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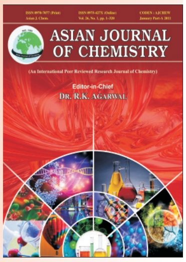

Bismuth as Internal Standard for Reliable Detection of Trace Lead at Screen-Printed Electrode

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In this paper, bismuth served as an internal standard used for reliable anodic stripping voltammetric determination of trace lead at screen-printed carbon electrodes. Besides its negligible concentration in water samples, bismuth can form alloy with lead and their anodic stripping peaks can be separated obviously. The influence of three electrode pretreatment methods and various experimental parameters upon the stripping signal was investigated. Under optimized conditions, the response ratio I_{Pb}/I_{Bi} against the concentration of lead was linear in the 2-200 μg L^{-1} concentration range with a correlation coefficient of 0.998 after 2 min deposition. The practical application of this method was carried out for the determination of lead in river water samples and the results were consistent with the values obtained by ICP-MS. The attractive behaviors of the low cost carbon strip electrodes coupled with the reliable quantitative strategy facilitates the development of portable electrochemical sensing platform.

Keywords: Bismuth, Internal standard, Screen-printed electrodes, Anodic stripping voltammetry, Lead.

INTRODUCTION

With the rapid development of economy, a large number of pollutants are poured into environment which causes great damage to ecosystem and human health. Among the multitude of chemical contaminates, heavy metals are considered potential hazardous contaminants in the biosphere to human health due to their high toxicity, unbiodegradation and can accumulate tens of thousands of times[1,2]. As one of the highly harmful heavy metals that pollute the natural environment, lead is still widely used in several industrial areas, *e.g.* storage batteries, cable sheath, solders, anticorrosion coatings and petrol additives[3,4]. Lead poisoning can affect nearly every system in the body including dysfunction of hemoglobin and neurological damage, in extreme case, can cause death[5]. Therefore, the directive is regulated by WHO that maximum allowable concentration for lead in drinking water[6] is 10 μg L^{-1}. To control the concentration of heavy metals, there is an urgent demand for analytical techniques that can be used on site and can measure concentrations at trace level[7,8].

Up to now, a variety of analytical methods for trace lead determination in environment samples have been developed. They include flame and graphite furnace atomic absorption spectrometry (FAAS, GFAAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), *etc.*[9-11]. Briefly, these methods are advantageous because multi-elements can be determined at the same time with good sensitivity and excellent selectivity. However, they are expensive, time-consuming and complicated. Besides, the analysis should be strictly carried out in a standard laboratory by qualified technical personnel. Thus they are unsuitable for on-site determination[12]. In contrast, the electroanalytical methods have more attractive features with low power demands and easy operation procedures lending themselves to the design of portable field-based instruments.

In electrochemical analysis, anodic stripping voltammetry has been widely regarded as a sensitive technique for trace heavy metal detection due to its combined preconcentration procedure. It can also be connected to portable instrumentations[13-15]. The working electrode plays an important role in electrochemistry system, as the quality and the reliability of measurements depend mainly on this sensor. Carbon-based substrates, such as glass carbon, carbon paste, carbon fiber, pencil lead, boron-doped diamond and screen printed carbon, are the most commonly used electrode materials[16]. Since the appearance of screen-printing technology in the late 19th century, screen-printed electrode has experienced remarkable progress due to its versatility, having miniaturized size and single-use characteristics. Up to now, numerous papers involving Hg-plated screen-printed electrodes and bismuth-plated screen-printed electrodes have been reported in the heavy metal analysis[17,18]. Because of the disposable characteristic, this electrochemical sensing platform does not require extensive polishing between measurements and thus simplifies the operation steps. However, a major drawback of stripping voltammetry is the lack of reproducibility due to fouling or passivation effects[19]. Difference also exists between batch and batch (*e.g*., surface area and electrode thickness) in the process of screen printing resulting in measurement deviation. Therefore, run-to-run variations should be correct due to uncertainties[20].

