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VOLTAMPEROMMETRIC METHODS FOR THE COPPER IONS DETERMINATION

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ABSTRACT. We have evaluated procedures to improve the reproducibility and sensitivity of the voltamperommetric methods for the copper ions determinations in wastewaters. The influence of the analytical parameters (pH, electrolyte composition, deposition time and potential) on the performances of the method has been investigated. The optimal analytical conditions were found. Using these methods the copper concentration in the wastewaters after the electrochemical synthesis of the m-amino sulphonic acid on copper electrode and after the copper recovery by electrochemical methods, was determinated. In these conditions, the limit of detection was 0.05 – 1.5 ppm copper, with standard deviation 2 - 10%, depending of the concentration range and method.

Key words: *copper ions determinations, stripping and voltammetry methods*

Introduction

Continuing our interest in the field of the electroanalytical determination of the heavy metal ions [1], this contribution compares the performances of different electrochemical methods, applied for copper ions determinations.

The data published in the field of environmental pollution and related effects of the heavy metals on the flower cultivation [2] have been reported the negative influence of the high concentration of copper and other ions on the bottom and flower system of the plant.

One important property of the cyclic voltamogramms (CV) or of the polarogramms corresponding to the reduction of the ions is the proportionality of the peak current with the solution concentration. The detection limit of cyclic voltammetry (CV) is relatively high (10^{-2} – 10^{-5} M), but the method could be used for the quantitative control of the composition of the wastewater in the specified concentration range. The quantitative use of CV has been limited by

the fact that the dependence of the i/E curves on electrochemical and chemical (concentration) parameters in general is very complicated. [3]. Stripping analysis is an analytical method that uses a bulk electrolysis step (preelectrolysis) to preconcentrate the electroactive species from solution into a small volume of a mercury drop, on mercury film or on the surface of other electrodes (e.g. glassy carbon electrode - GCE) followed by the oxidation step. The major advantage of the stripping method, as compared to direct voltammetric analysis is the high surface concentration responsible for a high peak current, so the answer is less perturbed by the small currents due to the impurities oxidation. The technique is useful for the analysis of trace concentration (ppm and ppb). There are a few stripping methods valuable for the Cu (II) and other ions determination, from anodic stripping voltammetry (ASV) to adsorptive stripping methods. Adsorptive stripping voltammetry (AdSV) has been known to give excellent sensitivity for a variety of trace (ppb) metals at the mercury electrode [4]. This method involves complexation of the metal ion with different ligands and adsorption of the resulting complex onto the mercury drop or mercury film surface. The adsorbed complex is removed by scanning the electrode potential, usually in a reductive direction – cathodic stripping analysis (CSA). The metal ions are reduced and simultaneously amalgamated. Due to the peak separation the mixture of different metals could be analysed. Other variants, such as stripping by a current or potential step or different combined procedures have been also proposed [5, 6].

The electrochemical techniques like the stripping methods ensure the determination of the traces –ppb- metals ions [1]. There are two main stages in the stripping analysis:

- Preconcentration (plating) consists in the application of a constant reductive potential for a period of time, when takes place the adsorptive accumulation of metal on Hg surface: $Me^{n+} + ne^- \Rightarrow Me(Hg)$
- Stripping, when the metal ions or metal-complex accumulated on Hg surface is oxidised and the oxidation current, proportional with the metal concentration, is determinated.

Copper could be determinated by the anodic stripping voltammetry directly in organic solvents [1]. There are two conditions for that: solubility of the copper (II) complex species in the given solvent and the possibility to assure the conductivity of the supporting organic electrolyte [6].

The most common pre-treatment of GCE is pre-anodisation and pre-cathodisation. The effect of treatment procedure on electrochemical response depends on the applied voltage, pH value of the electrolyte solution and the duration of the treatment. The treated GCE usually behaves as a metal film-coated electrode (MFCE) [7].

The aim of this paper is to compare the performances of copper ions determination by different voltamperommetric methods.

