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Coupling of cold vapor generation with atmospheric pressure glow microdischarge sustained between miniature flow helium jet and flowing liquid cathode for the determination of mercury by optical emission spectrometry

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Abstract

A direct current atmospheric pressure glow microdischarge (dc-µAPGD), generated between a miniature flow He jet nozzle anode and a small-sized flowing liquid cathode, was combined with a continuous flow cold vapor generation (CVG) system to improve sensitivity of the determination of Hg by optical emission spectrometry (OES). In this arrangement, Hg(II) ions were converted to cold vapor in the reaction with $NaBH_4$ and subsequently delivered in a stream of He carrier/ jet-supporting gas to the microdischarge through the nozzle anode. Additional He shielding gas was used to prevent discharge zones from the access of ambient air. A vertical distribution of emission from the Hg I 253.7 nm line between both electrodes was acquired, and the highest response for Hg was established in the near-anode region of the microdischarge. Several operating parameters that affect the CVG reaction and discharge were optimized. Under compromised conditions, the intensity of the Hg I line was improved over 4000 times as compared to this obtained in a µAPGD-OES system without the CVG system. The efficiency of CVG of Hg and its transport to the microdischarge was evaluated to be 98±1%. For comparison, in the µAPGD system without CVG, the efficiency of sputtering was merely lower by about 20%, i.e., 77±4%. A likely explanation of the enhancement of Hg response observed for CVG-µAPGD was discussed. The detection limit (DL) of Hg assessed for CVG-µAPGD-OES was 0.14 µg L^{-1} (3σ criterion). To assess accuracy of the new method, Hg was quantified in a certified reference material (CRM) of human hair (NCS ZC 81002). An excellent agreement between certified and measured concentrations of Hg was obtained. In addition, recoveries of Hg added to samples of different waters were evaluated. They were in the range of 96-103% proving good accuracy of CVG-μAPGD-OES. Repeatability of the signal over the linearity concentration range of 5-500 μg L^{-1} of Hg was within 2.1-4.1% (as relative standard deviation, RSD).

1. Introduction

Atmospheric pressure glow discharges (APGD) generated in contact with a flowing liquid cathode solution has been applied as an alternative excitation source in optical emission spectrometry (OES) since mid-90s.[1-3] Main advantages of such APGD are low-energy consumption, the possibility of analysis of samples at atmospheric pressure without the need for using discharge-sustaining gases and simple design of discharge devices. Since analyzed samples are used as flowing liquid cathode solutions, they are sputtered in contact with a discharge phase and, therefore, no nebulizers and spray chambers are required for introduction of sample solutions to this excitation source. This certainly reduces costs of the equipment and its operation.[3-5] In recent years, APGD has been successfully used for spectrochemical analysis of different samples, e.g., vaccines,[6] tea,[7] tap water[7,8] as well as spruce needles, soils and lake waters[9]. Commonly, this kind of excitation sources provides favorable conditions for excitation of alkali metals, therefore, detection limits (DLs) of Li and Na are typically better than 1 μg L^{-1}.[7-10] Values of DLs of alkaline earth metals and transition metals are higher and usually span the range of 1-25 μg L^{-1}.[7-14]

Considering achievements made in last 3 years in application of APGD generated in contact with the liquid cathode as an efficient excitation source for analytical OES, it is evident that a more effort has been devoted to improving the DL of Hg. This element is usually present in food and water samples at very low concentrations. Due to extremely high toxicity and tendency to accumulate in tissues, Hg is recognized as a serious environmental pollutant that concentrations should be routinely monitored and controlled in environmental and food samples. Modifications of existing techniques, the improvement of their analytical performance or the development of new methods are necessary because of the vital necessity of reliable determinations of Hg at very low levels. This also includes the development of figures of merit of APGD-OES operated in contact with the flowing liquid cathode.

Apparently, Shekhar studied effects of the concentration of low molecular weight organic compounds, i.e., ethanol (CH_3CH_2OH), formic acid (HCOOH) and acetic acid (CH_3COOH), added to a solution of the liquid cathode on response of the Hg I 253.7 nm emission line.[15] The researcher established that the presence of 5.0% (m/v) CH_3COOH in solutions led to a 5-fold enhancement of the intensity of the mentioned line. It was presumed that the effect observed was due to an increase in the sputtering rate of the liquid cathode solution. As a result, the efficiency of transport of Hg to the discharge phase was higher. For that, the DL of Hg was improved (2 μg L^{-1}). A similar experiment was carried out by Doroski et al.,[16] who examined the influence of the addition of CH_3CH_2OH, HCOOH and CH_3COOH to the liquid cathode solution on response of Hg and Ag, Pb and Se. Each compound, separately added to the solution, was found to enhance (10-13 times) the intensity of the Hg I 253.7 nm emission line, likely due to changes in physicochemical properties of the solution. Although there was no evidence to credit CVG of Hg for observed signal improvements, authors did not exclude such a possibility. The DL of Hg evaluated for this system was 2 μg L^{-1}. It was improved by one order of magnitude as compared to conditions without low molecular compounds in the liquid cathode solution.

Improvements of APGD generated in contact with the liquid cathode reported in the literature mostly concern modifications of the composition of liquid cathode solutions. A less frequent modification, with a considerable impact on excitation conditions in APGD and its performance, was a change of the composition of the discharge gas atmosphere. Replacing a conventional metallic pin electrode with a miniature flow of He from a nozzle anode, Shirai et al. sustained APGD in the air-H_2O vapor-He atmosphere between a bulky solution liquid cathode and a miniature flow He jet.[17] In addition, a glass tube was used to surround discharge zones and prevent them from penetration of ambient air. Authors observed that the intensity of N_2 molecular bands, e.g., with the band head at 337.1 nm, was strongly suppressed in such semi-closed discharge system. They also noted that the concentration of nitrate ions in the solution of the liquid cathode treated with APGD was decreased. The intensity of NO molecular bands was simultaneously declined. Unfortunately, analytical performance of the modified semi-closed APGD system has not been evaluated. It could be expected that operation of APGD in a system with the flowing liquid cathode in the atmosphere of H_2O vapor and He but without access of air to discharge zones would be quite desirable. It could result in reduction in the level of the background and its fluctuation as well as in the increase in the intensity of atomic emission lines of metals. In addition, by applying the miniature flow He jet nozzle anode, a new opportunity to broaden the way of analytes' delivery to the discharge, e.g., as cold vapor of Hg formed in the CVG reaction and purged from a reaction/ separation system by a stream of He carrier/ jet-supporting gas, would be opened.

Considering eventual benefits, the investigation of such new excitation source, its analytical performance and suitability for the determination of Hg seems to be interesting. Therefore, in this paper, the coupling of CVG with µAPGD sustained between the miniature flow He jet and the small-sized flowing liquid cathode was proposed to improve the sensitivity of the determination of Hg by OES. To shelter microdischarge zones from penetration by ambient air, µAPGD was operated in a semi-closed chamber and the atmosphere of He shielding gas. Various operating parameters related to the CVG reaction and discharge were optimized. Under optimized conditions, figures of merit for CVG-µAPGD-OES were assessed. The proposed method was successfully applied for analysis of a certified reference material (CRM) of human hair and different water samples spiked with Hg.

