Antimony (Sb) is widely distributed in the environment. In general, concentration of antimony is 0.2–0.3 mg/kg in the earth crust. In the last decades, however, the Sb concentrations in environment were elevated due to human activities. The Sb pollution mainly originates from mining, industrial emission sources, fossil fuel combustion and waste incineration. Antimony is toxic and harmful to human health seriously, for example, prolonged exposure to Sb or its compounds can induce dermatitis, keratits, conjunctivits, and gastritis. Antimony trioxide is suspected of being carcinogenic in humans. Antimony and its compounds are now considered as pollutants of priority interest by Environmental Protection Agency of the United States (USEPA) and the Council of the European Communities.

There are various methods reported for environmental measurements of antimony levels, such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), gas chromatography (GC), high performance liquid chromatography (HPLC), high performance liquid chromatographic separation and inductively coupled plasma spectrometric detection (HPLC-ICP-MS) and spectrophotometry. Electroanalytical methods, due to their accuracy, sensitivity, relative simplicity, low costs and portable field-based equipment, have also been frequently used for analyzing trace antimony. Among these electrochemical techniques, adsorptive cathodic stripping voltammetry (AdCSV) is a significantly sensitive and effective technique for the determination of trace amount of metal ion. The AdCSV procedures developed for the determination of antimony were based on the adsorptive accumulation of an antimony complex on the electrode surface with different organic complexing ligands such as 2,3,4,5,7-pentahydroxyflavone (morin), pyrogallol, 4-(2-thiazolylazo)-resorcinol, catechol. The majority of these electrochemical procedures were traditionally conducted on a hanging mercury drop electrode (HMDE) or the mercury film electrode (MFE) prepared by electroplating a thin film of mercury on a suitable substrate such as glassy carbon electrode. Despite the advantages of mercury electrodes for stripping voltammetry, the toxicity of mercury or mercury salts causes risks to public health and unavoidable contamination of the environment in practice. So it is significant to develop alternative electrodes to replace the mercury electrode. Recently, bismuth-film electrode (BiFE), consisting of a thin bismuth film deposited on a suitable substrate material such as glassy carbon electrode, has been shown a similar performance with mercury electrode. Since the toxicity of bismuth and its salts is negligible, the BiFE was considered to be environmentally friendly and might be a satisfying alternative to MFE. In addition, the BiFE offers other advantages such as good mechanical stability that makes it be particularly suitable for on-line monitoring in flow systems. Recently, Ping Zong et al. applied the in situ plated bismuth-film electrode to determine antimony by Osteryoung square-wave cathodic stripping voltammetry. However, there is no report about the determination of antimony by using ex situ prepared BiFEs under mild acid conditions.

In this study, a new analytical technique was developed for the determination of antimony. The new protocol is based on square-wave AdCSV (SWAdCSV) by using an ex situ BiFE as the working electrode and gallic acid as the complexing ligand. All the antimony species in the samples were reduced to Sb(III), and then formed stable complex with gallic acid. The optimization of this method was achieved by testing the relevant experimental parameters such as deposition time, deposition potential and gallic acid concentration. Trace antimony in several environmental samples were determined by applying this developed method.

### Experimental

**Apparatus and reagents.—** An Autolab PST050 electrochemistry workstation (Radiometer, France) and a MARS microwave digestion system (CEM ModelMDS-2000, USA) were used. The working electrode was a bismuth film electrode (BiFE), the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a platinum wire. A magnetic stirrer was used for stirring the solution during the preconcentration period.

All the reagents used were of analytical grade purity unless otherwise mentioned. The 100 mg/L bismuth solution was prepared by dissolving proper amount of Bi(NO₃)₃·5H₂O (Siopharm Chemical Reagent Co., Ltd, China) in 1 M HAc-NaAc (pH 4.5). The 1000 μg/L Sb(III) was prepared by dissolving an appropriate amount of SbCl₅ (Siopharm Chemical Reagent Co., Ltd, China) in a small amount of HCl and diluting with 10% of HCl solution. A 0.1 M HAc-NaAc (pH 4.8) served as a supporting electrolyte in the analysis step. Stock solution (2 × 10⁻² M) of gallic acid was prepared in ethanol. A pH meter (PB-10 Sartorius, China) was used for pH measurements. All aqueous solutions were prepared using ultra-pure water (Milli-Q systems, USA).

