Combining chemical reduction with an electrochemical technique for the simultaneous detection of Cr(VI), Pb(II) and Cd(II)

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This work herein reports the approach for the simultaneous determination of heavy metal ions including cadmium (Cd(II)), lead (Pb(II)), and chromium (Cr(VI)) using a bismuth film electrode (BFE) by anodic stripping voltammertry (ASV). The BFE used was plated *in situ*. Due to the reduction of Cr(VI) with H_2O_2 in the acid medium, on one hand, the Cr(III) was produced and Cr(VI) was indirectly detected by monitoring the content of Cr(III) using square-wave ASV. On the other hand, Pb(II) was also released from the complex between Pb(II) and Cr(VI). Furthermore, the coexistence of the Cd(II) was also simultaneously detected with Pb(II) and Cr(VI) in this system as a result of the formation of an alloy with Bi. The detection limits of this method were 1.39 ppb for Cd(II), 2.47 ppb for Pb(II) and 5.27 ppb for Cr(VI) with a preconcentration time of 120 s under optimal conditions ($S/N = 3$), respectively. Furthermore, the sensitivity of this method can be improved by controlling the deposition time or by using a cation-exchange polymer (such as Nafion) modified electrode.

Introduction

Electrochemical stripping voltammetry has been established as a powerful tool for the determination of trace metals.[1–4] It showed remarkable sensitivity due to the combination of an effective preconcentration step and advanced electrochemical measurements of the accumulated analytes. The choice of the working electrode is crucial for the success of the stripping operation.[5] Most commonly, mercury film electrodes (MFEs) have been used because of high reproducibility and sensitivity.[6] However, the dramatic toxicity of mercury has prevented it from being popular. Therefore, extensive research efforts have been focused on finding new mercury-free electrode materials. Recently, bismuth film electrodes (BFEs) have been identified as alternatives to MFEs due to their remarkably low toxicity and their performance, which has proved to be equal to or even superior to that of MFEs.[7–9]

As we know, cadmium (Cd(II)), lead (Pb(II)), and hexavalent chromium (Cr(VI)) are harmful to the human beings, especially Cr(VI), which has been recognized as a known human respiratory carcinogen and toxic pollutant.[10–13] Furthermore, the issue of the restriction of the use of certain hazardous substances (RoHS) in electronics and electronic equipment in 2003 also makes it more imperative for the detection of these heavy metal ions.

Recently, considerable efforts have been devoted to the investigation of the determination and quantification of trace Cr(VI) in solution. Some of these methods rely on spectroscopic methods,[14–18] such as, atomic absorption spectrometry (AAS), where Cr(VI) was detected with 1,5-diphenylcarbazide[15] and total chromium by AAS.[18] In addition, electrochemical techniques have attracted more interests[19–27] due to high sensitivity, portability, and the ability to distinguish Cr(VI) from Cr(III). Among all the electrochemical detections, adsorptive stripping voltammetry (AdSV) has been commonly adopted due to the spontaneous adsorption of surface-active complexes of chromium with diethylenetriamine pentaacetic acid (DTPA)[19,20] or cupferron.[21] Lately, the BFE has also been developed to detect Cr(VI) using catalytic adsorptive stripping voltammetry by Wang and co-workers.[26]

However, the simultaneous electrochemical detection of Pb(II), Cd(II) and Cr(VI) has never been reported using the BFEs. This may be attributed to two factors. On one hand, the electrochemical technique adopted for the detection of Cr(VI) was different from that used for Pb(II) and Cd(II) due to the different redox processes. Anodic stripping voltammertry (ASV) is usually used for the detection of Pb(II) and Cd(II) at bismuth film coated electrodes due to the formation of alloys with bismuth, whereas AdSV is commonly applied to detect Cr(VI), which can not form an alloy with bismuth. On the other hand, the formation of the complex ($PbCrO_4$) between Pb(II) and Cr(VI) makes it insensitive and inaccurate for the determination of both heavy metal ions.

In order to achieve the simultaneous detection of Pb(II), Cd(II) and Cr(VI), the work presented combined chemical reduction with an electrochemical technique. By reducing the Cr(VI) using H_2O_2 in an acid medium, Cr(III) was produced and Pb(II) was released from $PbCrO_4$. Then the square-wave ASV (SWASV) was followed to simultaneously detect Cr(III), Pb(II) and Cd(II) due to the formation of alloys with bismuth (Fig. 1). Furthermore, the sensitivity of this method can be improved by controlling the deposition time and by modifying the electrode surface with a cation-exchange polymer, such as Nafion.

