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Determination of Trace Bismuth(III) by Stripping Voltammetry at Antimony-Coated Carbon Paste Electrode

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A new procedure was elaborated to determine trace bismuth(III) using an anodic stripping square-wave voltammetry at the antimony film carbon paste electrode (SbF-CPE). The method is realized in highly acidic medium of hydrochloric acid in which antimony peak is negligible, and apparently catalyzed by presence of cadmium(II), thus allowing the determination at ppb levels. Calibration dependence was linear up to 110 ppb Bi with a detection limit (3σ) of 1.55 ppb. Applicability of the method was tested on the real sample of river water.

Keywords: bismuth(III) determination, stripping voltammetry, antimony film electrode, carbon paste electrode, Cd(II)-assisted catalysis

1. INTRODUCTION

According to results of soil measurements, bismuth belongs to the rarest elements. This agrees with its content from 0.1 ppm in coal to 3 ppm in sandstone. Sediments in rivers contain 2.4 ppm and in an ocean bay 0.27-0.64 ppm. Levels of bismuth in drinking and river waters are not reported [1]. On the contrary, large quantities of bismuth are produced annually in different areas, such as semiconductors, cosmetic products (e.g. pigments in eye shadow, lipsticks and hair dyes), medicines, alloys with low melting points, byproduct of copper and tin refining, metallurgical additives, and preparation and recycling of uranium in nuclear fuels [2]. Concerning toxicity, all lethal intoxications are attributed to therapeutic uses of bismuth compounds, mostly injections or long-lasting treatments; single cases of poisonings were reported [3,4]. On the other hand, organobismuth compounds are extremely toxic; several of them are used for bactericidal and fungicidal applications [5]. Concerning analytical control of environment, determination of bismuth is mostly ignored and two official methods only are recommended for its determination in drugs: gravimetric and polarographic [6].

In the last period, modern electroanalytical methods like stripping voltammetry and stripping chronopotentiometry at mercury film electrodes (MFEs) were recognized as one of the most powerful tools in trace and ultratrace analysis of heavy metals [7,8]. However, the use of MFE is usually disclaimed due to toxicity of mercury or more precisely, well-known toxicity of its salts. This initiated researches and electrochemists to search for new electrode materials. For example, heterogeneous carbon electrochemical sensors, namely carbon paste electrodes, were applied for bismuth determination [9-14]. At the down of 2000, the bismuth film electrode was introduced in anodic stripping voltammetry but as evident, this cannot be applied for bismuth(III) determination.

In this contribution, determination of bismuth(III) using the antimony-based electrode is first described. Although known since 1923 as one of the metal | metal oxide sensors used for potentiometric pH measurements [15], antimony film electrodes (SbFEs) were successfully introduced into stripping electrochemical methods in 2007 [16,17] after preliminary studies [18]. Since that time, antimony-based electrodes were analytically applied in various ways on different substrates and different modifications [19-31]. Considering some interesting characteristics of SbFEs such as, favourably negative overvoltage of hydrogen evolution, wide operational potential window, convenient operation in relatively strong acidic medium (pH≤2) and very low voltammetric peak corresponding to anodic reoxidation of antimony provoked us to elaborate the procedure for Bi(III) determination although its peak appears practically at the same potential.

2. EXPERIMENTAL

2.1. Chemicals and Solutions

Standard stock solutions of antimony(III) and cadmium(II) (1000 mg L^{-1}, atomic absorption standard solutions) were obtained from Merck, whereas standard stock solutions of bismuth(III) (1000 mg L^{-1}, atomic absorption standard solutions) were provided by Aldrich and Alfa Aesar, respectively, and diluted as required.

