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Application of the catalytic properties of methionine to the determination of Bi(III) as well in the presence of Cu(II) ions at low levels by square wave voltammetry

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ABSTRACT

A simple and fast method for the determination of Bi(III) in the presence Cu(II) in non-complexing solution was proposed. The catalytic activity of L-methionine on Bi(III) ions electroreduction as well as lack of this amino acid influence on Cu(II) ions electroreduction process were utilised. The calibration graph of Bi(III) in 4 mol dm^{-3} chlorate (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine is linear in the range of concentrations of Bi(III) from 3×10^{-7} to $1 \times 10^{-4}\,\text{mol dm}^{-3}$. The detection and quantification limits were found to be 1.53×10^{-7} and $5.12 \times 10^{-7}\,\text{mol dm}^{-3}$, respectively. Precision and recovery of the method were investigated by determination of Bi(III).

Keywords: L-methionine; Bismuth (III) determination; Copper; Square wave voltammetry

1. Introduction

Water is a unique solvent because of the specific physical and physicochemical properties, which decide its role in biological life on Earth and its versatility as an environment. The complex studies of elements properties in aqueous environment allow to appoint the conditions of chemical and electrochemical processes equilibrium and to indicate the areas of thermodynamic stability of the different forms of an element.

Bismuth is a strongly dispersed element belonging to the group of less toxic heavy metals. It concentrates mostly in lungs and hard tissues and causes disturbances in metabolic processes and the nervous system [1]. This makes monitoring its content in the natural environment extremely important. In medicine bismuth compounds are used for their disinfecting, astringent and anti-inflammatory action [2–5]. The application of this element for the treatment of helicobacter pyloric-induced gastritis [6,7] is particularly interesting.

Determination of bismuth has been carried out using spectroscopic and electrochemical techniques such as, for example, anodic stripping voltammetry (ASV) [8,9], cathodic stripping voltammetry [10] potentiometric stripping analysis [11] or differential pulse anodic stripping voltammetry [12].

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The electrochemical methods for determination of Bi(III) have important advantages including high sensitivity, low detection limit, relative simplicity as well as inexpensive costs of sample measurement.

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. The increase of the Bi(III) electroreduction reversibility in the solutions of strongly complexing properties was used, even though the stripping voltammetry methods [8–10,12,13] were employed. In order to increase the sensitivity and selectivity of the voltammetric methods of Bi(III) determination except the mercury electrode other working electrodes were applied for example, carbon paste electrodes (CPEs) [14–18]. A limited number of studies on the use of CPEs for voltammetric determination of Bi(III) with detection limits ranging from 3×10^{-7} mol/dm^{-3} to subnanomolar concentrations have been reported [17,18]. Guo et al. [16] determined bismuth (III) by adsorptive ASV method using a CPE. The detection limit was found to be 5×10^{-10} mol/dm^{-3}. Chemically modified gold electrodes were employed as well [19].

However from an 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.

One of the problems during the process of Bi(III) determination is the presence of interferants, mainly Cu(II) ions, occurring often in much higher concentrations comparing to Bi(III) [20–22]. The advantage of the highly sensitive stripping techniques is often overshadowed by the interference of Cu(II), the peak of which overlaps with the Bi(III) peak [20]. Khaloo et al. [21] proposed a method for the determination of bismuth and copper in the presence of each other based on adsorptive stripping voltammetry of Bi(III)-chromazorul-S and Cu(II)-chromazorul-S complexes using a hanging mercury drop electrode. The detection limits were 0.1 and 0.05 ng/dm^{-3} for bismuth and copper, respectively.

In this paper a simple and fast method of Bi(III) determination, also in the presence of Cu(II), by square wave voltammetry was proposed.

In agreement with the cap-pair effect [23,24] the organic substances introduced into the supporting electrolyte can catalyse one type of electrode process and simultaneously have no influence or even inhibit the other electrode processes. Such a behaviour enables the determination of different elements near each other without the necessity for analyte accumulation, what considerably simplifies the analysis procedure.

Such a manner was proposed earlier for the determination of In(III) ions in the presence of Cd(II) and Pb(II) [25]. By applying square wave voltammetry it was possible to determine 3×10^{-7} mol/dm^{-3} In(III) in the presence of 5×10^{-5} mol/dm^{-3} Cd(II) and 1×10^{-4} mol/dm^{-3} Pb(II) in 5 mol/dm^{-3} $NaClO_4$.