2. Experimental

2.1. Instrumentation

dc-µAPGD was sustained in the open-to-air atmosphere between the surface of an acidic solution overflowing a small-sized quartz tube (the liquid cathode) and a stainless steel nozzle fed with a miniature flow of He (the anode). A liquid cathode compartment consisted of a polytetrafluoroethylene (PTFE) tube (ID 9.0 mm), working as a waste reservoir, and a quartz delivery tube (ID 2.0 mm). An additional graphite tube (ID 4.0 mm) was inserted into the quartz tube in such way that its side was about 2 mm above the edge of the quartz tube and the PTFE tube (see details in Fig. 1a). A 0.4% (m/v) HCl solution was delivered through the quartz tube using a 2-channel peristaltic pump. This solution overflowed the graphite-quartz tube and was drained out of the cathode compartment with the same peristaltic pump. A miniature flow of He was introduced through a nozzle using a Tylan General (CA, USA) FC-2900 flow controller and an RO-28 digital flow meter. The length of the nozzle was 70 mm while its diameters were 1.15/0.75 mm (OD/ID). The nozzle and the graphite-quartz tube were vertically oriented. The gap between them (the discharge gap) was 5.0 mm. A Pt wire attached to the graphite tube was used for maintaining electric contact to the liquid cathode solution. The stable microdischarge was formed when a miniature flow of He was passed through the nozzle and a potential of 1000-1500 V from an HV dc power supplier was applied to both electrodes. This resulted in a discharge current of 15-40 mA flowed through electrodes, additionally stabilized by a 10 kΩ ballast resistor placed in an anode circuit. The discharge cell was placed in a holder that enabled to move it in two directions. Therefore, it was possible to collect emission spectra from different zones of the microdischarge.

A continuous flow CVG system is shown in Fig. 1b. It consisted of a 4-channel peristaltic pump with delivery tubes, and a home-made cylindrical (ID 20 mm, the total volume 20 mL) reactor/ gas-liquid phase separator (GLS). The GLS had a glass frit at the bottom and a drainage tube inserted from the top. To generate cold vapor of Hg, a $NaBH_4$ solution alkalized with NaOH (0.1% (m/v)) and a sample solution acidified with HCl to a concentration of 16% (m/v) were pumped in two separate streams to a Y-junction where reagents were mixed and immediately reacted. The reaction mixture was subsequently passed into the GLS. Gaseous products were separated from a post-reaction solution by purging the GLS with He carrier gas. The flow of this gas was introduced through the glass frit. Vapor of Hg along with H_2 were directly swept into the microdischarge through the nozzle. To simplify coupling of CVG with μAPGD realized between the liquid cathode and the miniature flow He jet, He carrier gas supported the gaseous jet and enabled to sustain the microdischarge. When the post-reaction solution level exceeded 15 mm above the glass frit, it was drained out of the GLS using a peristaltic pump.

In some experiments, μAPGD was sustained in the atmosphere of H_2O vapor and He but without contact with ambient air. In this case, the cathode compartment and the nozzle anode were inserted into a cylindrical glass chamber (ID 50 mm, the total volume 250 mL) through which an additional flow of He shielding gas was passed. He shielding gas was introduced to this semi-closed system (see Fig. 1c) next to a quartz observation window. Its flow rate was controlled by a rotameter. This prevented from awkward condensation of H_2O vapor on the observation window. He and H_2O vapor were leaked outside the chamber through a hole (ID 5 mm.), the same that was used to introduce the nozzle.

Radiation emitted by μAPGD was imaged (1: 1) on the entrance slit (100 mm) of a 320 mm focal length single grating imagining spectrometer Triax 320 (HORIBA Jobin Yvon, France) using an achromatic UV lens. The spectrometer was equipped with an in-build diaphragm (1.0 mm or fully opened), a 1200 grooves mm^{-1} holographic grating and a Hamamatsu R-928 photomultiplier. A voltage of -700 V was used to bias the photomultiplier. Emission spectra of microdischarge were measured with a step of 0.01 nm. The output signal of the photomultiplier, integrated at 0.1 s, was amplified using an HORIBA Jobin Yvon SpectraAcq2 single photon counting acquisition system. A SpectraMax/32 for Windows software (Instruments SA, Inc.), version 3.2, was used to handle the spectrometer and control its configuration. Acquisition and data processing were made using the same computer program.

2.2. Reagents and solutions

Doubly distilled water was used throughout the work. He (99.999% grade) was supplied by Air Products (Poland). A stock standard solution of Hg (1000 mg L^{-1}), NaOH and $NaBH_4$ were supplied by Sigma-Aldrich Chemie GmbH (Germany). Single-element solutions of Hg were prepared by appropriate dilutions of the stock standard solution. To stabilize the reducing agent, solid $NaBH_4$ was dissolved in a 0.1% (m/v) NaOH solution. Solutions of $NaBH_4$ were freshly prepared and filtered through cellulose filter papers (grade 595). A concentrated HCl solution (37-38% (m/m)) obtained from J. T. Baker (Netherlands) was used to acidify all sample solutions. In addition, J. T. Baker 65% (m/m) HNO_3 and Sigma-Aldrich 30% (m/m) H_2O_2 solutions were used for open-vessel wet oxidative digestion of samples. All reagents were of analytical grade or better. A CRM of human hair (NCS ZC 81002), approved by the Chinese National Analysis Center for Iron and Steel, was used for validation.

2.3. Measurements and sample preparation

For optimization of operating parameters of CVG-µAPGD, an univariate method was used, examining the effect of one given parameter at a time and keeping other parameters unchanged. Each measurement, related to the intensity of the Hg I 253.7 nm emission line and the background in the vicinity of this line, in certain experimental conditions, was repeated 3 times and the final background-corrected signal of Hg (net intensity) was averaged.

To assess the efficiency of evaporation of the liquid cathode solution and the efficiency of sputtering of Hg, a 25 mg L^{-1} Hg solution (50.0 g) acidified with HCl to a concentration of 0.4% (m/v) was delivered to the µAPGD system. The whole waste solution was collected and weighted. The efficiency of evaporation of the liquid cathode was evaluated basing on the mass loss of this solution. In addition, the concentration of Hg in the waste solution was determined by CVG-ICP-OES using calibration by the double standard solution addition. Both efficiencies were averaged for 3 independent experiments. The efficiency of CVG of Hg was evaluated by sampling a portion of the waste solution drained from the GLS. The concentration of Hg in this solution was determined in the same way as described above (n=3).

The human hair CRM (NCS ZC 81002) was initially heated at 90°C in a stove for 4 h.