**Procedure.—** Before bismuth film formation, the glassy carbon electrode (GCE) was polished with 0.30 to 1.05 μm alumina slurry
on a felt pad, thoroughly rinsed with water, and then sonicated in 5% HNO₃, ethanol and distilled water. After being cleaned, a bismuth film or a mercury film was prepared on a GCE by applying −1.0 V for 5 min in 1 M acetate buffer media (pH 4.5) with 0.08 M sodium citrate containing 100 mg/L bismuth(III)(or mercury(II)). And then the three electrodes system was immersed into 30 mL of 0.1 M HAc-NaAc solution containing Sb(III) and gallic acid. The preconcentration was carried out at −0.38 V under stirring. After accumulation, the solution was left to equilibrate for 10 s, and a cathodic SW scan to a final potential of −0.70 V was applied on the working electrode while the voltammogram was recorded. The parameters of square wave mode were as follows: frequency: 25 Hz; scan increment: 5 mV; pulse height: 50 mV. During each measurement, the ex situ prepared BiFE was cleaned by keeping the potential of the electrode at −1.3 V for 15 s to prevent memory effects. The temperature was maintained at about 25°C throughout the measurements.

The sample analysis procedure was as follows: the 0.30 g sample, 9 mL 16 M HNO₃, 1 mL concentrated HF and 1 mL 30% H₂O₂ were placed into a microwave digestion tank over night and then digested according to the microwave digestion procedure (5 min at 180°C and then 30 min at 200°C). After cooling down naturally, the seal pot of the digestion tank was opened, and each solution was heated to empty it of HNO₃ on a hotplate. Then the digestion tank was cooled down to room temperature and diluted to 25 mL in a volumetric flask with double-distilled water for analysis by SWAdCSV as mentioned above. Before analysis, the antimony(V) in the digested sample solutions were reduced to antimony(III) by reacting with proper sodium sulfite, then the solution was heated for 30 min to release the excess sulfur dioxide in boiling water.

**Results and Discussion**

**Electrochemical behavior of antimony(III) - GA complex at the bismuth film electrode.**— A cyclic voltammogram (in the range from −0.40 to −0.70 V) of the Sb(III)-GA complex with and without Sb(III). The GA (Line a in Figure 1A) shows neither oxidation peak nor reduction peak in the selected experiment condition. After adding Sb(III), a cathodic peak at −0.53 V (Line b in Figure 1A) appeared. According to V. Mirceski et al. and X. Jiang, et al. the process of the electrode reactions might be that Sb(III) and GA formed complexes in the solution after adding Sb(III), and then the Sb(III)-GA complexes were aborbed onto the surface of BiFE. The Sb(III) in Sb(III)-GA complexes was reduced into Sb(0) during the potential scanning, resulting in the reduction peak. No peak was observed in the anodic scan, suggesting that the reduction of the complex was an irreversible process.

In comparison with the ex situ prepared MFE, the SWAdCSV analysis was performed in a solution containing Sb(III) and GA at an ex situ prepared BiFE in the presence of dissolved oxygen (Figure 1B). It was obvious that the ex situ prepared BiFE (solid line) showed a better electroanalytical performance for determination of Sb(III) than the ex situ prepared MFE(dotted line). The position of peak on the ex situ prepared MFE (−0.57 V) was more negative than the counterpart on ex situ prepared BiFE (−0.53 V). There was no significant difference between peak heights in deoxygenated and non-deoxygenated solutions on the ex situ prepared BiFE, and it might be because of the insensitivity of ex situ prepared BiFES to the dissolved oxygen. Therefore, for the rest of this work, direct measurements without solution purging were adopted. In addition, the ex situ prepared BiFE was cleaned by keeping the potential of the electrode at −1.3 V for 15 s during each measurement to prevent memory effects. The change of background current in the voltammogram was used to check for hydrogen evolution. It was observed that there was no hydrogen evolution reaction during cleaning BiFE.

**The selection of optimum experimental conditions.**— In order to establish the optimum experimental conditions for a SWAdCSV method to determine antimony(III) using the ex situ prepared BiFE, the following parameters that might affect the voltammetric signal of the complex were investigated: pH, GA concentration, adsorptive accumulation time and deposit potential of the Sb(III)-GA complex.

**The effect of pH.**—The effect of pH on the stripping peak current of Sb(III)-GA complex was investigated in 0.1 M HAc-NaAc supporting electrolytes at different pH values, and each solution contained 10 μg/L Sb(III) (Figure 2). The pH of solution had an influence on the peak potentials of Sb(III)-GA complex, which changed to more negative values for higher pH values. The peak currents of Sb(III)-GA complex also varied with the change of pH from 4.0 to 5.2, and the stripping peak current reached the maximum at pH 4.8. When pH was higher than 4.8, the stripping peak currents began to decrease. Thus, the optimum condition of pH value was 4.8.

**The effect of gallic acid concentration.**—In our experiment, the stripping behaviors of the complexes that Sb(III) complexed with different ligands including gallic acid, pyrogallol, methyl gallate, catechol and catechol at the ex situ bismuth film electrode were determined in 0.1 M HAc-NaAc (not shown). The result was that the stripping peak of Sb(III)-gallic acid complex was the highest, and the shape of its peak was better than that of other complexes.