In this research the catalytic activity of L-methionine on the electroreduction of Bi(III) ions in chlorate (VII) solutions [26] and a lack of this activity referring to Cu(II) ions were utilised.

2. Experimental

2.1. Apparatus

The experiments were performed using a three-electrode cell with a hanging controlled growth mercury drop electrode (Entech, Cracow, Poland) as the working electrode (electrode area was 0.009487 cm^2, 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 the electrochemical analyzer Autolab/GPES (Version 4.9) (Eco Chemie, Utrecht Netherlands).

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

2.2. Reagents and solutions

Analytical-grade reagents: $NaClO_4$ (Fluka), $HClO_4$ (Fluka), $Bi(NO_3)_3$ (Aldrich), $Cu(NO_3)_2$ (Aldrich) and L-methionine (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. Nitrogen was passed over the solution during the measurements.

The supporting electrolyte was 3 mol dm^{-3} $NaClO_4$ + 1 mol dm^{-3} $HClO_4$. Due to the weak solubility of $Bi(NO_3)_3$ in 4 mol dm^{-3} chlorates (VII) the solutions were treated by ultrasonic machining. The methionine solutions were prepared just before the measurements.

3. Results and discussion

It was found that the reversibility of the Bi(III) ions electroreduction in 1–8 mol dm^{-3} chlorates (VII) increases with the decrease in water activity [27]. Introduction of methionine into the solutions of Bi(III) ions in 1–8 mol dm^{-3} chlorates (VII) causes the increase in the peak current of electroreduction of Bi (III) ions. The magnitude of this effect depends on the methionine and the chlorates (VI) concentration [26].

As it was demonstrated earlier [26] the peaks current of electroreduction of the Bi(III) ions increases with the increase in methionine concentration (in the range of 5×10^{-4}–$1 \times 10^{-2}\,\text{mol dm}^{-3}$) for all the studied chlorates (VII) concentrations. Above the $1 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine concentrations the plateau on the $i_\text{p} = f$ ($c_\text{methionine}$) [26] curves is observed, hence $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine was recognized as the optimum. The highest catalytic activity of methionine was observed in 4 mol dm^{-3} solution of chlorates (VII).

Fig. 1(a) and (b) presents the peaks of electroreduction of $1 \times 10^{-6}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII) as well as $1 \times 10^{-7}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine.

As seen in Fig. 1(a) the lowest Bi(III) concentration for which the defined swv peak was obtained amounts to $1 \times 10^{-6}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII). The introduction of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine into 4 mol dm^{-3} solution of chlorate (VII) causes the increase in the reversibility of Bi(III) ions electroreduction which is expressed by a considerable increase in the peak height and enables the determination of $1 \times 10^{-7}\,\text{mol dm}^{-3}$ Bi(III) (Fig. 1(b)).

Fig. 2 presents the peaks of electroreduction of 1×10^{-7}–$1 \times 10^{-3}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine.

The calibration curve of Bi (III) in 4 mol dm^{-3} chlorate (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine is linear in the range of concentrations of Bi(III) from 3×10^{-7} to $1 \times 10^{-4}\,\text{mol dm}^{-3}$. At higher concentrations of Bi(III) there are substantial deviations from linearity.

Determination of Bi(III) was carried out in the presence of $1 \times 10^{-4}\,\text{mol dm}^{-3}$ Cu(II). The considerably higher reversibility of Cu(II) ions electroreduction processes compared with Bi(III) ions, as well as the fact that the differences in the reduction potentials of Bi(III) and Cu(II) ions are low cause the Bi(III) determination to be strongly interfered by Cu(II).

As seen in Fig. 3 in a solution of 4 mol dm^{-3} chlorates (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine the peaks current of electroreduction are present, both Bi(III) $E_\text{p} = 0.090\,\text{V}$ and Cu(II) $E_\text{p} = -0.145\,\text{V}$. It should be noticed that the height of the Bi(III) peak increases with an increase in its concentration, whereas the presence of methionine has no influence on the height of the peak current of

