Underpotential Deposition Study and Determination of Bismuth on Gold Electrode by Using Voltammetry

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The cyclic voltammetry (CV) and the semidifferential anodic stripping voltammetry (SdASV) were used for investigation of bismuth(III) underpotential deposition (UPD) on gold electrode. Based on the excellent electrochemical properties of Au/Bi UPD system, a new method for determining bismuth(III) was established. A solution of 0.1 mol/L HNO_3 was selected as the supporting electrolyte. Factors affecting the Bi(III) UPD and stripping steps were investigated and an optimized analytical procedure was developed. The calibration plots for Bi(III) concentration in the range 1.25×10^{-8}—1.0×10^{-7} mol/L were obtained. The detection limit, calculated as three times the standard deviation of the analytical signal of 8.3×10^{-8} mol/L for a 90 s electrodeposition at 0.00 V (while the solution magnetically stirred at a speed of 300 rpm), was 7.5×10^{-9} mol/ L. For 8 successive determinations of 1.25×10^{-7} mol/L Bi(III), the obtained RSD (relative standard deviation) was 0.4%. The developed method was applied to bismuth determining in medicine and urine samples. The analytical results were compared with that of atomic emission spectrometry (AES) method.

Keywords bismuth, underpotential deposition, determination, gold disk electrode, cyclic voltammetry, semidifferential anodic stripping voltammetry

The combination of stripping voltammetry with UPD can lead to the improvement of sensitivity, selectivity and reversibility for electroanalytical purpose and avoid the use of toxic mercury as the work electrode[1] and then analytical applications have been described.[2-4] In this work, we develop a new method to quantify bismuth based on the UPD properties of Au/Bi system.

Bismuth is a medicine element generally used for curing gastric disease, so it is necessary to evaluate the existence of the element in some pharmaceuticals. Conventional anodic stripping voltammetry (ASV), because of its higher sensitivity, simple equipment and lower cost, has been adopted to study and determine bismuth with carbon paste electrode in practice samples.[5]

The general UPD properties of bismuth on gold,[6-8] platinum[8,9] and iridium[10,11] have been investigated. The aim of this work is to develop a high sensitivitive and selectivitive analytical method for the determination of bismuth based on the concept of UPD combining the semidifferential anodic stripping voltammetry (SdASV) which usually possesses more well-defined peak shape and higher sensitivity.[12,13]

Experimental

Instrument

A CHI660 Electrochemical workstation (USA) for CV measurements and a MP-1 potentiometric stripping analyzer (Jining, Shandong Province, China) for SdASV testing were used.

Chemicals

The stock solution of Bi(III) (0.10 mol/L) was prepared by dissolving 4.8507 g of $Bi(NO_3)_3 \cdot 5H_2O$ (Shanghai, AR) in 2.5 mol/L HNO_3. All standard solutions of Bi(III) were diluted with 0.1 mol/L HNO_3(Sha-

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nghai, AR) from the stock solution. A solution of HNO_3 (0.1 mol/L) served as the supporting electrolyte. A double-distilled water was used in all above solution.

Cell

A 25 mL of glass cell was used in a 3-electrode configuration. The work electrode was a gold disk electrode. The counter electrode was a platinum wire and the reference electrode was a Hg/Hg_2Cl_2 electrode (SCE).

Preparation of the gold disc electrode

The gold disc electrode with a surface area of 0.0314 cm^2 was polished with 0.5 μm aluminum oxide powder to mirror-like finish. The electrode was then rinsed with water, immersed in an ultrasonic bath for 5 min and rinsed again. The newly treated electrode can be used to determine SdASV curves in a week. While the electrode was not in use it stored in pure water.

Pretreatment of samples

A 0.1000 g of sample powder of stomach medicine (bisuc stomach tablets, the marked composition per tablet: bismuth aluminic 200 mg, sodium bicarbonic 200 mg, succus liquiritiae 300 mg, cortex frangulae 25 mg, magnes carbonic 400 mg, fructus foeniculi 10 mg, produced by Shiquan Medicine Limited Company, Harbin, China, license number is 20000453) was transferred to a quartz beaker and then 4.0 mL of concentrated HNO_3 was added. The sample was decomposed on a temperature-adjustable sand-bath at about 200 ℃. After 30 min, 2 mL of concentrated $HClO_4$ was added. Until the sample was near dryness, 3 mL of concentrated HNO_3 was added. After cooled to room temperature, the sample was diluted to 250 mL with HNO_3 (0.1 mol/L). Aliquots of 0.01—1.00 mL of the diluted sample solutions were added to 20 mL of HNO_3 (0.1 mol/L). Then the bismuth was directly determined by using SdASV with the three standard additions methods.

