Supporting Information

Determination of bismuth by optical emission spectrometry with liquid anode/cathode atmospheric pressure glow discharge.

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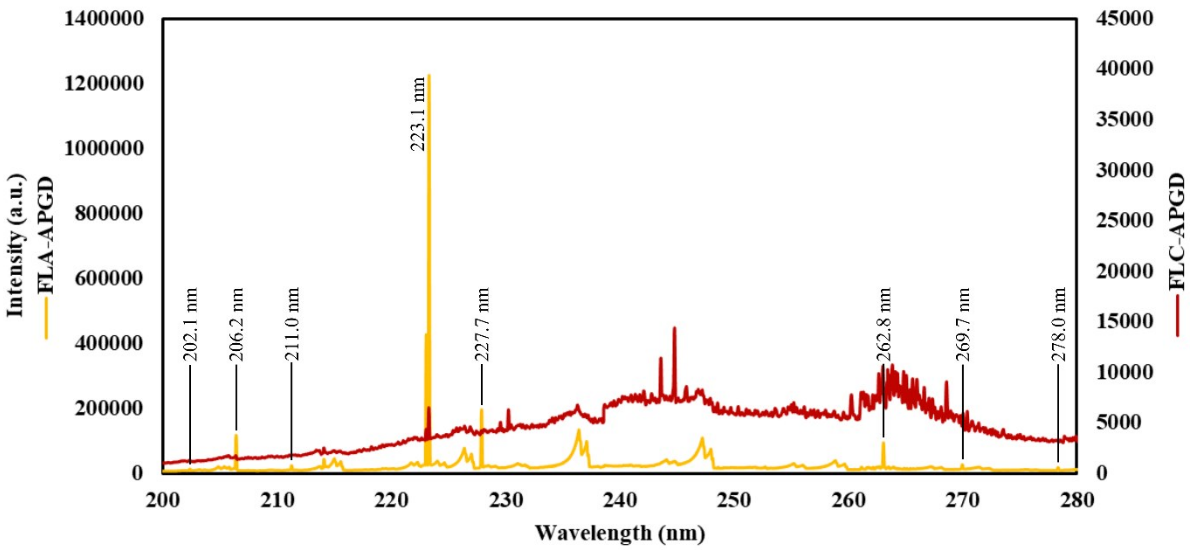

Fig. SI-1. Emission spectra of APGD generated in contact with a Bi-containing solution (serving as the FLA or the FLC) in the spectral range of 200-280 nm.

