



# The improvement of the analytical performance of direct current atmospheric pressure glow discharge generated in contact with the small-sized liquid cathode after the addition of non-ionic surfactants to electrolyte solutions

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## ABSTRACT

A low power direct current atmospheric glow discharge sustained in the open to air atmosphere in contact with a small-sized flowing liquid cathode was used as an excitation source in optical emission spectrometry. The composition of electrolyte solutions served as the liquid cathode was modified by the addition of non-ionic surfactants, namely Triton x-45, Triton x-100, Triton x-405 and Triton x-705. The effect of the concentration of each surfactant was thoroughly studied on the emission characteristic of molecular bands identified in spectra, atomic emission lines of 16 metals studied and the background level. It was found that the presence of both heavy surfactants results in a significant increase in the net intensity of analytical lines of metals and a notable reduction of the intensity of bands of diatomic molecules and the background. In conditions considered to be a compromise for all metals, selected figures of merit for this excitation source combined with the optical emission spectrometry detection were determined. Limits of detection for all metals were within the range of 0.0003–0.05 mg L<sup>-1</sup>, the precision was better than 6%, while calibration curves were linear over 2 orders of the magnitude of the concentration or more, e.g., for K, Li, Mg, Na and Rb. The discharge system with the liquid cathode modified by the addition of the surfactant found its application in the determination of Ca, Cu, Fe, K, Mg, Mn, Na and Zn in selected environmental samples, i.e., waters, soils and spruce needles, with the quite good precision and the accuracy comparable to that for measurements with flame atomic absorption spectrometry (FAAS) and flame atomic emission spectrometry (FAES).

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## 1. Introduction

When almost 20 years ago Cserfalvi and Mezei [1,2] introduced a new concept of atmospheric pressure glow discharge (APGD) realized by a direct contact of the discharge with a conductive sample solution acting itself as cathode, no one could expect that this type of the discharge would nowadays be one of the most promising and alternative excitation sources in optical emission spectrometry (OES). From the very beginning, developed low power direct current (dc) APGD, operated between a metallic anode and an electrolyte solution that overflowed an inlet tube or a capillary, was characterized by a very simple design of the discharge cell and low operating costs [1–7]. Indeed, the electric power used to sustain the discharge is relatively low, i.e., within 20–80 W, and mostly dissipated at the liquid-discharge interface to evaporate water and sputter dissolved metal ions from analyzed

solutions [8–12]. Despite a small size and a compact geometry of the discharge, excitation phenomena occurring in its near-cathode zone result in a simple atomic emission line spectra for a quite large number of metals, less common spectral overlaps of these lines and a relatively low level of the background intensity in their vicinity [1,2,11]. All this makes that dc-APGD generated in contact with the liquid cathode is a very convenient excitation source for the direct analysis of sample solutions by OES on the concentration of different metals present in them at the level of major and minor components or impurities [3–5,7,10–13].

The analytical performance of early dc-APGD systems with liquid cathodes was unfortunately unsatisfactory [2,3,5]. The short-term precision, referring to the reproducibility of consecutively measured intensities of atomic emission lines of metals, was commonly poor. Since this figure of merit was closely associated with an inability to reproduce the distance between the metallic anode and the surface of overflowing electrolyte solutions, fluctuations in their flow rate and the size of the cathode surface were critical for the overall performance of these systems [1–7]. Despite high flow rates used to neglect this

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inconvenience, any alterations of the discharge gap usually resulted in limits of detection (LODs) for measured metals, i.e., Al, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb and Zn, within the 0.01–1 mg L<sup>-1</sup> range [3]. Additionally, linearity ranges obtained for early dc-APGD discharge systems with liquid cathodes were short and only spanned about 2 orders of the concentration. That is why analytical applications of these devices were at the beginning limited to identifying Ca, K, Mg and Na ions in tap waters, which were simply used in these systems as electrolyte and/or carrier solutions [1–3,6,14,15]. Additionally, to demonstrate the suitability and the usefulness of this unique excitation source for the determination of a wider group of metals, mentioned tap waters were enriched with Cd, Cu, Ni, Pb and Zn ions [1–3,14,15].

Changes in the design of electrolyte solution delivery capillaries made in last several years led to the improvement of the optical thinness of the discharge and its stability [4,10–13,16–21]. A better reproducibility of the discharge gap results in a much better analytical performance of such modified discharge systems. This is primarily reflected by LODs of determined metals (0.001–0.01 mg L<sup>-1</sup>) that are actually better by 1 to 2 orders of the magnitude as compared to those achieved when using earlier constructions of discharge cells. Linearity ranges reported for these systems typically vary from 2 to at least 4 orders of the concentration, while the precision in most cases is better than 6%. All these improved figures of merit make dc-APGD generated in contact with the liquid cathode a highly desirable instrumental method for the spectrochemical analysis of food samples, including tap, drinking and mineral waters [4,7], tea infusion [4], tea leaves [4], fresh milk [7], tuna fish [20–22], oyster tissue [20] or aquatic plant [22].

