Voltammetric Determination of Copper(II) Using Antimony Film Electrodes

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Abstract: Possibility of determination of Cu(II) at antimony modified carbon paste electrode and its application in determination of trace amount of copper in real sample has been investigated. According to obtained results, it was found that SbF-CPE can be used for these purposes successfully. Both detection limit of 1.45 ppb (evaluated as 3σ) and RSD 4.8 (for 10 ppb Cu and 10 different measurements) were also evaluated. Antimony-based electrodes are environmentally friendly which is their most important advantage rather than mercury-based ones. BiFEs have been used for determination of copper before but because of decrease of the Bi peak with increasing Cu(II) concentration which causes irreproducibility. As known, it was solved by additions of high concentration of a gallium salt or hydrogen peroxide. Using this antimony film electrode, no addition of other chemicals was necessary.

Keywords: Antimony film electrode; Carbon paste electrode; Anodic stripping voltammetry; Copper(II) determination.

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Introduction

The great importance of copper in environmental [1] and industrial [2] system has attracted considerable interest. Copper is also an essential trace element in biological system [3–7]. It is both vital and toxic to many biological systems depending on the level of concentration [8]. Copper can be tolerated by human beings at relatively large concentration but excessive

intake of this element manifests certain diseases in humans as Menkes Syndrome and Wilson disease [9–10] and it is also toxic to aquatic organisms even at very small concentrations in natural water.

Therefore sensitive, reproducible and accurate analytical methods are required for determination of trace Cu(II) in various materials such as water, biological, environmental, medical and industrial samples in the presence of other cations. The most currently used method for determination of copper are atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP) or mass spectroscopy (MS). However, its real concentrations in natural samples - especially natural waters - are frequently lower than corresponding limits of detection of these techniques. Therefore, some troublesome preconcentration procedure must be carried out. Furthermore, these techniques have some disadvantages such as complicated operation, high cost of maintenance and expensive apparatus.

Stripping voltammetry represents an alternative method for determination of trace levels of metal ions. Since invention of polarography, various types of mercury electrode played dominant role also in stripping voltammetry thanks of its behaviour in the reductive potential region .However, mercury electrodes are often considered undesirable due to the toxicity of metallic mercury and especially, of mercury(II) salts employed for the preparation of mercury film electrodes.

A new type of electrode, the bismuth film electrode (BiFE) formed by coating a carbon substrate with a thin layer of bismuth was introduced in 2000 allowing determinations of trace metals by anodic stripping voltammetry [11]. Since that time, many researches carried out the use of Bi-based electrodes in various demensions and configuration [12].

Copper is a problematic element to be directly quantified by anodic stripping voltammetry using BiFEs since standard potential of the copper is higher than that of bismuth. It has also been discovered that increasing copper concentration resulted in a significant decrease in bismuth signal. This finding was postulated to result from the competition for surface sites on the electrode surface between the deposited copper and bismuth [13-16, 18]. This fact can be responsible for irreproducibility and high detection limit in determination copper at BiFEs which can be resolved by addition of gallium [15] or hydrogen peroxide [16] to the solution.

In 2007, antimony-based electrode was introduced [17]. Antimony oxidation peak is located at more positive potential rather than that of bismuth and and thus, Sb film electrodes can advantageously be applied [19]. Its application in determination of Cu(II) in real sample is presented in this contribution.

Experimental

Chemicals and Reagents

All chemicals used in this work were of analytical grade. Standard stock solutions of antimony(III), Cu (II), Ag(II) and Au(II) were prepared from *Fluka* (1000 mg·L^{-1}, atomic absorption standard solutions) and other metals (1000 mg·L^{-1}, atomic absorption standard solutions) .

Apparatus and Other Instrumentation

A modular electrochemical analyzer AUTOLAB equipped with PGSTAT12 (*EcoChemie*, Utrecht, The Netherlands) controlled by GPES software (*EcoChemie*) 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/3M 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.

The pH values were measured with a CPH 52 pH-meter (*Elteca*, Turnov, Czech Republic) with combined glass electrode (OP-0808P; *Radelkis*, Budapest, Hungary) and calibrated using commercially available standard buffers.

Comparative study was carried out using the Optimass 8000 ICP-oa-TOFMS instrument (*GBC Scientific Equipment Pty Ltd.*, Australia). Concentric nebulizer Micro Mist (*Glass Expansion Pty. Ltd.*, Camberwell, Victoria, Australia) coupled to a 70 mL thermostated (15 °C) cyclonic spray chamber (*Glass Expansion*) was used for sample introduction. Liquid uptake rate was controlled by selection of the instrument peristaltic (12 roller) pump speed and set for approximately 1 mL·min^{-1}. Microwave system SpeedwaveTM MWS-3+ (*Berghof*, Germany) was used for digestion of reference samples as well as of river water sample for ICP-oa-TOFMS measurement. The maximum total output of the microwave generator was 1450 W.