Then, 0.2 g samples were weighed into 25-mL glass beakers, and concentrated HNO_3 (5.0 mL) was added. Beakers were covered with watch glasses and left overnight for pre-digestion at room temperature. Subsequently, resulted sample suspensions were heated on a hot plate (at 60-70°C) for about 3 h and then brought to boil and heated for additional 3 h. During this step, additional portions of concentrated HNO_3 (2.0 mL) were added. When sample solutions were almost colorless, 30% (m/v) H_2O_2 (3.0 mL) was added. After next 30 min of heating, sample solutions were evaporated to near dryness and diluted to 30 mL with 16% (m/v) HCl. The determination of Hg in solutions of the digested CRM was made using CVG-µAPGD-OES. Double standard solution addition was used for calibration. Each spectrum was recorded 5 times and the signal of Hg (net intensity of the Hg I line) was averaged. Three independent samples of the CRM and respective blank samples were prepared.

Water samples from Purple and Azure lakelets, located in the Rudawy Landscape Park (Lower Silesian Voivodeship, The Sudetes mountains, Poland), a water sample from the Oder river (Wroclaw, Poland) and a sample of tap water (Wroclaw, Poland) were collected into 200 mL pre-cleaned polyethylene containers. After sampling, samples were acidified with concentrated HCl to a final concentration of 16% (m/v). Next, they were filtered through cellulose filter papers (grade 595) and divided into 2 equal aliquots. One of the aliquots was spiked with a 10 mg L^{-1} Hg solution to a final concentration of 50 µg L^{-1}. Each spectrum was recorded 5 times and the signal of Hg was averaged. For each water, 3 samples and blanks were independently prepared.

3. Results and discussion

3.1. Emission characteristics of different µAPGD systems

At outset, vertical distributions of the sensitivity of the Hg I line, the background intensity, the background intensity fluctuation (expressed as the standard deviation, SD), and the DL of Hg along the discharge gap (5.0 mm) were studied. The µAPDG system was operated between the miniature flow He jet and the liquid cathode in the open-to-air atmosphere. The flowing liquid cathode was a solution of 25 mg L^{-1} Hg in 0.4% (m/v) HCl. This solution was introduced to the microdischarge at a flow rate of 1.2 mL min^{-1}. The flow of He used to support the gaseous jet was 100 mL min^{-1}. In these conditions, after applying a potential of 1450 V, the discharge current was 35 mA. Emission spectra of µAPGD were recorded using a 1.0-mm diaphragm.

It was found that the vertical distribution of the sensitivity of the Hg I line (see Fig. 2a) was related to particular distributions of Zn I 213.8 nm, Cd I 228.8 nm, Mg I 285.2 nm, Cu I 324.7 nm, Pb I 405.8 nm, Na I 589.0 nm and K I 766.5 nm emission lines measured by Webb et al.[10] and Mezei et al.[18] in APGD systems with conventional metallic anodes. The highest sensitivity of the Hg I line was seen 2 mm above the surface of the liquid cathode in the near-cathode zone. Close to the anode, the sensitivity of the Hg I line was strongly suppressed. The background surrounding the Hg I line was dominated by the presence of the NO molecular band with the band head at 255.9. The background intensity and its SD were found to increase gradually when the observation zone moved towards the anode (in the range of 0-3 mm above the surface of the liquid cathode). A wide maximum of the background intensity occurred within 3-4 mm from the surface of the liquid cathode. When the 1.0-mm diaphragm was used, the sensitivity of the Hg I line (in a. u. per $\mu g\ L^{-1}$), the background intensity (in a. u.) near this line, the SD of the background intensity (in a. u.) as well as the DL of Hg (in $\mu g\ L^{-1}$) measured (n=10) in the near-cathode region, i.e., 2 mm above the surface of the cathode, were 28×10^{-3}, 198, 9.9 and 1.1×10^{3}, respectively (see Table 1). When acquisition of emitted radiation from the near-cathode region was made with the fully opened diaphragm, the sensitivity of the Hg I line was 2.9-fold improved but concurrently, the background intensity and its SD were increased, respectively, by 5.5 and 3.8 times. The DL of Hg in these conditions was $1.4\times10^{3}\ \mu g\ L^{-1}$. As compared to a corresponding APGD system described in our earlier work,[9] where non-ionic surfactants were used to increase detection power for Hg and other elements, the DL of Hg obtained here was disappointingly high.

Similarly as in the previous experiment, the vertical distribution of the sensitivity of the Hg I line, the background intensity and the SD of the background intensity, and the DL of Hg were also evaluated for μAPDG operated between the miniature flow He jet and the liquid cathode in the open-to-air atmosphere but combined with CVG of Hg. Except for the composition of the liquid cathode solution (a 0.4% (m/v) HCl solution without Hg), all other operating parameters set to the μAPGD system were the same as before. A sample solution for the CVG reaction (a 100 $\mu g\ L^{-1}$ Hg solution in 10% (m/v) HCl) and an alkaline 0.1% (m/v) $NaBH_4$ solution were both delivered to the Y-junction at a flow rate of 3.0 $mL\ min^{-1}$. After separation in the GLS, Hg vapor was introduced into the microdischarge through the nozzle anode in the stream of He carrier/ jet-supporting gas at 100 $mL\ min^{-1}$. As can be seen from Fig. 2b, the vertical distribution of the sensitivity of the Hg I line is different from that described before. The Hg I line reached the highest sensitivity in the near-anode region (4.0

mm above the surface of the liquid cathode), likely due to introduction of Hg vapor through the nozzle anode. However, distributions of the background intensity and the SD of the background intensity are similar to those seen in the previous experiment. Surprisingly, coupling CVG with μAPGD operated between the miniature flow He jet and the flowing liquid cathode resulted in a 600-fold improvement of the sensitivity of the Hg I line. Simultaneously, the background intensity and the SD of the background intensity were increased only by 50 and 30%, respectively. In consequence, when the 1.0-mm diaphragm was used for collecting emitted radiation from the near-anode zone, the DL of 2.3 μg L^{-1} of Hg was achieved for CVG-μAPGD-OES. It was 480-fold improved as compared to the DL obtained for μAPGD without the CVG system. With the fully opened diaphragm, the sensitivity of the Hg I line was found to be additionally twice increased but the SD of the background intensity was over 3 times higher than this obtained when the 1.0-mm diaphragm was used. Hence, the DL of Hg evaluated in these conditions was just a little higher, i.e., 3.2 μg L^{-1}.

Afterwards, the μAPGD device was closed in the semi-closed glass chamber and He shielding gas (2.0 L min^{-1}) was passed through it to remove air. Vertical distributions of the sensitivity of the Hg I line, the background intensity, the SD of the background intensity and the DL of Hg assessed were corresponding to those obtained for the CVG-μAPGD system operated in the open-to-air atmosphere. However, by sustaining the microdischarge in the H_2O vapor-He atmosphere with the absence of air, a noticeable suppression of the intensity of emission bands of the NO molecule in the spectral range of 200-270 nm was observed (see Fig. 3) in addition to an increase in the sensitivity of the Hg I line. The DL of Hg evaluated for CVG-μAPGD-OES using this arrangement and measuring the near-anode region was 1.9 and 1.4 μg L^{-1} (n=10), correspondingly, with 1.0-mm or fully opened diaphragms. This indicates that it is reasonable to collect emission spectra from a larger discharge area (using the fully opened diaphragm). As a result, more regular profiles of the Hg I line were obtained. It is also noteworthy that repeatability of signals of Hg obtained for the microdischarge combined with the CVG system was better than 4% (as the relative standard deviation, RSD) and more than 2 times lower as compared to the RSD evaluated for the arrangement without the CVG system. Since then, μAPGD combined with CVG of Hg and sustained in the system with He shielding gas was thoroughly studied to improve its analytical performance. Suitability of this system for determining traces of Hg in environmental samples was also evaluated. In all further experiments, emission spectra of the near-anode zone of the microdischarge were acquired with the fully opened diaphragm.

