

Determination of trace amount of antimony (III) by adsorption voltammetry on carbon paste electrode

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Abstract: A sensitive method is described for the determination of trace antimony based on the antimony-bromopyrogallol red (BPR) adsorption at a carbon paste electrode (CPE). Three steps were involved in the overall analysis: preconcentration, reduction and stripping. Optimal conditions were found to be an electrode containing 25% paraffin oil and 75% high purity graphite powder as working electrode; a 0.10 mol/L HCl solution containing 40 $\mu\text{mol/L}$ BPR as accumulation medium; a 0.20 mol/L HCl solution as reduction and stripping electrolyte; accumulation time, 150 s; reduction potential and time, -0.50 V, 60 s; scan range from -0.50 to 0.20 V. Interferences by other ions were studied as well. The detection limit was found to be 0.5 nmol/L for 150 s preconcentration. The linear range was from 1.0 nmol/L to 0.50 $\mu\text{mol/L}$. Application of the proposed method to the determination of antimony in water and human hair samples gave good results.

Key words: antimony; bromopyrogallol red; carbon paste electrode; adsorptive voltammetry

Antimony (Sb), in trace and ultra trace amounts, is an important element in biological and environmental systems. It is a toxic element, and harmful to human health seriously. It is considered as pollutant of priority interest by the Environmental Protection Agency of the United States and the Council of the European Communities. Therefore, it is not surprising that various techniques have been employed for Sb determination^[1-4], among which electrochemical stripping analysis is favored for its high sensitivity, low cost, as well as easy and rapid operation.

The application of carbon paste electrodes (CPEs) has attracted considerable attention in recent years. CPEs have several advantages such as nontoxicity, low background current, wide range of used potential, rapid renewal, and easy fabrication^[5,6]. We have reported a pyrogallol red modified carbon paste electrode for the determination of Sb (III)^[7]. Even though this method is found to be sensitive, it is only applied to spiked samples due to the interference of Cu (II). The aim of this work is to develop a simple, selective and sensitive method for the determination of Sb (III) by adsorptive voltammetry on CPE in real samples.

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1 Experimental

1.1 Apparatus

A JP-303 polarographic analyzer made by Chengdu Instrument Factory was used throughout the electrochemical experiment. A working CPE, with an inner diameter of 4 mm, was prepared by packing carbon paste in a glass tube with a stainless steel rod as the electric contact. This working electrode was used together with a platinum wire counter electrode and a saturated calomel electrode (SCE) reference electrode. A magnetic stirrer made by Shanghai Analytical Instrument Company with a teflon-coated stirring bar was used in the accumulation, cleaning, and rinsing steps.

1.2 Reagents and solutions

Chemicals were of analytical reagent grade unless otherwise stated. A 10.0 mmol/L antimony (III) stock solution was prepared by dissolving antimony oxide in 6 mol/L HCl. A 1.0 mmol/L stock solution of bromopyrogallol red (BPR) (Merck) was prepared by dissolving an appropriate amount of BPR in double distilled water.

Carbon paste was prepared by thorough mixing of 0.5 g of paraffin oil with 1.5 g of high purity graphite powder. The working electrode surface was polished on a piece of graph paper.

All other solutions were prepared using standard laboratory procedures. Double distilled water was used throughout.

1.3 Procedure

The electrode was first immersed in a preconcentration solution containing an appropriate concentration of Sb (III) and 40 $\mu\text{mol/L}$ BPR in 0.10 mol/L HCl, where the accumulation of Sb (III)-BPR complex onto the electrode was achieved, at open circuit, under constant stirring. After accumulation, the electrode was removed, rinsed with water and dried with absorbent paper. Then it was introduced into the separate voltammetric cell containing only a supporting electrolyte (0.20 mol/L HCl). A cathodic potential (-0.50 V) was applied for 60 s in the quiescent supporting medium to ensure the reduction of the accumulated species. Finally, the second-order derivative voltammogram was recorded by applying a positive-going potential scan at 100 mV/s from -0.50 V to 0.20 V. The same electrode surface could be reused without any treatment for at least 30 successive experiments. Further use required a renewal of the electrode surface by mechanical smoothing, similarly as reported elsewhere^[5,6]. All experiments were performed at room temperature and it was not necessary to remove oxygen from the solution.