For testing recovery of bismuth in urine samples, 2.5 mL of urine and 0.10 mL of Bi^{3+} (1.0×10^{-5} mol/L) were transferred to a quartz beaker immediately. After the addition of 2.0 mL of concentrated HNO_3 to sample collection, it was heated on a temperature-adjustable sand-bath at about 100 ℃. Aft0er 30 min, 1.0 mL of $HClO_4$ was added to the beaker. Then the tempera-ture was increased to 200 ℃ till the volume was reduced to about 0.5 mL. The sample was added to 1.0 mL of H_2O_2 and heated till near dryness. After the sample was cooled to room temperature, 20 mL of HNO_3 (0.1 mol/L) was added. The sample solution was directly determined by using SdASV. The analysis of the sample was performed with three standard additions. Each addition should contribute an analytical signal of about 30% of that of the sample. The results were corrected for the amount of bismuth contributed by the chemicals used in the sample pretreatment.

SdASV *analytical procedure*

The analysis was performed with removal of oxygen in a 20 mL of supporting electrolyte of HNO_3 (0.1 mol/L). The SdASV analytical procedure consisted of the following steps: (a) conditioning of the electrode: a potential (E_{cond}) is applied for a period of time (T_{cond}) to ensure dissolution of remaining deposits. The optimum condition parameter is: $E_{cond} = 0.45$ V (vs SCE) and $T_{cond} = 10$ s; (b) the UPD step: deposition potential (E_{dep}) = 0.00 V (vs SCE), deposition time (T_{dep}): 90 s $\leqslant T_{dep} \leqslant$ 240 s, stirring speed : 300 rpm; (c) equilibrium time (T_{rest}) = 30 s; (d) the stripping step was performed with semidifferential voltammetry, initial potential (E_{in}) is 0.00 V, fine potential (E_f) is 0.45 V.

Evaluation of the analytical signal of the SdASV

The semidifferential current corresponding to the stripping peak of UPD Bi (e, $\mu A \cdot s^{-1/2}$) was used to quantify the content of bismuth.

Investigations of UPD *characteristics*

Cyclic voltammetry (CV) was used to understand the basic UPD property of bismuth so as to optimize the analysis conditions. The procedure is as follows. After polishing and cleaning as indicated in the section of "preparation of gold disc electrode", the gold electrode was immersed in the 20 mL of solution of supporting electrolyte without oxygen (oxygen was removed previously by using nitrogen). The CV curves were recorded by applying a cyclic potential scan model in the range of −0.45—0.45 V.

Results and discussion

Underpotential and bulk deposition of bismuth(III) *on* Au

Figs. 1, 2 and 3 show the cyclic voltammograms of Bi^{3+} at different concentrations. For 10^{-5} mol/L Bi^{3+} (Fig. 1), only one pair of peaks was observed. The UPD process displayed a peak potential ($E_{p,UPD}$) at −0.090 V and the stripping reaction displayed a peak potential ($E_{p,UPD\text{-}S}$) at 0.290 V. There are no bulk deposition (BD) and corresponding stripping (BD-S) peaks to be observed at this lower concentration level. It is interesting to note that the change of the Bi^{3+} concentration (c_{Bi}) has obvious effect on the $E_{p,UPD}$, $E_{p,UPD\text{-}S}$ and bulk deposition as seen in voltammograms which was displayed in Figs. 2 and 3. Both $E_{p,UPD}$ and $E_{p,UPD\text{-}S}$ shifted to a positive direction with increasing c_{Bi}. At the same time, another pair of peaks corresponding to the bulk deposition gradually occurred in a more negative potential range. For 1×10^{-4} mol/L Bi^{3+} (Fig. 3), the $E_{p,UPD}$ shifted to 0.045 V and $E_{p,UPD\text{-}S}$ to 0.320 V. The peak potential of bulk deposition (E_{BD}) occurred at −0.180 V and the peak potential of bulk stripping ($E_{BD\text{-}S}$) at 0.068 V. The reduction peak of the bulk deposition is too low to be observed in Fig. 2. This phenomenon of peak potential shift with increasing c_{Bi} can be observed repeatedly in the millimolar range. On the other hand, the peak currents of UPD ($I_{p,UPD}$) and UPD-S ($I_{UPD\text{-}S}$) keep roughly unchanged with the increasing of c_{Bi}. This feature indicates the typical monolayer property because of the saturated covering of the adsorbed atoms at that concentration range. The effect of c_{Bi} on cyclic voltammetric results is briefly summarized in Table 1.