Experimental

Instrumentation and software

The computer aided instruments used for potential control was BAS 100W equipped with Controlled Growth Mercury Electrode (CGME) West Lafayette, USA and the Portable Trace Element Analyser, PTEA –WAGTECH equipped with glassy carbon electrode, GCE. The classical three electrodes cell has been used for the cyclic voltammetry determinations (WE- GCE; CE- Pt wire and RE - Ag/AgCl). Reference (Ag/AgCl) and Pt wire auxiliary electrodes used to this work, were from BAS Co. The UNICAN Helios β UV-VIS spectrometer has been used to control the results of the electrochemical methods.

Reagents

All solution were prepared with MiliQ purified water and analytical grade chemicals (Merck).

Procedure

PTEA is equipped with a classical three electrodes cell, all built into the unit. The sample volume is 20 cm^{-3}.

The glassy carbon electrode (GCE) has been activated according to literature data [8], before the copper determination. The reactivation procedure has been according to the PTEA producer [9]. All the measurements have been made in the appropriate supporting electrolyte (ASE), containing :117g NaCl, 35.5g ascorbic acid, 7.7 g NaOH in 500 mL MiliQ purified water.

Results and discussions

We compared the results obtained by different electrochemical techniques:

- Direct voltammetric and polarographic measurements on mercury electrode;
- Stripping voltammetric analysis (SVA) on the CGME

Prior the Cu (II) determination with CGME, Hg (II) has been added into the sample, when the following reactions take place:

$$Hg(II) + 2e^- \rightarrow Hg \text{ and } Cu(II) + 2e^- \rightarrow Cu(Hg).$$

The reduced species Cu (Hg) is then re-oxidized:

$$Cu(Hg) \rightarrow Cu(II) + Hg + 2e^-$$

Influence of the Cu (II) concentration

The electrochemical answer depending on Cu (II) concentration has been investigated by polarography, cyclic voltammetry and stripping techniques. The reversible one electron reduction of Cu (II) in (ASE) supporting electrolyte, demonstrated the proportionality of peak current with the concentration – figure 1.

The effect of Cu (II) concentration on peak current, (Figure 1) and on polarographic limiting current (Figure 2) is demonstrated by the linear increasing of the current with increasing concentration.

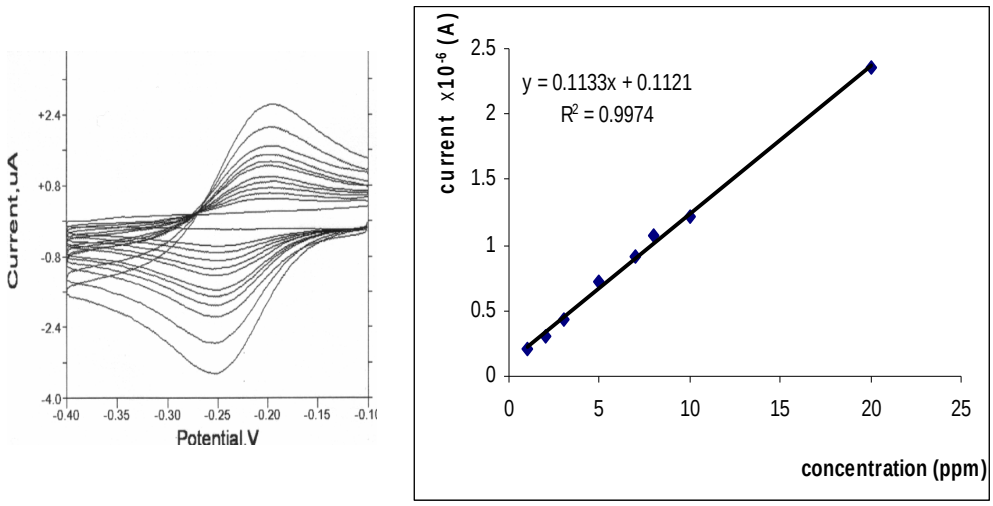

Figure 1. Cyclic voltammograms (CV) of Cu(II) with increasing concentration from 0-25 µgmL^{-1} along with the resulting calibration plots.