2.2. Apparatus

A modular electrochemical analyzer AUTOLAB equipped with PGSTAT12 controlled by GPES software (EcoChemie, Utrecht) was used for all voltammetric measurements. The conventional three-electrode configuration with antimony film-plated carbon paste electrode (SbF-CPE) was employed throughout the work. The Ag/AgCl/3 M KCl and a Pt plate served as the reference and auxiliary electrodes. All electrochemical experiments were carried out in one-compartment voltammetric cells (10-20 mL) at conditioned room temperature (23±1 °C). In voltammetric stripping measurements, a magnetic stirrer (approximately 300 rpm) was employed during the electrochemical deposition step.

2.3. Preparation of the Carbon Paste Substrate Electrode

The carbon paste was prepared by intimately hand-mixing of graphite powder (0.5 g; CR-5, Maziva Týn nad Vltavou) with highly viscous silicone oil (0.3 mL; LUKOIL MV 8000, Lučební závody Kolín). Both components were homogenized to obtain a mixture that was subsequently packed into a piston-driven carbon paste holder [32], thus providing a carbon paste electrode support for plating with antimony film.

3. RESULTS AND DISCUSSION

3.1. Effect of the Cadmium(II) Presence

As reported very recently, a favourable catalytic effect of cadmium(II) on the reoxidation peak of mercury was observed during the determination of mercury [30]. Therefore, our first experiments

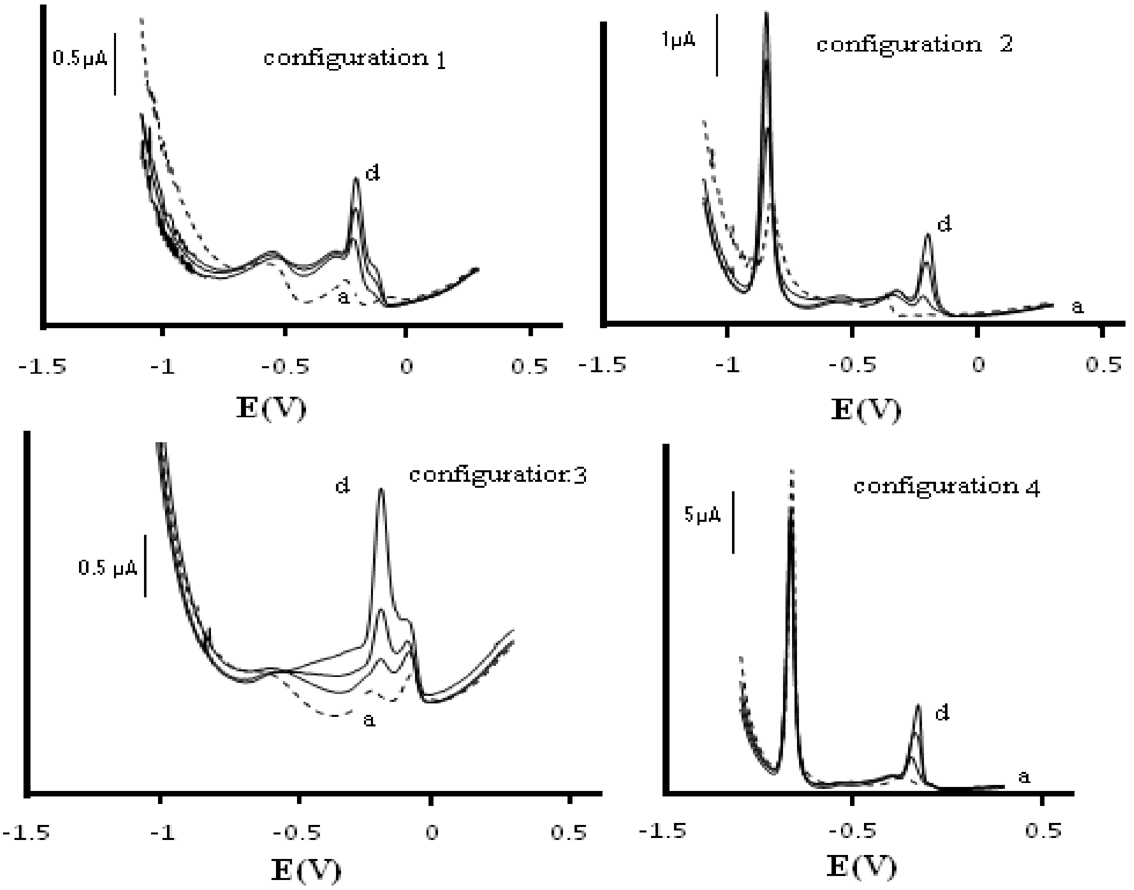
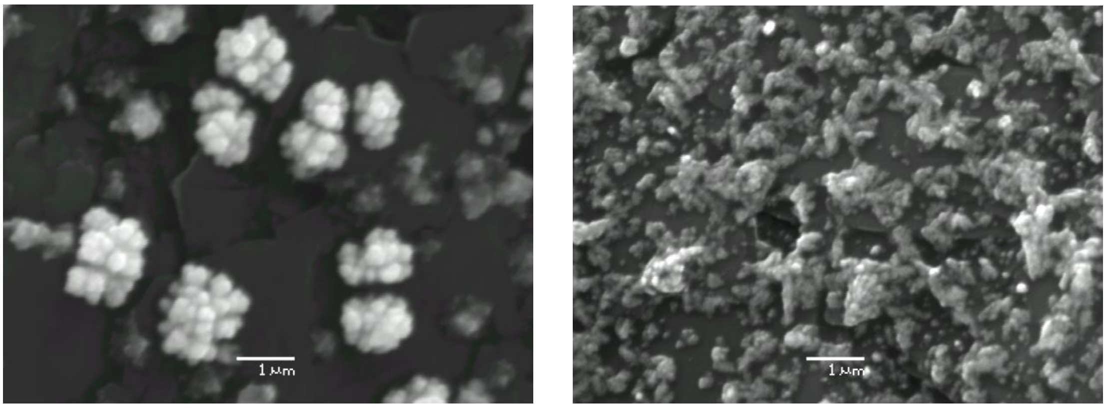


