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# Simultaneous Determination of Bismuth and Copper by Square Wave Voltammetry in The Presence of Ethylenediaminetetraacetic Acid

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## ABSTRACT

A sensitive and selective method for the simultaneous determination of copper and bismuth by square wave voltammetry (SWV) was developed using ethylenediaminetetraacetic acid (EDTA) as complexing agent. Factors affecting the pH and concentrations ratios of copper and bismuth were investigated. Optimal analytical conditions were found to be: pH of 8.0, the ratio of  $[Cu^{2+}]/[Bi^{3+}]$  was 0.13-2.5. The limit of detection ( $\delta$ ) was  $1.26 \times 10^{-7}$  mol dm<sup>-3</sup> for copper,  $1.30 \times 10^{-7}$  mol dm<sup>-3</sup> for bismuth.

**Key Words:** Copper; Bismuth; Simultaneous determination; SWV; EDTA; Water.

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## 1. INTRODUCTION

Bismuth and copper are environmentally important. There is a growing necessity to measure several analyses simultaneously in the same sample in various fields like environmental analysis and industrial control. Therefore, the development of simple, inexpensive, and easily handled procedures with the ability of multi-element analysis for trace metal monitoring in real samples is urgently needed for quality assessments. Typical simultaneous trace metal analyses have been based on chromatography [1,2], continuous flow analysis [3], X-ray fluorescence spectrometry [4], inductively coupled plasma atomic emission spectroscopy [5], inductively coupled plasma mass spectrometry [6] and anodic stripping voltammetry [7, 8].

Copper is an essential element for the normal metabolism of many living organisms. It is a constituent of numerous proteins and enzymes. Bismuth has been used in medicines for the treatment of helicobacter pyloric induced gastritis [9, 10]. Many electro analytical stripping procedures have been proposed for the individual determination of nanomolar concentration of copper [10-18] and bismuth [19-22] with anodic stripping voltammetry (ASV) and adsorptive cathodic stripping voltammetry (AdCSV). Although these

procedures offer the desired sensitivity, they suffer from some practical difficulties such as nearness of reduction peaks potential of bismuth and copper metal ions with oxidation peak potential of the electrode, formation of the intermetallic compound and the overlapping of the anodic stripping voltammograms of these peaks of two metal ions [23]. In spite of this fact, there are three reports on simultaneous determination of copper and bismuth [23-25].

This paper describes a procedure for simultaneous determination of copper and bismuth with SWV by using EDTA as complexing agent due to separation of these cations peak. Various factors (such as pH and ratio) influencing the simultaneous determination of copper and bismuth were investigated.

## 2. EXPERIMENTAL

### 2.1. Chemicals

All chemicals used were of analytical reagent grade. A 0.1 mol dm<sup>-3</sup> EDTA was prepared by dissolving 3.722 g Na<sub>2</sub>H<sub>2</sub>Y.2H<sub>2</sub>O in water and diluting to 100 mL in volumetric flasks. Double distilled water was used throughout. Stock solution of bismuth (0.1 mol dm<sup>-3</sup>) was prepared by dissolving 4.85 g of bismuth nitrate

[Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O] in 10mL 1.0 M nitric acid and diluting to 100.0mL with water. A 0.1 mol dm<sup>-3</sup> copper (II) stock solution was prepared by dissolving 2.41 g of [Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O] (Merck) in water and diluting to 100 mL in a volumetric flask. pH 8.0-11.5 NH<sub>3</sub>/NH<sub>4</sub>Cl buffer solutions were prepared by dissolving 5.4 g of [NH<sub>4</sub>Cl] (Merck) in water, diluting to 100 mL in a volumetric flask, adding to concentrated NH<sub>3</sub> or HCl and using pH meter. Argon gas with %99.99 purity was used to de-aerate solutions.

## 2.2. Apparatus

Square wave voltammetry was conducted with a Chemical Work Station model CHI 660 B. Measurements were carried out with a hanging mercury electrode in a three electrode arrangement. The auxiliary electrode was a wire of platinum. An Ag/AgCl was used as reference electrode. Inolab WTW-720 digital pH meter was used for pH measurements. The parameters were designated; frequency: 10 Hz, pulse amplitude: 0.0025 V, potential increment: 0.004 V.