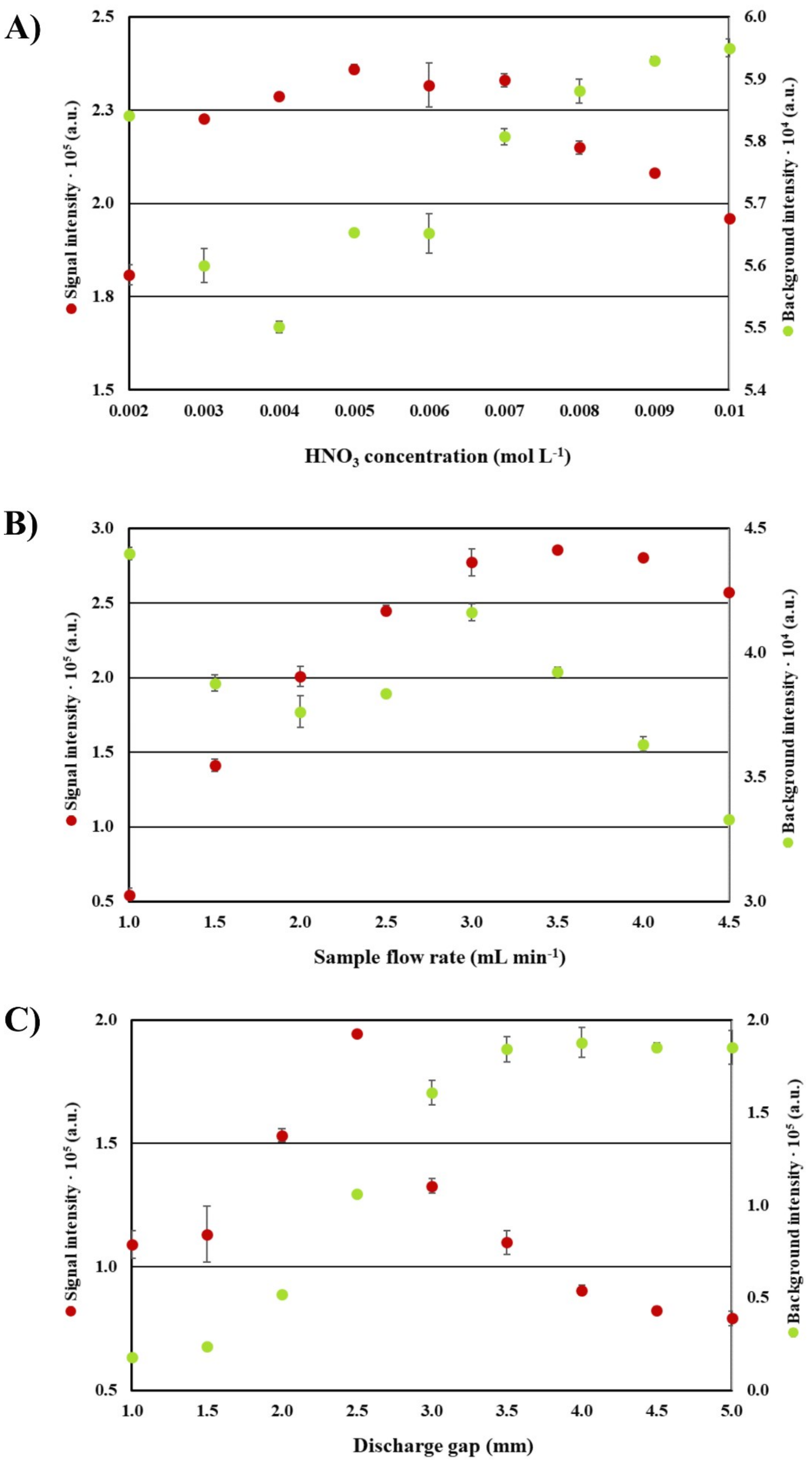

Fig. SI-2. The effect of the acid concentration (A), the sample flow rate (B), and the discharge gap (C) on the intensities of the Bi emission line and the background emission in the case of the FLA-APGD system.

