

Research Article

Determination of Total Germanium in Chinese Herbal Remedies by Square-Wave Catalytic Adsorptive Cathodic Stripping Voltammetry at an Improved Bismuth Film Electrode

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A catalytic adsorptive cathodic stripping voltammetric method on an improved bismuth film electrode (BiFE) for the determination of trace germanium in the presence of pyrogallol has been investigated. A well-defined and sensitive stripping peak of Ge(IV)-pyrogallol complex was observed at -0.79 V (versus SCE) in a 0.1 M acetate buffer solution (pH 4.8) at a deposition potential of -0.34 V. The reduction current is catalytically enhanced by adding KBrO_3 . The experimental variables and potential interference were studied. Compared with the BiFE plated in the solution prepared based on HAC-NaAc without trisodium citrate, the improved BiFE electrodeposited in the solution of HAC-NaAc containing trisodium citrate displayed a better electroanalytical performance for the determination of germanium(IV). Under the optimized conditions, the detection limit of Ge(IV) was 60 ng L^{-1} , and the relative standard deviation (RSD) was 3.73% at $5 \mu\text{g L}^{-1}$ level ($n = 9$). This method was successfully applied to determine the total germanium in several Chinese herbal remedies.

1. Introduction

Germanium is an essential trace element in human body and very important for our health. Either overaccumulation or deficiency of germanium could result in various diseases, such as acute renal failure [1]. Germanium compounds display a number of biological activities [2] and are described as antioxidants and immunostimulatory medicine that are used to inhibit the progress of cancer and destroy cancer cells [3]. Organogermanium compounds are considered to promote health and cure diseases [4].

Various analytical methods for determining the trace and ultratrace levels of germanium in medicine [4], food [5–7], water [8], and soil [5] have been reported, for example, inductively coupled plasma-mass spectrometry (ICP-MS) connected with solid phase extraction [4, 8] and combination

of hydride generation [9], graphite furnace atomic absorption spectroscopy (GF AAS) [6, 10], the spectrophotometric method [11], the hydride generation atomic fluorescence spectrometry method [12], the luminol chemiluminescence flow method [13], and electrochemical methods [5, 7, 14–16]. Among these methods, electrochemical methods show obvious advantages in accuracy, sensitivity, simplicity, low cost, and analytical speed [7]. Adsorptive stripping voltammetry (AdSV) is well suited to determine the trace metal elements. The AdSV procedures developed for the determination of germanium were based on the adsorptive accumulation of a germanium complex on the hanging mercury drop electrode (HMDE) [5, 14–18] or the mercury film electrode (MFE) [7]. Despite the advantages of mercury electrodes for stripping voltammetry, the toxicity of mercury or mercury salts could not be neglected since mercury causes risks to public health

and unavoidably contaminates the environment in practice. So it is significant to develop alternative electrodes to replace the mercury electrode. In recent decades, bismuth film electrode (BiFE), consisting of a thin bismuth film deposited on a suitable substrate material such as glassy carbon electrode, has been developed and shown a similar performance with mercury electrode [19, 20]. Since the toxicity of bismuth and its salts is negligible, the BiFE is considered to be environment friendly and might be a satisfying alternative to MFE. Moreover, the BiFE has been widely used to determine many trace elements such as Cr(VI) [21, 22], As(III) [23], Co(II) and Ni(II) [24], and Cd(II) and Pb(II) [19]. However, there is no report about the determination of germanium in Chinese herbal remedies by using BiFEs so far. And our group found that the analytical performance of bismuth film electrode was significantly improved by adding citrate to a relatively higher pH electrodeposition solution [25].

In this study, a new and sensitive analytical method was developed for the determination of germanium based on square-wave catalytic adsorptive cathodic stripping voltammetry using an improved BiFE as the working electrode and pyrogallol as a complexing ligand. The optimization of the developed technique was achieved by testing the relevant experimental parameters such as pH value, deposition time, deposition potential, and pyrogallol concentration. The method was successfully applied to determine the trace germanium in several Chinese herbal remedies.

