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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

Krzysztof Gręda, Piotr Jamróz*, Paweł Pohl

Department of Chemistry, Division of Analytical Chemistry, Wroclaw University of Technology, Wybrzeze Stanislawa Wyspianskiego 27, 50-370 Wroclaw, Poland

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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^{-1}, 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).

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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* Corresponding author. Tel.: +48 71 320 3807; fax: +48 71 320 2494.
E-mail address: piotr.jamroz@pwr.wroc.pl (P. Jamróz).

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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^{-1} 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^{-1}) 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^{-1} 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 and 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 imagining spectrometer Triax 320 (HORIBA Jobin Yvon) using an achromatic UV lens (details about the optical emission

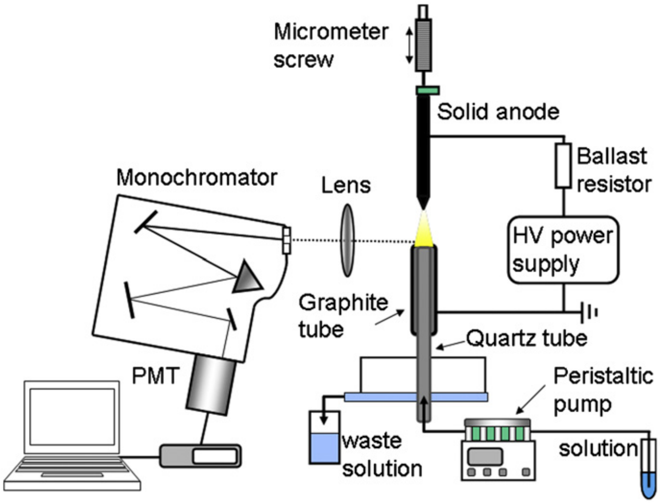

Fig. 1. The experimental set-up of the excitation source (not to scale).

spectrometry system in Table 1). A SpectraMax/32 for Windows software (Instruments SA, Inc.), version 3.2, was used to handle the spectrometer and control its configuration. The acquisition and the data processing were done with the same computer program. Most prominent and free from interferences atomic emission lines of metals were measured. A Perkin Elmer 1100 B flame atomic absorption spectrometer (FAAS) was used as a reference method for the quantification of the concentration of Ca, Cu, Fe, K, Mg, Mn, Na and Zn in analyzed environmental samples. Working conditions recommended by the manufacture of the FAAS instrument were used in all determinations. In case of K and Na, the concentration of these metals was measured using an atomic emission mode. A time-average integration mode with an integration time of 1 s and 3 read cycles was selected for the signal processing.

2.2. Reagents and solutions

Doubly distilled water was used throughout. Single-element 1000 mg L^{-1} standard solutions of Ca, Cd, Co, Cr, Cs, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr and Zn were supplied by Sigma-Aldrich Chemie GmbH (Germany). Non-ionic 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycols, i.e., Triton x-45 [$C_{14}H_{22}(C_2H_4O)_{4.5}$], Triton x-100 [$C_{14}H_{22}(C_2H_4O)_{9.5}$], and 70% (m/v) water solutions of Triton x-405 [$C_{14}H_{22}(C_2H_4O)_{35}$] and Triton x-705 [$C_{14}H_{22}(C_2H_4O)_{55}$], were also provided by Sigma-Aldrich. Single-element or mixed standard solutions of studied metals at concentrations within the range of 0.1–100 mg L^{-1} were prepared by appropriate dilutions of bulk standard solutions. All solutions were acidified with a concentrated HCl solution (ACS reagent, 36.5–38.0%) obtained from J. T. Baker. The final concentration of HCl in these solutions was 0.1 mol L^{-1}. Triton x-45, Triton x-100 and Triton x-405 were separately added to standard solutions and their final concentrations corresponded to ½, 1, 2, 5, 8 and 10 times their critical micelle concentrations (CMCs). In case of Triton x-705, its concentration in standard solutions was lower, i.e., ¼, ½, 1, 2, 3 and 5 times its CMC, due to difficulties in handling more concentrated solutions of this surfactant. Values of CMCs were 0.10, 0.24, 0.81 and 1.04 mmol L^{-1}, respectively, for Triton x-45, Triton x-100, Triton x-405 and Triton x-705 [25].