## 2.3. Procedure

Five milliliters of NH<sub>3</sub>/NH<sub>4</sub>Cl buffer solution was pipetted into the volumetric cell. Then 0.1 M EDTA was added, giving a final concentration more than copper and bismuth. The solution was purged with water-saturated argon for 5 min in the first cycle and 30 s for each successive cycle. Copper and bismuth peaks were observed at about -0.4 V and -0.7 V, respectively. All experiments were carried out at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Characteristic of the Cu-EDTA and Bi-EDTA Complexes

Preliminary experiments were carried out to identify the general features that characterize the behavior of the Cu-EDTA, Bi-EDTA systems on hanging mercury electrode. Fig.1 displays the voltammograms of  $9.9 \times 10^{-6}$  mol dm<sup>-3</sup> of each metal ion (copper and bismuth). And Fig.2 displays the voltammograms of  $1.96 \times 10^{-5}$  mol dm<sup>-3</sup> of each metal ion (copper and bismuth) in the presence of EDTA at pH 10 and Fig.3 at pH 8.

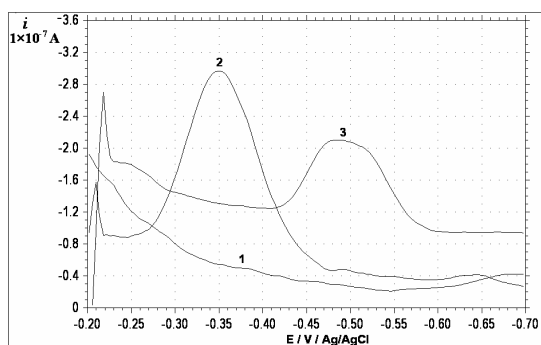


Figure 1. Voltammograms of copper and bismuth in NH<sub>3</sub>/NH<sub>4</sub>Cl, pH 10, 1. 5 mL NH<sub>3</sub>/NH<sub>4</sub>Cl, 2. 1 + 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> copper, 3. 1 + 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> bismuth.

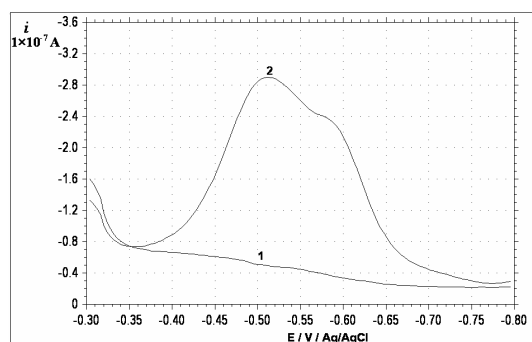


Figure 2. Voltammograms of copper and bismuth in NH<sub>3</sub>/NH<sub>4</sub>Cl, pH 10, 1. 5 mL support electrolyte + 0.1 mL 0.1 mol dm<sup>-3</sup> EDTA, 2. 1 + 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> copper and 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> bismuth.

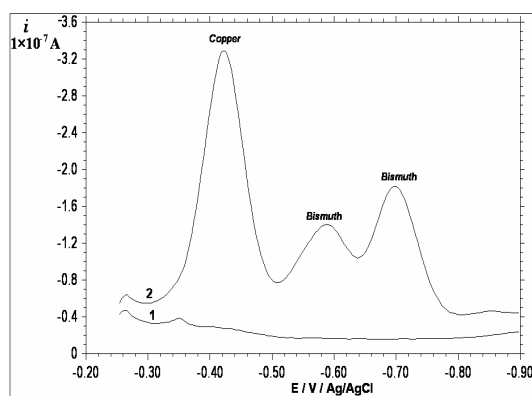


Figure 3. Voltammograms of copper and bismuth in NH<sub>3</sub>/NH<sub>4</sub>Cl, pH 8, 1. 5 mL support electrolyte + 0.1 mL 0.1 mol dm<sup>-3</sup> EDTA, 2. 1 + 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> copper and 0.05 mL 10<sup>-3</sup> mol dm<sup>-3</sup> bismuth.

### 3.2. Optimization of Parameters

#### 3.2.1. Effect of pH

The influence of pH on the reduction peaks current of copper and bismuth was studied in the pH range of 8.0–11.5 for NH<sub>3</sub>/NH<sub>4</sub>Cl-EDTA. It was seen from Table 1 the peaks potential of copper and bismuth shifted toward more negative values and distance between them decreased with increasing pH of the mixture of metal ions solution. Therefore, pH 8 was selected for subsequent uses, because at pH 8 copper and bismuth's reduction peaks were separated very well. And bismuth's second reduction peak was used for its determination, because this peak was sensitive for standard addition of bismuth than bismuth's first reduction peak.