2 Results and Discussions

2.1 Adsorptive and voltammetric characteristics of the Sb (III)-BPR complex on CPE

As shown in Fig.1, no peak was found when the CPE was processed as the procedure shown above in a solution containing 0.10 $\mu\text{mol/L}$ Sb (III). Anodic stripping voltammograms (ASVs) were obtained in the solution of BPR without and with Sb (III). The ASV in the solution of BPR without Sb (III) did not show any current peak in the potential range used, whereas the ASV in the solution of BPR with Sb (III) illustrated a sensitive anodic peak at about 0.06 V. It seems clear

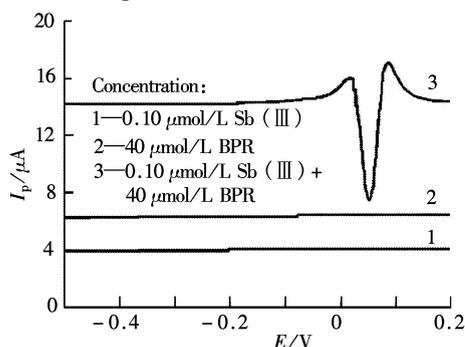


Fig.1 Anodic stripping curve (Preconcentration medium: 0.10 mol/L HCl; preconcentration time: 150 s; reduction and stripping medium: 0.20 mol/L HCl; reduction time and potential: 60 s, -0.50 V; scan rate: 100 mV \cdot s⁻¹)

that the Sb (III)-BPR complex in the solution can be accumulated on the electrode surface during the preconcentration period, and then reduced to Sb (0) during reduction interval. The anodic peak at about 0.06 V corresponds to the oxidation of Sb (0) on the electrode surface to Sb (III).

Fig.2 shows the plots of the peak current of the complex varying with accumulation time t_a for 0.10 $\mu\text{mol/L}$ and 0.050 $\mu\text{mol/L}$ Sb (III), respectively. The trends were generally the same as those obtained for this type of electrode^[5-7], i.e., both curves showed initially linear behavior, stripping peak height increased with an increasing accumulation time until the peak height reached a plateau, indicating adsorption equilibrium was achieved. The plots in Fig.2 also displays steeper slopes at higher concentrations of Sb (III), pointing to the higher rate of uptake of Sb (III)-BPR complex onto the electrode surface and also the longer accumulation time required to reach the current plateau at lower Sb (III) concentrations. A preconcentration time of 150 s was used for further studies in order to keep the linear relation under more concentration of antimony condition.

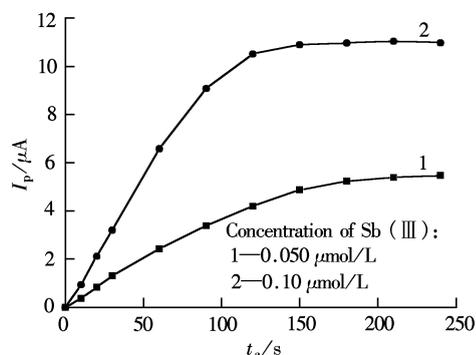


Fig.2 Effect of preconcentration time on the peak current (Other conditions are the same as in Fig.1)

In order to further investigate the behavior of the Sb (III)-BPR complex on the CPE, cyclic voltammetry was adopted. Fig.3 displays cyclic voltammograms (CVs) after preconcentration for 150 s on CPEs in 0.10 mol/L HCl solution containing 1.0 $\mu\text{mol/L}$ Sb (III) and 40 $\mu\text{mol/L}$ BPR (solid line). The anodic peak at 0.06 V corresponded to the oxidation of Sb (0) on the electrode surface to Sb (III), while the cathodic peak at -0.30 V corresponded to the reduction of Sb (III) in the Sb (III)-BPR complex to Sb (0). The fact that the peak current rapidly decreased upon repetitive scanning (dashed line) showed the Sb (0) precipitated on the electrode surface could be completely stripped into the supporting electrolyte, which conduced to the renewal of the electrode surface.

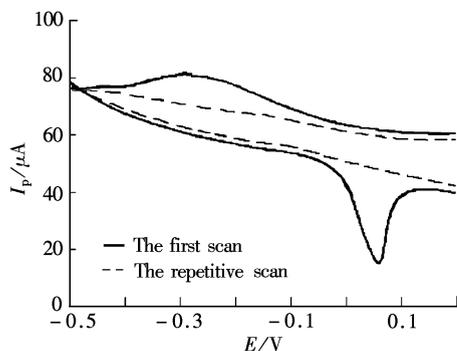


Fig.3 Cyclic voltammograms of the CPE preconcentration in 0.10 mol/L HCl solution containing 1.0 $\mu\text{mol/L}$ Sb (III) and 40 $\mu\text{mol/L}$ BPR (Scan rate is 50 mV/s, other conditions are the same as in Fig.1)

2.2 Selection of the adhesive in the electrode

The mineral butter, silicon oil, solid paraffin and liquid paraffin were used as the adhesive of the CPE. It was found that liquid paraffin was the best choice for the highest sensitivity.