2.3. Sample preparation and measurements

Two water samples (2 L of each water) from Purple and Azure lakelets, located in the Rudawy Landscape Park (Lower Silesian Voivodeship, Sudetes Mountains, Poland), were collected into pre-cleaned polyethylene bottles. Both ponds are artificially formed in place of former (the turn of the 18th and the 19th centuries) mines of metal ores. Water samples were immediately acidified with a 2.0 mol L^{-1} HCl solution and filtered through pre-conditioned quantitative cellulose filter papers (grade 2). Before measurements, portions of resulting filtrates were appropriately diluted and Triton x-405 was added to resulting sample solutions so that the final concentration of HCl was 0.1 mol L^{-1}, while the concentration of the surfactant corresponded to its 5 × CMC. Two soil samples (~500 g of each soil) from the area of mentioned lakelets were collected at a depth of 10–20 cm from the surface. They were thoroughly disaggregated and dried in an oven at 60–80 °C for 16 h and next grounded using an agate mortar and a pestle. Ground soil samples were sieved through a 250 μm size sieve to obtained finely homogenized powders. Sample portions (4 g) of the <250 μm size fraction were shaken with 40 mL of a 1.0 mol L^{-1} HCl solution for 48 h at room temperature. Resulting leachates were separated from samples using the filtration through pre-conditioned quantitative cellulose filter papers (grade 2). Finally, collected filtrates were 10-fold diluted and Triton x-405 was added to them to reach the concentration corresponding to its 5 × CMC. Needles of spruces (~100 g for each location) growing near both lakelets were analyzed as well. Their leachates were prepared in the same way as described above. All sample solutions were analyzed by dc-APGD-OES on the concentration of Ca, Cu, Fe, K, Mg, Mn, Na and Zn. The method of four standard additions was used for the calibration to compensate for any matrix effects. For each material three parallel samples and respective procedural blank samples were prepared.

Sample solutions analyzed by FAAS/FAES were prepared in the same way as for the analysis by dc-APGD-OES except for the addition of Triton x-405 to them. The five-point calibration with simple standard solutions at the concentration range of 0.1–5.0 mg L^{-1} (Ca, Cu, Fe, Mg, Mn and Zn) or 0.01–1.0 mg L^{-1} (K and Na) was carried out. Final results were averaged for three parallel samples and values of corresponding blank samples were considered in calculations.

3. Results and discussion

3.1. Effect of the concentration of non-ionic surfactants on band emission characteristic of identified molecules

As can be seen from Fig. 2, giving exemplary emission spectra of miniaturized dc-APGD generated in contact with an overflowing 0.1 mol L^{-1} HCl solution and the same solution but containing Triton x-100 and Triton x-705 at a concentration corresponding to 5 × CMC of these surfactants, the addition of non-ionic surfactants to electrolyte solutions results in considerable changes in the morphology of the emission spectrum of this excitation microsource. It is reflected by an overall decrease in the intensity of molecular bands and the background level. Accordingly, intensities of emission bands of the NO molecule identified within

Table 1
Experimental conditions of the acquisition of emission spectra of the miniaturized dc-APGD excitation source generated in contact with flowing liquid cathode.

Triax 320 imaging spectrometer with SpectraAcq2 single photon counting acquisition system (HORIBA Jobin Yvon)	
Focal length	320 cm
Grating	Holographic, 1200 grooves mm^{-1}
Spectral range	190–900 nm
Entrance slit width	100 μm
Exit slit width	100 μm
Photomultiplier	Hamamatsu R-928
Bias voltage	−700 V
Integration time	100 ms
Wavelengths	Ca I 422.7 nm, Cd I 228.8 nm, Co I 240.7 nm, Cr I 359.3 nm, Cs I 852.1 nm, Cu I 324.8 nm, Fe I 248.3 nm, Hg I 253.7 nm, K I 766.5 nm, Li I 670.8 nm, Mg I 285.2 nm, Mn I 279.5 nm, Na I 589.0 nm, Ni I 232.0 nm, Pb I 368.3 nm, Rb I 780.0 nm, Sr I 460.7 nm and Zn I 213.9 nm.