Table 1. Effect of pH on peaks potential and separation (np\* no peak).

pH	-E, mV		
	Cu <sup>2+</sup>	Bi <sup>3+</sup>	
8.0	420	600	800
8.5	468	580	708
9.0	496	592	708
9.4	516	600	723
9.8	516	580	733
10.0	520	590	700
10.5	584	620	790
11.0	620	680	800
11.5	625	np*	868

### 3.2.2. Influence of [Cu<sup>2+</sup>]/[Bi<sup>3+</sup>] ratios

In first study, [Cu<sup>2+</sup>]/[Bi<sup>3+</sup>]= 1 and 1.92x10<sup>-5</sup> mol dm<sup>-3</sup> in pH 8 NH<sub>3</sub>/NH<sub>4</sub>Cl-EDTA solution was investigated. The results are shown in Table 2.

After than have worked with samples which presented different [Cu<sup>2+</sup>]/[Bi<sup>3+</sup>] ratios. This method was given more error when we used more amount of copper than bismuth (Table 3, last row). Due to the copper reduction peak overlapped on bismuth's first peak. So bismuth's second peak (-0.7 V) was effected from this interaction. After these situation is thought determination of copper and bismuth can do more successful when amount of bismuth is more than copper. All results for this study are shown in Table 2.

Table 2 Determination of copper and bismuth (n=5).

	Added (10 <sup>-5</sup> mol dm <sup>-3</sup> )		Found (10 <sup>-5</sup> mol dm <sup>-3</sup> )		Standard Deviation (10 <sup>-5</sup> )		$\bar{x} \pm \frac{t^a_s}{\sqrt{N}}$		% Error	
	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>
$\frac{1}{1}$	1.92	1.92	1.85	2.00	0.09	0.25	1.85±0.09	2.0±0.28	3.6	4.0
$\frac{2}{1}$	1.94	0.97	1.84	1.01	0.28	0.14	1.84±0.27	1.01±0.13	5.0	4.0
$\frac{2.5}{1}$	2.40	0.97	2.56	0.99	0.16	0.01	2.56±0.15	0.99±0.01	6.6	2.0
$\frac{5}{1}$	2.40	0.48	2.62	0.38	0.33	0.07	2.62±0.31	0.38±0.07	9.0	20
$\frac{7.5}{1}$	7.28	0.97	6.70	0.78	1.10	0.12	6.7±1.00	0.78±0.11	8.0	19
$\frac{10}{1}$	4.85	0.48	5.42	0.33	0.26	0.06	5.42±0.25	0.33±0.06	12	32
$\frac{1}{2}$	0.97	1.94	1.00	1.89	0.32	0.24	1.0±0.30	1.89±0.28	3.1	2.5
$\frac{1}{2.5}$	0.97	2.40	0.99	2.35	0.06	0.39	0.99±0.06	2.35±0.45	2.0	2.1
$\frac{1}{5}$	0.48	2.40	0.49	2.40	0.02	0.02	0.49±0.02	2.40±0.02	1.4	0.0
$\frac{1}{7.5}$	0.97	7.28	1.04	7.17	0.04	0.38	1.04±0.04	7.17±0.36	7.0	1.5
$\frac{1}{10}$	0.48	4.85	0.52	4.54	0.06	0.33	0.52±0.06	4.54±0.30	7.0	6.0

% 90 Confidence level

#### 4. DETECTION LIMITS OF METHOD

To verify the linear relationship between peaks current and metal concentrations five calibration graphs were constructed under optimum conditions (pH 8 NH<sub>3</sub>/NH<sub>4</sub>Cl buffer, frequency 10 Hz, pulse amplitude 0.0025 V, potential increment 0.004 V). Under the selected conditions the detection limits (3σ) of 1.26×10<sup>-7</sup> mol dm<sup>-3</sup> and 1.30×10<sup>-7</sup> mol dm<sup>-3</sup> were obtained for copper and bismuth, respectively.

