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Short communication

Stripping voltammetric determination of mercury(II) at antimony-coated carbon paste electrode

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ABSTRACT

A new procedure was elaborated to determine mercury(II) using an anodic stripping square-wave voltammetry at the antimony film carbon paste electrode (SbF-CPE). In highly acidic medium of 1 M hydrochloric acid, voltammetric measurements can be realized in a wide potential window. Presence of cadmium(II) allows to separate peaks of Hg(II) and Sb(III) and apparently catalyses reoxidation of electrolytically accumulated mercury, thus allowing its determination at ppb levels. Calibration dependence was linear up to 100 ppb Hg with a detection limit of 1.3 ppb. Applicability of the method was tested on the real river water sample.

1. Introduction

As known, mercury contamination in the environment derives predominantly from natural sources. One could mention so-called Minamata disease; high mercury levels in fish and shellfish still cause health risks to human communities [1–3]. Thus, there is no doubt about analytical control of environment directed to determine mercury compounds. Cold vapor atomic absorption spectrometry seems to be the most frequently applied method for this purpose but presently, more sophisticated (and more expensive) techniques (such as, for example, inductively coupled plasma mass spectrometry) are also used.

Voltammetric methods offer to be a proper alternative since they allow the analytical determination without too expensive equipment. Gold [4–15], colloidal gold paste [16] or gold film-plated carbon paste electrodes [17] were the most often used ones successfully employed for the determination of mercury. Considering that gold is not a cheap material, procedures employing glassy carbon electrodes [18–25] had also to be mentioned. In this contribution, application of the antimony-based electrode is first described. Since 1923, the material is known as a metal/metal oxide sensor used for potentiometric pH measurements [26]. After preliminary studies [27], antimony film electrodes were successfully introduced into stripping electrochemical methods using a glassy carbon and carbon fiber substrates [28] followed by antimony film carbon paste electrodes (SbF-CPEs) [29–31]. Since that time, antimony-based electrodes were analytically applied in various ways on different substrates and different modifications [32–39].

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade purity. Atomic absorption standard solutions (1000 $\mu g\,L^{-1}$) of antimony(III) and other metals were provided by Aldrich and diluted as required. Hydrochloric acid (1 M, pH near 0) was used as a supporting electrolyte. All solutions were prepared from doubly deionized water obtained by passing through a laboratory purification system (Milli-Q, Millipore).

2.2. Preparation of the working 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 [40], thus providing a carbon paste electrode support for in situ platting with antimony film.

2.3. Instrumentation

A modular electrochemical analyzer AUTOLAB equipped with PGSTAT12 controlled by GPES software (EcoChemie, Utrecht) was used for all voltammetric measurements. The conventional

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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 was employed during the electrochemical deposition step.

2.4. Procedure

A cell containing Sb(III) (500 ppm) and desired concentration of Cd(II) and Hg(II) salts was subjected to the accumulating voltage. Following the electrochemical deposition step and a short equilibration period (15 s), a square-wave (SW) voltammogram was recorded by applying corresponding potential scan toward more positive potentials. Before each measurement, the cleaning step was performed by keeping the working electrode for 30 s at +0.2 V in 1 M HCl. When needed, the carbon paste surface was mechanically renewed extruding ca. 0.5 mm of the paste out of the electrode holder and smoothed with a wet filter paper. Usually, this simple operation was made before starting a new set of experiments.

3. Results and discussion

3.1. Voltammetric behaviour of antimony-coated electrodes in acidic media

One redox couple corresponding to reduction (deposition of Sb film at −0.5 V) and oxidation to Sb(III) (its dissolution at 0.0 V) were recorded on a bar carbon paste substrate when media of either 0.01 M or 0.1 M HCl were used (Fig. 1b and c). In more concentrated acid (1 M), these peaks decreased but another peaks could be seen at more positive potentials (Fig. 1a), which could be allocated to redox couple Sb(V)/Sb(III) [41]. However, these peaks are very small as well. Small dissolution peaks of antimony were also observed in anodic stripping voltammograms. It seems that on the contrary to other metal films (Hg, Bi), products of the Sb film reoxidation are insoluble in 1 M HCl medium (it is known that antimony itself does not dissolve in acids that have no oxidation ability). Thus, it can be used in much wider potential window limited by hydrogen evolution on the cathodic and chlorine evolution on the anodic sides.