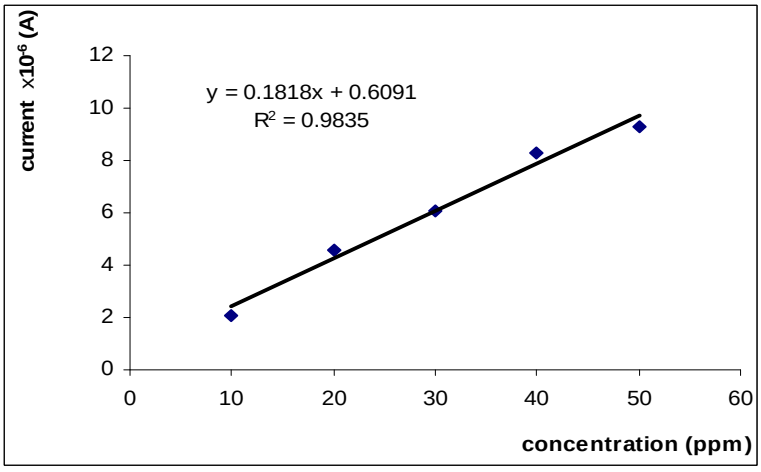

Figure 2. Calibration curve obtained from polarographic data; drop size: 6 µm;v: 10 mVsec^{-1}.

In the concentration range from 1–25 ppm, figure 1 and 10–60 ppm, figure 2, the slope is 0.1133, respectively 0.1818 µA/ppm. The detection limit is higher for cycic voltammetry.

The reproducibility of the CV response is good, with R^2 = 0,99. A 4.5% relative standard deviation of peak currents was obtained under 6 measurements of 20.0 µgmL^{-1}.

Influence of mercury drop size

In order to find the optimal conditions for the Cu (II) determination we investigated the influence of Hg drop size on the peak current – Figure 3.

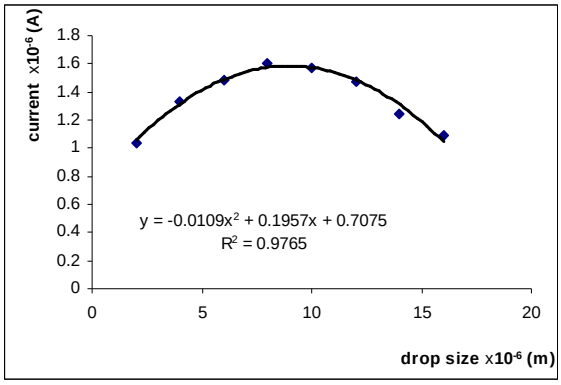

Figure 3. Influence of drop size on the polarographic current.

The dependence follows the equation of $y = -0.0109x^2 + 0.1957x + 0.7075$ and the drop size of 8-10 µm gives higher currents.

Stripping analysis

The best results have been obtained on CGME, by stripping techniques (Figure 4), when the calibration curve is described by the equation y = 3.2566x + 3.012, for the smaller concentration (1-12 ppm).

The peak area for Cu oxidation can be used to estimate the adsorbed amount of ions at the CGME. From the equation $\Gamma = Q/nFA$, the surface coverage Γ of the adsorbed species can be calculated from the values of the charge *Q* (the area of the peak) and electron transfer number n - the value 2 is taken into account for the oxidation of Cu to Cu(II).

The voltammogram of 20.0 µgmL^{-1} adsorbed at CGME gives a peak area of 7.3 µC and the surface coverage *Γ of* 3.01x10^{-10} molcm^{-2} can be obtained.

Obviously, the surface coverage of adsorbed species is close to the theoretical value of a monolayer.

The slope indicates that the electrode process is simultaneously controlled by surface adsorption and heterogeneous electron transfer rate.