2. Experimental

2.1. Apparatus and Reagents. An Autolab PST050 electrochemistry workstation (Radiometer, France) and a microwave digestion system (CEM Model MDS-2000, USA) were used. A three-electrode electrochemical cell system was used with the multimode electrode: 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. PGENERAL TAS-990 atomic absorption spectrophotometer (Chengdu Superman S&T Co., Ltd., China).

All the reagents used were of analytical grade purity unless otherwise stated. The 1000 mg L^{-1} bismuth solution was prepared by dissolving proper amount of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., China) in 5% HNO_3 . The germanium standard solutions were made from a stock of $1000 \mu\text{g mL}^{-1}$ Ge(IV) (China Iron & Steel Research Institute) by dilution with water as required. A 0.1 M HAc-NaAc (pH 4.8) served as a supporting electrolyte in the analysis step. Stock solution (0.02 mol L^{-1}) of pyrogallol was prepared weekly and was stored at 4°C in a refrigerator. A pH meter (PB-10 Sartorius, China) was used for pH measurements. All aqueous solutions were prepared using ultrapure water (Milli-Q systems, USA).

2.2. Procedure

2.2.1. SWAdCSV Measurements of Germanium(IV). Prior to bismuth film formation, the glassy carbon electrode (GCE)

was polished with a $0.3\text{--}0.05 \mu\text{m}$ alumina slurry on a felt pad, thoroughly rinsed with water, and then sonicated in 5% HNO_3 , ethanol, and distilled water. A bismuth film was prepared on a GCE by applying -1.0 V for 5 min in a 100 mg L^{-1} bismuth(III) and 1 mol L^{-1} acetate buffer media (pH 4.5) with 0.08 mol L^{-1} sodium citrate. Then the three-electrode system was immersed into 30 mL 0.1 mol L^{-1} HAc-NaAc (pH 4.8) solution that contained $3 \times 10^{-4} \text{ mol L}^{-1}$ KBrO_3 ; $1.3 \times 10^{-3} \text{ mol L}^{-1}$ pyrogallol was added into the volumetric cell. The preconcentration potential (-0.34 V versus SCE) was applied while the solution was stirred for 150 s. The solutions were stopped and followed by a 15 s equilibration time. And then the voltammogram recorded by applying a negative scan from -0.5 to -1.0 V using the square-wave mode with the following parameters: frequency: 25 Hz; scan increment: 4 mV; pulse height: 50 mV. After the ground voltammogram has been obtained, the adsorptive stripping experiment was repeated for the addition of proper germanium stock solution. The electrode was cleaned at -1.3 V for 10 s before each measurement.

2.2.2. Determination of Germanium(IV) in Real Samples. The analysis procedure of Chinese herbal remedies sample was as follows: the 0.5 g sample, 5 mL HNO_3 , and 1 mL H_2O_2 were placed into a microwave digestion tank overnight and then digested according to a microwave digestion procedure (5 min at 180°C and then 15 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 HNO_3 on a hotplate (120°C). Then the digestion tank was cooled down to room temperature and diluted to 25 mL in a volumetric flask with double-distilled water. These sample solutions were analyzed by SWAdCSV as mentioned above.

3. Results and Discussion

3.1. Electrochemical Behavior of Germanium(IV)-Pyrogallol Complex at the Improved Bismuth Film Electrode. Figure 1 shows the SWAdCSV response for $10 \mu\text{g L}^{-1}$ Ge(IV) obtained at (c) BiFE plated in 1 mol/L acetate buffer (pH 4.5) without trisodium citrate and (d) the improved BiFE plated in 1 mol/L acetate buffer (pH 4.5) containing 0.08 mol/L trisodium citrate. And it was obvious that the BiFE (d) electrodeposited in HAc-NaAc medium containing sodium citrate also showed a better electroanalytical performance for determination of Ge(IV) than the BiFE (c). According to Zhang et al. [25] and Nunes and Faria [26], the significant improvement was due to the addition of trisodium citrate that helped form a homogeneous structure by aggregates of spherical particles with a few nanometers in diameter. We also investigated the effect of KBrO_3 on the electrochemical behavior of germanium(IV)-pyrogallol complex at the improved bismuth film electrode. No stripping peak of pyrogallol was observed (see Figure 1(a)). When Ge(IV) was present together with pyrogallol in the solution, a well-defined stripping peak of the Ge(IV)-pyrogallol complex was observed at a potential of -0.79 V (see Figure 1(b)). When KBrO_3 was added into the above solution, the reduction peak current of the complex