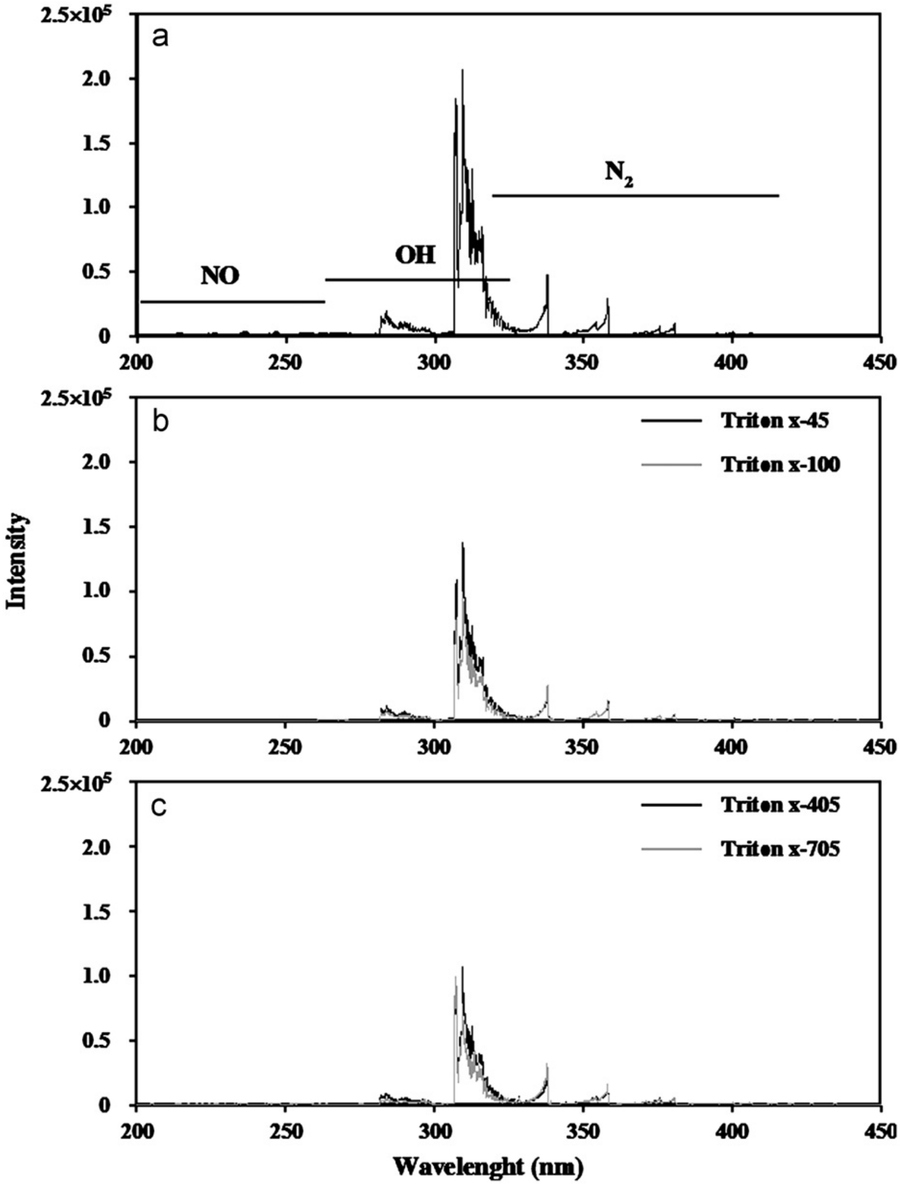

Fig. 2. Emission spectra of dc-APGD generated in contact with the small-sized liquid cathode within the 200–450 nm spectral range when using 0.1 mol L^{-1} HCl electrolyte solutions with the addition of (a) no surfactant, (b) Triton x-45 and Triton x-100 (at its 5 × CMC) and (c) Triton x-405 and Triton x-705 (at its 5 × CMC).

the spectral range of 203–260 nm and belonging to the $A^2\Sigma^+ \rightarrow X^2\Pi$ system, the OH molecule identified within the spectral range of 259–321 nm and belonging to the $A^2\Sigma^+ \rightarrow X^2\Pi$ system and the N_2 molecule identified within the spectral range of 315–406 nm and belonging to the $C^3\Pi_u \rightarrow B^3\Pi_g$ system were significantly reduced, however, the magnitude of this reduction was established to depend on the size of the surfactant and its concentration in the electrolyte solution. It is clearly evidenced by the dependence of the net intensity of band heads from the concentration of the surfactant in the electrolyte solution found for (0-1) NO, (0-0) OH and (0-1) N_2 systems, at 247.9, 309.3 and 357.7 nm, respectively. As can be seen from Fig. 3(a), giving the relative net intensity of mentioned band heads of NO, OH and N_2 molecules versus the concentration of Triton x-45 and Triton x-405, greater and more rapid decreases in the net intensity of these band heads (by 50 to more than 90% as compared to values assessed using the electrolyte solution with no surfactant added) were achieved when Triton x-405 was used even at its relatively low concentration in electrolyte solutions, i.e., ½ × CMC and 1 × CMC. A similar trend was established for Triton x-705. In case of Triton x-45 and Triton x-100, the drop of the net intensity of selected band heads of NO, OH and N_2 molecules was more gradual and lower in terms of its value.

The intensity of the background in the vicinity of these band heads was found to decrease as well in these conditions (see Fig. 3(b) for (0-1) NO and (0-1) N_2 molecular bands and the addition of Triton x-45 or Triton x-405 to electrolyte solutions). This effect was also faster and stronger in case of the presence of heavy surfactants in electrolyte solutions. Accordingly, a decrease in the background intensity by 20–40% as compared to this acquired in conditions without the addition of the surfactant was established. Light surfactants, i.e., Triton x-45 and Triton x-100, were found to produce a 10–30% reduction of the background intensity when present in electrolyte solutions at the concentration corresponding to their 2 × CMC or 5 × CMC.