One approach to counter these variations resulting from uncertainties at once is to introduce an internal standard. The internal standard peaks are affected in the same way that the analyte peaks are affected by such fluctuations in the measurement system. Therefore, measuring the ratio of the analyte/standard stripping peaks response can improve the reproducibility. Usually, the internal standard method is used in separation techniques such as gas and liquid chromatography and capillary electrophoresis[19], also in mass spectrometry[21] and infrared analysis[22]. Among anodic stripping voltammetry, only few studies have utilized the internal standardization technique[23-27]. However, in the above cases, there need extra addition of internal standards, such as indium, thallium or zinc. There are also articles involving bismuth as internal standard using mercury as modifying solution[28] or on glass carbon electrode[29]. Fernando and Kratochvil[30] reported the use of lead and cadmium as internal standards for each other on a polarographic analyzer coupled with a stationary mercury drop electrode. Brown *et al*.[31] used the analytes themselves as internal standards for stripping voltammetry on a hanging mercury drop working electrode, this method omitted the addition of extra internal standard.

In this work, a portable electrochemical sensing platform is put up by connecting screen-printed electrodes to a miniaturized workstation for rapid and reliable quantitation of trace lead. Bismuth is added as a useful internal standard for the quantitative analysis of lead due to its negligible concentration in real waters, the formation of an alloy between lead and bismuth[18] with significant increase in stripping current signals and the obviously separated anodic stripping peaks between lead and bismuth. Square wave anodic stripping voltammetry (SWASV) is used because of its advantages of low background current and insensitivity to solutions containing dissolved oxygen[10]. The optimization of various parameters and attractive analytical performance of the sensing platform are reported. Moreover, the practical application of the method is verified in real samples with satisfactory results.

EXPERIMENTAL

The stock and standard solution were prepared from analytical grade chemicals which were used as received. Lead nitrate and bismuth(III) nitrate penta-hydrate were purchased from Shanghai Reagent Corporation (Shanghai, China). Stock solution of 1000 mg L^{-1} Pb^{2+} was prepared in buffer solution and 100 mg L^{-1} Bi^{3+} stock solution was prepared in HNO$_3$ (pH 2.0) solution. A series of working solution were prepared by diluting the stock solution. 0.1 M (pH 4.5) acetate buffer solution was used all the time unless otherwise stated. Electrochemical characterization was performed in 1 mM potassium hexacyanoferrate(III) dissolved in 0.1 M potassium chloride solution. Deionized water with resistance no less than 18.2 MΩ cm^{-1} from a Pall Cascada laboratory water system was used throughout.

A USB 2.0 ElectroChemistry System (PLAB Instruments, Changchun, China) was employed to perform cyclic voltammetry (CV) and SWASV. Screen-printed electrodes (SPCEs) were purchased from Suzhou Yangtze Delta Academy of Bio-X Science Ltd. (Suzhou, China) which included a three electrode configuration printed on the same strip. A 3 mm diameter carbon working electrode, a carbon counter electrode and an Ag reference electrode were printed on one strip. An insulating layer was also printed onto it to define the working area. A specific connector was used to connect the electrochemical strip to the portable ElectroChemistry System. A polyethylene voltammetric cell which has the volume of 10 mL was used to carry out the analysis. The electrochemical results were compared with ICP-MS results which were obtained on a Perkin Elmer ELAN DRCII ICP-MS spectrometer (USA).

Electrode pretreatment: Prior to each determination approach, the SPCEs were pretreated in 0.1 M (pH 4.5) acetate buffer solution at +1.6 V for 120 s and then +1.8 V for 60 s, after that the electrode were thoroughly rinsed with water. The resulted electrode was named as SPCE-I. SPCE-II was pretreated in 0.1 M (pH 4.5) acetate buffer solution at the potential of +1.7 V for 180 s and then thoroughly rinsed with water. SPCE-III was pretreated in the buffer solution by cyclic potential scanning from -1.6 V to + 1 V for 15 cycles and then thoroughly rinsed with water. Scan rate (100 mV s^{-1}) used for the three pretreatment methods were the same. After dried at room temperature, the pretreated SPCEs was placed in an electrochemical cell for the voltammetric measurement of the target analyte or cyclic voltammetric measurement in 0.1 M potassium chloride solution containing 1 mM potassium ferricyanide.

Measurement procedure: The electrochemical analysis of lead ions by disposable SPCEs was performed with an *in situ* deposition of target metals without removal of dissolved oxygen, at the same time, bismuth ions were also deposited. The pretreated electrode was immersed in a 10 mL electrochemical cell, containing 0.1 M acetate buffer (pH 4.5) and 120 μg L^{-1} bismuth ions. Then deposition was performed under the constant potential of -1.4 V for 120 s keeping the solution stirring. After the deposition step, the stirring was stayed still for 30 s, square-wave anodic stripping voltammetric scan was recorded from -1 V to 0.2 V. Other parameters were as follows: frequency of 20 Hz, amplitude of 50 mV and scan rate of 200 mV s^{-1}. After recording the background voltammograms, a series of lead standard working solutions were added. Conditioning step used to remove the target metals and bismuth was conducted by applying a positive potential of + 0.6 V for 50 s under the stirring condition prior to the next cycle.