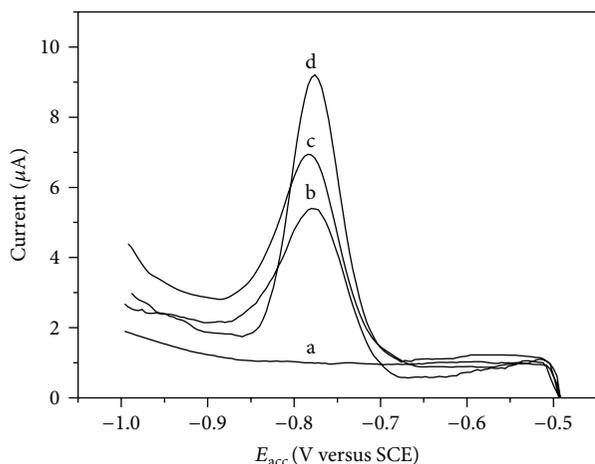


FIGURE 1: Square-wave stripping voltammograms recorded at the improved BiFE plated in 1 mol L^{-1} acetate buffer (pH 4.5) containing 0.08 mol/L trisodium citrate (a, b, and d) and the BiFE (c) plated in 1 mol/L acetate buffer (pH 4.5) without trisodium citrate: (a) 0.1 mol L^{-1} HAC-NaAc (pH 4.8) + pyrogallol ($1.3 \times 10^{-3} \text{ mol L}^{-1}$); (b) a + $10 \mu\text{g L}^{-1}$ Ge(IV); (c, d) b + $2 \times 10^{-4} \text{ mol L}^{-1}$ KBrO_3 ; deposition potential: -0.34 V ; deposition time: 150 s; SW frequency: 25 Hz; scan increment: 4 mV; pulse height: 50 mV.

significantly increased (see Figure 1(d)). The catalytic current occurred at the reduction potential of the Ge(IV)-pyrogallol complex owing to the addition of BrO_3^- . On the basis of the experimental results, the possible reaction mechanism is that Ge(IV) forms complex with pyrogallol, which subsequently is adsorbed on surface of the BiFE. During the voltammetric scan, Ge(IV) in the complex is reduced to Ge(0), which is then oxidized chemically to Ge(IV) by BrO_3^- . And then the reoxidized Ge(IV) contributes to the reduction current again, producing the catalytic cycle (see Figure 2).

Cyclic voltammograms (in the range from -0.5 to -1.0 V) of the Ge(IV)-pyrogallol complex with and without Ge(IV) after preconcentration at the BiFE were shown in Figure 3. The pyrogallol (see Figure 3(a)) shows that neither oxidation peak nor reduction peak was observed in the potential window studied here under the selected experiment condition. After adding Ge(IV), the Ge(IV)-pyrogallol complex showed a cathodic peak, at -0.79 V (see Figure 3(b)), arising from the reduction of the Ge(IV) in Ge(IV)-pyrogallol complexes to Ge(0). There was no peak observed in the anodic scan, indicating that the reduction of the complex was an irreversible process.

3.2. The Selection of Optimum Experimental Conditions. In order to establish the optimum experimental conditions for a SWAdCSV method to determine germanium(IV) using BiFE, the following parameters that might affect the voltammetric signal of the complex as variables were investigated: pH, pyrogallol and KBrO_3 concentrations, adsorptive accumulation time (t_{acc}), and accumulation potential (E_{acc}) of the germanium(IV)-pyrogallol complexes.