3.2. Areas of stable operation of CVG-µAPGD

The influence of the discharge current (within 15-40 mA) and the flow rate of the liquid cathode solution (within 0.9-2.1 mL min^{-1}) on stable operation of CVG-µAPGD was investigated using 3 different flow rates of He shielding gas, i.e., 1.0, 1.75 and 2.5 L min^{-1}. Other operating parameters of the CVG-µAPGD system were the same as before (see the section 3.1).

In general, it was found that large discharge currents resulted in increased production of H_2O vapor. In consequence, H_2O vapor condensed on the quartz observation window and the nozzle anode causing the microdischarge to extinguish. A higher (>2 L min^{-1}) He shielding gas flow rate was used to avoid this problem. The increase in the flow rate of the liquid cathode solution was also effective. In these conditions, the efficiency of vaporization of H_2O was lower. When the flow rate of the liquid cathode solution was too low (<0.9 mL min^{-1}), the microdischarge was unstable because of sparkles with the graphite tube. Maps of stable operation areas found for the CVG-µAPGD system are shown in Fig. 4.

Webb et al.[19,20] previously reported that a movement of air in the atmosphere surrounding APGD generated in contact with the flowing liquid cathode deteriorates its analytical performance, i.e., repeatability of signals of elements, the level and fluctuation of the background. In the CVG-µAPGD system studied in the present contribution, the increase in the flow rate of He shielding gas did not cause such problems, probably because the use of the miniature flow He jet instead of the metallic pin electrode stabilized the microdischarge. Indeed, it was found that the SD of the background intensity in the vicinity of the Hg I line was not affected by the flow rate of He shielding gas, though the background intensity was increased by 35% when the flow rate of this gas was changed from 1.0 to 2.5 L min^{-1}. As can be seen from Fig. 4, high flow rates of He shielding gas were responsible for extended ranges of stable operation of CVG-µAPGD and a desirable 2.2-fold improvement of the sensitivity of the Hg I line when the flow rate of He shielding gas was increased from 1.0 to 2.5 L min^{-1}.

Results related to the effect of the discharge current on the sensitivity of the Hg I line were completely unexpected. In previously published papers, analytes were delivered to discharge cells as components of the flowing liquid cathode solution[1,2,6-16,21] and sputtered to the discharge core by bombardments of its surface. Higher discharge currents commonly led to an improvement of the efficiency of transport of elements from the solution to the discharge and, in consequence, an increase in the intensity of their emission lines.[2,10,12] In the

CVG-μAPGD system studied here, the microdischarge was fed with Hg vapor present in He carrier/ jet-supporting gas that passed through the GLS and was introduced to the nozzle anode. For that reason, sputtering of the liquid cathode solution did not play a significant role in analyte transport. On the other hand, it could be expected that the growing discharge current would result in an increase in energy density and an enhancement of the efficiency of excitation of Hg atoms. Surprisingly, it was found that the optimal discharge current was relatively low, i.e., 20-25 mA (U=1100 V). What is more, its further increase resulted in a decreased sensitivity of the Hg I line. So far, such behavior of APGD has not been described in the literature. A detailed explanation of this singularity requires further investigations.

As mentioned before, higher flow rates of the liquid cathode solution were advantageous for stable operation of CVG-μAPGD. Although the reduction of the flow rate of the liquid cathode solution from 2.1 to 0.9 mL min^{-1} resulted in the increase in the sensitivity of the Hg I line, this improvement was low, i.e., only 20% on the whole. Hence, as compromise, a flow rate of 1.5 mL min^{-1} was chosen for the study.

Under compromised conditions, i.e., for the discharge current of 25 mA, the He shielding gas flow rate of 2.5 L min^{-1} and the liquid cathode solution flow rate of 1.5 mL min^{-1}, the DL of Hg was 0.45 μg L^{-1}.

3.3. Effect of $NaBH_4$ and HCl concentrations

To select optimum parameters related to the CVG reaction, the sensitivity of the Hg I line, the background intensity and the DL of Hg were examined versus different concentrations of $NaBH_4$ and HCl. Three different flow rates of He carrier/ jet-supporting gas were used, i.e., 100, 200 and 300 mL min^{-1}.

As can be seen from Fig. 5, the sensitivity of the Hg I line is strongly affected by the increasing $NaBH_4$ concentration within 0.05-0.5% (m/v). A gradual reduction in response for Hg with the concentration of the reducing agent could be explained by an increase in the concentration of H_2 in He carrier/ jet-supporting gas. Although APGD with the liquid cathode can be operated in the atmosphere of H_2,[2] a negative impact of this gas on the efficiency of excitation of Hg atoms seems to be undeniable. It is well know that H_2, as a by-product of the $NaBH_4$ decomposition, impairs analytical performance of inductive coupled (ICP) and microwave induced (MIP) plasmas.[22] Gielniak et al. reported that H_2 introduced into He-APGD sustained between two metallic electrodes also led to a decrease in the sensitivity of the Hg I line.[23]

In the case of the influence of the HCl concentration in the sample solution on performance of CVG-μAPGD, the sensitivity of the Hg I lines was increased by about 20-30% when the HCl concentration was changed from 2.0 to 16% (m/v), irrespectively of the $NaBH_4$ concentration.

The intensity of the background near the Hg I line was heightened by 50-65% when the $NaBH_4$ concentration was increased from 0.05 to 0.5% (m/v), and declined by about 10% when the HCl concentration was increased from 2.0 to 16% (m/v). The SD of the background intensity appeared not to change with the concentration of HCl in the sample solution. However, it was increased by about 25% when the $NaBH_4$ concentration was changed from 0.05 to 0.5% (m/v).