The effect of paraffin oil content in the CPE was investigated as well. It was found that too high oil contents would increase the hydrophobic character of the electrode surface, limiting somewhat the Sb (III)-BPR complex adsorption on the CPE, but, however, too low loadings resulted in rather poor reproducibility due to the lack in compaction of the electrode material. Hence the CPEs containing 25% paraffin oil were employed in all subsequent experiments.

2.3 Effect of the supporting medium

Seven media, namely sodium hydroxide, phosphate buffer, Britton-Robinson buffer, acetate buffer, sulfuric acid, nitric acid and hydrochloric acid were tested as accumulation media. Of these, sulfuric acid, nitric acid and hydrochloric acid were outstanding in terms of peak shape and sensitivity. Among these three, hydrochloric acid gave the best peak shape. When the concentration of hydrochloric acid was 0.10 mol/L, the highest peak was obtained. Therefore, a 0.10 mol/L HCl solution was chosen as accumulation supporting media.

Solutions discussed above were also examined as stripping electrolyte medium. A sensitive and shape peak was obtained when a 0.20 mol/L HCl solution was used. Therefore, a 0.20 mol/L HCl solution was selected as reduction and stripping medium for further studies.

2.4 Effect of BPR concentration

Fig.4 shows the effect of variation of BPR con-

centration on the peak current. The peak current increased with increasing BPR concentration up to 30 $\mu\text{mol/L}$ BPR and remained constant when the concentration of BPR was in the range from 30 $\mu\text{mol/L}$ to 50 $\mu\text{mol/L}$. Higher concentration of BPR led to somewhat decrease of the peak current, probably due to the competitive adsorption of BPR and Sb (III)-BPR complex on the CPE surface. Thus, an optimum BPR concentration of 40 $\mu\text{mol/L}$ was selected for further experiments.

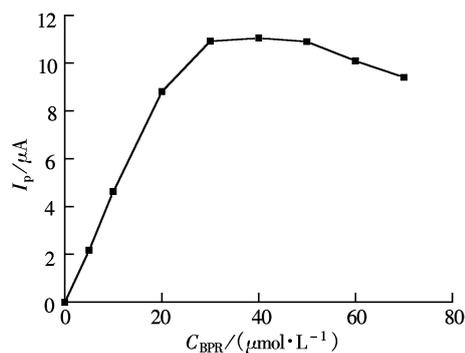


Fig.4 Effect of BPR concentration on the peak current (Other conditions are the same as in Fig.1)

2.5 Effect of reduction potential and time

Fig.5 illustrates the influence of the reduction potential E_r on the peak current. The peak current increased sharply with negative-going reduction potential up to -0.40 V and then remained constant till -0.55 V. But when the reduction potential was more negative than -0.60 V, the peak current decreased rapidly, which was due to the fact that hydrogen ions in the aqueous solution were reduced to hydrogen and, therefore, led to the exfoliation of the Sb (0) from the electrode surface. Accordingly, -0.50 V was selected as the reduction potential for all subsequent studies. Under this reduction potential, a 60 s reduction time t_r was judged to be sufficient and was therefore favored (see Fig.6).

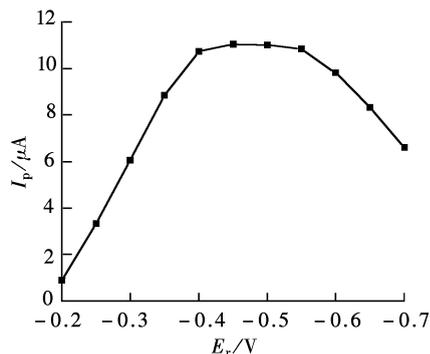


Fig.5 Effect of reduction potential on the peak current (Other conditions are the same as in Fig.1)

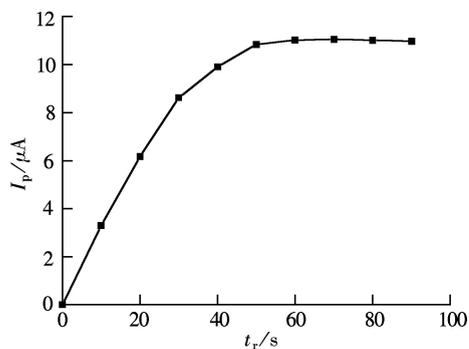


Fig.6 Effect of reduction time on the peak current (Other conditions are the same as in Fig.1)

2.6 Linear range and detection limit of the method

The second-order derivative peak current increased linearly with Sb (III) concentration in the range from 1.0 nmol/L to 0.50 $\mu\text{mol/L}$. The detection limit (three times signal to noise) was found to be 0.50 nmol/L for 150 s preconcentration. After the CPE was activated, the relative standard deviation (RSD) of 3.8% was obtained by ten successive determinations of 0.10 $\mu\text{mol/L}$ Sb (III).