Analysis of real river water samples: River water samples were collected from two different sites (Wulong river in Laiyang and Wang river in Laizhou, Shandong). Both samples were filtered by 0.45 μm Mixed Cellulose Ester (MCE) membrane filter to separate particulate matter and acidified to pH 2.0 with HNO_3, then were placed in quartz tubes for UV digestion. The treated river water was adjust to pH 4.5 and spiked with ferricyanide ions to a final concentration of 0.1 mM. Acetate buffer was made by dilution in the solution. At the same time, ICP-MS was used as a comparative method to quantify the lead concentration in the real samples.

RESULTS AND DISCUSSION

Electrochemical characterization of pretreated SPCEs: Printing inks usually contain graphite, solvent, polymer binder, which have a dramatic effect on the electrochemical performance, especially polymer binder for dispersion and adhesion onto the substrate is closely related with the electrode surface's electron transfer rate[32,33]. Electrochemical pretreatment is an extensively used procedure to improve the slow electron transfer rate of various carbon electrode materials due to its simplicity, effectiveness and can be performed *in situ*.

First, changes of the electron transfer properties at the electrode surface after the three electrochemical pretreatment methods were investigated by using cyclic voltammetric profiles. The outer-sphere redox couple potassium ferricyanide was used to assess three electrochemical pretreatment methods, they were the potential cycling, one-step pre-anodization and two successive oxidation steps. As it was observed in Fig. 1, the electrochemical response of potassium ferricyanide at fresh SPCEs was poor for the separation (ΔEp) of oxidation and reduction peak potential was large, indicating that the electron transfer was hindered by nonconductive polymer binder and the electrochemical reaction was irreversible. In sharp contrast to untreated SPCEs, cyclic voltammetric studies indicated that the enhanced electrochemical response signal can be obtained at pretreated SPCEs. Especially after two successive oxidation steps, ΔEp was only 160 mV and peak currents were greatly increased, indicating that the electrochemical performance was largely increased with fast electron transfer rate and reversible electrochemical reaction, which was due to the removing of contaminates at the electrode surface or polymer binder filled in the ink and the more explosion of micrometer-sized graphite particles at the electrode surface. This observation is similar to that reported by Kadara *et al.*[34] who electrochemically evaluated a variety of commercially available screen-printed carbon electrodes from Dropsens, Zensor and Kanichi. Kadara *et al.*[34] also analyzed the reasons why the ΔEp was not close to the ideal value (59 mV). Taking peak separation and peak current into account, two successive oxidation pretreatment method was preferred.

Voltammetry behavior of lead at SPCEs with bismuth as internal standard: To evaluate the suitability of Bi(III) as internal standard, experiments were carried out by spiking a known amount of standard Bi(III) during the preconcentration of lead at the SPCEs. Almost no stripping signals appeared at the bare SPCEs (Fig. 2 curve a) for 0.1 M acetate buffer (pH 4.5). And a small lead stripping peak at -0.71 V appeared (Fig. 2 curve b) when 15 μg L^{-1} lead was added into the background supporting electrolyte of 0.1 M (pH 4.5) acetate buffer solution. In contrast, after adding 120 μg L^{-1} bismuth into the above solution and simultaneously co-depositing, there appeared a sharp and big lead stripping peak at -0.70 V. The peak current was 5.3 times larger than that obtained at the bare SPCEs. The appearance of sharp and large stripping peak for bismuth (Fig. 2 curve c) at -0.28 V was also presented. Clearly, the carbon electrodes with the addition of bismuth as internal standard can dramatically improve the detection sensitivity to trace lead. On the other hand, it was obvious that the potentials of oxidation peaks between bismuth and lead were highly resolved (430 mV). This result indicated that bismuth not only can be used as an internal standard but also a good modifier. Although the deposition time was short (only