Although less frequently reported, the improvement of the analytical performance of dc-APGD systems generated in contact with the liquid cathode can also be attained through the modification of the composition and physicochemical properties of electrolyte solutions delivered. Accordingly, it was lately established that formic or acetic acids added to these solutions in the amount not higher than 10% (v/v) was responsible for a 3- to 4-fold increase in the sensitivity of the determination of Hg, likely due to changes of the boiling point and the surface tension of analyzed solutions [22].

Considering the possibility of changes of the rate of chemical reactions and the distribution of reaction products by the addition of surfactants to analyzed solutions as described in case of various atomic spectrometry applications [23,24], it could be expected that the presence of these compounds may enhance the sputtering efficiency of dissolved ions and the transfer rate of metals to the near-cathode zone of the discharge.

Since, to the best of our knowledge, the analytical performance of dc-APGD generated in contact with the liquid cathode modified by the addition of surfactants to electrolyte solutions has not been examined so far, the investigation of the behavior of such a discharge system seems to be important for its practical application in the trace element analysis. Therefore, in this present study, miniaturized dc-APGD generated in the open to air atmosphere in contact with a small-sized liquid cathode was used and the effect of the concentration of non-ionic surfactants, namely Triton x-45, Triton x-100, Triton x-405 and Triton x-705, added to electrolyte solutions on the net intensity of atomic emission lines of 16 metals and the background intensity in the vicinity of these lines for this system was thoroughly examined. Under conditions which are a compromise for all metals and relate to the type and the concentration of the surfactant, selected figures of merit, i.e., linearity ranges, LODs and the precision, distinctive for this excitation source were determined using OES and compared to those achieved in conditions without the addition of the surfactant. Additionally, the suitability of the system for the trace

analysis was evaluated by its application to measurements of the concentration of selected metals in environmental samples, i.e., water samples from two lakelets located in disused workings of metal ores, extracts of needles of spruces growing on slopes of these two excavations and extracts of soils collected from this area. The reliability of results of the analysis of these samples made with the miniaturized dc-APGD system with the liquid cathode modified by the addition of Triton x-405 and combined with the OES detection was assessed by comparing them with results obtained using flame atomic absorption spectrometry (FAAS) and flame atomic emission spectrometry (FAES).

## 2. Experiment and materials

### 2.1. Instrumentation

In an open to air miniaturized dc-APGD system used in this work, a quartz tube with an internal diameter of 2 mm, mounted in a glass-Teflon housing, was applied to introduce electrolyte solutions to the system at a flow rate of 1.2 mL min<sup>-1</sup> via a two channel peristaltic pump (LabCraft, France) [4,17] (see Fig. 1). In a cathode compartment of the housing, a graphite tube with an internal diameter of 4 mm was fixed on the mentioned quartz tube in such a way that its edge was 2 mm above the edge of the internal quartz tube. The electrolyte solution overflowing the quartz tube acted in this system as the liquid cathode. It was collected in a reservoir formed at the bottom of the housing and instantly drained using the same peristaltic pump. A molybdenum rod with an external diameter of 2 mm, attached to a regulated micrometer screw, was used as the anode. The molybdenum rod and the graphite tube were vertically oriented and the gap between them was 5 mm. A platinum wire, directly bonded to the graphite tube, was used to provide the electrical contact. A stable abnormal dc-APGD between the surface of the electrolyte solution overflowing the graphite tube and the anode was sustained after applying a positive potential (1500 V) to the rod from a high-voltage dc power supplier and bringing it to a distance of 1 mm from the solution surface. A 10 kΩ ballast resistor was immersed in the electric circuit of the discharge to stabilize the discharge current (30 mA).

An unmagnified (1:1) image of the near-cathode zone of the discharge was collimated at the entrance slit single grating imaging spectrometer Triax 320 (HORIBA Jobin Yvon) using an achromatic UV lens (details about the optical emission

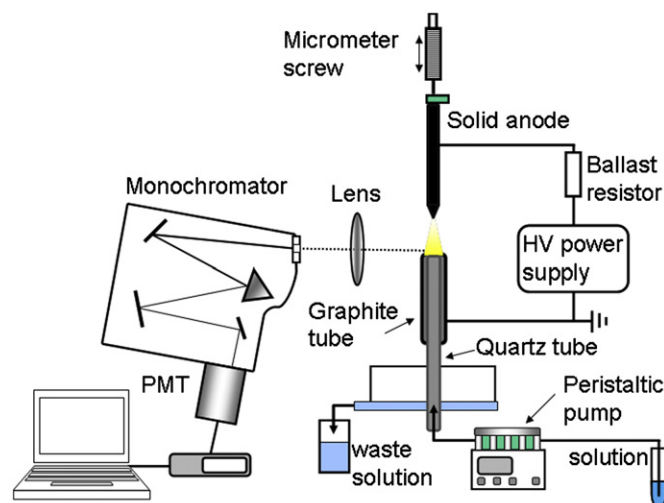


Fig. 1. The experimental set-up of the excitation source (not to scale).

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