Interestingly, no band structures originating from common and well marked carbon containing molecules, i.e., the C_2 $A^3\Pi_g \rightarrow X^3\Pi_u$ system appearing in the 469–516 nm spectral range (for the most intensive 0-0, 1-0, 2-1 and 3-2 transitions bands), the CH $A^2\Delta \rightarrow X^2\Pi$ system with the most intensive (0-0) transition band at 431.4 nm or the CN $A^2\Sigma \rightarrow A^2\Pi$ system appearing in the

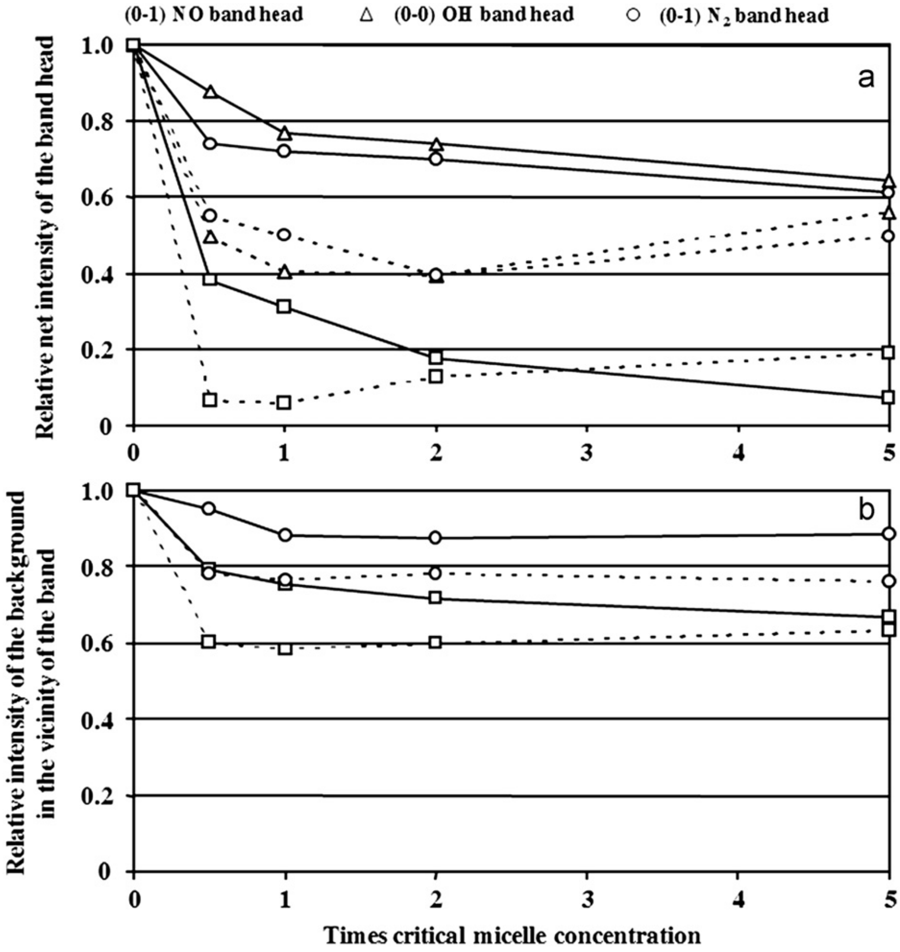

Fig. 3. The dependence of (a) the relative net intensity of band heads and (b) the relative intensity the background in the vicinity of bands from the concentration of Triton x-45 (solid line) and Triton x-405 (dotted line) in the electrolyte solution.

358–422 nm spectral range (for the most intensive 0-0, 0-1, 1-0, 1-1, 1-2, 2-1, 2-2 and 2-3 transitions), were identified in emission spectra of miniaturized dc-APGD generated in contact with electrolyte solutions with added surfactants. This is likely to the fact that products of the decomposition of these non-ionic surfactants in conditions of the dc-APGD treatment are relatively large in size [26].

3.2. *Effect of the concentration of non-ionic surfactants on atomic emission characteristic of metals*

When analyzing electrolyte solutions containing metals added at concentrations ranged from 1 to 10 mg L^{-1}, it was established that the net intensity of their analytical lines was enhanced in different ways, depending on the type of the surfactant and its concentration in the electrolyte solution. The mentioned increase in the net intensity of these lines was found to be the highest for Triton x-405 and Triton x-705 when they were present in electrolyte solutions at the concentration close to their 5 × CMC. This can be seen for instance for Ca, Co, Cr, Cs, Cu, Fe, Hg, K, Li, Mn, Na, Ni, Pb, Sr and Zn in Fig. 4, which gives net intensity amplification factors for these metals defined as ratios of net intensities of their atomic emission lines achieved in conditions when a surfactant was added to the electrolyte solution to net intensities of these lines obtained in conditions with no surfactant present in the electrolyte solution. Apparently, the highest enhancements of net intensities of atomic emission lines of studied metals were obtained for Pb (~9–10), Cu, K and Na (~5–6) and Hg (~5), then for Co, Fe and Mn (~4–5), Cs and Ni (~4) and finally for Cd, Mg and Rb (~3–4). A lower amplification of net intensities of atomic emission lines was determined for Cr (~3), Ca, Li and Zn (~2–3) and Sr (~2). For a half of metals, i.e., Cr, Cs, Hg, Li, Mg, Ni, Rb and Sr, net intensity amplification factors obtained for Triton x-405 and Triton x-705 at the concentration corresponding to their 5 × CMC, were similar. In case of Ca, Cd, Co, Cu, Fe, K, Mn, Na, Pb and Zn, respective amplification factors achieved for Triton x-705 at its 5 × CMC were slightly better than those obtained when Triton x-405 was present in the electrolyte solution.