A typical concentration of $NaBH_4$ used in CVG of Hg in combination with ICP or MIP is within 0.1-1.0% (m/v).[22,24,25] Our additional trials indicated that the optimal concentration of $NaBH_4$ for CVG-μAPGD could be much lower than 0.1% (m/v). Indeed, examining the effect of the $NaBH_4$ concentration in the lower concentration range than in the beginning, i.e., 0.005-0.05% (m/v), on the sensitivity of the Hg I line, it was found that response for Hg was inversely proportional to the $NaBH_4$ concentration. The HCl concentration in the sample solution was kept at 16% (m/v) and different flow rates of He carrier/ jet-supporting gas were used, i.e., 100, 200 and 300 mL min^{-1}. Accordingly, the less concentration of $NaBH_4$ was used the greater amplification of the Hg signal was recorded, i.e., by about 7.5% per each 0.01% (m/v) of $NaBH_4$. This effect was irrespective of the flow rate of He carrier/ jet-supporting gas. Lower concentrations of $NaBH_4$ were not examined, but it was expected that a further decrease in the $NaBH_4$ concentration, i.e., <0.005% (m/v), would probably result in an improvement of the sensitivity of the Hg I line. Considering the possibility of competitive reactions of $NaBH_4$ with other ingredients of sample solutions, it was decided to use slight excess of the reducing agent. Based on all obtained results, 0.005% (m/v) $NaBH_4$ and 16% (m/v) HCl concentrations were considered as optimal for the CVG reaction.

3.4. Effect of flow rates of He carrier/ jet-supporting gas and reagents

The impact of the flow rate of He carrier/ jet-supporting gas on the sensitivity of the Hg I line was examined within 40-340 mL min^{-1}. As can be seen from Fig. 6, the sensitivity of Hg I line strongly improves with the increasing He flow rate up to 150 mL min^{-1}. Apparently, at low He flow rates, residence time of Hg in the microdischarge core was the longest, but excitation conditions of Hg atoms were possibly unfavorable due to a relatively high concentration of H_2 in He carrier/ jet-supporting gas. When the He flow rate exceeded 150 mL min^{-1}, the sensitivity of the Hg I line reached a plateau (150-340 mL min^{-1}). DLs of Hg evaluated for

CVG-μAPGD when it was operated using He carrier/ jet-supporting gas at 100, 200 and 300 mL min^{-1} were 0.19, 0.18 and 0.22 μg L^{-1}, respectively. The flow rate of He carrier/ jet supporting gas of 200 mL min^{-1} was preferred in further experiments.

The influence of flow rates of reagents for the CVG reaction (within 0.3-6.0 mL min^{-1}) and He carrier/ jet-supporting gas (within 40-340 mL min^{-1}) was also examined on the sensitivity of the Hg I 253.7 nm line, the background intensity and the DL of Hg. As can be seen from Fig. 7, the sensitivity of the Hg I line strongly increases in the beginning (up to 3.5 mL min^{-1}) and then, the increase in response for Hg is much slower. This could be explained by an increase in the concentration of H_2 in discharge gas. Although the lowest DL of Hg (0.14 μg L^{-1}) was ascertained when the highest flow rate of reagents was used, i.e., 6.0 mL min^{-1}, the flow rate of 3.0 mL min^{-1} was considered as optimal to reduce unacceptably high consumption of the sample solution.

3.5. Effect of the liquid cathode solution composition

It is well known that the composition of the liquid cathode solution plays a significant role in processes of sputtering of analytes and their excitation in APGD.[9,13,15,16,21,26] In our latest papers,[9,21] physicochemical properties of the liquid cathode solution were modified by addition of non-ionic Triton surfactants. The effect of size and the concentration of Triton surfactants was investigated on analytical performance of APGD-OES. It was acknowledged that heavy Triton x-405 enabled to reduce DLs of Hg and other elements examined at least several times. Under optimized conditions, response for Hg was enhanced more than 5 times. Furthermore, the background intensity and its fluctuation in the vicinity of the Hg I 253.7 nm emission line and atomic emission lines of other elements were considerably decreased. As a result, the DL of 0.13 mg L^{-1} of Hg, although relatively high, was 15 times lower than this assessed before addition of the surfactant.

The effect of the HCl concentration in the liquid cathode solution on Hg response for the CVG-μAPGD system was examined in the range of 0.05-8.8% (m/v). It was established that for the acid concentration lower than 0.05% (m/v) it was impossible to sustain the microdischarge. Unlike in other papers,[1,2,11,12] the increase in the HCl concentration from 0.05 to 8.8% (m/v) resulted in a very slight linear decrease in the sensitivity of the Hg I line, i.e., only by 8% on the whole. In addition, it was observed that the microdischarge became unstable, and the SD of the background intensity was gradually increased when the HCl concentration in the liquid cathode solution exceeded 1.1% (m/v). The background intensity decreased by over 15% when the HCl concentration was changed from 0.05 to 1.8% (m/v), and then, above the latter concentration, it was practically unchanged. In effect, DLs of Hg evaluated when 0.05 and 8.8% (m/v) HCl solutions were used as flowing liquid cathodes were similar, i.e., 0.16 and 0.25 µg L^{-1}, respectively.

The effect of addition of Triton x-405 (within its 0.05-10×CMC, where CMC is the critical micelle concentration of 0.81 mmol L^{-1})[9] to the liquid cathode solution was also examined. It has already been reported that addition of non-ionic and ionic surfactants to liquid cathode solutions allows decreasing DLs of most metals at least by one order of magnitude.[9,21,27,28] In the present contribution, the presence of Triton x-405 at low concentrations (0.05-1.5×CMC) did not lead to any changes in the sensitivity of the Hg I line and the DL of Hg obtained with the CVG-µAPGD system. When the amount of the surfactant was increased from its 1.5×CMC to 7.0×CMC, the sensitivity of the Hg I line was gradually decreased by about 5.0% per each 1.0×CMC. Afterwards, above 7.0×CMC of Triton x-405, the sensitivity of the Hg I line practically remained unchanged. In the case of the SD of the background intensity, it slightly increased when the amount of added Triton x-405 exceeded its 1.5×CMC. In effect, DLs of Hg evaluated in conditions of the Triton x-405 presence in solutions of the liquid cathode in amount of its 1.5×CMC and 10×CMC were not much differentiated, i.e., 0.15 and 0.20 µg L^{-1}, respectively.

The only positive effect of addition of the non-ionic Triton x-405 surfactant was a linear suppression of the background intensity in the vicinity of the Hg I line. Such decay of the background level in the whole studied range (from 0.05×CMC to 10×CMC) was higher than 25%. Based on these results, the composition of the liquid cathode solution was not modified in further experiments by adding Triton x-405. A 0.4% (m/v) HCl solution was used as the liquid cathode in the coupled CVG-µAPGD system.

3.6. Transport efficiency and excitation conditions of Hg

The efficiency of CVG of Hg assessed under initial operating conditions ($NaBH_4$ and HCl concentrations of 0.01% (m/v) and 10% (m/v), respectively, the flow rate of He carrier/ jet-supporting gas of 100 mL min^{-1}) was 97.0±3.0% (n=3). Under optimized operating conditions ($NaBH_4$ and HCl concentrations of 0.005% (m/v) and 16% (m/v), respectively, the flow rate of He carrier/ jet-supporting gas of 200 mL min^{-1}), the efficiency of transport of Hg was practically the same, i.e., 98±1% (n=3). In both cases, considering very low concentrations of $NaBH_4$, both CVG efficiencies were unexpectedly high. However, it was evident that the increase in the concentration of the reducing agent did not lead to the improvement of the sensitivity of the Hg I line (see Fig. 5).

