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ADSORPTIVE CATHODIC STRIPPING VOLTAMMETRIC DETERMINATION OF ANTIMONY IN THE PRESENCE OF COPPER AND BISMUTH BY USING HEMATOXYLIN

İbrahim Şahin[1] and Nuri Nakiboglu[2],*

[1] Chemistry Education Division, Necatibey Education Faculty, Balıkesir University, 10100 Balıkesir, Turkey
[2] Chemistry Department, Sciences and Arts Faculty, Balıkesir University, 10145 Balıkesir, Turkey

ABSTRACT

This study describes a new adsorptive cathodic stripping voltammetric method using hematoxylin as complexing reagent for determination of antimony in the presence of Cu(II) and Bi(III). The method is based on the accumulation of Sb(III)-hematoxylin complex onto a hanging mercury drop electrode (HMDE), and reduction of the antimony in the adsorbed complex by using square wave cathodic stripping voltammetry. The effects of chemical (pH, supporting electrolyte, concentration of hematoxylin) and instrumental (accumulation potential, accumulation time, stripping mode and scan rate) parameters on the measured current as response are discussed. The linear relationship was obtained in the concentration range of 2.7-80 $\mu g\ L^{-1}$ (r = 0.998, $n = 10$). The detection ($3s$) and the quantification ($10s$) limits were estimated to be 0.8 $\mu g\ L^{-1}$ and 2.7 $\mu g\ L^{-1}$, respectively. The method was applied to determination of Sb(III) in water samples.

KEYWORDS: Antimony, hematoxylin, adsorptive cathodic stripping voltammetry, water

1. INTRODUCTION

Antimony is a natural element and used in various industrial fields. The Agency for Toxicological Substances and Diseases Registry (ATSDR) in the United States accepted that antimony and its compounds are pollutants (*http://www.atsdr.cdc.gov/mrls.html*). The antimony value in drinking water is recommended to be 0.02 mg/L by The World Health Organisation [1] Therefore, accurate determination of antimony is important in various samples and matrices.

Antimony has been determined using many methods in various matrices. Among these, hydride generation atomic absorption spectrometry (HGAAS) [2] and inductively coupled plasma optical emission spectrometry (ICP OES) have been favoured to minimize the problems associated with matrix interferences for the determination of antimony at trace and ultra-trace levels. Advantages and disadvantages of these techniques have been discussed in the literature [3]. Additionally, review articles including analytical methods for the speciation and determination of antimony are available [4-7]. On the other hand, a variety of electroanalytical methods, such as anodic stripping voltammetry (ASV) [8-11], adsorptive cathodic stripping voltammetry (AdCSV) [12-14], and adsorptive anodic stripping voltammetry (AdASV) [15], have also been used for determination of Sb(III) in various samples. Sb(III) is preconcentrated in acidic medium as Sb(0) at the electrode for a particular time period, and subsequently oxidized to Sb(III) in ASV methods. Morin [12], chloranilic acid [13], pyrogallol [14] and alizarin red s [15] have been used as complexing agents in AdSV determination of Sb(III). The detailed information about electroanalytical determination of antimony can be found in the review reported by Toghill *et al.* [16]. Generally, the main interfering ions in voltammetric determination of Sb(III) are Cu(II), Bi(III) and As(III). Therefore, alternative voltammetric procedures, free from these interferences, are needed.

Hematoxylin (HMT,) widely used in the field of histology and pathology as a staining agent, is a natural compound obtained by extraction from the logwood tree, *Haematoxylon campechianum* [17]. The interactions between HMT and various metal ions, such as aluminum (III), chromium (III), iron (III), copper (II), lead (II), nickel (II), osmium (III) and tin (II), have been known. These complex compounds have a variety of colours, depending on the metal ions (*http://stainsfile.info/ StainsFile/stain/ hematoxylin /hxintro.htm*). There are few reports for developing new analytical methods using HMT. One of these, reported by Niazi *et al.* [18], is a spectrophotometric method using HMT as complexing agent for simultaneous determination of Al(III) and Fe(III). The other one is a voltammetric method using a HMT modified carbon paste electrode for determination of nicotinamide adenine dinucleotide (NADH) [19]. However, there is no study using HMT

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* Corresponding author

as complexing agent for the determination of Sb (III) and other metal ions by voltammetry.

The aim of the study is to develop an alternative method, free from interference of common ions, using a new complexing agent for the determination of Sb (III) by adsorptive stripping voltammetry.