At the same time, it was established that all studied surfactants rapidly decreased the background intensity in the vicinity of atomic emission lines of studied metals. Accordingly, even at the lowest concentration of Triton x-405 in the electrolyte solution, i.e., ½ × CMC, decreases in the background level by about 50–60% (Cd, Co, Hg, Zn), 30–40% (Cu, Fe, Mg, Mn, Ni, Pb), and 10–20% (Ca, Cr, Cs, Li, Rb, Sr) were noted and found to remain at the same level (±5) at higher concentrations of this surfactant in the electrolyte solution. Corresponding results were obtained in case of the addition of Triton x-705 to analyzed electrolyte solutions. Surprisingly, a similar behavior of the background intensity of atomic emission lines of studied metals was also observed for Triton x-45 and Triton x-100. Only in case of Mg and Ni, the drop of the background level of atomic emission lines of these two metals was established to be lower by about 10% as compared to this achieved in case of Triton x-405.

Considering the emission behavior of diatomic molecules and atoms of metals present in spectra of dc-APGD generated in

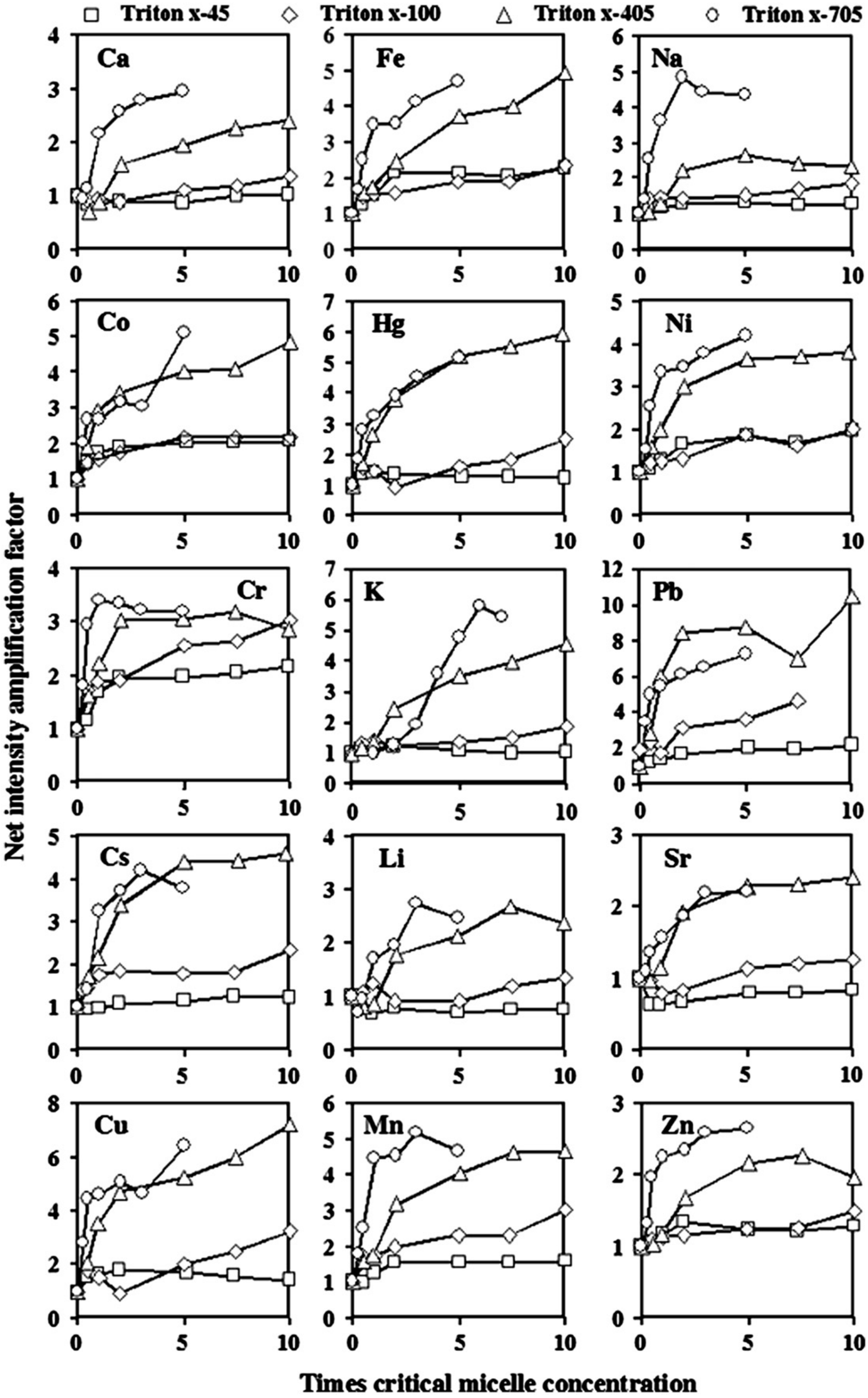

Fig. 4. The dependence of the net intensity amplification factor for atomic emission lines of selected (Ca, Co, Cr, Cs, Cu, Fe, Hg, K, Li, Mn, Na, Ni, Pb, Sr and Zn) metals from the concentration of Triton x-45, Triton x-100, Triton x-405 and Triton x-705 in the electrolyte solution.