Figure 1. Voltammograms for 10–30 ppb Bi(III) (in 10 ppb steps) utilizing the electrode configurations defined in Table 1. Voltammograms show blank (a) and 3 successive additions of 10 ppb Bi(III) (b–d). Supporting electrolyte as specified in Table 1. Deposition potential -1.1 V, deposition time 160 s. Square wave voltammetric stripping scan with frequency 25 Hz, amplitude 25 mV and step height 5 mV. A 30 s cleaning step at +0.3 V while stirring was applied to the electrode between measurements.

were oriented to further investigation of the significance of Cd(II) and Sb(III) concentration in the system and their effect on the bismuth calibration (10–30 ppb bismuth with 10 ppb additions). The analysis of bismuth utilizing different electrode configurations is shown in Fig. 1 with the associated electrode configurations reported in Table 1. As seen in the figure, configurations 1 and 2 (not containing antimony) generated currents of much lower intensity than those in the presence of antimony. In addition, although an increased bismuth signal can be seen with increasing concentration, this increase is unreliable, producing poor calibration data. The introduction of antimony(III) into the system (configurations 3 and 4) resulted in marked improvement. In the presence of Sb(III) and the absence of Cd(II), two overlapped peaks were registered with their heights simultaneously increased with increasing Bi(III) concentration.

Table 1. Electrode set-ups and sample matrices used to investigate the stripping performance of bismuth at different electrode configurations

Configuration	Electrode	Matrix
1	Bare carbon paste electrode	1 M HCl
2	Bare carbon paste electrode	1 M HCl, 50 ppb Cd(II)
3	Carbon paste electrode, antimony-plated in situ	1 M HCl, 1 ppm Sb(III)
4	Carbon paste electrode, antimony-plated in situ	1 M HCl, 1 ppm Sb(III), 50 ppb Cd(II)



A B

Figure 2. SEM images of in situ deposits obtained (A) in the absence and (B) in the presence of Cd(II). Deposited from 1 M HCl containing 100 ppm Sb (A) without and (B) with addition of 30 ppm Cd, deposition potential -1.1 V, deposition time 120 s.