3.2.1. The Effect of the Supporting Electrolyte and pH. In our experiment, the stripping behavior of the Ge(IV)-pyrogallol complex at the improved bismuth film was determined in different supporting electrolytes, including HAC, HAC-NaAc, HNO_3 , HCl, H_2SO_4 , $\text{NH}_3\text{-NH}_4\text{Cl}$, and NH_4Ac . The results showed that HAC-NaAc buffer solution was more suitable for the stripping of Ge(IV)-pyrogallol complex due to the well-defined stripping peak, low background current, and high sensitivity.

The effect of pH on the stripping peak current of Ge(IV)-pyrogallol complex was investigated in 0.1 mol L^{-1} HAC-NaAc solutions at different pH values (see Figure 4). The peak currents of the complex varied with the change of pH from 4.0 to 5.4. The pH of the solution also had an influence on the peak potentials, which changed to more negative values for higher pH values. For example, for a pH of 4.0, the peak potential of Ge(IV) was -743 mV ; for a pH of 5.4, the peak potential was -821 mV . 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 values is pH 4.8.

3.2.2. The Effect of Pyrogallol Concentration. The effect of the pyrogallol concentration on peak current of the Ge(IV)-pyrogallol complex was investigated in the range 3.0×10^{-4} – $1.5 \times 10^{-3} \text{ mol L}^{-1}$ (see Figure 5). At low pyrogallol concentrations, the complexation of Ge(IV) with pyrogallol was not completed. So the peak currents increased with increasing pyrogallol concentration up to $1.3 \times 10^{-3} \text{ mol L}^{-1}$. When pyrogallol concentration was higher than $1.3 \times 10^{-3} \text{ mol L}^{-1}$, the peak current started to decrease. It is possible that there was competitive adsorption of the free pyrogallol on the electrode surface. Therefore, for the following work, a pyrogallol concentration of $1.3 \times 10^{-3} \text{ mol L}^{-1}$ was used.

3.2.3. The Effect of KBrO_3 Concentration. The effect of KBrO_3 concentrations on the stripping peak current of the Ge(IV)-pyrogallol complex was studied. The results indicated that KBrO_3 enhanced the stripping sensitivity of the complex. At KBrO_3 concentrations smaller than $3 \times 10^{-4} \text{ mol L}^{-1}$, the peak height increased rapidly with increasing KBrO_3 concentration, but, subsequently, it increases slowly, and distortion of the cathodic side of the peak was observed. Therefore, the concentration $3 \times 10^{-4} \text{ mol L}^{-1}$ was used in the further experiments.

3.2.4. The Effect of Accumulation Potential and Accumulation Time. The effects of the accumulation potential and accumulation time on the stripping peak current of Ge(IV)-pyrogallol complex on the improved bismuth film electrode were studied. The preconcentration potential was examined over the range from -0.34 to -0.38 V in the experiment with a deposition time 180 s and is shown in Figure 6. The largest peak current was obtained at a deposition potential of -0.34 V , and the peak current decreased slowly at more negative potentials. Electrostatic exclusion may be responsible for the observed effect. Since the germanium(IV)-pyrogallol