contact with the small-sized liquid cathode containing non-ionic surfactants, it can be presumed that the positive effect observed for the addition of heavy analogs, especially at the concentration corresponding to their 5 × CMC, is likely related to a decrease in the pressure of the water vapor over overflowing solutions and a reduction of their surface tension. This expectedly results in favorable conditions for the sputtering of dissolved metal ions from the surface of electrolyte solutions and hindered conditions for the vaporization of water. In consequence, the concentration of positive ions of studied metals available for recombination processes in the near-cathode zone of the discharge is increased while the concentration of the water vapor in the core of the discharge is rather decreased. A lower contribution of the water vapor in the phase of the discharge seemingly leads to an increase in the energy and/or the number of free electrons responsible for recombination and excitation processes [1,27–30]. Certainly, a combination of both phenomena would directly influence the analytical performance of the examined discharge system. In addition, it could be presumed that products of the decomposition of non-ionic surfactants studied (hydrocarbons like species) may be transferred into discharge zones and participate in various processes, e.g., inelastic collisions. In these conditions, the collisional quenching of excitation states of diatomic species, i.e., OH and N_2 molecules, by means of mentioned hydrocarbons should be considered. A similar decrease in the molecular band emission of OH and N_2 species, resulted from the quenching by simple hydrocarbons, was reported by Frentiu et al. [31] after the addition of CH_4 to argon capacitively coupled plasma (Ar-CCP).

Considering the magnitude of increases in the net intensity of atomic emission lines of all metals and decreases in the background level achieved in conditions of the presence of Triton x-405 or Triton x-705 in electrolyte solutions, it was expected that the analytical performance of the dc-APGD-OES system with the small-sized liquid cathode modified by the addition of these non-ionic surfactants to electrolyte solutions at the concentration corresponding to their 5 × CMC would be enhanced. Although somewhat higher amplification factors of the net intensity were obtained for Triton x-705, the handling of standard solutions containing this surfactant was in a long run uncomfortable due to their high viscosity and difficulties in a smooth drainage of the cathode compartment. Hence, a compromised setting for all metals was Triton x-405 at the concentration corresponding to its 5 × CMC.

3.3. *Analytical figures of merit and application in trace analysis of environmental samples*

To assess the suitability of the dc-APGD-OES system with the small-sized liquid cathode being electrolyte solutions containing Triton x-405 at the concentration corresponding to its 5 × CMC, the following figures of merit were determined: linearity ranges of calibration curves for analytical lines of studied metals, their LODs and the reproducibility of net intensities of these lines (values of the two latter parameters are given and compared in Table 2). The calibration was carried out over concentration intervals given in Table 2 and considering the net intensity at the maximum of the analytical line profile. As compared to calibration curves obtained using standard solutions without the addition of Triton x-405, linear to 100 $mg\,L^{-1}$ in case of all studied metals, linearity ranges of calibration curves recorded using standard solutions containing this surfactant were shorter, i.e., to 50 $mg\,L^{-1}$ for all metals except for Cu, Mg, Na and Zn. In case of these four metals, upper linearity concentration ranges were lower. In all cases, linearity correlation coefficients (R^2) were better than 0.990.

LODs were calculated as concentrations corresponded to 3 × standard deviations of the background level acquired for 10 consecutive measurements of a blank solution (a 0.1 $mol\,L^{-1}$ HCl solution containing Triton x-405 at the concentration corresponding to its 5 × CMC). Their values for all metals were in the range from 0.0003 $mg\,L^{-1}$ in case of Li to 0.40 $mg\,L^{-1}$ in case of Cr. The best LODs, ranging from 0.0003 to 0.05 $mg\,L^{-1}$, were established for Ca, Cd, Cu, K, Li, Mg, Mn, Na, Ni, Rb and Zn. The greatest enhancement of LODs, i.e., by more than one order of the magnitude as compared to those obtained in conditions with no surfactant added to the electrolyte solution, was also found for Ca, Cd, Cu, Mg, Mn and Ni, in addition to Hg and Pb. It was presumed that such an enhanced detection power of the miniaturized dc-APGD system was mainly related to a strengthening of the net intensity of atomic emission lines of these metals and a decline in the background level of these lines and its fluctuation in conditions of the presence of the surfactant in the liquid cathode. The improvement of LODs for other metals was also noticeable but not so marked, i.e., from 2 (Na), through 3 (K, Li), 4 (Cs), 5 (Sr) to 6–8 times (Co, Cr, Fe, Zn). It can be seen that values of LODs assessed in the present work using a 0.1 $mol\,L^{-1}$ HCl electrolyte solution well correspond to those achieved using a comparable discharge cell [4], although, they are about from about 3 (Mg, Zn), 4 (Ca) to 5 (Cd, Cu, Mn) times higher. This could be explained by the use of twice higher discharge gap (5 mm) and sample flow rate (1.2 $mL\,min^{-1}$) as compared to the mentioned work [4]. For Li and Rb, the same LODs as in cited work were obtained.