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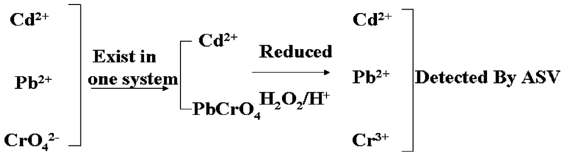

Fig. 1 The schematic illustration of simultaneous detection of Cr(VI), Pb(II) and Cd(II).

Experimental

Chemical and reagents

All solutions were prepared with double-distilled water. All chemicals employed in this work were of analytical reagent grade and used as received. Cr(VI), Cr(III), Cd(II) and Pb(II) were prepared by diluting the corresponding standard stock solutions prepared with $K_2Cr_2O_7$, $CrCl_3 \cdot 6H_2O$, $CdCl_2$ and $Pb(NO_3)_2$, respectively. $Bi(NO_3)_3$ was used for the bismuth film electrode by diluting the corresponding standard stock solution. 0.1 M acetate buffer (pH 4.5), prepared by mixing appropriate amounts of CH_3COOH and CH_3COONa, and was used to prepare solutions of the supporting electrolyte. The reductant reagent H_2O_2 was freshly prepared prior to experiments.

Apparatus

SWASV was performed with a conventional three-electrode system, with a CHI 630 electrochemical workstation (CH Instruments, USA). A bismuth coated glassy-carbon (GC) electrode (3 mm diameter) was used as the working electrode, with an Ag/AgCl (saturated KCl) electrode and a platinum wire acting as the reference and counter electrodes, respectively. Prior to each experiment, the GC electrode was polished with water slurry of 0.3 and 0.05 µm Al_2O_3 powders, and then rinsed with HNO_3 solution, ethanol and water, respectively.

Nafion film modified electrode

A 6 µL drop of the Nafion (1%) solution was placed on the electrode surface and the solvents were left to evaporate at room temperature for 10 min.

Real sample preparation

0.1 g polypropylene was acidified in a mixture of 1 mL 30% H_2O_2 and 8 mL concentrated nitric acid for 5 hours, and then the sample was solubilized by a microwave-accelerated reaction system MARS-X (CEM). Finally, the sample was transferred into flasks and diluted to 25 mL as the stock solution. For the analysis, 5 mL of polypropylene (adjusting the pH of the solution to 4.5 when used), 2.5 mL of 1.0 M acetate buffer and 17.5 mL de-ionized water were prepared.

The sewerage sample was supplied from a sewage treatment plant in Changchun, and was filtered through a 0.22 µm membrane (Millipore). The sample was prepared with 0.2 M acetate buffer and treated by H_2O_2 in acid media before determination.

Procedure for SWASV analysis

The three electrodes were immersed into the electrochemical cell, containing 5 mL 0.1 M acetate buffer (pH 4.5), 1.0 ppm Bi(III) and the target metal ions. The BFE was prepared *in situ* by spiking the sample with the required concentration of Bi(III) and simultaneously depositing Bi and the target metals on the surface of the electrode at −1.4 V under stirring for 120 s. Following the preconcentration step, the stirring was stopped, and after 20 s, the voltammogram was recorded by applying a positive-going square-wave voltammetric potential scan (with a frequency of 15 Hz, amplitude of 25 mV and potential step of 5 mV). The scan was terminated at 0.3 V. A cleaning step (120 s at 0.3V, with solution stirring) was used to remove the target metals and Bi prior to the next cycle.

Pre-plating of the Bi film was carried out according to a previous report.[28]

Results and discussion

Effect of the concentration of bismuth solution on the SWASV response

The effect of the concentration of bismuth on the stripping peak currents of Pb(II), Cd(II) and Cr(III) was studied in the range from 0 to 3.0 ppm, each containing 20 ppb Pb(II), Cd(II) and Cr(III) with a deposition time of 120 s. Well defined and sharp stripping peaks for Cd(II), Pb(II) and Cr(III) were observed when the Bi(III) was present in the electrochemical cell (Fig. 2, inset). The stripping peak currents of Pb(II), Cd(II) and Cr(III) increase rapidly at first with the increase of the bismuth concentration, and then decrease slightly, as shown in Fig. 2. In this case, the concentration of the bismuth solution controlled the thickness of the Bi film. When the concentration of the bismuth solution increased, the Bi film coated on the electrode surface was thicker, which influenced the heights of the peaks of Pb(II), Cd(II) and Cr(III). In