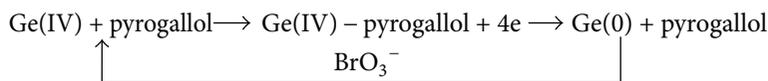


FIGURE 2

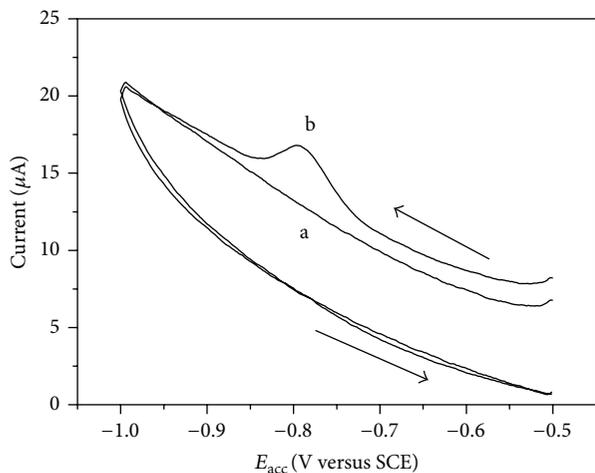


FIGURE 3: Cyclic voltammograms recorded at a BiFE plated in 1 mol L^{-1} acetate buffer (pH 4.5) containing 0.08 mol/L trisodium citrate: (a) 0.1 mol L^{-1} HAc-NaAc (pH 4.8) + pyrogallol ($1.3 \times 10^{-3} \text{ mol L}^{-1}$) + $2 \times 10^{-4} \text{ mol L}^{-1}$ KBrO_3 ; (b) a + Ge(IV) ($20 \mu\text{g L}^{-1}$); deposition potential: -0.34 V ; deposition time: 150 s ; potential scan rate: 50 mV s^{-1} .

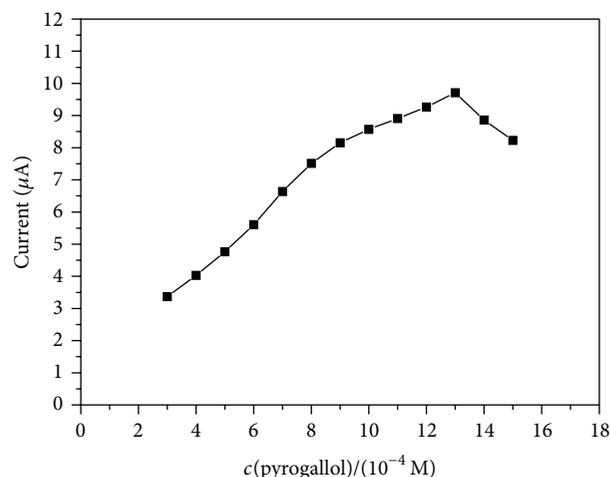


FIGURE 5: The effect of the pyrogallol concentration on the stripping peak current of Ge(IV)-pyrogallol complex in 0.1 mol L^{-1} HAc-NaAc + $3 \times 10^{-4} \text{ mol L}^{-1}$ KBrO_3 ; Ge(IV) concentration: $10 \mu\text{g L}^{-1}$. Other conditions as in Figure 1.

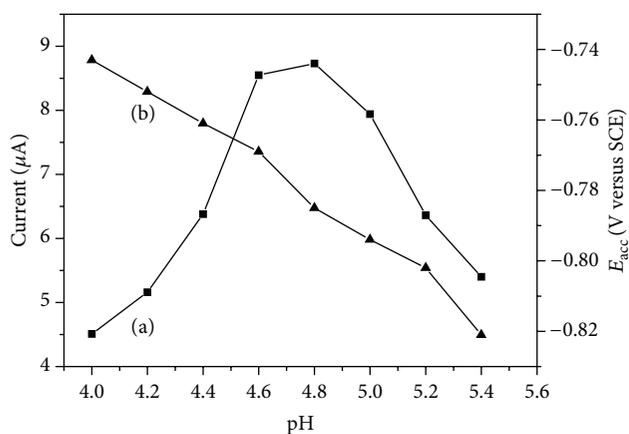


FIGURE 4: The effect of pH of the supporting electrolyte on the stripping peak current (a) and the position of peak (b) of Ge(IV)-pyrogallol complex in 0.1 mol L^{-1} HAc-NaAc + pyrogallol ($1.3 \times 10^{-3} \text{ mol L}^{-1}$) + $3 \times 10^{-4} \text{ mol L}^{-1}$ KBrO_3 ; Ge(IV) concentration: $10 \mu\text{g L}^{-1}$. Other conditions as in Figure 1.

complex appears to be negatively charged, a more positive potential is favorable for its adsorption at BiFE, but too positive potential would damage the BiFE. Thus, -0.34 V was selected as the accumulation potential in the further procedures.