Somewhat surprising was a high value of the efficiency of sputtering of Hg from the liquid cathode solution in the case of the µAPGD system without CVG. In this case, the microdischarge was operated under the following conditions: the discharge current of 35 mA, the flow rate of He jet-supporting gas of 100 mL min^{-1}, the solution flow rate of 1.2 mL min^{-1}, the concentration of Hg of 25 mg L^{-1} in 0.4% (m/v) HCl. The efficiency of sputtering was 77±4% (n=3), while the efficiency of sample vaporization was merely 28±1% (n=3). The very high value of this efficiency of Hg from the liquid cathode solution to APGD operated in contact with a conventional metallic pin anode was previously reported by Cserfalvi et al..[29] Zhu et al. suggested that transport of Hg from the liquid cathode solution to the discharge phase could be enhanced due to production of vapor of this element.[30]

The coupling of µAPGD with CVG of Hg increases the efficiency of transport of this element but just by about 20% in relation to the sample delivery by sputtering in the case of the µAPGD system without CVG. Therefore, it appears that more effective transport of Hg cannot be the only one explanation for the observed enhancement of the sensitivity of the Hg I line (over 3 orders of magnitude). According to Kim et al.,[12] just above the surface of the liquid cathode, H_2O vapor is the main component of discharge gas. APGD with the liquid cathode seems to be resistant to saturation with H_2O vapor thanks to high energy density (several kW cm^{-3}).[3] On the other hand, most of supplied energy is consumed by H_2O molecules in their vaporization, ionization and dissociation processes. Stable µAPGD can be operated in these conditions but suffers from a small number of electrons with sufficiently high energy to excite Hg atoms. When Hg is delivered to the microdischarge as a component of the liquid cathode solution, it reaches the highest concentration in the near-cathode region. H_2O vapor saturation of this region is extremely high and, in consequence, energy of electrons ready for excitation of Hg atoms is dissipated.

The main component of µAPGD in the near-anode region was He atoms that likely promoted formation of high energy electrons. In a result, supplied energy was not consumed in mentioned side processes and could be used for efficient excitation of Hg atoms in µAPGD coupled with CVG.

3.7. Analytical performance

Under optimal conditions, the DL of Hg evaluated for CVG-µAPGD-OES was 0.14 µg L^{-1}. Due to such low DL, the studied method can be easily adapted for the monitoring of water quality (according to the US Environmental Protection Agency the maximum contaminant level for inorganic Hg in drinking water is 2 µg L^{-1}). The comparison of DLs of Hg assessed for other competitive analytical methods reported in the literature (without pre-concentration of Hg with an Au trap) is given in Table 2. As it can be seen, in most cases, the DL of Hg evaluated for the method proposed is improved by 4 to over 80 times as compared to DLs of Hg obtained for other methods. This DL can be even improved by prolonging integration time of measurements (in this work it was merely 0.1 s).

It was found that, for the studied CVG-µAPGD-OES method, the upper linearity range of the calibration curve was 500 µg L^{-1}. Repeatability of the signal (n=10) at 5, 10, 25, 50 and 100 µg L^{-1} of Hg were 4.1, 3.0, 2.9, 3.5 and 2.1%, respectively. The method was successfully applied for the determination of Hg in the CRM of human hair (NCS ZC 81002). The result obtained, i.e., 2.17±0.08 µg g^{-1} (n=3), was consistent with the certified value, i.e., 2.16±0.21 µg g^{-1}. Additionally, samples of tap water, Oder river water, Azure Lakelet water and Purple Lakelet water, which contained Hg below 0.14 µg L^{-1}, were spiked with known amounts of this element (50 µg L^{-1}) and analyzed. Average recoveries (n=3) of added Hg for these waters (n=3) were 96, 103, 102 and 102%, respectively. All these results proved good precision and accuracy of CVG-µAPGD-OES.

4. Conclusions

A novel analytical method, i.e., optical emission spectrometry with excitation in atmospheric pressure glow microdischarge sustained between the miniature flow He jest and the small-sized flowing liquid cathode, and combined with cold vapor generation of Hg (CVG-µAPGD-OES), was described. As compared to the µAPGD system without CVG, the efficiency of excitation of Hg atoms in the microdischarge combined with CVG was several thousand times higher. In consequence, the DL of Hg was improved by 4 orders of magnitude. Increasing the integration time or using an Au trap could achieve a further improvement of the DL of Hg. To improve the sensitivity of the determination of Hg, the concentration of H_2 in discharge gas has to be reduced, e.g., by replacing $NaBH_4$ with $SnCl_2$. However, an essential factor improving the efficiency of excitation of Hg atoms is also the limitation of saturation of discharge gas with H_2O vapor. To increase application possibilities of the new device, its design should be modified to limit the consumption of He shielding gas. In spite of this, CVG-µAPGD-OES was shown to be suitable to determine Hg concentrations of several to doze µg L^{-1}.

At present, as compared to CVG heated quartz tube atomic absorption spectrometry (HQT-AAS), where Ar is used for purging Hg vapor, CVG-μAPGD-OES described in the present contribution uses He as discharge and carrier gas and seems to be about 3 fold more expensive. However, consumption of gases in CVG-ICP-OES or CVG-MIP-OES is much higher and therefore, the proposed alternative is relatively cheaper. In our opinion, there is place for the improvement of the system by decreasing the flow rate of He or replacing the latter gas with Ar. Certainly, the cost of the device of the newer method, i.e., CVG-μAPGD-OES, is much lower as compared to devices for CVG-HQT-AAS, CVG-ICP-OES and CVG-MIP-OES.

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Table 1. Comparison of the sensitivity of the Hg I 253.7 nm line, the background intensity, and the detection limit of Hg evaluated for µAPGD-OES and CVG-µAPGD-OES systems. Emission spectra were collected in near-cathode (µAPGD-OES) and near-anode (CVG-µAPGD-OES) regions. The liquid cathode solution flow rate: 1.2 mL min^{-1}, the He carrier/ jet-supporting gas flow rate: 100 mL min^{-1}, the discharge gap: 5.0 mm, the discharge current: 35 mA, the $NaBH_4$ concentration: 0.1% (m/v), the HCl concentration in the sample solution: 10% (m/v), the HCl concentration in the liquid cathode solution: 0.4% (m/v), the flow rate of reagents: 3.0 mL min^{-1}, the He shielding gas flow rate: 2.0 L min^{-1}.

Studied method (surrounding gas)	Diaphragm	Sensitivity, a. u. per µg L^{-1}	Background intensity, a. u.	Detection limit, µg L^{-1}
µAPGD-OES (open-to-air)	1.0 mm	$(28.1\pm2.2)\times10^{-3}$	198±4	$(1.1\pm0.1)\times10^{3}$
	fully opened	$(81.8\pm9.9)\times10^{-3}$	$(1.09\pm0.05)\times10^{3}$	$(1.4\pm0.3)\times10^{3}$
CVG-µAPGD-OES (open-to-air)	1.0 mm	16.7±0.7	294±17	2.3±0.5
	fully opened	35.4±1.5	$(1.42\pm0.04)\times10^{3}$	3.2±0.4
CVG-µAPGD-OES (He shielding)	1.0 mm	28.4±1.8	235±7	1.9±0.4
	fully opened	60.6±2.2	986±22	1.4±0.3

Average values (n=10) ± SD.

