G.U. Journal of Science
23(1): 33-39 (2010)

GUJS
www.gujs.org

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

Erdoğan Hasdemir[1], Kuddusi Karaboduk[1♣]

[1] *Gazi University, Faculty of Art and Sciences, Department of Chemistry, Ankara, Turkey*

Received: 03.03.2009 Revised: 14.07.2009 Accepted: 20.10.2009

ABSTRACT

A sensitive and selective method for the simultaneous determination of copper and bismuth by square wave voltammetry (SWV) was developed using ethylenediaminetetraacedic 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 (3δ) was 1.26×10^{-7} mol dm^{-3} for copper, 1.30×10^{-7} mol dm^{-3} for bismuth.

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

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^{-3} EDTA was prepared by dissolving 3.722 g $Na_2H_2Y.2H_2O$ in water and diluting to 100 mL in volumetric flaks. Double distilled water was used throughout. Stock solution of bismuth (0.1 mol dm^{-3}) was prepared by dissolving 4.85 g of bismuth nitrate

---

Corresiponding author: kuddusi82@gmail.com

[$Bi(NO_3)_3 \cdot 5H_2O$] in 10mL 1.0 M nitric acid and diluting to 100.0mL with water. A 0.1 mol dm^{-3} copper (II) stock solution was prepared by dissolving 2.41 g of [$Cu(NO_3)_2 \cdot 3H_2O$] (Merck) in water and diluting to 100 mL in a volumetric flask. pH 8.0-11.5 NH_3/NH_4Cl buffer solutions were prepared by dissolving 5.4 g of [NH_4Cl] (Merck) in water, diluting to 100 mL in a volumetric flask, adding to concentrated NH_3 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_3/NH_4Cl 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 9.9×10^{-6} mol dm^{-3} of each metal ion (copper and bismuth). And Fig.2 displays the voltammograms of 1.96×10^{-5} mol dm^{-3} of each metal ion (copper and bismuth) in the presence of EDTA at pH 10 and Fig.3 at pH 8.

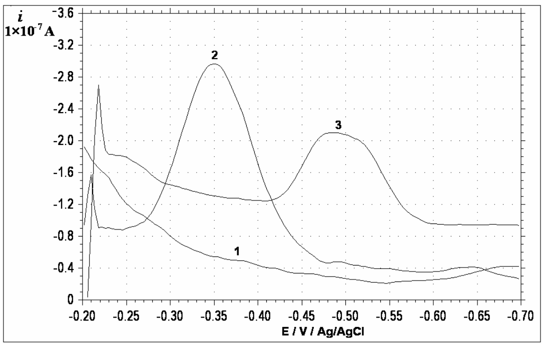

Figure 1. Voltammograms of copper and bismuth in NH_3/NH_4Cl, pH 10, 1. 5 mL NH_3/NH_4Cl, 2. 1 + 0.05 mL 10^{-3} mol dm^{-3} copper, 3. 1 + 0.05 mL 10^{-3} mol dm^{-3} bismuth.

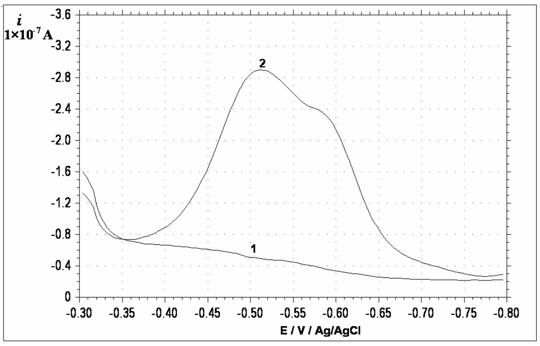

Figure 2. Voltammograms of copper and bismuth in NH_3/NH_4Cl, pH 10, 1. 5 mL support electrolyte + 0.1 mL 0.1 mol dm^{-3} EDTA, 2. 1 + 0.05 mL 10^{-3} mol dm^{-3} copper and 0.05 mL 10^{-3} mol dm^{-3} bismuth.

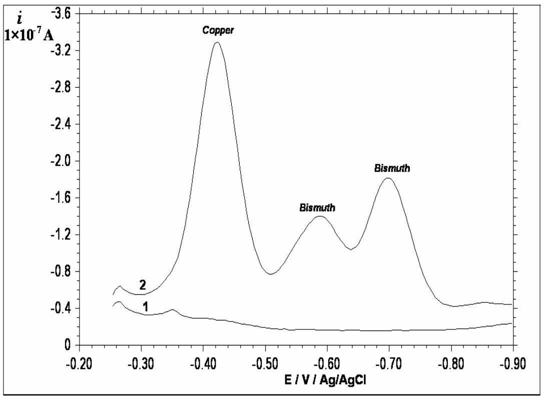

Figure 3. Voltammograms of copper and bismuth in NH_3/NH_4Cl, pH 8, 1. 5 mL support electrolyte + 0.1 mL 0.1 mol dm^{-3} EDTA, 2. 1 + 0.05 mL 10^{-3} mol dm^{-3} copper and 0.05 mL 10^{-3} mol dm^{-3} bismuth.