An addition of Cd(II) (configuration 4) highlights the advantages of the antimony film coating. In the presence of this ion, namely the Bi peak increased drastically which resulted in the improved resolution of the bismuth signal. Hence, the use of the antimony film electrode in the presence of cadmium produces superior results when compared to them registered in the absence of cadmium(II).

The most probable reason is that intermetallic compounds are formed when Sb film is deposited in the presence of Cd(II); it should be mentioned that the formation of CdSb and Cd_3Sb_2 was reported very early [33] but revised data from SGTE alloy databases [34] indicate that in the presence of excess antimony, only CdSb is formed. This can be documented by microstructural analysis; as can be seen (Fig. 2), the structure of the deposit in the presence of cadmium(II) (right) is completely different from that obtained from pure Sb(III) solution (left).

A formation of the intermetallic alloy may be confirmed also by records presented in Fig. 3; as seen, the small Sb peak occurring at -0.1 V is even smaller and shifted to more negative potentials in the presence of Cd(II). Similarly, a record of cyclic voltammogram (Fig. 4) shows the Sb peak completely suppressed in the presence of Cd(II). Based on these evidences, it seems that there is no pure antimony film but a new intermetallic film having its own characteristics suitable for the bismuth(III) determination (Fig. 5). As illustrated, Cd(II) ions compete with Bi(III) when deposited at the antimony film; a result is that Bi is much easily released during the stripping step. Very recently, such apparent catalytic effect of cadmium(II) was observed also in case of determination of mercury(II) [30] and can advantageously be utilized for determination of Bi(III) on trace levels as well.

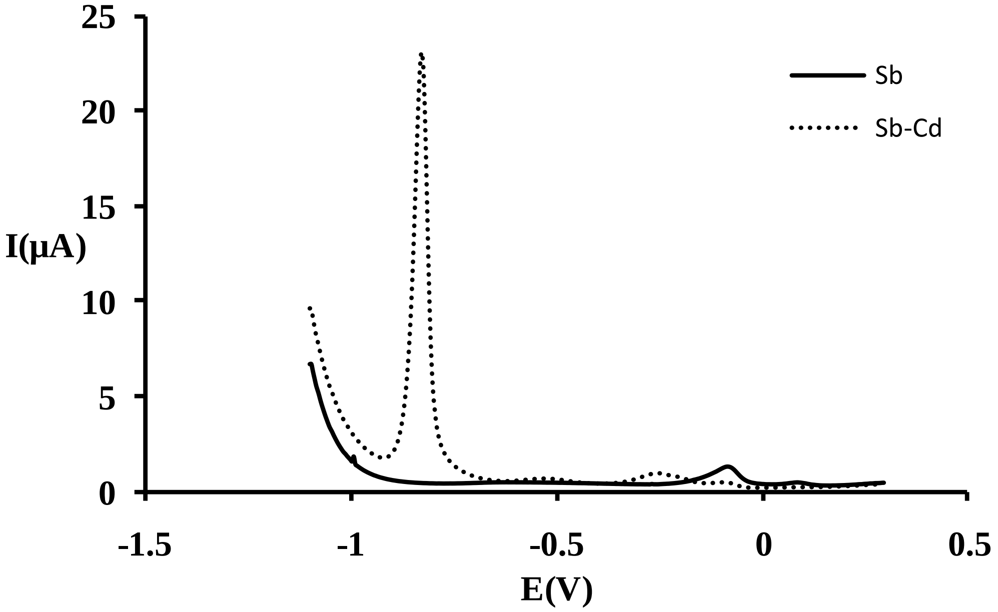


Figure 3. Effect of addition of cadmium(II) on the antimony square wave voltammogram.Solid line recorded for 1 ppm Sb(III), dashed line after addition of 50 ppb Cd(II), SW scan with frequency of 25 Hz, amplitude 25 mV and step height 5 mV. A cleaning step of 30 s at +0.3 V was applied to the electrode under stirring between measurements.