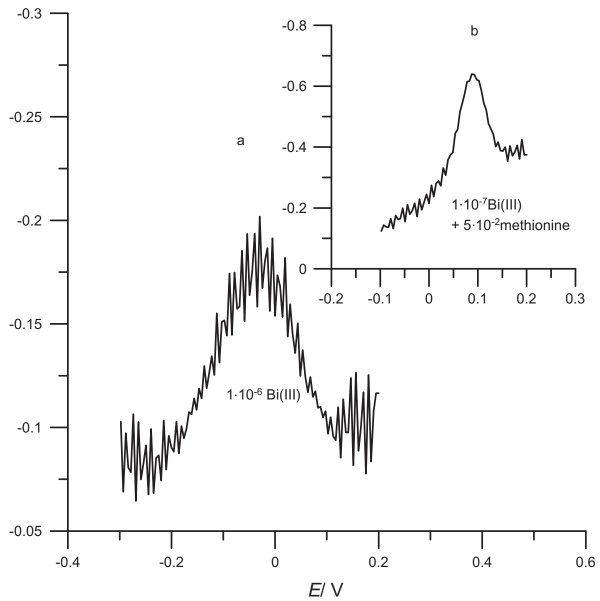

Fig. 1a,b. Square wave voltammograms obtained for solutions containing: $1 \times 10^{-6}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII) (a) as well as $1 \times 10^{-7}\,\text{mol dm}^{-3}$ Bi(III) in 4 mol dm^{-3} chlorates (VII) and $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine (b).

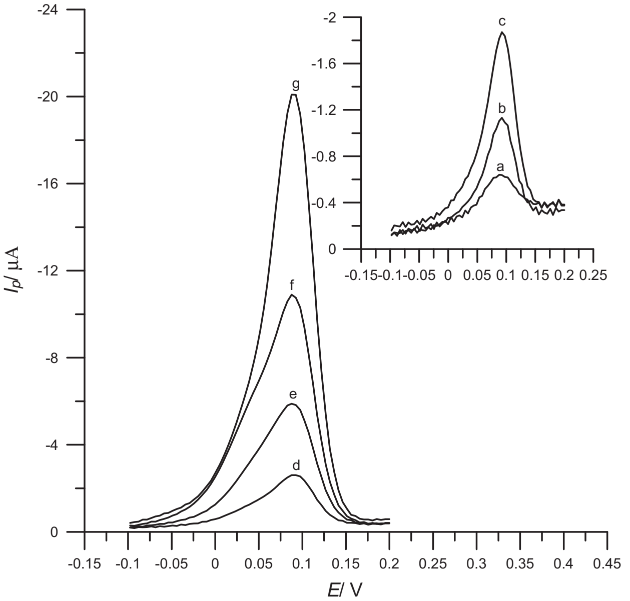

Fig. 2. Square wave voltammograms obtained for chosen solutions containing: 1×10^{-7} (a), 1×10^{-6} (b), 5×10^{-6} (c), 8×10^{-6} (d), 1×10^{-5} (e), 1×10^{-4} (f), 1×10^{-3} (g) mol dm^{-3} Bi(III) in 4 mol dm^{-3} chlorates (VII) in the presence of $5 \times 10^{-2}\,\text{mol dm}^{-3}$ methionine.

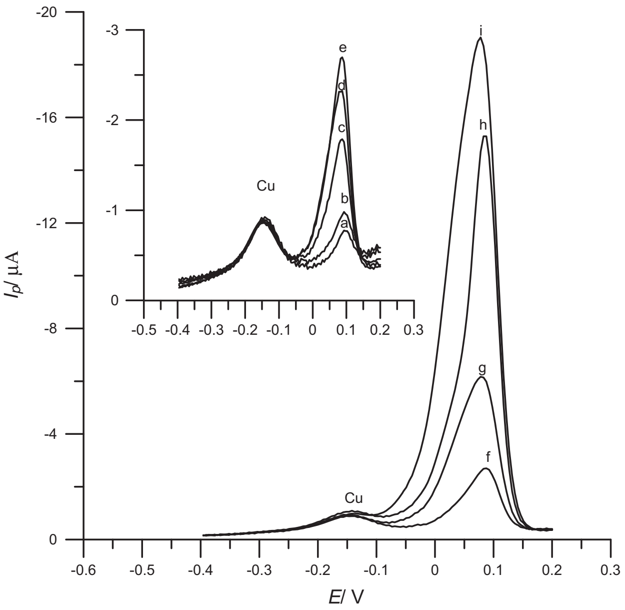

Fig. 3. Square wave voltammograms obtained for chosen solutions containing: 1×10^{-6} (a), 3×10^{-6} (b), 1×10^{-5} (c), 5×10^{-5} (d), 1×10^{-4} (e), 3×10^{-4} (f), 5×10^{-4} (g), 1×10^{-3} (h), 3×10^{-3} (i) mol dm^{-3} Bi(III) in 4 mol dm^{-3} chlorates (VII) in the presence of 5×10^{-2} mol dm^{-3} methionine and 1×10^{-4} mol dm^{-3} Cu(II).

electroreduction of Cu(II) ions. The lowest bismuth concentration for which the well-defined peak in 4 mol dm^{-3} chlorate (VII) in the presence of 5×10^{-2} mol dm^{-3} methionine and 1×10^{-4} mol dm^{-3} Cu(II) was obtained is equal to 1×10^{-6} mol dm^{-3}.