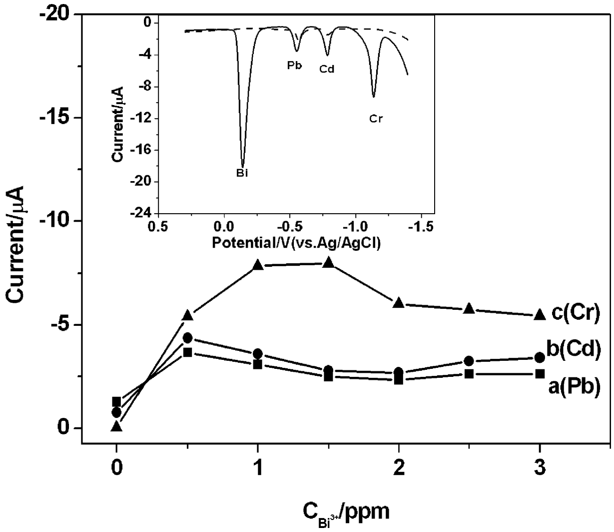

Fig. 2 The effect of the concentration of bismuth on the stripping peak currents of calibration samples of 20 ppb Pb(II), Cd(II) and Cr(III). Inset: the different SWASVs responses of calibration samples of 20 ppb Pb(II), Cd(II) and Cr(III) in the absence of Bi (dotted line) and in the presence of 0.5 ppm Bi (solid line) at GC electrode.

order to get good sensitivity, 1.0 ppm Bi(III) was chosen as optimal concentration for the subsequent determinations.

SWASV responses of samples of Pb (II), Cd (II) and Cr(III) and samples of Pb (II), Cd (II) and Cr(VI) after reducing by H_2O_2 at the bismuth film electrodes

Fig. 3 shows the different SWASV responses of the sample of 40 ppb Pb(II), Cd(II) and Cr(III) (solid line) and the sample of 40 ppb Pb(II), Cd(II) and Cr(VI) after adding H_2O_2 in acid medium (dotted line) at the BFEs, respectively. The BFEs were modified by *in situ* depositing of bismuth and the metals on the bare GC electrode. At both BFEs, three peaks at −1.13 V for Cr(III), −0.78 V for Cd(II) and −0.54 V for Pb(II) were obtained. As depicted in Fig. 3, the responses of the two samples show similar SWASV behaviors and almost equal peak heights. This phenomenon may be attributed to the reaction between H_2O_2 and CrO_4^{2-} in acid medium.[29] The reaction can be represented by the eqn (1):

$$3H_2O_2 + 10H^+ + 2CrO_4^{2-} \rightarrow 2Cr^{3+} + 8H_2O + 3O_2 \qquad (1)$$

Therefore, by reducing the Cr(VI) using H_2O_2 in the acid medium, on one hand, the production of Cr(III) made the simultaneous detection with Pb(II) and Cd(II) by SWASV possible, on the other hand, it released the Pb from the complex between Pb(II) and CrO_4^{2-}. In order to confirm further, we also compared the SWASV responses of a standard sample of Pb(II), Cd(II) and Cr(VI) before and after reduction by H_2O_2. The SWASV responses reduced if the sample was not reduced by H_2O_2, especially for Pb(II). The SWASV responses for Pb(II) reduced 71%. This phenomenon may be attributed to the interactions between Pb(II) and CrO_4^{2-} which makes the determination of heavy metal ions inaccurate and insensitive.

Effect of the concentrations of H^+ and H_2O_2

To our knowledge, H_2O_2 is usually used as oxidant in basic medium,[30] whereas, in acidic medium, reduction may be performed.[31] The concentrations of H^+ and H_2O_2 are very important for the reduction of Cr(VI) to Cr(III) completely, according to eqn (1). The concentration of acid solution (C_{H^+}) in the range of 0.05 mM–0.5 mM was investigated, as shown in Fig. 4. The highest SWASV respons of sample was obtained when C_{H^+} was 0.125 mM. When C_{H^+} was more than 0.125 mM, the SWASV responses were relatively low. The effect of concentration of H_2O_2 ($C_{H_2O_2}$) was also studied in the range of 0.125 mM–1.0 mM. The maximum SWASV response of the sample was obtained when the $C_{H_2O_2}$ was 0.25 mM (Fig. 5). When the concentration of H_2O_2 was more than 0.25 mM, the SWASV responses reduced slightly.