3.2. Optimization of Experimental Conditions

As observed, very acidic medium of hydrochloric acid must be used to avoid hydrolysis of Sb(III). In 0.01 and 0.1 M HCl, a peak corresponding to reoxidation of antimony was somewhat higher and overlapped with that of bismuth even in the presence of Cd(II) (not shown). The best results were obtained in 1 M HCl in which the Sb peak (a base line) was very small; for that reason, all further experiments were realized in this medium.

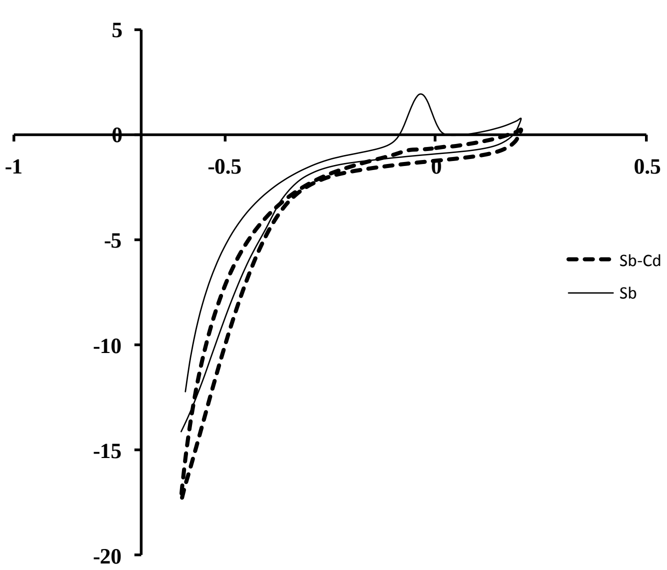


Figure 4. Cyclic voltammograms of antimony(III) in the potential range from +0.2 to -0.6 V in 1 M HCl containing 6 ppm Sb(III) (solid line) and after addition of 2 ppm Cd(II) (dashed line). CV scan with a scan rate of 100 mV s^{-1}, potential step of 10 mV.

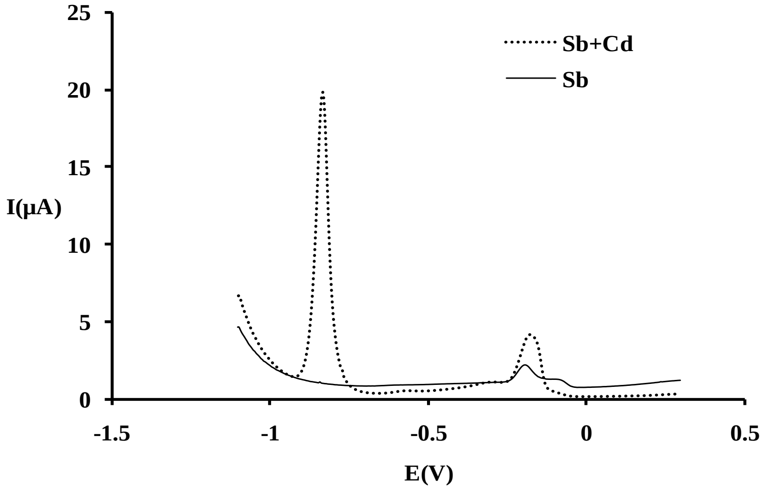


Figure 5. Effect of addition of cadmium(II) on the magnitude of bismuth peak. Recorded at Sb film (solid line) and at the presence of Cd(II) (50 ppb, dashed line), both for 20 ppb Bi(III). Further experimental data as under Fig. 3.