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_3/NH_4Cl-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^{2+}	Bi^{3+}	
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 $[Cu^{2+}]/[Bi^{3+}]$ ratios

In first study, $[Cu^{2+}]/[Bi^{3+}]$= 1 and $1.92x10^{-5}$ mol dm^{-3} in pH 8 NH_3/NH_4Cl-EDTA solution was investigated. The results are shown in Table 2.

After than have worked with samples which presented different $[Cu^{2+}]/[Bi^{3+}]$ 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^{-5} mol dm^{-3})		Found (10^{-5} mol dm^{-3})		Standard Deviation (10^{-5})		$\bar{x} \pm \frac{t^a s}{\sqrt{N}}$		% Error	
$[Cu^{2+}]/[Bi^{3+}]$	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}
$\frac{1}{1}$	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_3/NH_4Cl buffer, frequency 10 Hz, pulse amplitude 0.0025 V, potential increment 0.004 V). Under the selected conditions the detection limits (3δ) of 1.26×10^{-7} mol dm^{-3} and 1.30×10^{-7} mol dm^{-3} 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^{-5} mol dm^{-3} 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
NO_3^- , NH_4^+ , Cl^- , Na^+	1000[a]
Pb^{2+} , Zn^{2+} , Cr^{3+} Al^{3+} , Fe^{3+} , Hg^{2+}	100
Ni^{2+}	25
Co^{3+}	10
Sb^{2+}, Sn^{2+}	1

[a]Maximum ratio of ions tested

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

Species	Tolerance ratio
NO_3^- , NH_4^+ , Cl^- , Na^+	1000[a]
Pb^{2+} , Zn^{2+} , Cr^{3+} Al^{3+} , Fe^{3+} , Hg^{2+}	100
Ni^{2+}	25
Sb^{2+}, Sn^{2+}	1

[a]Maximum ratio of ions tested

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.

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

Sample No		Added (10^{-5} mol dm^{-3})	Founded (10^{-5} mol dm^{-3})	Standard Deviation (10^{-5})	$\bar{x} \pm \frac{t^a s}{\sqrt{N}}$
1	Cu^{2+}	0.97	0.90	0.08	0.90±0.07
	Bi^{3+}	1.45	1.50	0.23	1.50±0.27
2	Cu^{2+}	1.45	1.45	0.07	1.45±0.08
	Bi^{3+}	0.97	0,90	0.06	0.90±0.06
3	Cu^{2+}	0.97	0.91	0.02	0.91±0.02
	Bi^{3+}	2.90	2.61	0.27	2.61±0.26
4	Cu^{2+}	2.90	2.99	0.30	2.99±0.28
	Bi^{3+}	0.97	0.94	0.08	0.94±0.08

[a] 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 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^{-3})		Founded (10^{-5} mol dm^{-3})		Recovery (%)	
	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}	Cu^{2+}	Bi^{3+}
Tap water[a]			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

[a] Ankara, Turkiye

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.

REFERENCES

[1] Threeprom, J., Purachaka, S., Potipan, L., ‘’Simultaneous determination of Cr(III)–EDTA and Cr(VI) by ion interaction chromatography using a C18 column’’, ***J. Chromatogr., A***, 1073:291-295 (2005).

[2] Yang, G., Zhang, C., Wang, Q, Yin, J., ’Simultaneous determination of four heavy metal ions in tobacco and tobacco additive by online enrichment followed by RP-HPLC and microwave digestion.’, ***J. Chromatogr. Sci.***, 41:195-199 (2003).

[3] Zolotov, Y.A., Morosanova, E.I., Zhalavannaya, S.V., Dyukarev, S.S., “Continuous flow analysis: Simultaneous spectrophotometric determinations of metals”, ***Anal. Chim. Acta***, 308:386-396 (1995).

[4] Hettipathirana, T.D., “Simultaneous determination of parts-per-million level Cr, As, Cd and Pb, and major elements in low level contaminated soils using borate fusion and energy dispersive X-ray fluorescence spectrometry with polarized excitation”, ***Spectrochim. Acta B***, 59:223-229 (2004).

[5] Karami, H., Mousavi, M.F., Yamini, Y., Shamsipur, M., “On-line preconcentration and simultaneous determination of heavy metal ions by inductively coupled plasma-atomic emission spectrometry”, ***Anal. Chim. Acta***, 509:89-94 (2004).