When the concentration of Sb(III) was 10 μg/L, the effect of the GA concentration on peak heights of the Sb(III)-GA complex...
The effect of pH of the supporting electrolyte on the stripping peak current of Sb(III)-GA complex in 0.1 M HAc-NaAc, Sb(III) concentration: 10 μg/L. Other conditions as Figure 1(B). The peak current of the Sb(III)-GA complex increased when the GA concentration increased up to $8 \times 10^{-5}$ M. At low concentrations, the complexation of Sb(III) with GA was not completed. So the peak currents increased with increasing GA concentration. For GA concentrations higher than $8 \times 10^{-5}$ M, the peak current started to decrease. It is possible that there was competitive adsorption of the free GA on the electrode surface. Therefore, for the following work, a GA concentration of $8 \times 10^{-5}$ M was used.

The effect of deposition potential.—When the concentration of Sb(III) was 10 μg/L, the effect of the preconcentration potential on the peak current of Sb(III)-GA complex at the bismuth film electrode was studied. It indicated that the adsorption efficiency of the complex was in the region $-0.34$ to $-0.44$ V, and it slightly increased in the range from $-0.34$ to $-0.38$ V with a maximum at $-0.38$ V, and then started to decrease. Therefore, the potential of $-0.38$ V was selected as the preconcentration potential in the following experiment.

The effect of preconcentration time.—The accumulation time was varied between 30–270 s. Figure 4 showed the influence of accumulation time vs. stripping peak current of the Sb(III)-GA complex with stirring. When the concentration of Sb(III) was 10 μg/L, the peak current increased with the deposition time from 0 to 120 s; at the higher deposition time, the peak current started to level-off since the equilibrium concentration of the adsorbed complex on the surface of the ex situ prepared BiFE was approached. When the concentration of Sb(III) was 5 μg/L, it took more time to reach the preconcentration equilibrium. Thus, a deposition time of 120 s was selected for the rest of this work. However, in the real sample analysis, the deposition time should be delayed due to the low concentration of antimony.

Linear range, detection limit and reproducibility.—Under the optimized experimental conditions, calibration plots for the determination of antimony(III) were constructed for different concentrations in the presence of dissolved oxygen. Figure 5 showed stripping voltammograms recorded for increasing Sb(III) concentration, ranging from 2 to $25 \mu$g/L (a-l). The linear regression equation was $i = 0.251 + 0.327 c$, in which $i$ and $c$ are peak current (μA) and Sb(III) concentration (μg/L), respectively, and the linear correlation coefficient ($R^2$) was 0.997. The limit of detection was 60 ng/L with a deposition time of 120 s. Other conditions as in Figure 1(B).
SMDE: static mercury drop electrode; ACSV: adsorptive cathodic stripping voltammetry; DPAdSV: differential pulse adsorptive stripping voltammetry; OWSCSV: Osteryoung square wave cathodic stripping voltammetry; CPE: carbon paste electrode; AdSV: adsorptive stripping voltammetry; CADSV: catalytic adsorptive stripping voltammetry.

Table I. The comparison of this work to some electrochemical methods of determination of antimony.

| SMDE | ACSV | HMD | DPAdSV | BiFE | CPE | HMDE | AdSV | BiFE | CADSV | HMDE | DPAdSV | BiFE | CPE | HMDE | AdSV | BiFE | CADSV | HMDE | DPAdSV | BiFE | CPE | HMDE | AdSV | BiFE | CADSV |
|------|------|-----|--------|------|-----|------|------|------|-------|------|--------|------|-----|------|------|------|-------|------|--------|------|-----|------|------|------|-------|
| Electrodes | Methods | Peak potential/ V | Linear range/ (mol/L) | Detection of limit/ (mol/L) | Real samples | References |
| SMDE | ACSV | −0.51 | 1.0 × 10⁻⁹ – 3.0 × 10⁻⁷ | 7.0 × 10⁻¹⁰ | steel and brass | 13 |
| HMDE | ACSV | −0.39 | 1.4 × 10⁻⁹ – 9.5 × 10⁻⁸ | 4.1 × 10⁻¹⁰ | red sea water wastewater | 14 |
| HMDE | DPAdSV | Sb (III) | −0.36 V | 7.8 × 10⁻⁸ – 2.0 × 10⁻⁷ | 1.0 × 10⁻¹⁰ | glucantime spiked tap water | 17 |
| HMDE | DPAdSV | Sb (V) | −0.25 V | 9.7 × 10⁻⁸ – 2.5 × 10⁻⁷ | 9.5 × 10⁻¹⁰ | | |
| HMDE | CADSV | −0.64 | 2.0 × 10⁻⁹ – 5.0 × 10⁻⁷ | 1.3 × 10⁻⁹ | gunshot residues | 18 |
| BiFE | OWSCSV | −1.15 | 8.2 × 10⁻¹⁰ – 8.2 × 10⁻⁹ | 1.6 × 10⁻¹¹ | coastal seawater river water | 23 |
| CPE | AdSV | 0.08 | 2.0 × 10⁻⁹ – 5.0 × 10⁻⁷ | 1.0 × 10⁻⁹ | water samples hair samples | 28 |
| HMDE | AdSV | −0.52 | 3.9 × 10⁻⁸ – 2.5 × 10⁻⁷ | 1.2 × 10⁻⁸ | drinking water | 29 |
| BiFE | SWAdCSV | −0.53 | 1.6 × 10⁻⁸ – 2.1 × 10⁻⁷ | 4.9 × 10⁻¹⁰ | soil limestone | Method shown in this paper |