Effects of accumulation potential and accumulation time were also evaluated. Concerning the first, studies were realized in the potential range of +0.2 to -0.6 V; the peak current exhibited a maximum at ca -1.1 V (Fig. 6 left) which was definitely set for all determinations. The dependence of the peak current on the accumulation time is also shown (Fig. 6 right). Not to prolong the experiment, an accumulation time of 160 s was selected for the analytical procedure.

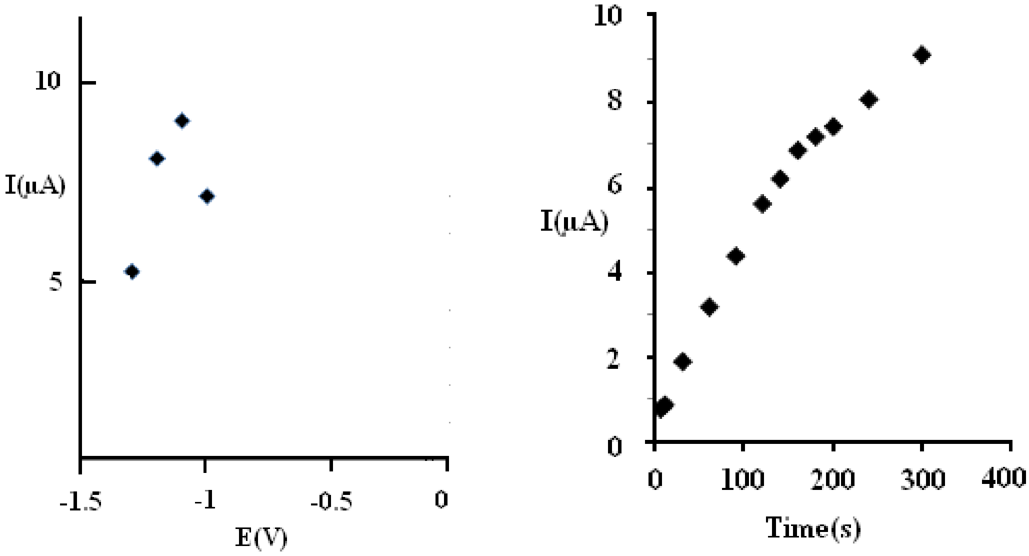


Figure 6. Effect of both the accumulation potential (left) and the accumulation time (right) on the peak current of bismuth. Measured for 50 ppb Bi(III) in the presence of 50 ppb Cd(II). Other parameters like given under Fig. 3.

3.3. Calibration and Interferences

Under optimized conditions mentioned above, calibration dependence was studied and corresponding graph constructed (Fig. 7). In the studied range of 10 to 110 ppb Bi(III), the linear calibration graph was obtained which could be described as I_{sw} [μA] = 0.180 c_{Bi} [ppb] – 0.358, with R^2 = 0.998; detection limit of 1.55 ppb (as 3σ) and RSD of 5.2 % (for 10 ppb Bi and 10 different measurements) were also evaluated.