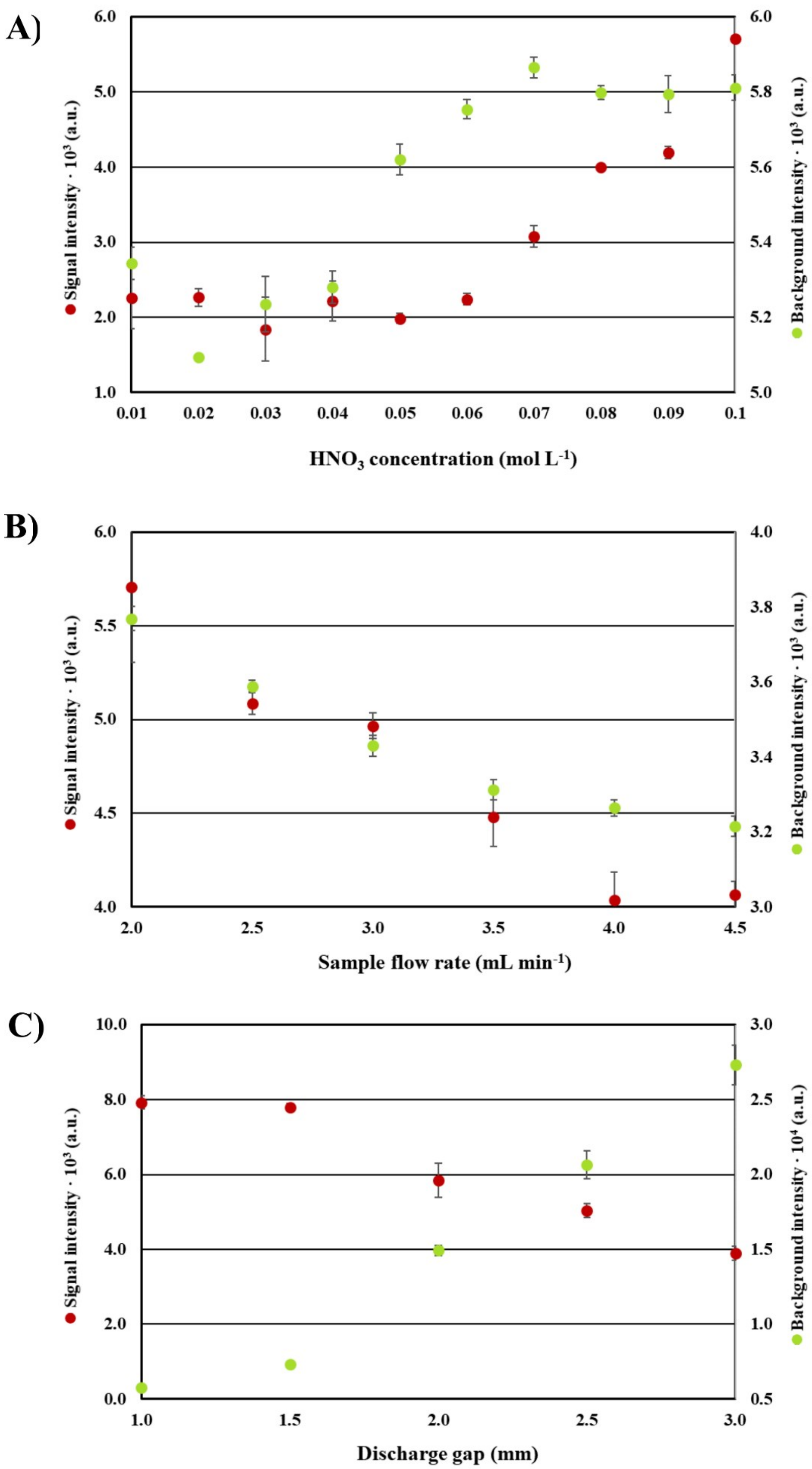

Fig. SI-3. The effect of the acid concentration (A), the sample flow rate (B), and the discharge gap (C) on the intensities of the Bi emission line and the background emission in the case of the FLC-APGD system.

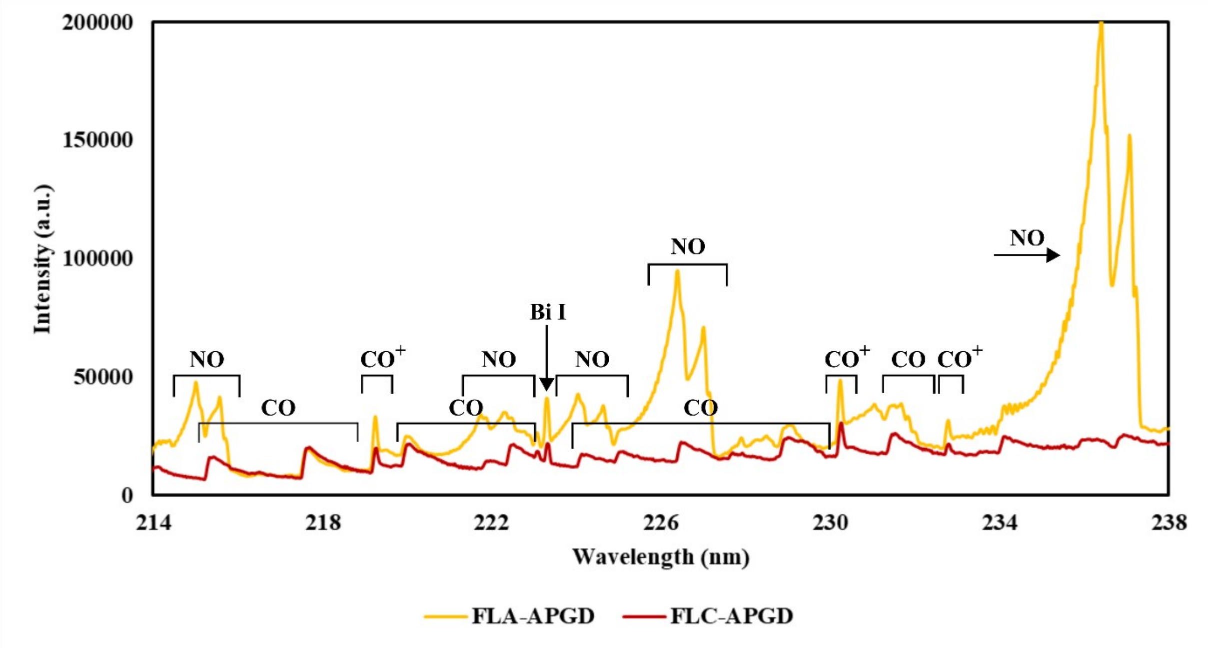

Fig. SI-4. The emission spectra of APGD generated in contact with a Bi-containing solution (serving as the FLA or the FLC) with the addition of 5% methanol, acquired in the spectral range of 214-238 nm.

Comment SI-1

The effect of acid kind and its concentration

The use of HCl for the sample preparation caused an inconvenience due to the reaction of the analyte with Cl^- ions, leading to the formation of BiOCl species. This resulted in a great suppression of the Bi signal intensity after some time since the sample preparation. That being so, the Bi standard solution in HCl had to be prepared just before measurements. Although it was not the aim of this work, it was established that after only a 3 hour storage from the preparation of the Bi solution acidified with HCl, the SBR of the Bi emission line was 4 times lower than the corresponding one obtained for a freshly prepared solution. Additionally, there was almost no measurable signal from Bi in the spectrum recorded the next day.