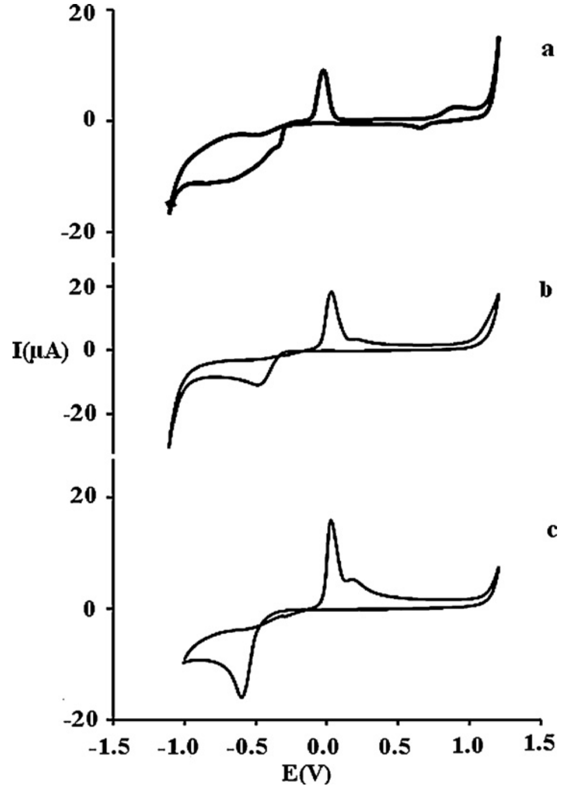

Fig. 1. Cyclic voltammograms of antimony(III) (10 ppb). Scan rate, 100 mV s^{-1}; potential step, 10 mV; initial potential, −0.3 V. Measured in medium of hydrochloric acid: (a) 1.0 M; (b) 0.1 M; (c) 0.01 M.

3.2. Stripping voltammograms of mercury(II)

Fig. 2a shows the square wave voltammograms of Hg at given condition; as can be seen, there are two peaks related to successive oxidation of mercury deposited at bare CPE. After accumulation in the presence of Sb(III), the Hg peak disappears and only a peak connected with oxidation of Sb to Sb(III) is recorded (Sb peak on Hg film electrode, Fig. 2b).

3.3. Positive effect of cadmium(II)

As described very early [42], intermetalic compounds CdSb and unstable Cd_3Sb_2 are formed in the cadmium–antimony system, but revised data from SGTE alloy databases [43] indicate formation of CdSb in the presence of excess antimony. As shown in Fig. 2c, presence of Cd(II) (giving a peak at −0.8 V) has also pos-

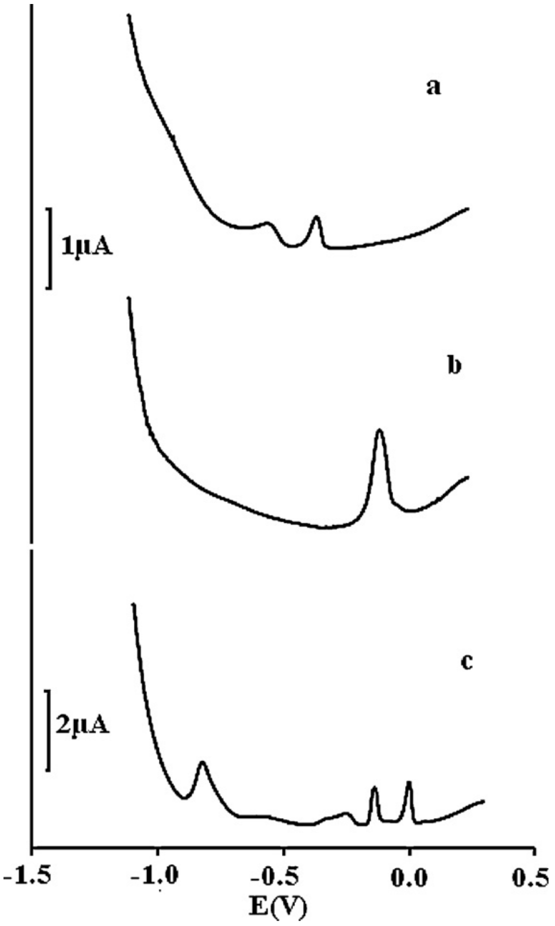

Fig. 2. Square wave anodic stripping voltammograms for various metal deposited at E_{acc} 150 s for t_{acc} 30 s; cleaning step 15 s at +0.2 V; SW stripping scan with 25 Hz frequency, 25 mV amplitude, and 4 mV potential step. Metals presented (a) 20 ppb Hg; (b) 20 ppb Hg + 500 ppb Sb; (c) 20 ppb Hg + 500 ppb Sb + 50 ppb Cd.