2. MATERIALS AND METHODS

2.1 Equipments and chemicals

A Radiometer Pol 150 Polarographic Analyzer connected with a Radiometer MDE 150 polarographic stand were used in voltammetric measurements. A combination consisting of a hanging mercury drop electrode (HMDE), Ag/AgCl (satd. KCl) reference electrode (Radiometer, B18C003) and platinum wire auxiliary electrode (Radiometer) were used as a three-electrode system. Hexa-distilled mercury (Radiometer-Copenhagen) was employed for HMDE. Measurements of pH were carried out using a WTW pH-meter with combined glass electrode. Standard buffer solutions were used for adjusting the meter prior to measurements. Titrisol ampoules were purchased from Merck for antimony and the other metal ions (1000 mgL^{-1}). HMT (Fig. 1) was obtained from Merck and used without purification. The other chemicals used throughout the study were of analytical grade. All of the solutions were prepared daily. Deionized water (18.2 MΩ) was obtained from an Sartorius Arium 611 ultrapure water purification system, and used for preparing all of the solutions
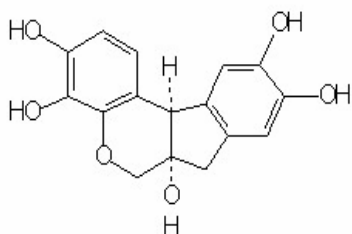

FIGURE 1 - Structure of HMT

2.2 Procedure

If not otherwise stated, the required aliquots of Sb(III) stock solution (or water sample), 1×10^{-4} mol L^{-1} HMT, and 1 mol L^{-1} acetic acid-phosphoric acid mixture (pH 5) were transferred into a 10-ml volumetric flask, and the volume was completed with deionized water. Then, the solution was decanted to a voltammetric cell and purged with nitrogen for 5 min. Accumulation at a new mercury drop was carried out with stirring the solution at a deposition potential of - 600 mV for 120 s. After a waiting time for 10 s, the potential was scanned from -200 mV toward the cathodic direction by using square wave (SW) modulation. Step duration, step amplitude and pulse amplitude were 0.04 s, 2 mV, and -25 mV, respectively. Measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Figure 2 displays the SW voltammograms of 8.2×10^{-8} mol L^{-1} Sb(III) in the absence of HMT (curve a), 1×10^{-6} mol L^{-1} HMT in the absence of Sb(III) (curve b), and the mixture of 8.2×10^{-8} mol L^{-1} Sb(III) and 1×10^{-6} mol L^{-1} HMT (curve c) in acetic acid-phosphoric acid mixture (pH 5), after 120 s of accumulation time at -0.600 V. Comparison of the voltammograms shows that a new peak appears at -0.520 V when Sb(III) is added to the solution containing HMT, which gives us an idea about the formation of Sb(III)-HMT complex in the solution. The peak current proportionally increases with the Sb(III) concentration (curve d). Cyclic voltammograms obtained affirm that the electrochemical reduction process of the antimony in the complex is irreversible. Additionally, logI-logv plot was drawn (see Fig. 3) using the data obtained from cyclic voltammograms recorded for 10, 20, 50, 100 and 200 mV/s scan rates (not shown herein). The slope of the linear graph is 0.9243, and this value is very close to 1 suggesting the adsorption process.
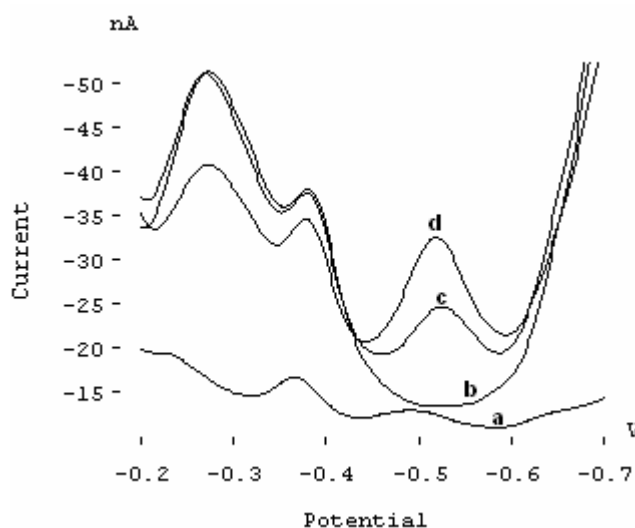