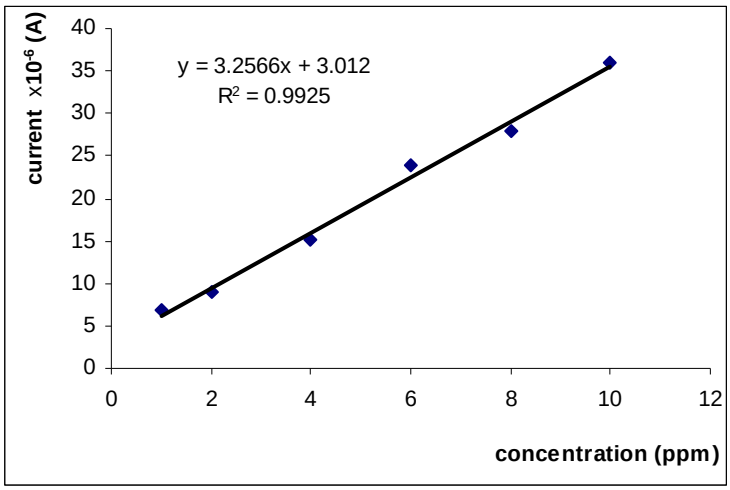

Figure 4. Plots of i_p – concentration for the oxidation of accumulated copper on CGME.

Influence of the Accumulation Time

With increasing accumulation time, the peak current initially increases and then trends to saturation value after 500 s, as illustrated in Figure 5.

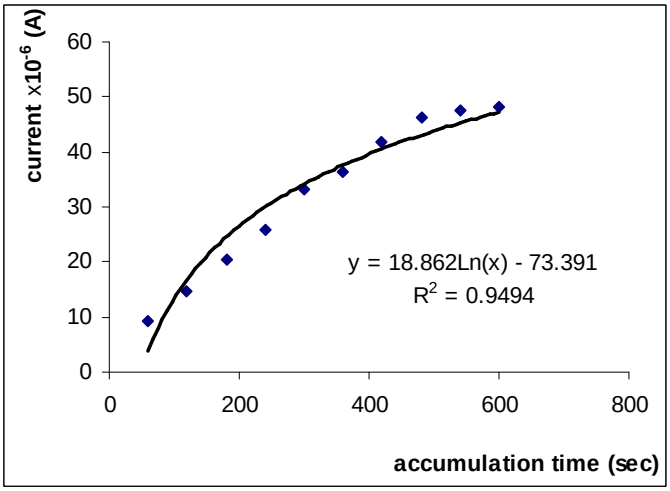

Figure 5. Effect of accumulation time on peak current. (500s was chosen as the accumulation time for all experiments).

The detection limit for stripping method is about 0.05 ppm, with a R^2 of 0.9992 and it is lower comparing to other electrochemical investigated methods. The stripping techniques seem to give the best results, comparing to other analytical methods – table 1.

Table 1.

Performance of the applied methods (* for 4 ppm)

Method	Detection limit [ppm]	Concentration range [ppm]	R^2	Standard deviation [%]
Spectrophotommetry*	>10	50-100	0.9600	3-6.8
Polarography	9	9-50	0.9752	4.2-4.5
Cyclic voltammetry	1	1-10	0.9928	2.25-3.23
Stripping (on CGME)	0.05	0.05-10	0.9992	1.37-1.91
Stripping (on MFGC)		0.05-10	0. 9880	7-10.33*

* comparing method

Conclusion

The proposed stripping method on CGME is selective and enough sensitive for the determination of low concentration of Cu (II), up to 0.05 ppm. Using the Wagtech PTEA (Portable Trace Element Analyser) equipped with thin mercury film on glassy carbon electrode (MFGC), the detection limit and the standard deviation are lower than those obtained using other electrochemical methods – Table 1. The obtained results were compared with the simple voltamperommetric (detection limite 1 ppm) and spectrophotometric methods (detection limite >10 ppm).

For the future, we propose to continue the research by using different complexing agents (azodyes) for the determination of other polluting ions; the preliminary data concerning the adsorptive stripping voltammetry using azodyes like ligands are promising. The stripping method on CGME will be used to control the depollution of wastewaters using PRIAM reactor.

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