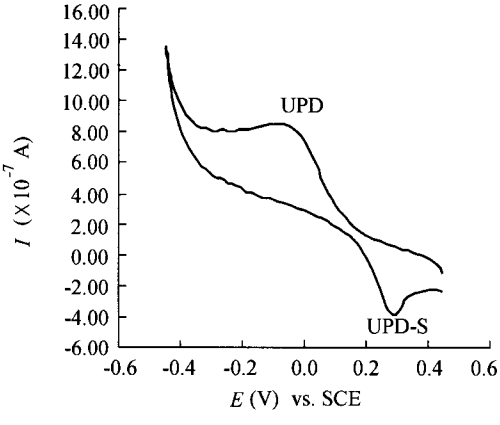

Fig. 1 Cyclic voltammograms of 1×10^{-5} mol/L Bi^{3+}. The supporting electrolyte is 0.1 mol/L HNO_3, scan rate: 10 mV/s.

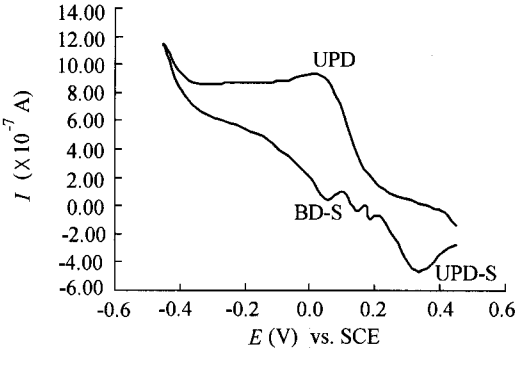

Fig. 2 Cyclic voltammograms of 5×10^{-5} mol/L Bi^{3+}. The supporting electrolyte is 0.1 mol/L HNO_3, scan rate: 10 mV/s.

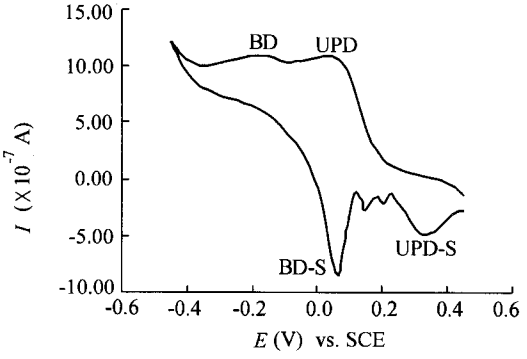

Fig. 3 Cyclic voltammograms of 1×10^{-4} mol/L Bi^{3+}. The supporting electrolyte is 0.1 mol/L HNO_3, scan rate: 10 mV/s.

UPD peaks, because they have more positive peak potentials and better reversibility than those of bulk deposition peaks, are very suitable to be used for analytical purpose. This approach can avoid as less as other coexisted metals to depositing on the electrode surface, which often take place in a relatively negative range of deposition potential, so it is advantageous to increase the selectivity.

SdASV *technique and working window*

The one aim of this work is to analyze bismuth at nanomolar concentration range with the aid of excellent characteristics of bismuth UPD monolayer Bi on gold sub-

Table 1 Effect of c_{Bi} on cyclic voltammetric results

c_{Bi} ($\times 10^{-5}$ mol/L)	$E_{p,UPD}$ (V)	$I_{p,UPD}$ ($\times 10^{-7}$ A)	$E_{p,UPD\text{-}S}$ (V)	$I_{p,UPD\text{-}S}$ ($\times 10^{-7}$ A)	$E_{p,BD}$ (V)	$I_{p,BD}$ ($\times 10^{-7}$ A)	$E_{p,BD\text{-}S}$ (V)	$I_{p,BD\text{-}S}$ ($\times 10^{-8}$ A)
1	-0.090	8.48	0.290	-3.86	—	—	—	—
5	-0.023	8.50	0.310	-3.92	—	—	0.060	5.0
10	0.045	8.55	0.320	-3.95	-0.18	1.0	0.072	-80

strate. Because of the technique with much better resolution and higher sensitivity, SdASV were used to determine bismuth. The obtained SdASV curves at different concentration level were displayed in Fig. 4. In contrast with that of in millimolar, only a well-defined single stripping peak with a stable peak potential was observed in the concentration range of ten fold nanomolar to hundred nanomolar as shown in the figure. This is the one of the reasons why UPD peak was chosen as the analytical signals. As seen from the SdASV curves in Fig. 4, the UPD Bi stripping peak is located at 280 mV.