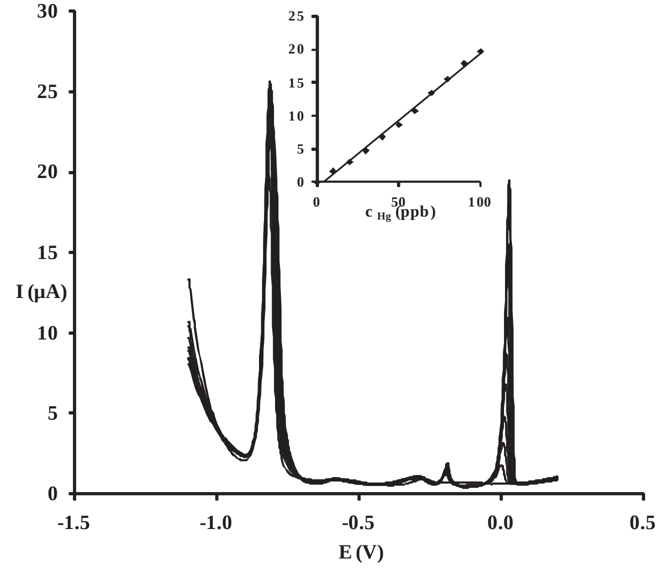

Fig. 3. SWASVs in the presence of 500 ppb Sb, 150 ppb Cd and successive additions of Hg(II) in 10 ppb steps. Inset depicts the corresponding calibration plot.

itive effect on the shape of stripping voltammogram, on which two separated oxidation peaks for antimony (at −0.2 V) and mercury (at 0.0 V) are observed. This phenomenon can hardly be attributed to the abovementioned alloy formation but anyway, it can be considered as catalytic effect of cadmium in determination of Hg(II) (probably amalgamation properties of mercury may also influence such behaviour). To obtain more insights into such electroanalytical performance of the SbF-CPE in highly acidic media, all parameters such as, accumulation potential, E_{acc}, accumulation time, t_{acc}, and effective Cd(II) concentration, c(Cd) were optimized. Resulting stripping voltammograms at such conditions (E_{acc}, −1.1 V; t_{acc}, 150 s; c(Cd), 150 ppb) are presented in Fig. 3 together with corresponding calibration plot (inset) which exhibited good linearity with a correlation coefficient (R_c) of 0.997. The repetitive measurements yielded excellent repeatability of 4.20% with the limit of detection (3σ) equals to 1.3 ppb (calculated for 10 ppb Hg from 10 measurements). It should be mentioned that at the presence of Cd(II), the Hg peak occurred at bare CPE at the same potential position but its magnitude increased roughly three times when SbF-CPE was employed (not shown).

3.4. *Analytical application*

Before analytical applications, interfering effects of foreign ions were examined. For a solution containing 30 ppb Hg(II), no interference was observed in the presence of 100 ppb Pb(II), Bi(III), or Cu(II). Presence of Ag(I) (100 ppb) caused a positive effect of about 27%. In case of Au(III) presence (100 ppb), the mercury peak completely disappeared.

The applicability of the optimized procedure was tested using a real water sample obtained directly from Labe river in Pardubice, Czech Republic. The sample was filtered with filter paper three times, and then acidified to pH ~ 0 with immediate addition of adequate amount of hydrochloric acid, and spiked with 20 ppb Hg (II) and 150 ppb Cd (II). A consecutive standard additions of 10 ppb Hg(II) were carried out; the respective voltammetric stripping analyses resulted in recoveries of 93.8%.

4. Conclusion

The antimony film carbon paste electrode was found usable in an unexpected application. Thanks of electroanalytical behaviour of Sb film, namely its relative resistance against reoxidation in highly acidic medium, determination of Hg(II) could be realized although it gives a voltammetric peak at more positive potential than Sb(III) itself. This was also possible thanks to presence of Cd(II) which functioned as an apparent catalyst. In this way, the SbF-CPE proved more competent than analogous bismuth-based electrodes. Thus, it can be concluded that some new applications of Sb film electrodes are under expectation soon.

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