Comment SI-2

The effect of acid kind and its concentration

In the FLA-APGD system, the growth in the acid concentration up to 0.005 mol L^{-1} resulted in an enhancement of the Bi signal intensity (by 30%) following by a gradual decline as the acid concentration was further increased. In the case of the FLC-APGD system, conversely, an initial fall of the Bi signal intensity was noted (by 12%) at acid concentrations up to 0.05 mol L^{-1} and then, it rocketed with a succedent growth in the acid concentration up to 0.1 mol L^{-1}.

Comment SI-3

The effect of acid kind and its concentration

Normally, solvated electrons take part in the reduction of the analyte ions, which the process is privileged at lower acidities of the FLA solution, and are responsible for the generation of the reduced forms of these analytes, as reported for Ag(I) and Cd(II).[1] Hence, alike for the latter analytes, it can be expected that at higher HNO_3 concentrations, *i.e.*, up to 0.01 mol L^{-1} as studied here, a contribution of the solvated electrons was very low, while other reactive species present in these conditions in the solution, *e.g.*, H radicals,[1] could react much slower or not at all with Bi(III) ions as compared to the solvated electrons. Therefore, the Bi signal intensity was decreased when the HNO_3 concentration was increased.

Comment SI-4

The effect of the discharge current and the He flow rate

Generally, as the discharge current increased, the background intensity in FLA-APGD was lifted; its behavior was akin to that reported for the FLC-APGD system. However, at the He flow rate of 100 mL min^{-1}, the background intensity did not depend on the discharge current, whereas at the lowest studied He flow rate (50 mL min^{-1}), the background intensity decreased with the increasing discharge current.

Comment SI-5

The effect of the discharge current and the He flow rate

The remarked background intensity growth was different for both investigated systems. In the case of FLA-APGD, it was noted that the background level enhanced around 4.5-fold as the gas flow rate rose from 150 to 350 mL^{-1} (lower He flow rates were not considered due to the discharge instability when the gas flow rates of 50-100 mL min^{-1} were applied at higher discharge currents), regardless of the discharge current used. However, for FLC-APGD, the observed background enhancement (assessed in the same range of the He flow rates) was much lower, *i.e.*, 2-fold (at discharge currents of 30-50 mA) or 1.4-fold (at discharge currents of 60-70 mA), apparently being slightly dependent on the discharge current applied and dropping with its growth.

Comment SI-6

The effect of the discharge current and the He flow rate

The results shown in Fig. 3 as well as the abovementioned intensity shifts of both the Bi emission line and the background level clearly indicate that there is a strong and intricate relationship between the discharge current and the He flow rate. This relationship could point that except for the collisions with electrons, the collisions with the excited He atoms and/or the metastable He atoms might play an important role in the excitation processes of Bi atoms, particularly in the case of the FLA-APGD system operated at higher He flow rates and higher discharge currents. As reported by Swiderski *et al.*[1], the later excitation source is more energetic than the FLC-APGD system and with a negligible contribution of the quenching processes due to the collisions of water molecules with the excited states of the molecular and atomic species. The water evaporation from the surface of the FLC solution and the flux of water molecules in the discharge phase was much higher than this in the FLA-APGD system, but its effect was less deteriorating at lower He flow rates and lower discharge currents.

Comment SI-7

The effect of the discharge gap

Considering the FLA-APGD system, the signal intensity of Bi was growing as the discharge gap was increased from 1 mm up to 2.5 mm (the observed intensity amplification was equal to 78% at the discharge gap of 2.5 mm) and then dropped with the further increase of the discharge gap up to 5 mm (by 60% at 5 mm). As for FLC-APGD, the signal intensity of Bi was decreasing up to 3 mm by 50%. At discharge gaps above that value, the response from Bi was not observed.

Regarding the background intensity, it was established that, with the rise of the discharge gap up to 3 mm, the background intensity was enhanced almost 5-fold in the case of FLC-APGD and over 9-fold in the case of FLA-APGD. Moreover, at discharge gaps of 4-5 mm, the background level for the FLA-APGD system was roughly constant, which resulted in an overall 10-fold background intensity enhancement as the discharge gap was changed from 1 to 5 mm.

References

1. K. Swiderski, A. Dzimitrowicz, P. Jamroz, P. Pohl, Influence of pH and low-molecular weight organic compounds in solution on selected spectroscopic and analytical parameters of flowing liquid anode atmospheric pressure glow discharge (FLA-APGD) for the optical emission spectrometric (OES) determination of Ag, Cd, and Pb, *J. Anal. At. Spectrom.*, 2018, **33**, 437–451.