Preparation of a 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*, Czech Rep.) with highly viscous silicone oil (0.3 mL; LUKOIL MV 8000, *Lučební závody Kolín*, Czech Rep.). Both components were homogenized to obtain a mixture that was subsequently packed into a piston-driven carbon paste holder, thus providing a carbon paste electrode support for in situ plating with antimony film. 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.

Procedures

Anodic stripping voltammetry (ASV) was performed as follows. Following the electrochemical deposition step and a short equilibration period (15 s), a square-wave (SW) voltammogram was recorded by applying a square-wave potential scan toward more positive potentials. Before each measurement, the "cleaning" step was performed by keeping the working electrode at +0.3 V for 30 s.

Results and Discussion

In this work, generating of the antimony film in situ was selected due to its simplicity. First of all, influence of the antimony film on the shape of the copper peak was investigated; the results are shown in Fig. 1.

It is can be observed that antimony film has very fine effect on copper peak. However, the positions potentials of re-oxidation for both Sb and Cu are almost the same. Thus, antimony film can be used for determination of copper successfully since the signal for the Sb peak is very small. Obviously from Fig. 1, the height of the copper peak in the presence of antimony increased significantly.

Optimization of Experimental Conditions

To obtain optimum conditions for ASV determination of copper(II), both Cu and Sb peaks should be considered because of practical identity of their anodic stripping potentials. In the optimum conditions, it is desirable to have the Cu peak much higher than that of Sb. In addition, very acidic solution must be used to avoid hydrolysis of antimony(III); for that reason, the solutions were acidified to a desired pH value (in the range of 1 − 3) using concentrated hydrochloric acid only. An acetate buffer (pH 4) was also applied but there were two overlapping peaks appearing on the voltammogram. Therefore, a medium acidified by HCl to pH 2 was found as optimum, in which all other measurements were performed.
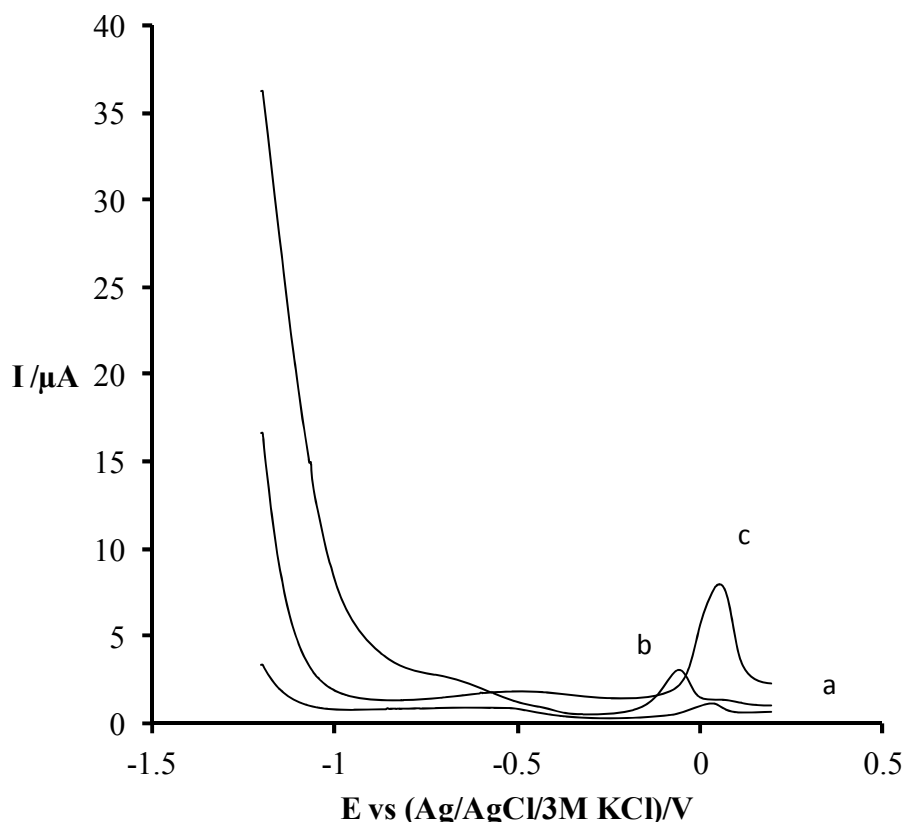
Fig. 1: *Anodic striping voltammograms obtained at an in situ prepared SbFE.* (a) 600 ppb Sb + 0.01 M HCl; (b) 50 ppb Cu + 0.01 M HCl; (c) 600 ppb Sb + 50 ppb Cu + 0.01 M HCl. $E_{acc} = -1.2$ V; $t_{acc} = 120$ s; $t_{ep} = 15$ s; ASV scan with frequency 25 Hz, amplitude 25 mV and potential step 4 mV. Reprinted form Ref. 19 with permission from Elsevier.