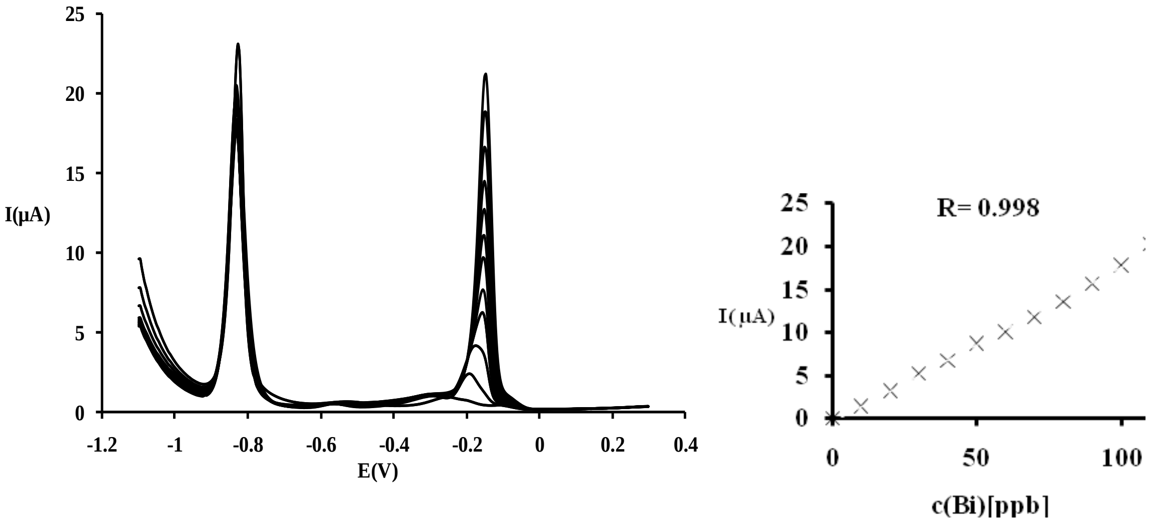


Figure 7. Square wave stripping voltammograms for increasing concentration of Bi(III) under optimized conditions in the presence of 1 ppm Sb, 50 ppb Cd and successive additions of Bi(III) in 10 ppb steps. Recorded at accumulation potential -1.1 V, accumulation time 160 s, other parameters as given under Fig. 3.

Concerning presence of foreign ions, no interferences were observed when Pb(II), Ag(I) or Hg(II) was added (all 40 ppb) into a solution of Bi(III) (20 ppb). In the presence of Cu(II) (also 40 ppb), the peak of bismuth decreased because of competition in electroplating between Cu(II) and Bi(III) as reported previously [35,36].

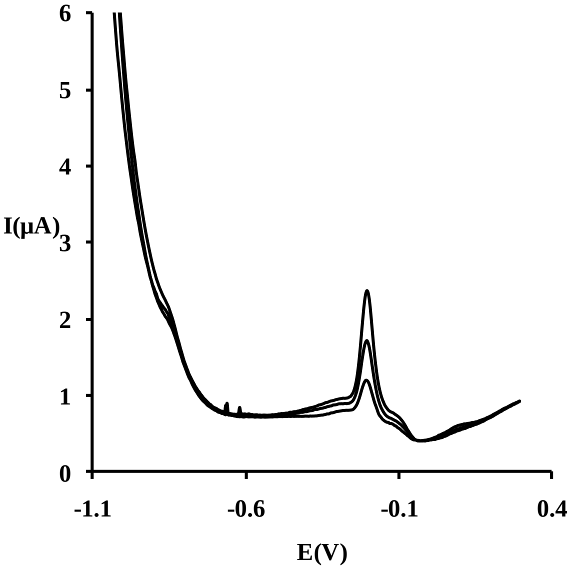


Figure 8. SWASVs of the real water sample obtained from Labe river spiked with 10 ppb Bi(III) after consecutive standard addition of of Bi(III) (each 10 ppb). All other data as given under Fig. 7.

3.4. Analytical Application

The applicability of the optimized procedure was tested using a real water sample taken directly from Labe river in Pardubice. The sample was filtered three times through a filter paper and then acidified to pH ~ 0 with addition of concentrated hydrochloric acid. The sample solution was spiked with 10 ppb of Bi(III) and then two consecutive standard additions of the same salt (each 10 ppb) were applied. Square wave anodic stripping voltammograms were recorded (Fig. 8) and the recovery calculated (93.7 ± 6.3 %).

4. CONCLUSION

The present study has demonstrated that the antimony film-plated carbon paste electrode is feasible for the voltammetric determination of trace amount of bismuth(III) in the presence of small amount of cadmium(II). The proposed method was found suitable for simple and low-cost determination of bismuth at ppb concentration levels.

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