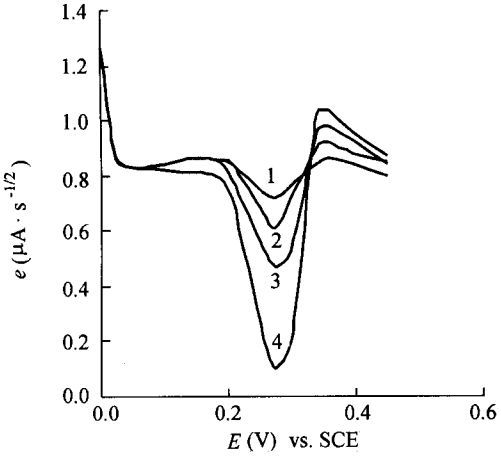

Fig. 4 SdASV curves of Bi^{3+}. A solution of 0.1 mol/L HNO_3 contains (1) 3.1×10^{-8} mol/L Bi^{3+}, (2) 8.3×10^{-8} mol/L Bi^{3+}, (3) 1.5×10^{-7} mol/L Bi^{3+} and (4) 2.7×10^{-7} mol/L Bi^{3+}. Supporting electrolyte: 0.1 mol/L HNO_3. $T_{dep} = 90$ s, scan rate: 88 mV/s.

The work window of the electrode for SdASV procedure is decided by the UPD behavior of Bi^{3+} as shown in Fig. 1. The most negative potential should not cause the bulk deposition at a higher Bi^{3+} concentration level, however it makes the reduction of adsorbed Bi^{3+} to be completed metal Bi. The dissolution of gold starts at 0.7 V, which decides the most positive potential. So a most suitable potential window from 0.00 V to 0.45 V was chosen in the experiment.

Saturated surface coverage of UPD *at millimolar concentration*

The surface coverage of UPD Bi was measured by using chronocoulometric method. A steady state Q_a of 3.97 μC was found, which corresponding to 126.4 $\mu C/cm^2$ charge and 4.37×10^{-10} mol/cm^2 surface coverage.

Reproducibility and detection limits

The reproducibility of the SdASV, expressed as the relative standard deviation (RSD) of 8 consecutive experiments performed. For the solution of HNO_3(0.1 mol/L) + Bi^{3+} (1.25×10^{-7} mol/L) with an electrodeposition condition of $E_{dep} = 0.00$ V, $T_{dep} = 90$ s, the obtained RSD was 0.4%.

The detection limit, calculated as three times the standard deviation of the analytical signal of 8.3×10^{-8} mol/L for a 90 s electrodeposition at 0.00 V, was 7.5×10^{-9} mol/ L.

Relationship between SdASV *signal e and* c_{Bi}

The SdASV method was applied to bismuth determination in the range of 1.25×10^{-8}—1×10^{-7} mol/L. A linear relationship was observed between the SdASV signal e and Bi^{3+} concentration (c_{Bi}). Linear regression analysis gave an equation,

$$e(\mu A \cdot s^{-1/2}) = 0.03723 + 3.274 \times 10^{6}\, c_{Bi}(mol/L)$$

The obtained correlation coefficient is 0.9991.

Determination of bismuth in the presence of coexisting ions.

According to the UPD behavior of Bi^{3+}, the ions possesses very closed peak potential to Bi^{3+} UPD may cause the possibility of interference. In the nanomolar concentration range, It was found that 100-fold Pb^{2+}, 20-fold Tl^{+},

100-fold Mg^{2+}, 100-fold Ca^{2+}, 500-fold Na^{+}, 500-fold K^{+} and 20-fold Cl^{-} didn't interfere the determination of bismuth. The serious interference was caused by Ag^{+}, Sb^{3+} and Cu^{2+}. 2-fold Cu^{2+}, 1-fold Sb^{3+} and 2-fold Ag^{+} made the stripping peak shape of UPD Bi obviously changed. The reason is that these three ions can undergo similar UPD process on the gold surface. So it is necessary for using a separation procedure when this method is to be used in a sample containing Ag^{+}, Sb^{3+} and Cu^{2+}. In this work, the medicine and urine samples were used to quantify bismuth. The obtained analytical results were compared with those of atomic emission spectrometry (AES). The sample analytical experiments indicated that there was no interference to be observed and the obtained analytical results were satisfactory.

Analysis of bismuth in medicine and standard spiked urine samples

The analytical results of the bismuth in medicine samples were shown in Table 2. The adaptability of this method to urine samples was tested by the degree of recovery. The obtained recovery data was shown in Table 3.

Table 2 Determination of bismuth in the gastric medicine

Content (%)	Average content (%)	RSD (%)	Average content(%) by AES[a]
6.03 5.65 5.78 5.89 6.27 6.02 5.94 5.61	5.90	3.6	6.01

[a] ICP/6500 (PE co. USA), wavelength 223.061 nm.

Table 3 Recovery of bismuth in urine samples

Testing time	Added Bi^{3+} (mg/mL)	Found ($\times 10^{-6}$ mg/mL)	Average ($\times 10^{-6}$ mg/mL)	RSD (%)	Average recovery (%)
9	1.04×10^{-5}	9.8 9.9 9.4 9.4 9.6 11.0 9.3 9.6 9.8	9.76	5.2	93.8

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