Table 2. Comparison of detection limits of Hg for different excitation sources used in optical emission spectrometric determinations of this element.

	Detection limit, µg L^{-1}	Integration time, s	Reference
CVG-µAPGD	0.14^{abc}	0.1	This work
ELCAD	15^{cd}	0.3	11
	10^{de}	-	
ELCAD	2^{de}	0.5	15
CVG-MIP	1.4^{abcf}	0.1	24
CVG-MSP	9^{acf}	0.1	25
	0.11^{cfg}	0.1	
SCGD-ICP	0.7^{cdf}	3.0	30
	1.2^{def}	0.2	
ECVG-MSP	1.1^{bc}	0.3	31
CVG-DBD	0.014^{bcg}	10	32
	0.043^{cfg}	10	
CVG-CCP	0.012^{cfg}	10	33

CVG Chemical vapor generation. µAPGD Atmospheric pressure glow microdischarge. ELCAD Electrolyte cathode discharge. MIP Microwave induced plasma. MSP. Microstrip plasma. SCGD Solution cathode glow discharge. ICP Inductively coupled plasma. ECVG Electrochemical cold vapor generation. DBD Dielectric barrier discharge. CCP Capacitively coupled plasma. [a] CVG with $NaBH_4$. [b] Operated in He. [c] Continuous flow mode. [d] Operated in the air. [e] Flow injection mode. [f] Operated in Ar. [g] CVG with $SnCl_2$.

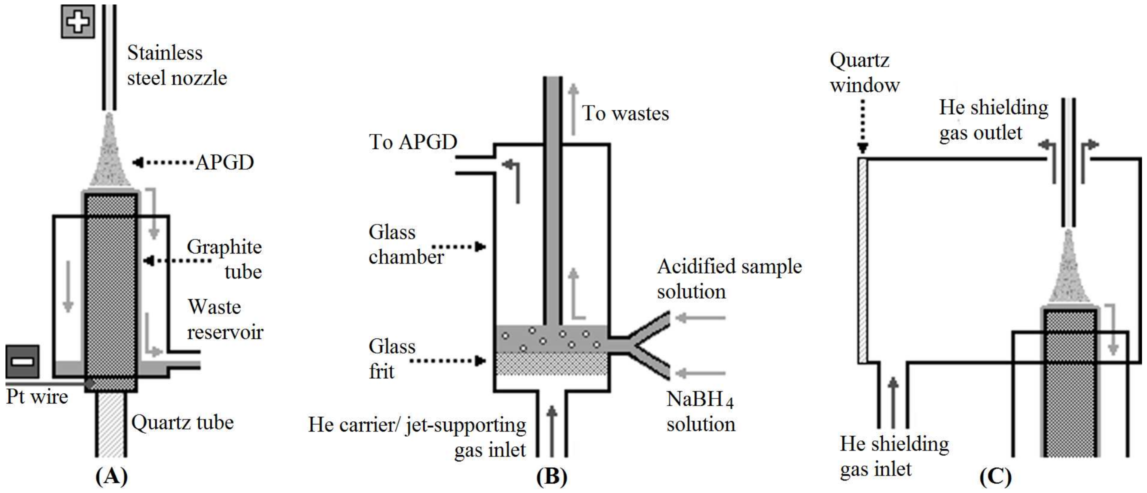

Fig. 1. Experimental set-up of µAPGD operated between the miniature flow He jet and the flowing liquid cathode (A), the reaction/ separation chamber (B) and the semi-closed chamber with shielding the microdischarge by the He flow (C).

1

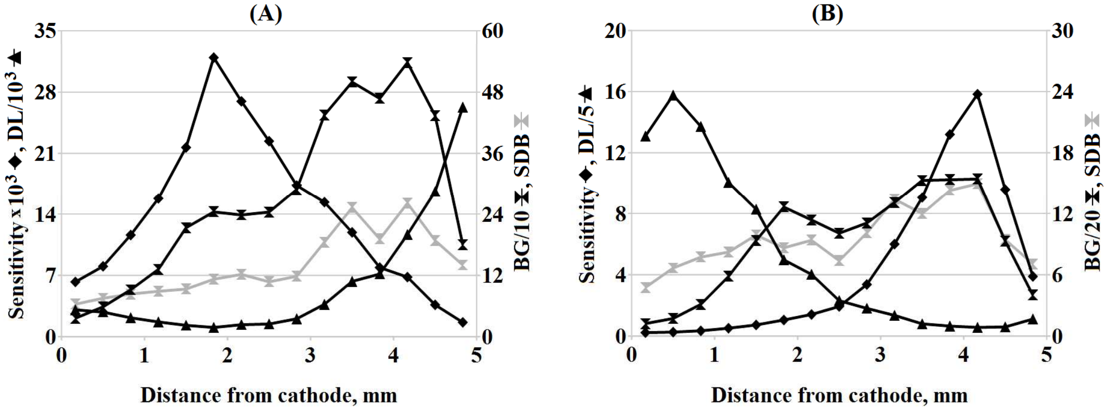

Fig. 2. Vertical distributions of the sensitivity of the Hg I 253.7 nm emission line (a. u. per µg L^{-1}), the detection limit of Hg (DL, µg L^{-1}), the background intensity (BG, a. u.) and its standard deviation (SDB, a. u.) for APDG systems operated between the miniature flow He jet and the flowing liquid cathode in open-to-air atmosphere. Hg is delivered as a component of the liquid cathode solution (A) or vapor produced in the cold vapor generation reaction (B). The liquid cathode solution flow rate: 1.2 mL min^{-1}, the He carrier/ jet-supporting gas flow rate: 100 mL min^{-1}, the discharge gap: 5.0 mm, the discharge current: 35 mA, the $NaBH_4$ concentration: 0.1% (m/v), the sample solution acidification: 10% (m/v) HCl, the flow rate of reagents: 3.0 mL min^{-1}, the He shielding gas flow rate: 2.0 L min^{-1}.

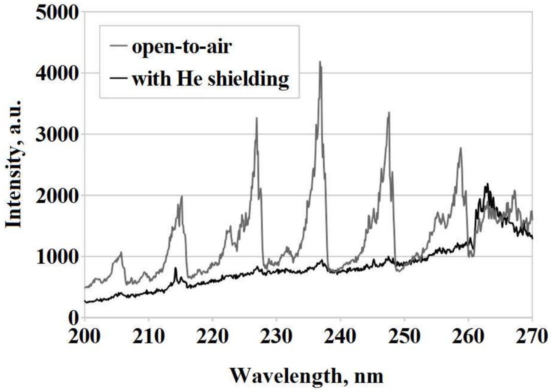

Fig. 3. Emission spectra of μAPGD operated between the miniature flow He jet and the flowing liquid cathode in the atmosphere of ambient air or He shielding gas. The liquid cathode solution flow rate: 1.2 mL min^{-1}, the He carrier/ jet-supporting gas flow rate: 100 mL min^{-1}, the discharge gap: 5.0 mm, the discharge current: 35 mA, the He shielding gas flow rate: 2.0 L min^{-1}.