The dependence of the maximum stripping peak current on the accumulation time was examined for samples

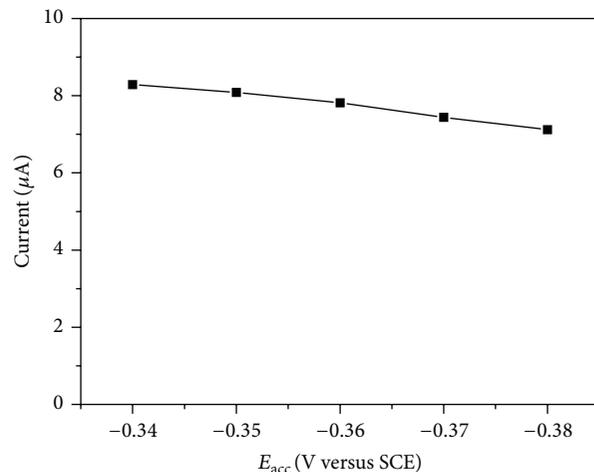
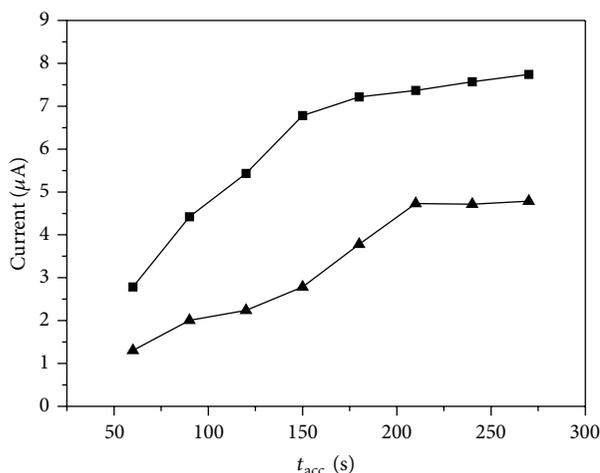


FIGURE 6: The effect of pre-concentration potential on the stripping peak current of Ge(IV)-pyrogallol complex. Other conditions as in Figure 1.

containing $5 \mu\text{g L}^{-1}$ and $10 \mu\text{g L}^{-1}$ germanium(IV) in the range of $0\text{--}270 \text{ s}$ (see Figure 7). The maximum peak height was observed at 150 s and 210 s for $10 \mu\text{g L}^{-1}$ and $5 \mu\text{g L}^{-1}$ germanium(IV), respectively, and was constant during the longer time. Therefore, a deposition time of 180 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 germanium(IV).

TABLE 1: Results for the determination of total germanium in several Chinese herbal remedies and the recovery rate.

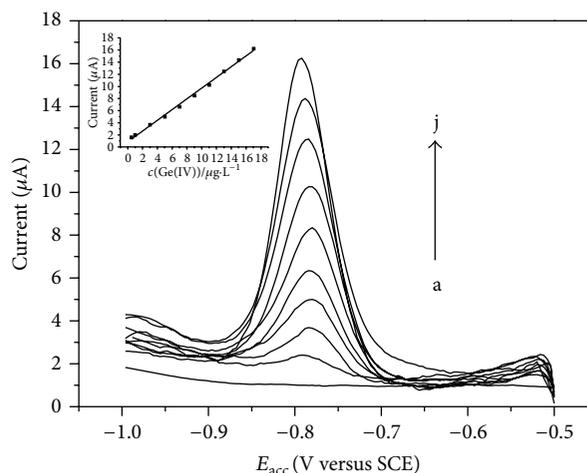
Sample	GF AAS	Found ^a	RSD (%)	Recovery		
				Addition	Found ^a	Recovery rate (%)
Cultivated ganoderma lucidum ($\mu\text{g g}^{-1}$) ^b	3.22	3.18	1.41	10.00	13.15	99.7
Wild ganoderma lucidum ($\mu\text{g g}^{-1}$) ^b	1.29	1.32	3.05	5.00	6.34	100.4
Polygonum multiflorum thunb ($\mu\text{g g}^{-1}$) ^b	0.47	0.49	3.62	5.00	5.38	97.8

^a $n = 3$.^bFrom a pharmacy, Beijing, China.FIGURE 7: The dependence of the stripping current of Ge(IV)-pyrogallol complex on the accumulation time, pyrogallol concentration $1.3 \times 10^{-3} \text{ mol L}^{-1}$, $5 \mu\text{g L}^{-1}$ (▲) Ge(IV), and $10 \mu\text{g L}^{-1}$ (■) Ge(IV). Other conditions as in Figure 1.

