 mL  $min^{-1}$ ) through the quartz tube using a 2-channel LabCraft (France) peristaltic pump, model Hydrys 05. A stable microdischarge was maintained after supplying the flow of gases through the nozzle and a 1000–1500 V potential to electrodes. In the latter case a Dora (Poland) HV-dc power supply was applied. The resultant discharge current ( $\sim 40$  mA) was additionally stabilized by using a 5 k $\Omega$  ballast resistor connected in series with the HV-dc power supply.

Using an achromatic UV lens, the radiation emitted by the near-cathode zone of  $\mu$ APGD was imaged (1:1) on the entrance slit (10  $\mu$ m) of a Shamrock SR-500i (Andor, United Kingdom) spectrometer equipped with Newton DU-920P-OE (Andor, United Kingdom) CCD camera. To handle the spectrometer and control its configuration, software provided by Andor (Solis-32 bit for Windows 7) was used. In all the experiments the integration time was 10 s; the intensities of the studied molecular bands and the atomic emission lines of metals were

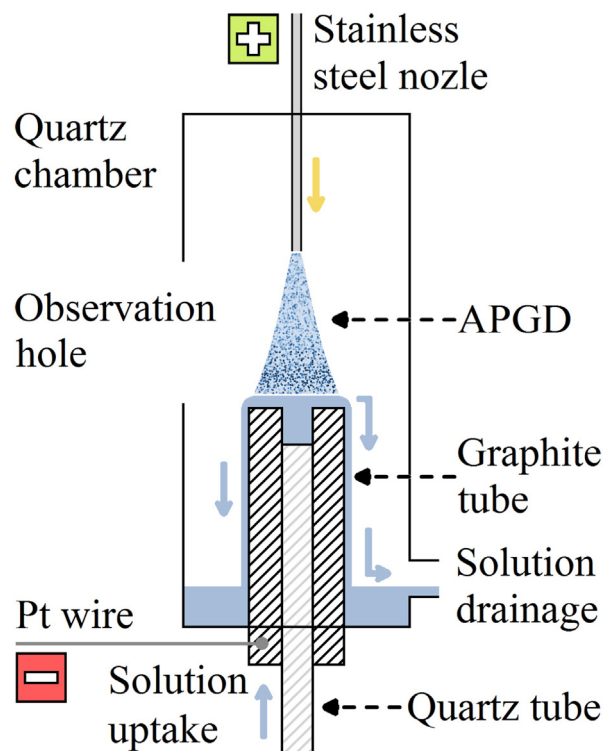


Fig. 1. The scheme of a semi-closed system for  $\mu$ APGD generated between a gaseous microjet and a flowing liquid cathode (not in scale).

background-corrected. Methods for measuring the excitation temperature of the hydrogen atoms ( $T_{exc}(H)$ ), the rotational and vibrational temperatures of the OH molecules ( $T_{rot}(OH)$ ,  $T_{vib}(OH)$ ), and the electron number density ( $n_e$ ) were described elsewhere [10,14].

### 2.2. Reagents and sample preparation

Compressed He (99.999%), Ar (99.999%) and  $CO_2$  (99.998%) were supplied by Air Products, Messer and Linde, respectively. Re-distilled water was used throughout. Single-element 1000 mg  $L^{-1}$  standard solutions of Ag, Ca, Cd, Co, Cr, Cs, Cu, Hg, In, K, Li, Mg, Mn, Na, Pb, Rb, Sr, Tl and Zn were supplied by Sigma-Aldrich (Germany). All the standards and samples solutions were acidified to a final concentration of 0.1 mol  $L^{-1}$  with a concentrated HCl solution (ACS reagent, 36.5–38.0%) obtained from J. T. Baker.

To assess the accuracy of  $\mu$ APGD-OES, the certified reference materials (CRMs) of the natural ground waters (ERM-CA615 and ERM-CA616) from the Joint Research Centre Institute for Reference Materials and Measurements (JRC-RMM) were analyzed. For each CRM, two parallel portions (10.0 mL) were sampled, acidified with concentrated HCl, and finally doubly diluted with re-distilled water. Resulting sample solutions were not filtered, the final HCl concentration was 0.1 mol  $L^{-1}$ . They were next directly analyzed by  $\mu$ APGD-OES on the content of Ca, K, Mg and Na versus the external calibration with standard solutions of these metals and respective blank sample solutions.

## 3. Results and discussion

### 3.1. Discharge appearance and spectra morphology

It was established that there were significant differences in the discharge appearance depending on the used microjet-supporting gases. In the case of Ar- $\mu$ APGD it looked like a thin thread expanding at its base to 2–3 mm, whereas for the He- $\mu$ APGD system a regular cone was formed with base diameter of about 4–5 mm. Both discharges

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