The addition of the surfactant to the electrolyte solution resulted as well in a better reproducibility of measured net intensities of analytical lines; in most cases it was better than 6%.

The dc-APGD-OES system with the small-sized liquid cathode modified by the addition of Triton x-405 was finally used for the analysis of selected environmental samples, i.e., waters and extracts of spruce needles and soils. At the beginning, the analysis of samples by this system was carried out using external calibration curves. Unfortunately, errors of the determination of concentrations of metals in relation to results obtained in FAAS/FAES measurements, treated as reference values were unacceptable. It was difficult to find any relation between the value of these errors and the kind of sample matrix or the element. Hence, it was decided to use the standard addition method for the calibration. The analysis of these samples revealed that they do not contain such metals as Cd, Co, Cr, Cs, Hg, Li, Ni, Rb, Pb and Sr, which were determined to be below their LODs. Results for Ca, Cu, Fe, K, Mg, Mn, Na and Zn are given in Table 3. To assess the accuracy of this analysis, results in all analyzed samples obtained with dc-APGD-OES for a given metal were compared to respective obtained with FAAS/FAES. The paired *t*-test at the 95% confidence level was applied for this purpose [32]. It was found that calculated values of the test ($|t_{calculated}|$) are lower than respective critical values ($t_{critical}$), i.e., 2.57 and 2.78 for 5 and 4 degrees of freedom, respectively, what proves the reliability of results achieved and the suitability of dc-APGD-OES system developed for the trace analysis of environmental samples.

4. Conclusions

The effect of the addition of non-ionic surfactants to the electrolyte solution on the analytical performance of dc-APGD with a small-sized liquid cathode was studied and assessed. It was found that the presence of Triton x-405 in sample and standard solutions results in convenient changes in the morphology of the emission characteristics of this excitation source. Accordingly, the intensity of molecular bands and the overall background level in addition to the magnitude of its fluctuations are substantially decreased. At the same time, the intensity of atomic emission lines of metals presents in electrolyte

Table 2
Signal reproducibility and limits of detection of metals established for the dc-APGD-OES system generated in contact with the small-sized liquid cathode.

Metal	Reproducibility (as RSD, %)			LOD (mg L^{-1})			LOD enhancement	Dynamic range[c] (mg L^{-1}) (R^2)[ad]	Dynamic range[c] (mg L^{-1}) (R^2)[bd]
	Ref. 4[a]	This work[a]	This work[b]	Ref. 4[a]	This work[a]	This work[b]			
Ca	3.2	3.6	3.5	0.09	0.36	0.04	10	1.2–100 (0.996)	0.13–100 (0.998)
Cd	3.5	6.2	6.2	0.05	0.27	0.02	14	0.90–80 (0.995)	0.07–50 (0.993)
Co	–	9.6	6.0	–	0.87	0.11	8	2.9–100 (0.995)	0.33–50 (0.991)
Cr	–	12	12	–	2.5	0.40	6	8.2–100 (0.990)	1.3–50 (0.995)
Cs	–	6.0	6.6	–	0.75	0.17	4	2.5–100 (0.996)	0.57–70 (0.997)
Cu	6.3	6.7	3.2	0.08	0.37	0.02	19	1.2–100 (0.992)	0.07–20 (0.991)
Fe	–	10.6	6.4	–	1.4	0.18	8	4.7–100 (0.998)	0.60–50 (0.995)
Hg	–	5.2	5.3	–	2.0	0.13	15	6.7–80 (0.993)	0.43–50 (0.998)
K	4.0	5.2	4.6	0.004	0.004	0.0012	3	0.04–100 (0.999)	0.01–50 (0.999)
Li	4.1	5.9	3.5	0.002	0.001	0.0003	3	0.003–100 (0.999)	0.001–70 (0.998)
Mg	6.5	5.0	2.2	0.04	0.10	0.008	12	0.33–100 (0.995)	0.03–40 (0.990)
Mn	3.7	5.2	4.4	0.10	0.50	0.02	25	1.7–100 (0.991)	0.07–50 (0.993)
Na	3.4	6.2	4.0	0.002	0.002	0.001	2	0.007–100 (0.999)	0.003–40 (0.996)
Ni	–	6.2	5.8	–	0.70	0.05	14	2.3–100 (0.991)	0.17–50 (0.992)
Pb	–	8.6	5.3	–	1.4	0.12	12	4.7–100 (0.992)	0.40–50 (0.995)
Rb	3.4	3.1	3.7	0.04	0.04	0.007	6	0.13–100 (0.998)	0.02–50 (0.998)
Sr	–	3.2	3.9	–	0.36	0.07	5	1.2–100 (0.996)	0.23–80 (0.994)
Zn	2.6	6.0	5.3	0.10	0.25	0.04	6	0.83–50 (0.994)	0.13–40 (0.990)

RSD: relative standard deviation for $n=7$ (a mixed 10 mg L^{-1} standard solution was used), LOD: limit of detection, LOQ: limit of quantification.