FIGURE 2 - SW voltammograms obtained in acetic acid-phosphoric acid mixture at pH 5: (a) 10 μg L^{-1} Sb (III) in the absence of HMT, (b) 1×10^{-6} mol L^{-1} HMT in the absence of Sb (III), (c) 10 μg L^{-1} Sb(III) in the presence of 1 × 10^{-6} mol L^{-1} HMT, and (d) c +10 μg L^{-1} Sb (III). Other conditions: E$_{ac}$=-600 mV, t$_{ac}$ = 120 s, scan rate = 50 mV/s.
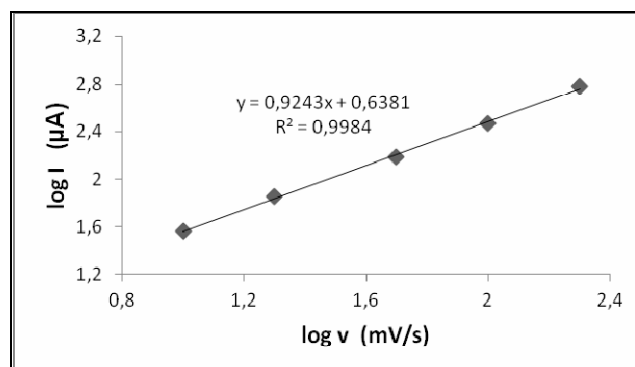

FIGURE 3 - LogI-logv plot for 10, 20, 50, 100 and 200 mV/s scan rates.

Preliminary experiments were performed for pH 4, 7 and 9 by using acetate, phosphate and ammonia buffers, respectively. Our previous studies indicated that boron can form a stable complex with polyhydroxy compounds, such as HMT. For this reason, Britton Robinson buffer was not preferred for avoiding complex formation between boron and HMT. The peak of Sb(III)-HMT complex overlaps with the free HMT, due to the competitive adsorption, at higher pHs more than pH 7, deteriorating the peak resolution. Therefore, further pH experiments were planned in neutral and acidic medium. The pH of the solution containing Sb(III)-HMT complex was varied in the range of 3.0 and 7.0 for examining the effect of pH on the peak current. No signal related to the complex was obtained below pH 3.0. The peak current gradually increases with pH and reaches a maximum value at pH 5.0, but then decreases (Fig. 4). Therefore, pH 5.0 was preferred as optimum. Additionally, sodium acetate, ammonium acetate and sodium acetate-phosphate mixture at pH 5 were tested, and a slightly high peak current was obtained in the case of acetate-phosphate mixture. The peak potential of both the free HMT and Sb(III)-HMT complex shifted linearly to negative values as the pH increases. A linear relationship between peak potential and pH for Sb(III)-HMT complex was observed (E_p = - 92, pH 5, R^2 = 0.9914).
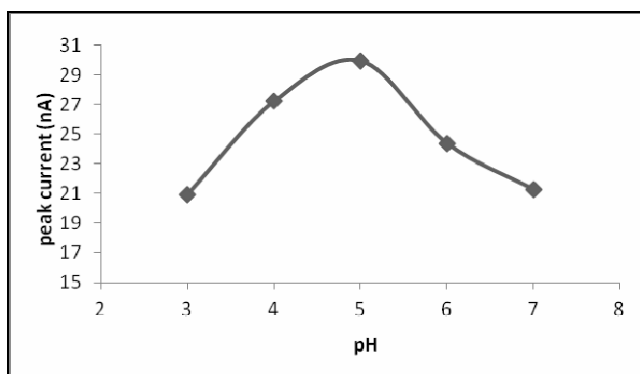

FIGURE 4 - The variation of complex peak current with pH (Conditions: $C_{Sb(III)}$: 20 µg L^{-1}, C_{HMT}: 1 × 10^{-6} mol L^{-1}, t_{acc} = 120 s, E_{acc} = -600 mV, pH 5, pulse amplitude: - 25 mV, scan rate: 50 mV/s).

The concentration of HMT is the other important solution parameter with respect to both complex formation degree and competitive adsorption on the electrode surface. For this reason, the effect of HMT concentration was studied. The peak current of Sb(III)-HMT complex rapidly increases with concentration of HMT up to 1 × 10^{-6} mol L^{-1} (not shown herein), and then, remains almost constant in the higher concentrations more than 1 × 10^{-6} mol L^{-1}. Therefore, this concentration was selected for subsequent measurements.