#### 5. INTERFERENCE STUDIES

Some interference ions by other ionic species in the square wave voltammetric determination of bismuth and copper was investigated by the addition of an interfering ion to a solution containing 1.92 × 10<sup>-5</sup> mol

dm<sup>-3</sup> of bismuth or copper using the optimized conditions. The addition of interfering ions into the solution was gone to with copper or bismuth peaks were overlapped and/or peaks currents were decreased. These points were called tolerance ratio. The results of this study are summarized in Table 3 and Table 4.

Table 3. Interference study of determination of copper under the optimum condition.

Species	Tolerance ratio
$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{Cl}^-$ , $\text{Na}^+$	1000 <sup>a</sup>
$\text{Pb}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Hg}^{2+}$	100
$\text{Ni}^{2+}$	25
$\text{Co}^{3+}$	10
$\text{Sb}^{2+}$ , $\text{Sn}^{2+}$	1

<sup>a</sup>Maximum ratio of ions tested

Table 4. Interference study of determination of bismuth under the optimum condition.

Species	Tolerance ratio
$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{Cl}^-$ , $\text{Na}^+$	1000 <sup>a</sup>
$\text{Pb}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Hg}^{2+}$	100
$\text{Ni}^{2+}$	25
$\text{Sb}^{2+}$ , $\text{Sn}^{2+}$	1

<sup>a</sup>Maximum ratio of ions tested

Table 5. Determination of copper and bismuth in synthetic samples (n=5).

Sample No		Added (10 <sup>-5</sup> mol dm <sup>-3</sup> )	Founded (10 <sup>-5</sup> mol dm <sup>-3</sup> )	Standard Deviation (10 <sup>-5</sup> )	$\bar{x} \pm \frac{t^a s}{\sqrt{N}}$
1	Cu <sup>2+</sup>	0.97	0.90	0.08	0.90±0.07
	Bi <sup>3+</sup>	1.45	1.50	0.23	1.50±0.27
2	Cu <sup>2+</sup>	1.45	1.45	0.07	1.45±0.08
	Bi <sup>3+</sup>	0.97	0.90	0.06	0.90±0.06
3	Cu <sup>2+</sup>	0.97	0.91	0.02	0.91±0.02
	Bi <sup>3+</sup>	2.90	2.61	0.27	2.61±0.26
4	Cu <sup>2+</sup>	2.90	2.99	0.30	2.99±0.28
	Bi <sup>3+</sup>	0.97	0.94	0.08	0.94±0.08

<sup>a</sup> 90 % Confidence level

## 7. ANALYSIS OF COPPER AND BISMUTH IN TAP AND SPRING WATER ENVIRONMENT

The utility of the developed method for copper and bismuth determination was tested by the determination of copper and bismuth in tap and spring water using the

## 6. SYNTHETIC SAMPLE ANALYSIS

The proposed method was successfully applied to the simultaneous determination of copper and bismuth in synthetic samples whose composition has been prepared according to known concentration. The results are shown in Table 5.

recommended procedure (Table 6). The concentration of copper and bismuth in tap and spring water was determined by the calibration graphic method. Solutions of known concentration of copper and bismuth were added to water samples. Five determinations were made on each addition.

Table 6 Determination of copper and bismuth in real samples environments(n=5).

Sample	Added ( $10^{-5}$ mol dm <sup>-3</sup> )		Founded ( $10^{-5}$ mol dm <sup>-3</sup> )		Recovery (%)	
	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>	Cu <sup>2+</sup>	Bi <sup>3+</sup>
Tap water <sup>a</sup>			no peak	no peak		
	1.75	1.75	1.77±0.03	1.71±0.16	101.0	98.0
	1.90	1.90	1.92±0.05	1.94±0.12	101.0	102.0
Spring water			no peak	no peak		
	1.75	1.75	1.79±0.09	1.79±0.07	102.2	102.2
	1.90	1.90	1.95±0.03	1.93±0.09	102.6	101.6

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## 8. CONCLUSION

The present study demonstrates that square wave voltammetry of copper and bismuth based on the reduction of copper-EDTA and bismuth-EDTA complexes on the hanging mercury electrode can be used for determination of trace amounts of both elements in the presence of each other. The method offers a practical separation of reduction potentials for simultaneous determination of trace amount of copper and bismuth in a single scan with high selectivity and sensitivity, simplicity and speed.

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