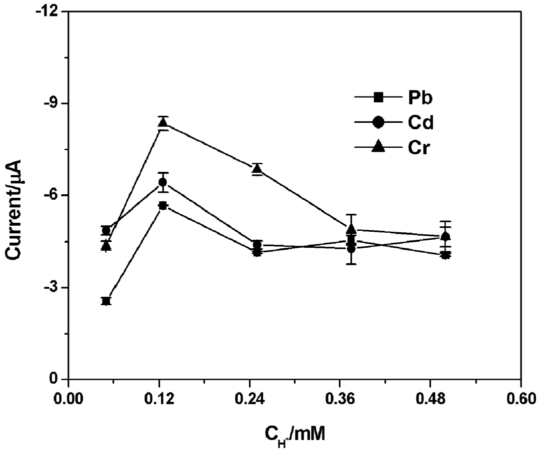

Fig. 4 The effect of the concentration of H^+ containing 1.0 mM H_2O_2 in the presence of 40 ppb Pb(II), Cd(II) and Cr(VI) in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1.0 ppm Bi^{3+}.

In addition, when the concentrations of H^+ and H_2O_2 were more than the optimal concentration, the stability was also decreased. Considering the reaction completely and good stability, the 0.125 mM H^+ and 0.25 mM H_2O_2 was chosen as optimal concentration for subsequent determinations.

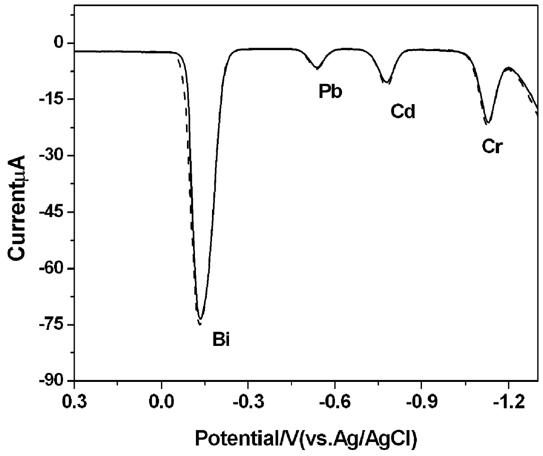

Fig. 3 The SWASVs of the sample of 40 ppb Pb(II),Cd(II) and Cr(III) (solid line) and the sample of 40 ppb Pb(II), Cd(II) and Cr(VI) after adding H_2O_2 in acid medium (dotted line) at BFE in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1.0 ppm Bi^{3+}.

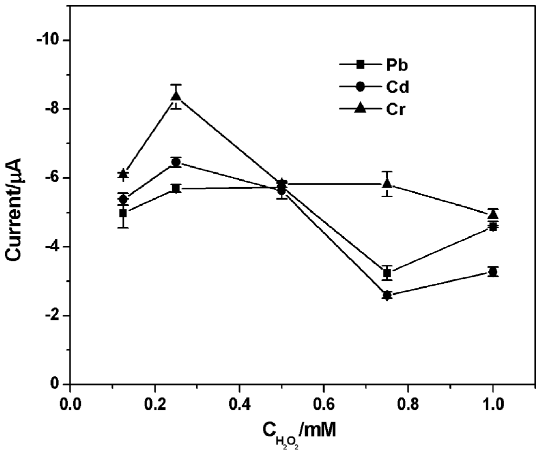

Fig. 5 The effect of the concentration of H_2O_2 containing 0.125 mM H^+ in the presence of 40 ppb Pb(II), Cd(II) and Cr(VI) in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1.0 ppm Bi^{3+}.

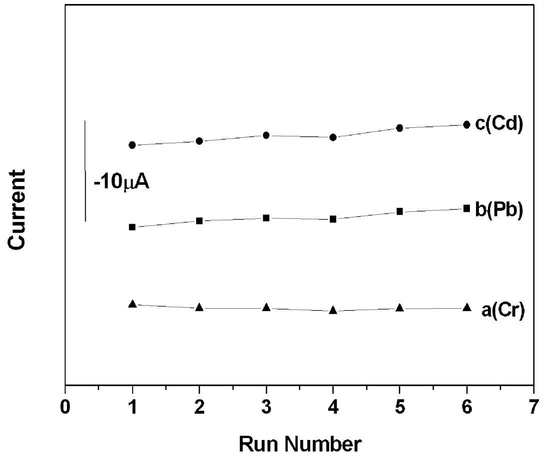

Fig. 6 The stability of 6 repetitive measurements of 100 ppb Pb(II), Cd(II) and Cr(VI) in 0.1 M HAc–NaAc (pH 4.5) buffer after adding 0.125 mM H^+ and 0.25 mM H_2O_2 containing 1 ppm Bi^{3+}.