The accumulation potential, accumulation time, stripping mode and scan rate are the important instrumental parameters affecting the peak current and, hence, sensitivity of the method. Figure 5 shows the effect of accumulation potential on the peak current of the Sb - HMT complex. Both the free HMT and the Sb(III) - HMT complex

peaks overlap at the potentials more positive than - 500 mV and more negative than - 900 mV resulting in bad peak resolution and low sensitivity. The peak current was maximum at - 600 mV, then decreased at more negative potentials because of competitive adsorption of the free ligand and the complex at the electrode surface.
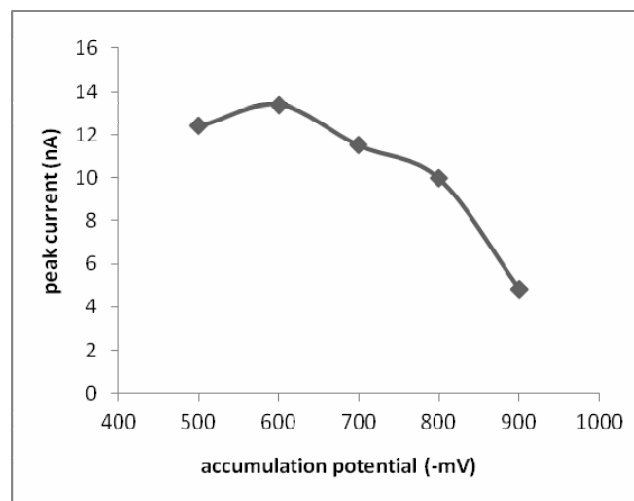

FIGURE 5 - The variation of complex peak current with accumulation potential (Conditions: $C_{Sb(III)}$: 10 µg L^{-1}, C_{HMT}:1 × 10^{-6} mol L^{-1}, pH 5, pulse amplitude:- 25 mV, scan rate: 50 mV/s).

The dependence of the peak current on the accumulation time, t_{ac}, is presented in Fig. 6. The peak current increases with the accumulation time up to 120 s, and then, slightly decreases for longer accumulation times. This is attributed to both saturation of the electrode surface and competitive adsorption of free HMT and Sb (III)-HMT complex on the electrode surface.
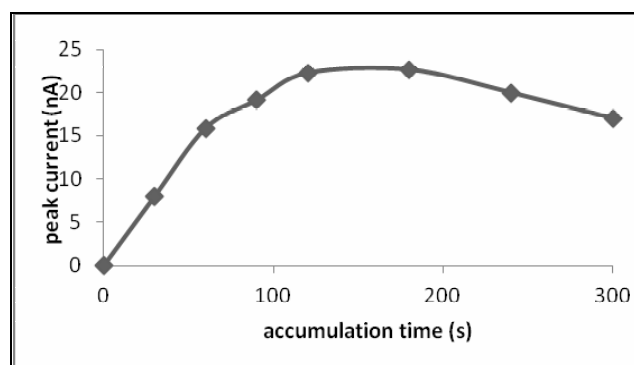

FIGURE 6 - The variation of complex peak current with accumulation time (Conditions: $C_{Sb(III)}$: 10 µg L^{-1}, C_{HMT} :1 × 10^{-6} mol L-1, pH 5, E_{acc} = - 600 mV, pulse amplitude: - 25 mV, scan rate: 50 mV/s).

The effect of the stripping modulation was investigated by using differential pulse and square wave (SW) potential scanning. SW modulation was chosen taking into account the highest peak current and the speed of the measurements. Additionally, the influences of scan rate on the peak current were studied while the other selected optimum conditions were kept constant. Scan rate was

varied from 10 to 50 mV/s. The results showed that the peak current increased by increasing scan rate; therefore, 50 mV/s was selected.

3.1 Validation and application of the method

As a result of the studies above, the optimum conditions for determination of antimony in the presence of HMT are as follows:

Supporting electrolyte and pH: acetic acid-phosphoric acid mixture and 5.0; concentration of HMT: 1×10^{-6} mol L^{-1}; accumulation potential: - 600 mV; accumulation time: 120 s; stripping mode: SW; scan rate: 50 mV/s.