The calibration curves of Bi(III) in 4 mol dm^{-3} chlorates (VII) containing 5×10^{-2} mol dm^{-3} methionine and 1×10^{-4} mol dm^{-3} Cu(II) were plotted. The dependences were linear in the range of concentration of Bi(III) from 3×10^{-6} to 3×10^{-4} mol dm^{-3}.

3.1. Quantitative studies

Validation of the procedure for the quantitative assay of Bi(III) in 4 mol dm^{-3} chlorates (VII) containing 5×10^{-2} mol dm^{-3} methionine as well as 1×10^{-4} mol dm^{-3} Cu(II) was examined by evaluation of the limit of detection, limit of quantification, repeatability, recovery and precision. The limits of detection and quantification were computed, as 3SB/m and 10SB/m, respectively, where "SB" is the standard deviation of the peak current for the blank and "m" is slope of the analytical curve [28].

Therefore the detection and quantification limits for Bi(III) ions determination in 4 mol dm^{-3} chlorates (VII) and in the presence of 5×10^{-2} mol dm^{-3} methionine were 1.53×10^{-7} mol dm^{-3} and 5.12×10^{-7} mol dm^{-3}.

Whereas for Bi(III) ions determination in 4 mol dm^{-3} chlorates (VII) containing 5×10^{-2} mol dm^{-3} methionine as well as 1×10^{-4} mol dm^{-3} Cu (II) the detection and quantification limits were 1.44×10^{-6} and 4.80×10^{-6} mol dm^{-3}.

The repeatability (1 day) of the proposed procedure was assessed on the basis of five measurements for a single Bi(III) concentration. In the concentration range of 1×10^{-7}–1×10^{-4} mol dm^{-3} in 4 mol dm^{-3} chlorates (VII) and in the presence of 5×10^{-2} mol dm^{-3} methionine the RSD of the peak current of Bi(III) is in the range from 0.6 to 5.77%.

In the concentration range from 1×10^{-6}–3×10^{-4} mol dm^{-3} in 4 mol dm^{-3} chlorates (VII) containing 5×10^{-2} mol dm^{-3} methionine and 1×10^{-4} mol dm^{-3} Cu(II) the RSD of the peak current of Bi(III) is in the range from 0.6 to 8.73%.

Precision and recovery of the method were investigated by determination of Bi(III) ions at three different concentrations in the linear range. The results are presented in Table 1.

Table 1
Recovery and precision obtained by square-wave voltammetry

Supporting electrolytes	Concentration of Bi(III)		Precision RDS (%)	Recovery[a] (%)
	Added/ mol dm^{-3}	Found/ mol dm^{-3}		
4 mol dm^{-3} chlorate (VII)+5×10^{-2} mol dm^{-3} methionine	3×10^{-7}	2.9×10^{-7}	1.01	99.9
	5×10^{-7}	5.3×10^{-7}	0.60	106.0
	5×10^{-6}	4.8×10^{-6}	3.21	96.0
4 mol dm^{-3} chlorate (VII)+5×10^{-2} mol dm^{-3} methionine +1×10^{-4} mol dm^{-3} Cu(II)	3×10^{-6}	3.05×10^{-6}	3.80	101.6
	5×10^{-6}	4.7×10^{-6}	0.85	94.0
	5×10^{-5}	5.07×10^{-5}	4.72	101.4

[a] Recovery = 100% + [(found-added)/added] × 100%.

4. Conclusion

The presented results allow for the following conclusions:

- L-methionine, in accordance with the cap-pair rule [23,24], accelerates the electroreduction of Bi(III) ions and has no influence on the electroreduction process of Cu(II) in chlorates (VII) solutions.
- The reversibility of Bi(III) ions electroreduction in chlorates (VII) depends on the methionine concentration and water activity.
- The optimal concentration of methionine and water activity for Bi(III) determination by voltammetric method were established.
- Bi(III) determination can be also carried out in the presence of 100-fold excess of Cu(II) ions.

The presented method is undoubtedly fast, simple, relatively inexpensive and with an easily accessible measurement system.

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