The stability of the bismuth film coated electrode

A series of 6 repeated measurements of 100 ppb Pb (II), Cd(II) and Cr(VI) in pH 4.5 acetate buffer after adding 0.125 mM H^+ and 0.25 mM H_2O_2, were used for demonstrating the stability of the BFE (Fig. 6). The relative standard deviation for the entire series is 3.21%, 2.67%, and 1.71% for Pb(II), Cd(II) and Cr(VI), respectively. The good stability may be attributed to the character of BFE which is less susceptible to oxygen background interference than MFE.

Calibration data

Calibration curves for the simultaneous determination of Pb(II), Cd(II) and Cr(VI) after adding H_2O_2 in acid medium at BFEs were achieved by SWASV under optimal conditions. The SWASV results for different concentrations of Pb(II), Cd(II) and Cr(VI) are illustrated in Fig. 7. The resulting calibration plots are linear over the range from 10 ppb to 100 ppb, 20 ppb to 100 ppb and 10 ppb to 70 ppb for Pb(II), Cd(II) and Cr(VI), respectively, with a preconcentration time of 120 s. The calibration curves and correlation coefficients are $y = 0.23x - 2.53$, $r = 0.990$, $y = 0.39x - 7.53$, $r = 0.990$ and $y = 0.19x + 0.80$ for Pb (II), Cd(II) and Cr(VI), respectively, with a deposition time of 120 s (x: concentration/ppb, y: current/μA). Based on three times the background noise (S/N), the limits of detection were 1.39 ppb for Cd(II), 2.47 ppb for Pb(II) and 5.27 ppb for Cr(VI). In order to improve the sensitivity of the approach, two strategies were investigated. One is controlling the deposition time, as depicted in Fig. 8(A).

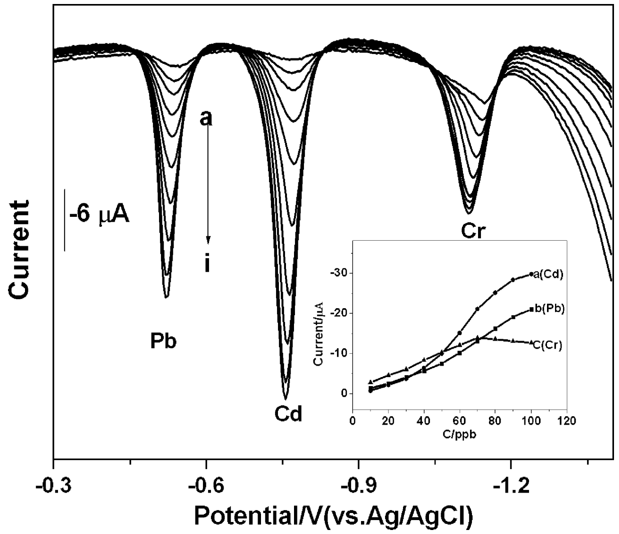

Fig. 7 The square-wave stripping voltammograms for increasing levels of Pb(II), Cd(II), and Cr(VI) in 10 ppb steps (a–i) after adding 0.125 mM H^+ and 0.25 mM H_2O_2 in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1 ppm Bi^{3+}. Inset: the calibration curves of Pb(II), Cd(II) and Cr(VI), respectively.