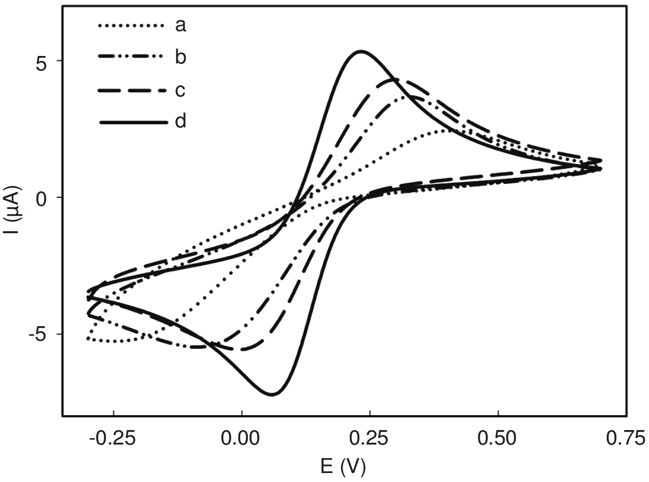

Fig. 1. Cyclic voltammograms obtained on: (a) fresh SPCE, (b) SPCE-III (potential cycling from -1.6 V to +1 V for 15 cycles in acetate buffer solution), (c) SPCE-II (one-step anodisation at 1.7 V in acetate buffer solution for 180 s), (d) SPCE-I (two successive anodisation, first at 1.6 V for 120 s and then at +1.8 V for 60 s in acetate buffer solution), in 1 mM potassium ferricyanide dissolved in 0.1 M potassium chloride solution. Scan rate used for the three pretreatment methods was the same, 100 mV s^{-1}

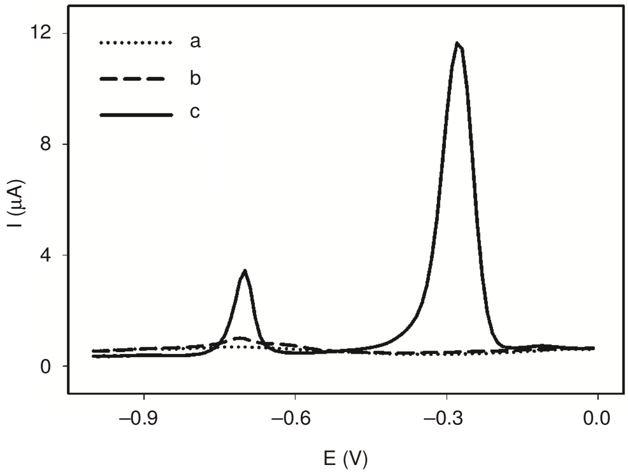

Fig. 2. Square wave anodic stripping voltammograms on SPCEs for 0.1 M (pH 4.5) acetate buffer (curve a), 0.1 M (pH 4.5) acetate buffer containing 15 μg L^{-1} lead (curve b), 0.1 M (pH 4.5) acetate buffer containing 15 μg L^{-1} lead and 120 μg L^{-1} bismuth (curve c). SWASV was performed from -1 V to 0.2 V, deposition at -1.4 V (120 s), conditioning at 0.6 V for 50 s, frequency: 20 Hz, amplitude: 50 mV, scan rate: 200 mV s^{-1}

2 min) in a nondeaerated solution, SPCEs with bismuth as internal standard displayed well-defined peaks and low background current.

Effect of experimental parameters on the response current: To enhance the electroanalytical performance of SPCEs with bismuth as internal standard for lead detection, several key operational parameters were optimized, including the concentration of bismuth ions, the supporting electrolyte pH, the preconcentration potential and the preconcentration time. In order to reflect the effect of various experimental variables on lead and bismuth peak intensities comprehensively, I_{Pb}/I_{Bi} (where I_{Pb} and I_{Bi} were denoted as the peak height of Pb and Bi against the baseline) was used as ordinate to evaluate and the results were shown in Fig. 3.

Concentration of bismuth ions: The effect of the bismuth ions concentration on the voltammetric stripping response was presented in Fig. 3(A). The stripping peak current of lead increased rapidly upon the increase of the concentration of bismuth ions in the range of 30 and 120 μg L^{-1} and then reached the maximum at 120 μg L^{-1}. When more than 120 μg L^{-1} bismuth ions were added into the solution, the stripping peak obviously decreased due to the difficulty of lead stripping from thicker bismuth film. Thereby, 120 μg L^{-1} bismuth was selected as suitable concentration, which resulted in an acceptable sensitivity for lead.