[a] With the addition of no surfactant.

[b] With the addition of Triton x-405 at the concentration corresponding to its 5 × CMC.

[c] From the LOQ to the upper linearity limit.

[d] Linearity correlation coefficient.

Table 3
Results (in μg g^{-1}) of the analysis of environmental samples carried out by dc-APGD-OES with the small-sized liquid cathode modified by the addition of Triton x-405 (at its 5 × CMC) and by FAAS/FAES.

	Waters		Soil leachates		Spruce needle leachates		$\lvert t\rvert$[a]
	Purple lakelet	Azure lakelet	Purple lakelet	Azure lakelet	Purple lakelet	Azure lakelet	
dc-APGD-OES							
Ca	106 (0.9)[b]	12.2 (0.7)	2.67×10^3 (3.1)	294 (4.0)	3.87×10^3 (5.3)	2.14×10^3 (1.5)	0.95
Cu	0.84 (5.4)	ND	44.6 (8.5)	25.6 (12.4)	10.3 (7.8)	4.18 (6.0)	2.27
Fe	58.0 (1.3)	ND	1.35×10^4 (0.5)	8.71×10^3 (0.9)	116 (2.0)	49.8 (5.3)	0.50
K	0.69 (4.1)	0.42 (13)	83.8 (6.3)	97.7 (2.0)	4.88×10^3 (5.4)	8.00×10^3 (5.0)	0.73
Mg	66.8 (2.1)	6.05 (3.8)	1.63×10^3 (6.7)	127 (10)	960 (3.7)	865 (4.0)	0.21
Mn	1.39 (2.1)	0.22 (4.8)	145 (2.9)	30.8 (3.5)	573 (1.3)	288 (5.4)	1.18
Na	2.59 (3.1)	2.84 (2.4)	10.8 (1.6)	26.4 (1.3)	14.9 (2.2)	12.8 (4.0)	0.79
Zn	0.27 (5.4)	ND	26.2 (7.6)	30.5 (5.2)	72.3 (2.1)	39.1 (14.1)	2.06
FAAS/FAES							
Ca	106 (0.6)	10.3 (0.6)	2.61×10^3 (1.0)	286 (1.2)	3.97×10^3 (0.2)	2.34×10^3 (0.1)	–
Cu	0.78 (1.8)	ND	38.9 (1.5)	21.7 (2.1)	3.08 (5.1)	3.45 (21)	–
Fe	57.1 (3.1)	ND	1.37×10^4 (0.6)	8.31×10^3 (1.5)	46.1 (0.5)	47.3 (5.9)	–
K	0.67 (0.9)	0.42 (4.5)	81.1 (2.0)	101 (2.1)	4.90×10^3 (1.7)	7.94×10^3 (1.2)	–
Mg	74.3 (0.5)	5.85 (0.6)	1.71×10^3 (0.2)	141 (0.4)	828 (0.5)	935 (0.2)	–
Mn	1.29 (0.8)	0.15 (1.5)	149 (1.5)	30.8 (2.1)	580 (0.8)	335 (1.2)	–
Na	2.58 (0.3)	2.11 (0.3)	10.8 (1.7)	7.00 (0.6)	15.2 (1.4)	15.4 (1.9)	–
Zn	0.21 (2.5)	ND	16.5 (4.1)	12.4 (4.9)	37.6 (1.8)	32.8 (1.4)	–

ND Not detected.

[a] Calculated values of the paired t-test ($p=0.05$) for the comparison of average concentrations of each metal obtained with dc-APGD-OES and FAAS/FAES (critical values of the paired t-test: 2.57 for 5 degrees of freedom in case of Ca, K, Mg, Mn and Na and 2.78 for 4 degrees of freedom for Cu, Fe and Zn).

[b] Relative standard deviation ($n=3$).

solutions is strengthened by 4–10 times with the exception of Ca, Cr, Li, Sr and Zn for which this increase is about 2–3 times lower as compared to other metals. Changes caused by the addition of Triton x-405 to electrolyte solutions are reflected the precision better than 6% for most of metals. The best LODs within the range of 0.0003–0.05 mg L^{-1} are achieved for Ca, Cd, Cu, K, Li, Mg, Mn, Ni, Na, Rb and Zn. Additionally, reasonably good precision and the accuracy similar to this obtained with FAAS/FAES are obtained in the analysis of complex environmental samples demonstrating the same the reliability of such modified discharge system and measurements made. It could be expected that changes in the composition of the electrolyte solution of the liquid cathode [12,22,33] or the replacement of a solid anode with a miniature gas flow through a nozzle electrode [12,29,34] would be beneficial for the performance of the dc-APGD excitation source and contribute to the extension of its applications in analytical atomic spectrometry.

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