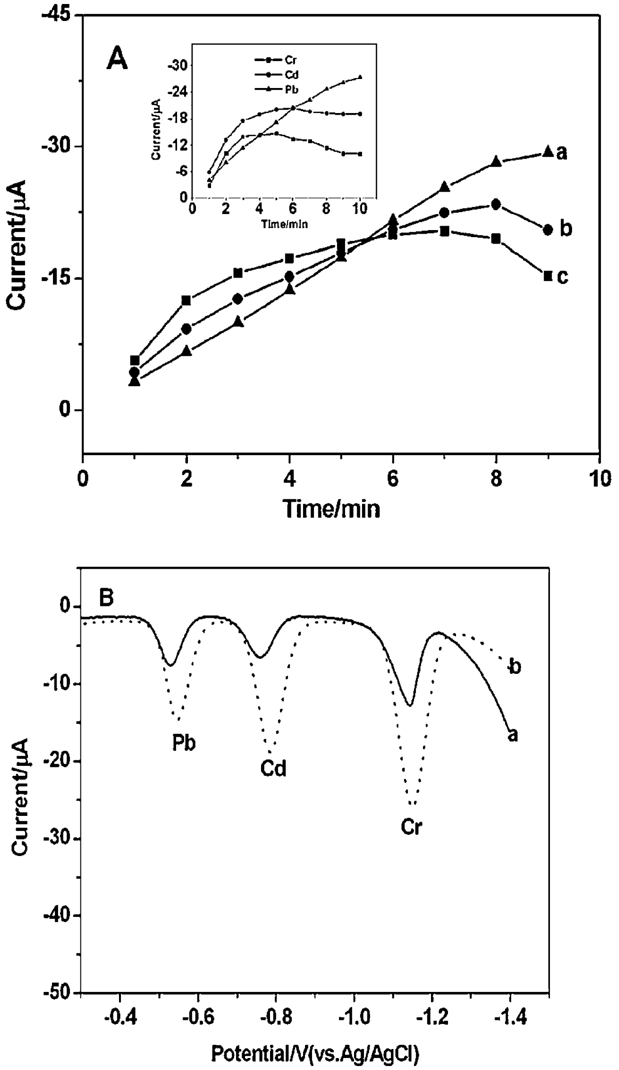

Fig. 8 (A) The effect of the deposition time in the presence of 50 ppb (a) Pb, (b) Cd and (c) Cr after adding 0.125 mM H^+ and 0.25 mM H_2O_2 in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1.0 ppm Bi^{3+}. Inset: results using the pre-plated Bi film electrode. (B) The different SWASVs of 50 ppb Pb(II), Cd(II) and Cr(VI) after adding 0.125 mM H^+ and 0.25 mM H_2O_2 in 0.1 M HAc–NaAc buffer (pH 4.5) containing 1.0 ppm Bi^{3+} at (a) BFE and (b) NCFE.

Table 1 Results for the determination of metal ions in the real samples by SWASV and ICP-OES/ICP-MS

	SWASV (ppb)			ICP-OES/ICP-MS (ppb)		
Sample	Pb	Cd	Cr	Pb	Cd	Cr
Polypropylene	83.2	41.7	45.0	82.6	50.6	52.6
Sewerage	7.69	6.55	—	7.91	6.29	—

At the initial deposition time, the stripping current for the three metal ions increased linearly with the preconcentration time. It may be attributed to the enhanced accumulation of the metals. However, as the deposition times increased, the thickness of the Bi film also increased and its effect became more primary. In addition, we also investigated the response with the pre-plated Bi film (Fig. 8(A), inset). It was found that the effect of the deposition time on each of the three analytical ions was nearly consistent with that obtained at the BFE plated *in situ*. We also investigated the effect of modified electrode surface with Nafion, as shown in Fig. 8(B). The Nafion-coated thin bismuth film electrode (NCBFE) can enhance the response of metal ions due to its ion-exchange character. Moreover, this modified electrode can offer higher resistance to the organic interferences.[5]

Application

The NCBFEs were applied for the determination of metal ions in different real samples. In all cases, the method of standard addition was selected for quantification. In the case of polypropylene, the use of the NCBFE did not show its superiority. This is maybe attributable to the low concentration of surfactants in this sample.[32] Therefore, in this case, the BFE was chosen to perform the detection. The results of analysis are shown in the Table 1. The result was satisfactory compared with that obtained by ICP-OES.

An attempt to determine metals ions in sewerage was also made. For this analysis, use of the bare BFE was impossible because of the presence of various surface-active compounds. In contrast, the NCBFE showed well-defined and stable peaks of Cd(II) and Pb(II), although the Cr was undetectable in this sample. The results of analysis by SWASV (Table 1) were consistent with those obtained by ICP-MS.

Conclusions

By combining chemical reduction with an electrochemical technique, the simultaneous detection of Cr(VI), Pb(II) and Cd(II) using one bismuth film coated electrode was implemented due to the formation of alloys between heavy metals and bismuth. Due to the production of Cr(III), on one hand, this method can be used to the indirect determination of Cr(VI), on the other hand, it can be used to monitor the total quantity of chromium. Moreover, this approach simplifies the detection process of heavy metal ions.

Acknowledgements

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