pH of the supporting electrolyte: In order to avoid hydrogen evolution and hydrolysis of bismuth, the pH of supporting electrolyte was investigated. Buffer solution has been widely used as supporting electrolyte to make sure the pH value constant as well as ionic strength in the analysis. In this experiment, 0.1 M acetate buffer was employed and its pH between 2.9 and 5.0 was evaluated. Fig. 3(B) showed the pH had an important effect on the I_{Pb}/I_{Bi} stripping current ratio of 120 μg L^{-1} Bi^{3+} and 15 μg L^{-1} Pb^{2+}. From pH 2.9 to 4.5, the anodic stripping current ratio (I_{Pb}/I_{Bi}) increased rapidly with the increase of pH value and then tended to increase gradually after pH 4.5. Considering that Bi^{3+} is easily hydrolyzed at higher pH value (above 5) and hydrogen dissolving will appear (at lower pH value) which would cause high background current that would partly overlapped the stripping signal, therefore, the buffer solution pH should be strictly adjusted to the appropriate value. In this work, we choose pH 4.5 for further experiments.

Deposition potential: The influence of accumulation potential on the I_{Pb}/I_{Bi} stripping peak current ratio of 15 μg L^{-1} Pb^{2+} and 120 μg L^{-1} Bi^{3+} was evaluated within the range of -0.9 to -1.5 V. As shown in Fig. 3(C), the I_{Pb}/I_{Bi} was rectilinear dependent on the deposition potential. When the deposition potential became negative, the stripping response increased rapidly until -1.4 V, where the response no longer increased even though more negative deposition potential than -1.4 V was applied, which probably due to the fact that the saturation was eventually reached and the stripping of lead was hindered when the bismuth film became thicker. Therefore, we preferred -1.4 V as deposition potential in the following experiments.

Deposition time: In anodic stripping voltammetric technique, the deposition time was another important parameter and its effect in this experiment was showed in Fig. 3(D).