Accumulation Potential

Effect of the accumulation potential on both Sb(III) alone and Cu peak in the presence of Sb(III) was investigated separately. Accumulation potential of −1.2 V was found as optimum at which the Cu peak was sufficiently high when compared with that of Sb (see Fig. 2).

Dependency of the Cu peak height on the accumulation time (t_{acc}, up to 300 s) was investigated for a solution containing 50 ppb Cu and 600 ppb Sb (0.01 M HCl, E_{acc} −1.2 V). No saturation was observed. Up to 120 s, a height of the Cu peak was sharp and increased linearly; further prolongation of the accumulation time gave higher but broader peaks. For that reason, t_{acc} of 120 s was applied in all subsequent measurements.

An effect of the Sb(III) concentration on the Cu peak altitude was also evaluated. Under abovementioned conditions, additions of 200 − 1000 ppb Sb(III) were applied to a solution containing 50 ppb Cu(II). There was not any special effect with Sb(III) concentration

but it is recommended to use at least 5 − 10 times higher concentration of the film forming Sb(III) salt rather than analyte. Therefore, an addition of 600 ppb Sb(III) was used for calibration.
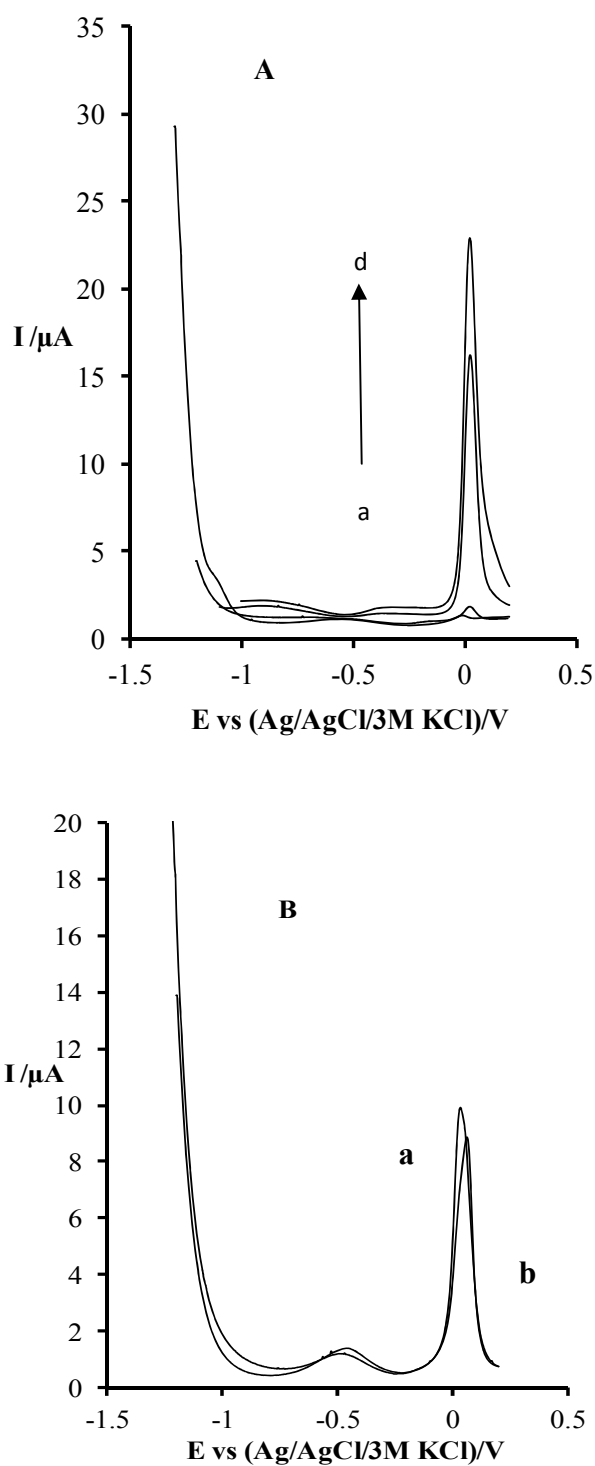
Fig 2: *Effect of deposition potentials*. **A)** 500 ppb Sb, 0.01 M HCl, deposition potential from **a)** to **d)** are −1.3, −1.2, −1.1, −1 V, respectively. **B)** A + 50 ppb Cu (II), a) −1.2 V and b) −1.3 V. Other parameters under Fig. 1. Reprinted form Ref. 19 with permission from Elsevier.