Figure 7 shows some voltammograms used for drawing the calibration curve. The linear relationship was obtained in the concentration range of 2.7 - 80 µg L^{-1} (22 - 657 nmol L^{-1}). The regression line equation (r = 0.998, n = 10) is I_p = 0.954 (±0.029) C_{Sb} + 7.570 (± 1.054) where I_p is the peak current (in nA) and C_{Sb} is the concentration of Sb(III) (in µg L^{-1}). The standard error of slope and intercept of the regression line are given in paranthesis. The estimated limit of detection (*3s*) and the limit of quantification (*10s*) based on the standard deviation of blank data (n = 7) were 0.8 µg L^{-1} (6.6×10^{-9} mol L^{-1}) and, 2.7 µg L^{-1} (2.2×10^{-8} mol L^{-1}), respectively. The relative standard deviation for 5 µg L^{-1} Sb (III) (n = 9) was calculated as 3.2 %.
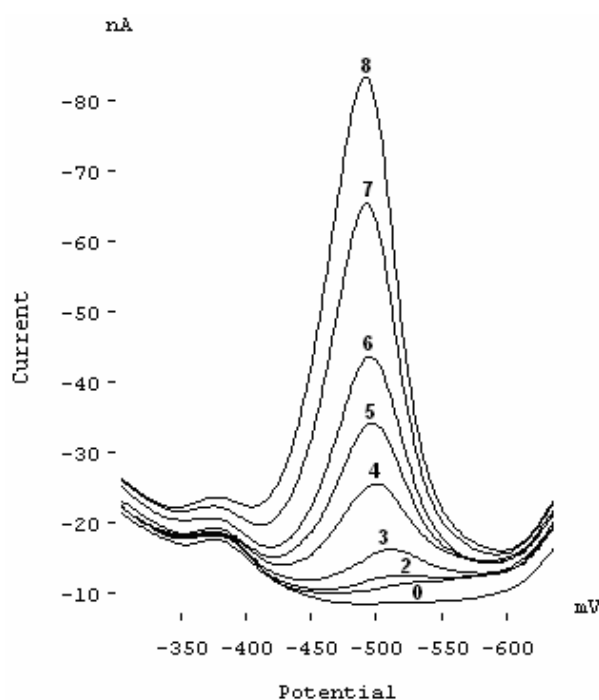
FIGURE 7- SW voltammograms of various concentration of antimony; (0) 1×10^{-6} mol L^{-1} HMT in acetic acid-phosphoric acid mixture (pH 5), (1) (0) + 3 µg L^{-1} Sb (III), (2) (0) + 5 µg L^{-1} Sb (III), (3) (0) + 10 µg L^{-1} Sb (III), (4) (0) + 20 µg L^{-1} Sb (III), (5) (0) + 30 µg L^{-1} Sb (III), (6) (0) + 40 µg L^{-1} Sb (III), (7) (0) + 60 µg L^{-1} Sb (III), and (8) (0) + 80 µg L^{-1} Sb (III).

The influence of various ions on the determinations of antimony was investigated in the presence of 20 µg L^{-1} of Sb (III). ± 5 % changing in the peak current was taken