[6] Sarmiento-González, A., Marchante-Gayon, J.M., Tejerina-Lobo, J.M., Paz-Jimenez, J., Sanz-Medel, A. “ICP-MS multielemental determination of metals potentially released from dental implants and articular prostheses in human biological fluids” ***Anal. Bioanal. Chem.***, 382:1001-1009 (2005).

[7] Farghaly, O.A., Ghandour, M.A., “Square-wave stripping voltammetry for direct determination of eight heavy metals in soil and indoor-airborne particulate matter”, ***Environ.Res.***, 97:229-235 (2005).

[8] Mamani, M.C.V., Aleixo, L.M., Abreu, M.F., Rath, S., “Simultaneous determination of cadmium and lead in medicinal plants by anodic stripping voltammetry”, ***J. Pharm. Biomed. Anal***,.37:709 (2005).

[9] Sadler, P.J. “Metal complexes in medicine: design and mechanism of action”, ***J. Inorg. Biochem.***, 67:4 (1997).

[10] Yang, L.B., Eshraghi, J., Fassihi, R., “A new intragastric delivery system for the treatment of Helicobacter pylori associated gastric ulcer: in vitro evaluation”, ***J. Controlled Release***, 57:215-222 (1999).

[11] Van Den Berg, C.M.G., “Determination of copper, cadmium and lead in seawater by cathodic

stripping voltammetry of complexes with 8-hydroxyquinoline", ***J. Electroanal. Chem.***, 215: 111-121 (1986).

[12] Yarnitzky, Ch., Schreiber-Stanger, R. "Adsorption stripping square-wave voltammetry of copper ions in the presence of thiourea", ***J. Electroanal. Chem.***, 214:65-78 (1986).

[13] Bilewicz, R., Kublik, Z. "The determination of traces of thiocyanate and copper(II) ions by cathodic stripping voltammetry", ***Anal. Chim. Acta***, 123: 201 (1981).

[14] Zhao, J., Sun, D., "Adsorption voltammetry of the copper-4-[(4-diethylamino-2-hydroxyphenyl)azo]-5-hydroxynaphthalene-2,7-disulphonic acid (Beryllon III) system", ***Anal. Chim. Acta***, 268: 293-299 (1992).

[15] Quentel, F., Madec, C., "Voltammetric study of the copper-1,10-phenanthroline complex", ***Anal. Chim. Acta***, 230: 83-90 (1990).

[16] Culjak, I., Mlakar, M., Branica, M., "Synergetic adsorption of the copper-phenanthroline-tributylphosphate complex at a mercury drop electrode", ***Anal. Chim. Acta***, 297:427-435 (1994).

[17] Safavi, A., Shams, E., "Determination of trace amounts of copper(II) by adsorptive stripping voltammetry of its complex with pyrogallol red", ***Anal. Chim. Acta***, 385:265-272 (1999).

[18] Shams, E., "Determination of trace amounts of copper by adsorptive stripping voltammetry", ***Anal. Lett.***, 33:465-478 (2000).

[19] Shams, E., "Determination of trace amount of bismuth(III) by adsorptive stripping voltammetry by alizarine red s", ***Electroanalysis***, 13:1140-1142 (2001).

[20] Gillain, G., "Studies of pretreatments in the determination of Zn, Cd, Pb, Cu, Sb and Bi in suspended particulate matter and plankton by differential-pulse anodic-stripping voltammetry with a hanging mercury drop electrode", ***Talanta***, 29:651-654 (1982).

[21] Jiang, M., Meng, F., Gong, C., Zhao, Z., "Simultaneous determination of bismuth and lead by single-sweep polarography of their glyoxalbis (2-hydroxyanil) complexes", ***Analyst***, 115:49-51 (1990).

[22] Wang, J., Lu, J., Luo, D., Wang, J., Tian, B., "Simultaneous adsorptive stripping voltammetric measurements of trace chromium, uranium, and iron in the presence of cupferron', ***Electroanalysis***, 9:1247-1251 (1997).

[23] Limson, J., Nyokong, T., "Substituted catechols as complexing agents for the determination of bismuth, lead, copper and cadmium by adsorptive stripping voltammetry", ***Anal. Chim. Acta***, 344: 87-95 (1997).

[24] Hajian, R., Shams, E., "Application of adsorptive stripping voltammetry to the determination of bismuth and copper in the presence of morin", ***Anal. Chim. Acta***, 491:63-69 (2003).

[25] Gholivand, M.B., Romiani, A.A., "Application of adsorptive stripping voltammetry to the simultaneous determination of bismuth and copper in the presence of nuclear fast red", ***Anal. Chim. Acta***, 571:99-104 (2006).