

## Selective, Simple and Economical Method for the Voltammetric Determination of Bi(III) in the presence Cystine in Non – Complexing Solution

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**Abstract.** The simple and fast method for the determination of Bi(III) in non-complexing solution was proposed. The catalytic activity of cystine on Bi(III) ions electroreduction process were utilized. The calibration graph of Bi(III) in 4 mol·dm<sup>-3</sup> chlorate (VII) in the presence of 1·10<sup>-2</sup> mol·dm<sup>-3</sup> cystine is linear in the range of concentrations of Bi(III) from 7·10<sup>-7</sup> to 4·10<sup>-5</sup> mol·dm<sup>-3</sup>. The detection and quantification limits were found to be 1.2·10<sup>-7</sup> mol·dm<sup>-3</sup> and 4.02·10<sup>-7</sup> mol·dm<sup>-3</sup>, respectively. Precision and recovery of the method were investigated by determination of Bi(III).

**Key words:** Bi (III) determination, cystine, square wave voltammetry

### Introduction

Bismuth is a strongly dispersed element belonging to less toxic heavy metals. It concentrates mostly in lungs and hard tissues and causes the disturbances in metabolic processes and nervous system (Burguera 2001). This means that monitoring its content in the natural environment is extremely important.

During the determination of bismuth using electrochemical methods we should also consider the composition of the supporting electrolyte because the process of Bi(III) ions electroreduction is irreversible. To increase the reversibility of Bi(III) the solutions of strongly complexing properties to the determination of Bi(III) were used, even then the stripping voltammetry methods (Guo 2005) (Zen 1996) are employed. In order to increase the sensibility and selectivity of the voltammetric methods of Bi(III) determination except the mercury electrode and the other working electrodes were also applied for example carbon paste electrodes (CPEs) (Ashrafi 2012). The chemically modified gold electrodes were employed as well (Profumo 2006). However from analytical point of view the proposed methods of Bi(III) determination were often not sufficient for use because of low sensitivities, complicated and time-consuming procedures or high costs of measurements.

In this paper the simple and fast method of Bi(III) determination by square wave voltammetry was proposed.

In agreement with cap – pair effect (Sykut 1978) (Dalmata 2005) the organic substances introduced to the supporting electrolyte can catalyze one type of electrode processes and simultaneously have no influence or even inhibit the other electrode processes. Such behaviour enables the determination of different elements near each other without necessity of analyte accumulation, what considerably simplifies the analysis procedure.

### Materials and Methods

The experiments were performed using a three–electrode cell with a hanging controlled growth mercury drop electrode (CGMDE) (Entech, Cracow, Poland) as the working electrode (electrode area was 0.009487 cm<sup>2</sup>, drop time was 3 s), Ag/AgCl/ saturated NaCl as the reference electrode and a platinum spiral as the counter electrode. The reference electrode was connected to the electrolytic cell via an intermediate vessel filled with the solution to be investigated. The measurements were carried out in thermostated cells at 298 K with electrochemical analyzer Autolab/ GPES (Version 4.9) (Eco Chemie, Utrecht Netherlands).

In the square wave voltammetric (swv) experiments optimal operating conditions were as follows; pulse amplitude 20 mV, frequency 120 Hz and step potential 2 mV.

Analytical - grade reagents: NaClO<sub>4</sub> (Fluka), HClO<sub>4</sub> (Fluka), Bi(NO<sub>3</sub>)<sub>3</sub> (Aldrich), and cystine (Aldrich) were

used without further purification. The solutions were prepared from freshly double distilled water. Before measurements the solutions were deaerated using high purity nitrogen. The supporting electrolyte was  $3 \text{ mol}\cdot\text{dm}^{-3} \text{ NaClO}_4 + 1 \text{ mol}\cdot\text{dm}^{-3} \text{ HClO}_4$ . For the sake of weak solubility of  $\text{Bi}(\text{NO}_3)_3$  in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) the solutions were treated by ultrasonic machining. The cystine solutions were prepared just before the measurements.

## Results and Discussion

It was found that the reversibility of the Bi(III) ions electroreduction in  $1 - 8 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) increases with the decrease of water activity (Nosal-Wiercińska 2010). Introduction of cystine to the solutions of Bi(III) ions in  $1 - 8 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) causes the increase of the peak current of electroreduction of Bi(III) ions. The magnitude of this effect depends on cystine and the chlorates (VII) concentration (Nosal-Wiercińska 2011). The highest catalytic activity of cystine was observed in  $3$  and  $4 \text{ mol}\cdot\text{dm}^{-3}$  solution of chlorates (VII). Figure 1 presents peaks of electroreduction of  $1\cdot 10^{-7} - 4\cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$  Bi(III) in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) in the presence of  $1\cdot 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  cystine. The calibration curve of Bi(III) in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorate (VII) in the presence of  $1\cdot 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  cystine is linear in the range of concentrations of Bi(III) from  $7\cdot 10^{-7}$  to  $4\cdot 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ . At higher concentrations of Bi(III) there are substantial deviations from linearity.