Table II. Results for the determination of antimony in different samples and recovery rate.

| Sample | Certified value | Founda | R.S.D. (%) | Recovery |
|--------|----------------|---------|------------|----------|
| Soilb (μg/g) (GBW07406) | 60 | 60.9 | 4.13 | 41.67 | 99.79 | 95.5 |
| Limestoneb (μg/g) (GBW07720) | 100 | 99.3 | 1.81 | 81.33 | 140.21 | 98.6 |
| Glucantime spiked tap water | 17 | 153.33 | 9.7 | 55.56 | 153.33 | 96.0 |
| TrAC Trends in Analytical Chemistry | 20 | 209.17 | 8.2 | 111.11 | 209.17 | 98.3 |

aMean of three determinations.

bFrom The Institute of Geophysical and Geochemical Exploration (IGGE) for Certified reference materials (GBW07406 and GBW07720, respectively), China.

300 s, and the relative standard deviation (RSD) from the ten parallel determinations of Sb(III) at 10 μg/L was 3.37%. Some voltammetric methods for the detection of Antimony were shown in the Table I and were compared with the new developed approach in this study.

The interference.— When 8% error was allowed, potential interferences in the determination of antimony were studied. Solutions containing 10 μg/L antimony(III) and various amounts of foreign ions were prepared and measured according to the above procedure. The experimental results showed that a 1000-fold excess of K(I), Na(I), 500-fold excess of Mg(II), Ag(I), Al(III), 100-fold excess of Ni(II), Mn(II), Zn(II), 50-fold excess of Cu(II), 20-fold excess of Cr(III), Cr(VI), Cd(II), Co(II), Fe(III), In(II), Ga(II), 10-fold excess of Sn(II), Ge(II) did not interfere with the determination of Sb(III) under the selected experimental conditions. The Fe(III) ion interfered seriously at the concentration more than 20-fold excess over antimony(III), its interference eliminated by masking with proper NaF.

Analysis of samples.— In our experiment, the developed method was applied to the determination of antimony in several practice samples: a certified limestone sample and a certified soil sample. The samples were pre-treated according to the procedure described in the experimental section, and then the sample solutions were used for total antimony determination. The results are listed in Table II. The concentration of antimony in certified soil sample (the certified value is 60 ± 7 μg/g) was 60.9 μg/g with a relative standard deviation (RSD) 4.13% (n = 3). And, after adding 41.67 μg/g and 81.33 μg/g Sb(III) into the soil, respectively, the obtained result was 99.79 μg/g and 140.21 μg/g, so the recovery rate was 95.5% and 98.6% by calculation, respectively. The similar processes were conducted to detect the concentration of antimony in the certified limestone sample. The concentration of antimony in limestone (the certified value is 100 ± 4 μg/g) was 99.3 μg/g with a relative standard deviation (RSD) 1.81% (n = 3). And, after adding 55.56 μg/g and 111.11 μg/g Sb(III) into the soil, respectively, the obtained result was 153.33 μg/g and 209.17 μg/g, so the recovery rate was 96.0% and 98.3% by calculation, respectively.

Conclusions

The present study demonstrates that the square-wave adsorptive cathodic stripping voltammetry is an excellent method for the determination of trace antimony in the presence of gallic acid. The optimum conditions of this method for determination of antimony were investigated. It is demonstrated that the ex situ bismuth film electrode was suitable for the quantification of antimony at trace level with high sensitivity and good reproducibility under mild acid conditions. The proposed method was applied to the determination of trace antimony in several environmental samples, and the results were satisfied. So this study revealed the possibility of considering the ex situ bismuth film electrode as a good alternative to the mercury-based electrode in determining antimony because of its more environmentally-friendly than mercury electrode.

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