2.7 Interference studies

To check the selectivity of the proposed stripping

voltammetric method for the Sb (III) ions, various metal ions, as potential interferences, were tested. The results showed that less than 500-fold molar excess of Ca^{2+} , Mg^{2+} ; 100-fold molar excess of Al^{3+} , Cr^{3+} , Zn^{2+} , Ba^{2+} , Mn^{2+} , Ti (IV); 50-fold molar excess of Fe^{3+} , Co^{2+} , Ni^{2+} , Ga (III), Ge (IV), Se (IV), V (V); 20-fold molar excess of Cd^{2+} , As (III), Sn (IV); 10-fold molar excess of Pb^{2+} , Bi^{3+} , and 5-fold molar excess of Cu^{2+} did not interfere the determination of 0.10 $\mu\text{mol/L}$ Sb (III). The sustainable coexistent concentration of Cu^{2+} , Bi^{3+} and Pb^{2+} could be increased up to 50-fold, 100-fold and 100-fold molar excess over Sb (III), respectively, by adding 1.0 mmol/L sodium oxalate into the accumulation medium.

2.8 Analytical applications

The proposed method was applied to the determination of antimony in water and human hair samples. Samples were pretreated according to Refs. [8, 9]. A suitable volume was transferred into a cell for the determination of antimony, using the procedure described above. The results, summarized in Tab. 1 and Tab.2 show satisfactory recoveries.

Tab.1 Determination results of antimony in water samples ($n=3$)

Sample	Found/($\text{nmol} \cdot \text{L}^{-1}$)	RSD/%	Added Sb (III)/($\text{nmol} \cdot \text{L}^{-1}$)	Total found/($\text{nmol} \cdot \text{L}^{-1}$)	Recovery/%
Tap water	2.31	3.9	2.00	4.34	101.5
River water	2.46	4.5	2.00	4.52	103
Waste water	12.84	4.1	10.00	22.56	97.2

Tab.2 Determination results of antimony in human hair samples ($n=3$)

Sample	Found/($\mu\text{g} \cdot \text{g}^{-1}$)	RSD/%	Added Sb (III)/($\mu\text{g} \cdot \text{g}^{-1}$)	Total found/($\mu\text{g} \cdot \text{g}^{-1}$)	Recovery/%
Human hair 1 [#]	6.46	4.3	5.00	11.32	97.2
Human hair 2 [#]	5.98	4.7	5.00	11.07	101.8

3 Conclusion

This paper presents that the bromopyrogallol red is a useful ligand for the highly sensitive and selective determination of Sb (III) by adsorptive stripping voltammetry on CPE. The cheap, nonpoisonous CPE was used instead of the severely toxic, expensive mercury electrode in this method. Thus, it has excellent environmental and economical benefit. In this method, the accumulation was achieved by non-electrochemical deposition step and the stripping analysis was performed in a pure electrolyte solution. This approach not only enhanced sensitivity but also eliminated the majority of the interferences from the sample background. Compared with the determination of antimony based on CPE previously^[7], the method presented here had a lower detection limit and was not

so strongly interfered with by other metal ions. The determination results of trace antimony in water and human hair samples gave good results.

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碳糊电极吸附伏安法测定痕量锑

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摘要: 根据锑与溴邻苯三酚红(BPR)生成的络合物在碳糊电极上的吸附特性, 建立了测定痕量锑的吸附伏安法. 整个分析过程分3个步骤: 吸附富集、还原和溶出. 用单因素变化法得出最佳试验条件为: 以含40 $\mu\text{mol/L}$ BPR的0.10 mol/L HCl为富集底液; 富集时间150 s; 还原和溶出介质为0.20 mol/L HCl; 还原电位为-0.50 V; 还原时间为60 s; 扫描范围为-0.5~0.20 V. 考察了共存离子的影响. 二次导数溶出峰电流与锑(III)浓度在1.0 nmol/L~0.50 $\mu\text{mol/L}$ 范围内呈良好的线性关系, 检出限达0.5 nmol/L. 该方法已成功应用于人发和水样中锑的测定.

关键词: 锑; 溴邻苯三酚红; 碳糊电极; 吸附伏安法

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