Interference Study

Influence of other metal ions on ASV determination of copper (II) was studied in the solution containing 50 ppb Cu(II); the results are shown in Table I.

Table I: *Effects of diverse ions on determination results of 50 ppb Cu(II).*

| Metal	Concentration	Effect on Cu peak
Cd	50 ppb	–42 %
Pb	150 ppb	–
Bi	50 ppb	– (In 100 ppb there were two overlapping peaks)
Hg	150 ppb	–
Ag	100 ppb	11 %
Au	50 ppb	23 % (In 100 ppb of Au the Cu peak decreased so much)

Calibration

Fig. 3 shows square wave anodic stripping voltammograms of SbFE for Cu(II) under the optimum conditions. The calibration graphs show linear range over the concentration of 10–120 ppb Cu(II) with the lower detection limits of 1.45 ppb and RSD 4.8 for 10 different measurements.

The linear dependence can be described by the equation I_{sw} [µA] = 0.199 c_{Cu} [ppb] + 2.259 with R^2 = 0.998, detection limit of 1.45 ppb (evaluated as 3σ) and RSD 4.8 (for 10 ppb Cu and 10 different measurements) were also evaluated.

Real Sample Analysis

The procedure elaborated was applied for determination of copper(II) in a real water sample. To verify its applicability, a sample of river water was tested representing quite complicated matrix (taken from Labe river in Pardubice, Czech Rep.).
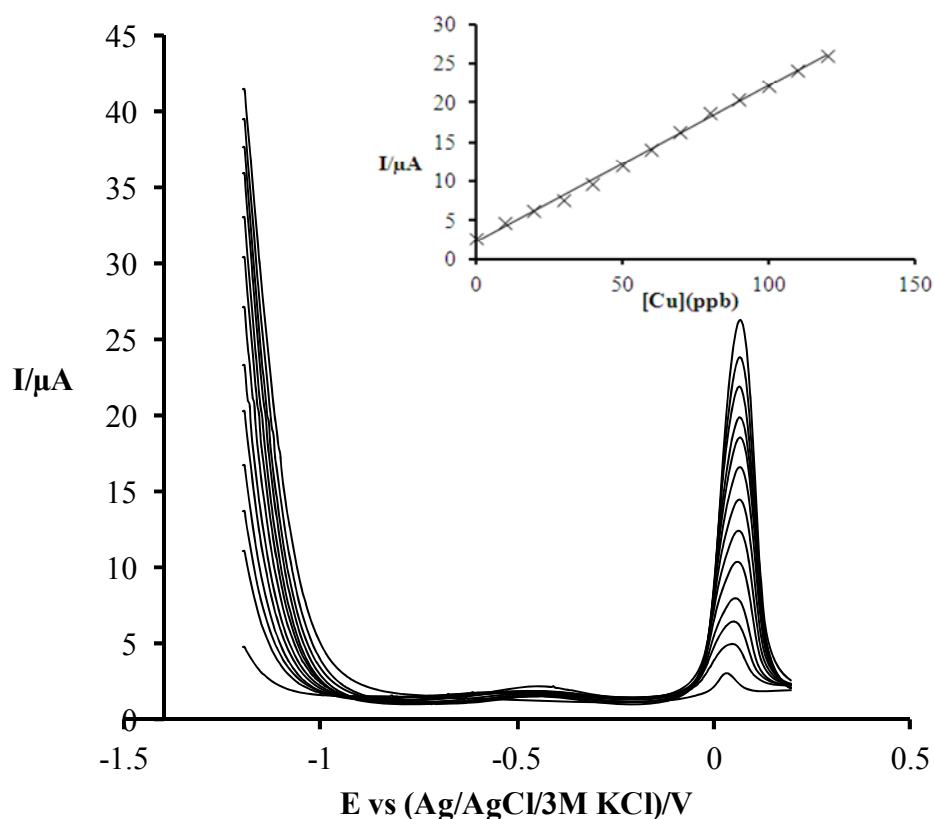
Fig. 3: *Square wave stripping voltammograms for increasing concentration of Cu(II) on the SbF in 10 ppb steps in optimum conditions*. Inset: corresponding concentration dependence. Reprinted form Ref. 19 with permission from Elsevier.