3.3. Linear Range, Detection Limit, and Reproducibility.

Under the optimum experimental conditions, a linear relationship between the peak current and the germanium(IV) concentration was obtained in the range of 0.5 to $17 \mu\text{g L}^{-1}$ (see Figure 8) in the presence of dissolved oxygen. The linear regression equation was $i = 0.886c + 0.856$, where i and c are peak current (μA) and Ge(IV) concentration ($\mu\text{g L}^{-1}$), respectively, and the linear correlation coefficient (R^2) was 0.995 . The voltammogram obtained for the lowest concentration with an accumulation time of 540 s was 60 ng L^{-1} , and the relative standard deviation from the nine parallel determinations of Ge(VI) at $5 \mu\text{g L}^{-1}$ was 3.73% .

3.4. The Interference. Two major sources of interference were investigated. First, potential interferences from other metal ions in the determination of germanium(IV) were studied. Various ions were examined as possible interferences by the addition of the interfering ions to a solution containing $10 \mu\text{g L}^{-1}$ Ge(IV) using the optimum experimental conditions. The results indicated that a 500-fold excess of Mg(II), a 200-fold excess of Cd(II), Co(II), Cr(III), Fe(III), Ni(II), Pb(II), Zn(II), and Mn(II), and a 5-fold excess of Sn(II), Sb(III) did not interfere in the determination of Ge(IV) with an error less than 5%.

FIGURE 8: Adsorptive stripping curves of Ge(IV) concentrations from 0 to $17 \mu\text{g L}^{-1}$ (a-j) (a: 0 , b: 0.5 , and c-j: 1 - 17 (in the step of $2 \mu\text{g L}^{-1}$)) obtained at the bismuth film electrode. Pyrogallol concentration $1.3 \times 10^{-3} \text{ mol L}^{-1}$. Other conditions as in Figure 1.

In addition, naturally occurring organic compounds can be adsorbed onto the electrode surface and interfere with the adsorptive voltammetric analysis. The interference of anionic surfactant sodium dodecylbenzene sulfonate (SDBS) and the cationic surfactant cetyltrimethylammonium bromide (CTMAB) was investigated. The Ge(IV) signal diminished by 49 and 67% after addition of 3.48 mg L^{-1} SDBS and 3.64 mg L^{-1} CTMAB, respectively.

3.5. Analysis of Samples. In our experiment, the developed method was applied to determine of total germanium in several Chinese herbal remedies: cultivated ganoderma lucidum, wild ganoderma lucidum, and polygonum multiflorum thunb. The samples were pretreated according to the procedure described in Section 2, and then the sample solutions were used for germanium determination. The results are listed in Table 1, and the recovery rate is from 97.8 to 100.4%. And the accuracy of the proposed method was assessed by comparing the results obtained by SWAdCSV with those obtained by GF AAS.

4. Conclusions

In this study, we developed a new method for determining the total germanium by square-wave catalytic adsorptive

stripping voltammetry at an improved bismuth film electrode. And we got the optimum condition for the germanium determination. Total germanium in several Chinese herbal remedies was determined by using this optimized method, and the results were consistent with those obtained by GF AAS. It is demonstrated that the catalytic adsorptive Ge(IV)-pyrogallol-KBrO₃ system is suitable for determining trace germanium with high sensitivity, simplicity, and good reproducibility and with being environment friendly.

Conflict of Interests

The authors have declared no conflict of interests.

Authors' Contribution

Shangwei Zhong and Jiali Su have equally contributed to this work.

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