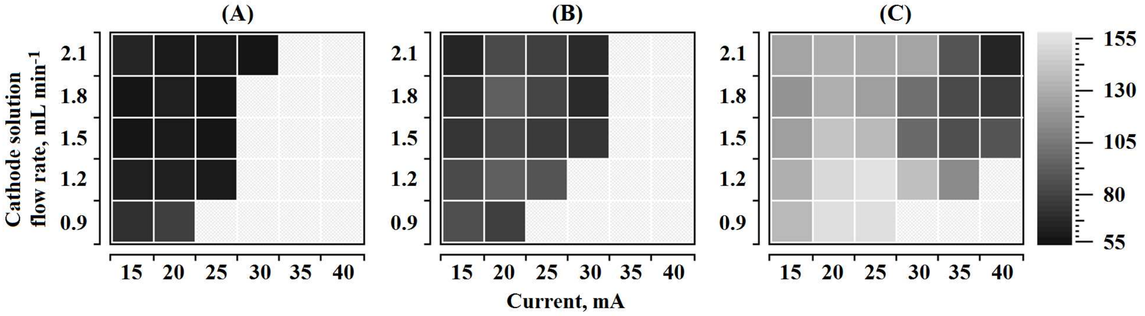

Fig. 4. Effect of the discharge current (15-40 mA), the liquid cathode solution flow rate (0.9-2.1 mL min^{-1}) and the He shielding gas flow rate (A: 1.0, B: 1.75, C: 2.5 L min^{-1}) on the sensitivity of the Hg I 253.7 nm emission line (a. u. per µg L^{-1}). The liquid cathode solution flow rate: 1.5 mL min^{-1}, the He carrier/ jet-supporting gas flow rate: 100 mL min^{-1}, the discharge gap: 5.0 mm, the $NaBH_4$ concentration: 0.1% (m/v), the sample solution acidification: 10% (m/v) HCl, the flow rate of reagents: 3.0 mL min^{-1}. Dashed area means instability of µAPGD.

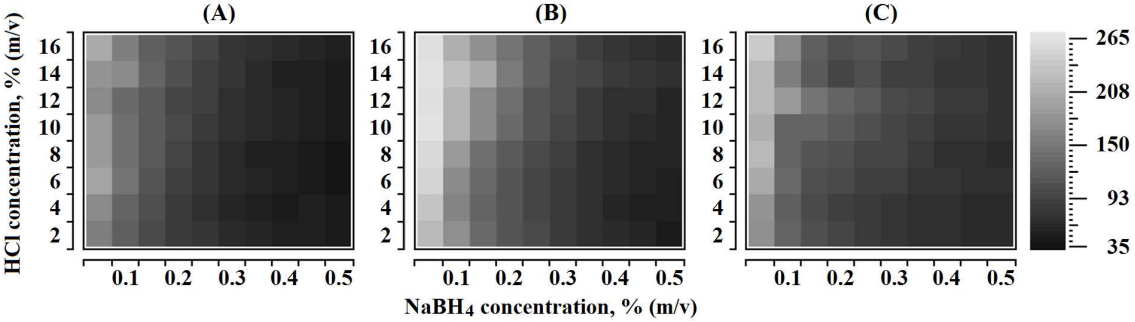

Fig. 5. Effect of the sample solution acidification (2.0-16% (m/v) HCl), the $NaBH_4$ concentration (0.05-0.5% (m/v)) and the He carrier/ jet-supporting gas flow rate (A: 100, B: 200, C: 300 mL min^{-1}) on the sensitivity of the Hg 253.7 I nm emission line (a. u. per µg L^{-1}). The liquid cathode solution flow rate: 1.5 mL min^{-1}, the discharge gap: 5 mm, the discharge current: 25 mA, the flow rate of reagents: 3.0 mL min^{-1}, the He shielding gas flow rate: 2.5 L min^{-1}.

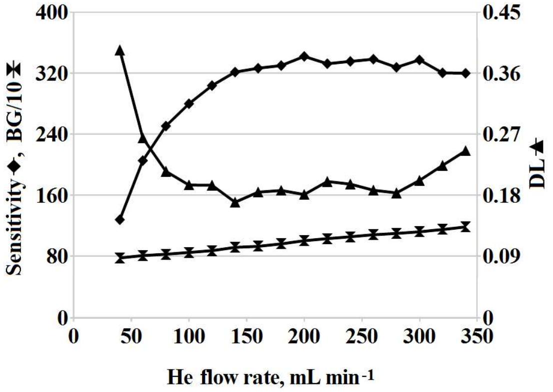

Fig. 6. Effect of the He carrier/ jet-supporting gas flow rate (40-340 mL min^{-1}) on the sensitivity of the Hg I 253.7 nm emission line (a. u. per µg L^{-1}), the detection limit of Hg (DL, µg L^{-1}) and the background intensity (BG, a. u.). The liquid cathode solution flow rate: 1.5 mL min^{-1}, the discharge gap: 5.0 mm, the discharge current: 25 mA, the NaBH$_4$ concentration: 0.005% (m/v), the sample solution acidity: 16% (m/v) HCl, the flow rate of reagents: 3.0 mL min^{-1}, the He shielding gas flow rate: 2.5 L min^{-1}.

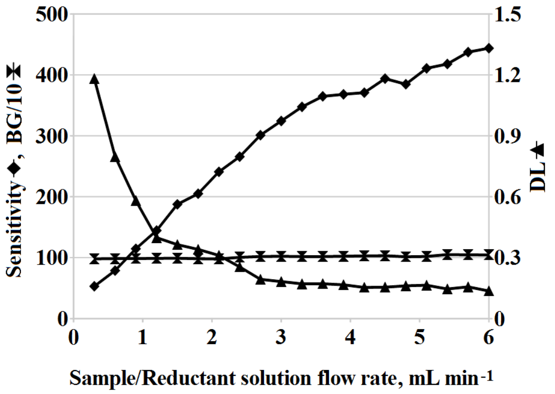

Fig. 7. Effect of the flow rate of sample and $NaBH_4$ solutions (0.3-6.0 mL min^{-1}) on the sensitivity of the Hg I 253.7 nm emission line (a. u. per µg L^{-1}), the detection limit of Hg (DL, µg L^{-1}) and the background intensity (BG, a. u.). The liquid cathode solution flow rate: 1.5 mL min^{-1}, the He carrier/ jet-supporting flow rate: 200 mL min^{-1}, the discharge gap: 5.0 mm, the discharge current: 25 mA, the $NaBH_4$ concentration: 0.005% (m/v), the sample solution acidity: 16% (m/v) HCl, the He shielding gas flow rate: 2.5 L min^{-1}.