Validation of the procedure for the quantitative assay of Bi(III) in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) containing  $1\cdot 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  cystine was examined by evaluation of the limit of detection (LOD), limit of quantification (LOQ), repeatability, recovery and precision. The detection and quantification limits at Bi(III) ions determination in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) and in the presence of  $1\cdot 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  cystine were  $1.2\cdot 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$  and  $4.02\cdot 10^{-7} \text{ mol}\cdot\text{dm}^{-3}$ , respectively.

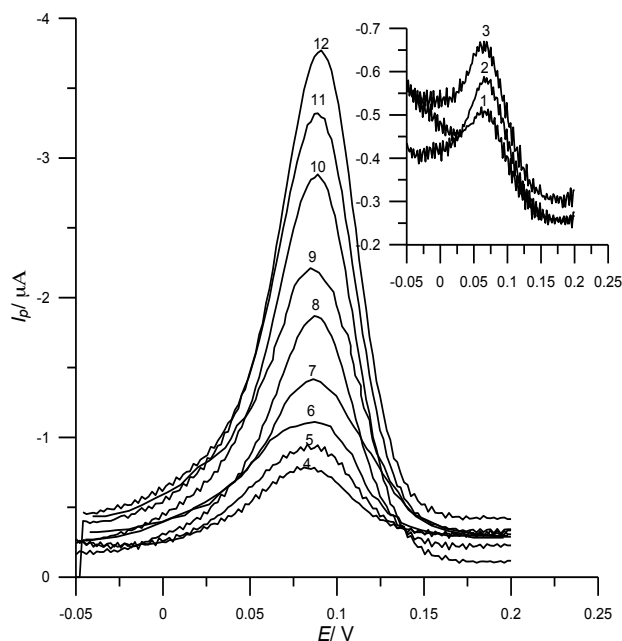


Fig. 1. Square wave voltammograms obtained for chosen solutions containing:  $1\cdot 10^{-7}$  (1),  $3\cdot 10^{-7}$  (2),  $5\cdot 10^{-7}$  (3),  $7\cdot 10^{-7}$  (4),  $9\cdot 10^{-7}$  (5),  $2\cdot 10^{-6}$  (6),  $4\cdot 10^{-6}$  (7),  $6\cdot 10^{-6}$  (8),  $8\cdot 10^{-6}$  (9),  $1\cdot 10^{-5}$  (10),  $2\cdot 10^{-5}$  (11),  $4\cdot 10^{-5}$  (12)  $\text{mol}\cdot\text{dm}^{-3}$  Bi(III) in  $4 \text{ mol}\cdot\text{dm}^{-3}$  chlorates (VII) in the presence of  $1\cdot 10^{-2} \text{ mol}\cdot\text{dm}^{-3}$  cystine.

## Conclusion

The presented results allow for the following conclusions:

- cystine, in accordance with cap – pair rule (Sykut 1978) (Dalmata 2005), accelerates the electroreduction of Bi(III) ions in chlorates (VII) solutions
- the reversibility of Bi(III) ions electroreduction in chlorates (VII) depends on the cystine concentration and water activity
- the optimal concentration of cystine and water activity for Bi(III) determination by voltammetric method were established. The presented method is fast, simple, relatively inexpensive and with easily accessible measurement system.

## References

- Burguera M., Burguera J.L., Rondón C., García M.I., De Peña Y.P., Villasmil L.M. Determination of bismuth in biological tissues by electrothermal atomic absorption spectrometry using platinum and tartaric acid as chemical modifier. *J. Anal. At. Spectrom.* 2001; 16:1190-1195.
- Guo H, Li Y., Xiao P., He N. Determination of trace amount of bismuth (III) by adsorptive anodic stripping voltammetry at carbon paste electrode. *Anal. Chim. Acta* 2005; 534, 143-147.
- Zen J., M., Chung M. Square-wave voltammetric stripping analysis of bismuth(III) at a poly(4-vinylpyridine)/mercury film electrode *Anal. Chim. Acta* 1996; 320, 43-51.
- Ashrafi A.M., Vytřas K. Determination of trace bismuth(III) by stripping voltammetry at antimony-coated carbon paste electrode. *Int. J. Electrochem. Sci.* 2012; 7:471-483.
- Profumo A., Fagnoni M., Merli D., Quartarone E., Protti S., Dondi D., Albin, A. Multiwalled carbon nanotube chemically modified gold electrode for inorganic as speciation and Bi(III) determination. *Anal. Chim. Acta* 2006; 78:4194-4199.
- Sykut K., Dalmata G., Nowicka B., Saba, J. Acceleration of electrode processes by organic compounds - cap-pair effect. *J. Electroanal. Chem.* 1978; 90: 299-302.
- Dalmata G. Kinetics and mechanism of Zn(II) ions electroreduction catalyzed by organic compounds. *Electroanalysis* 2005; 17:789-793.
- Nosal-Wiercińska A. The kinetics and mechanism of the electroreduction of Bi(III) ions from chlorates (VII) with varied water activity. *Electrochim. Acta* 2010; 55:5917-5921.
- Nosal-Wiercińska A. The catalytic activity of cysteine and cystine on the electroreduction of Bi(III) ions. *J. Electroanal. Chem.* 2011; 662:298-305.