The sample was filtered with filter paper three times and then acidified to pH 2 with HCl as described above. The filtrate was spiked with 20 ppb Cu before three consecutive standard additions of 10 ppb Cu and SW anodic stripping voltammograms were gradually recorded after each addition; the resulting records together with corresponding standard addition plot are presented in Fig. 4. The analysis indicated the copper content of 6.4 ppb ($\sigma = 0.17$), for 3 different measurments.

The control analysis by independent ICP method using isotope [63]Cu gave the result in 5.6 ppb for 5 replications. Table II contains statistical data about measurement of Cu(II) in two different methods.
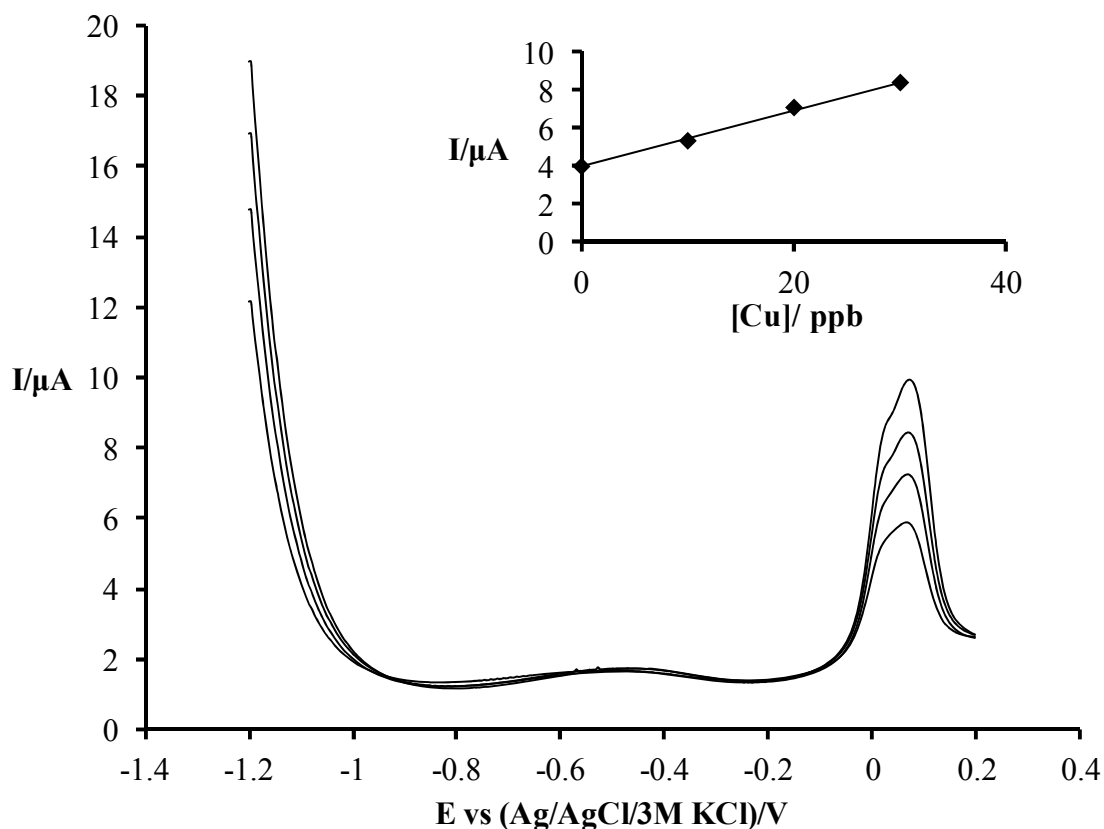
Fig. 4: *ASV of the real water sample obtained from Labe river in Czech spiked with 20 μg·L^{-1}of Cu(II) together with three ASVs recorded after consecutive standard addition of 10 μg·L^{-1}of Cu(II).*

Table II: *Statistical data about measurements Cu(II) in two different methods.*

Parameter	ICP	SbF stripping voltammetry
Number of replications	5	3
Average	5.6	6.4
Standard deviation	0.71	0.17
Confidence interval (95%)±ts/√n	±0.885112	±0.422543
Pooled standard deviation		0.588
Calculated t		1.87
Critical t (95%)		2.45

Conclusions

In the present paper, the possibility of determination Cu(II) at antimony film electrode was checked and according to obtained results, it was found out that this SbFE can be used for these purposes. Application in real sample analysis was also investigated; the results agreed well with those obtained in comparative measurements with ICP-MS.

Acknowledgements

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