into account as interference criterion. The results showed that B(III), Bi(III), Cr(III) and Cu(II) did not affect the peak current. The obtained voltammograms in the absence and presence of Cu(II) and Bi(III) are given in Fig. 8. The peak current and the peak potential remain almost constant in the presence of 1800 µg L^{-1} of Cu(II) and Bi(III) suggesting the selectivity of the proposed method in point of these ions (Fig. 8). Additionaly, 30-fold Al(III), 10-fold Co(II) and 10-fold Ni(II) did not interfere but 2-fold Fe(III), Pb(II) and Zn(II) decreased the peak current while Cd(II) increased the signal because of overlapping its peak with the signal. EDTA (2×10^{-3} mol L^{-1}) was added to the sample solution for eliminating the interference of the Cd(II), Fe(III), Pb(II) and Zn(II) ions.
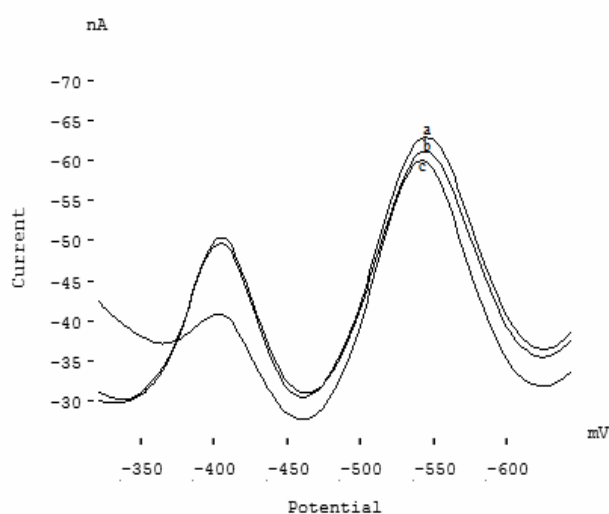
FIGURE 8 - SW voltammograms obtained in the absence and presence of Cu(II) and Bi(III) ions: (a) 1×10^{-6} mol L^{-1} HMT in acetic acid-phosphoric acid mixture (pH 5) and 30 µg L^{-1} Sb(III), (b) a + 30 µg L^{-1} Cu(II) and 30 µg L^{-1} Bi(III), and (c) a + 1800 µg L^{-1} Cu(II) and 1800 µg L^{-1} Bi(III)).
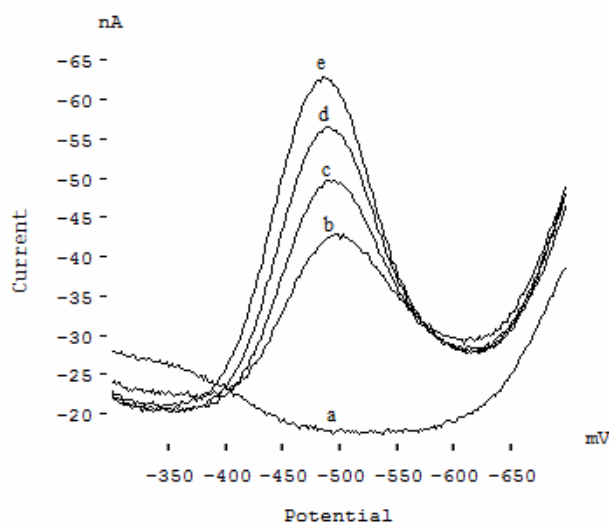
FIGURE 9 - Standard addition voltammograms for fortified drinking water sample: (a) 1×10^{-6} mol L^{-1} HMT in acetic acid-phosphoric acid mixture (pH 5), (b) water sample spiked with 20 µg L^{-1} Sb(III), (c). b + 10 µg L^{-1} Sb(III), (d) b + 20 µg L^{-1} Sb(III), and (e) b + 30 µg L^{-1} Sb(III)).

TABLE 1 - The obtained results in water samples spiked with Sb(III).

Water Samples	Sb(III) added ($\mu g\ L^{-1}$)	Sb(III) found ($\mu g\ L^{-1}\pm s$, N=3)	Bias (%)	R (%)
	-	n.d.[c]		-
DW 1[a]	3.0	2.63 (±0.28)	12.3	88
	10.0	9.18 (±0.40)	8.2	92
	20.0	21.10 (±1.10)	5.5	106
DW 2[b]	20.0	21.65 (±1.60)	8.3	108

[a] DW 1: Drinking water; [b] DW 2: Drinking water fortified with 50 $\mu g\ L^{-1}$ Cu(II), Bi(III), Co(II), Zn(II), Pb(II), Fe(III), Cr(III), Mn(II), Ni(II), Mo(VI), Hg(II), Al(III), Se(IV) and 500 $\mu g\ L^{-1}$ Na(I), K(I), Ca(II), Mg(II); [c] n.d. = not detected.

The proposed method was applied to the drinking water and fortified drinking water samples. Standard addition voltammograms obtained for the fortified drinking water sample are shown in Fig. 9. The accuracy check of the method in water samples was characterized by the use of recovery tests, and the results obtained were summarized in Table 1.

4. CONCLUSIONS

A new, selective, sensitive and accurate voltammetric method for the determination of Sb(III) in the presence of HMT was described. As far as we know, this is the first time that HMT is used in voltammetry for the determination of a cation. The method has advantages over some existing voltammetric methods [9, 12, 15] as it is free from the interference of Cu(II) and Bi(III). The method can be used with satisfactory results for the trace determination of Sb(III) in water samples, and is particularly recommended for the samples containing Cu(II) and Bi(III).

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CORRESPONDING AUTHOR

Nuri Nakiboglu
Balıkesir University
Science and Art Faculty
Chemistry Department
10145 Balıkesir
TURKEY

Phone: ++90 0266 612 10 00
Fax: ++90 0266 612 12 15
E-mail: nnuri@balikesir.edu.tr