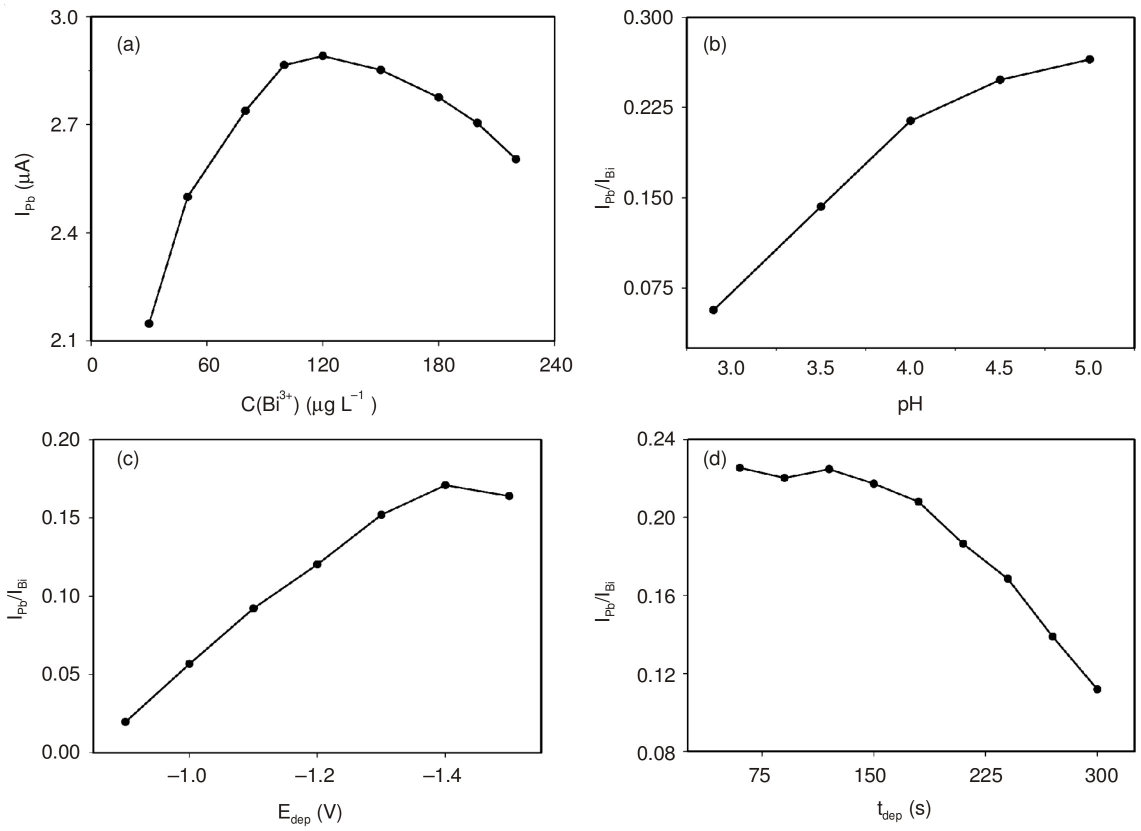

Fig. 3. Optimization of (a) the concentration of bismuth ions in 0.1 M (pH 4.5) acetate buffer containing 15 μg L^{-1} lead, and (b) the pH of supporting electrolyte, (c) the deposition potential and (d) the deposition time in 0.1 M (pH 4.5) acetate buffer containing 15 μg L^{-1} lead and 120 μg L^{-1} bismuth. Other parameters were as in Fig. 2

The variation of the I_{Pb}/I_{Bi} stripping peak current ratio was examined with the accumulation time from 60 s to 300 s. The response peak current of lead increased rapidly with the increase of accumulation time until 180 s was reached (not shown) and then gradual leveling-off due to the saturation of lead on the electrodes surface. While the response current of bismuth increased rapidly with the accumulation time increasing all the time (until 300 s) and the speed was much faster than lead. As shown in Fig. 3(D), a platform between 60 and 120 s can be observed. The decrease of I_{Pb}/I_{Bi} peak current ratio was obtained with the longer accumulation time (above 120 s). Therefore, 120 s was preferred for the following experiments.

Determination of lead at SPCEs with bismuth as internal standard: The electroanalytical performance of SPCEs with bismuth as internal standard was accessed and the results were depicted in Fig. 4(A) which exhibited a highly linear response when the response current ratio I_{Pb}/I_{Bi} was used as ordinate. The lead concentration varied from 2 to 200 μg L^{-1} in the experiments. Well-defined sharp peaks were observed and with the increase of the concentration of lead, the lead peak current increased while the bismuth peak height stayed almost constant when the concentration of bismuth was fixed at 120 μg L^{-1} level. Using the ratio I_{Pb}/I_{Bi} as the measured response, the variations such as the stirring and electrode surface between samples and sensors were reduced. As shown in Fig. 4(B), the calibration curve constructed using I_{Pb}/I_{Bi} against the concentration of lead was linear in the range of 2-200 μg L^{-1} and the slope calculated was 0.0198 with a correlation coefficient of 0.998.

Moreover, reproducibility was also a key characteristic due to its disposable measurement. The relative standard deviation (7.4 %) obtained for six SPCEs of 15 μg L^{-1} lead (calculated from I_{Pb}/I_{Bi}) was indicated. Precision was another key parameter in analytical chemistry. Ten repetitive measurements for a solution containing 15 μg L^{-1} lead along with 120 μg L^{-1} bismuth added resulted in highly repeatable peak current and the relative standard deviations was 3.5 %. The I_{Pb}/I_{Bi} was highly accurate and reproducible, which indicated that a detailed calibration plot for each run was unnecessary. Such good precision may be attributed to the removal of uncertainties between electrodes and physical parameter effect.

Interference: The effect of many ions potentially present in natural waters as interfering species was studied by analyzing a standard solution (15 μg L^{-1} Pb^{2+}). Under the optimized conditions, a certain amount of interfering ions was added until they produced a change in peak current of less than or more than 5 % of the initial response current (max. 2,000 fold higher than the concentration of Pb^{2+}). It was shown that Na^+, K^+, OAc^-, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Mn^{2+} had no effect on response current. No interference was also observed for more 10-fold Zn^{2+}, 5-fold Cd^{2+}, Co^{2+}, 2-fold Ni^{2+} on the peak current. However, 1-fold Cu^{2+} was found to cause severe interference which was probably attributed to the formation of the intermetallic compound between copper and lead deposited on the electrode as well as to the competition between the electrodeposited bismuth and copper for surface sites on the electrode[35, 36]. The monitored lead voltammetric peak current was changed with quantities of Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} added to the solution, which probably due to the active sites competition with Pb^{2+} on the limited electrode surface during the deposition procedure. However, for real samples analysis, the effect caused by interferences can be alleviated effectively by using masking reagents, such as ferricyanide for copper interference[8] or the standard addition calibration procedure. The interferences effect caused by organic matters which controlled heavy metal speciation can be eliminated by UV digestion.

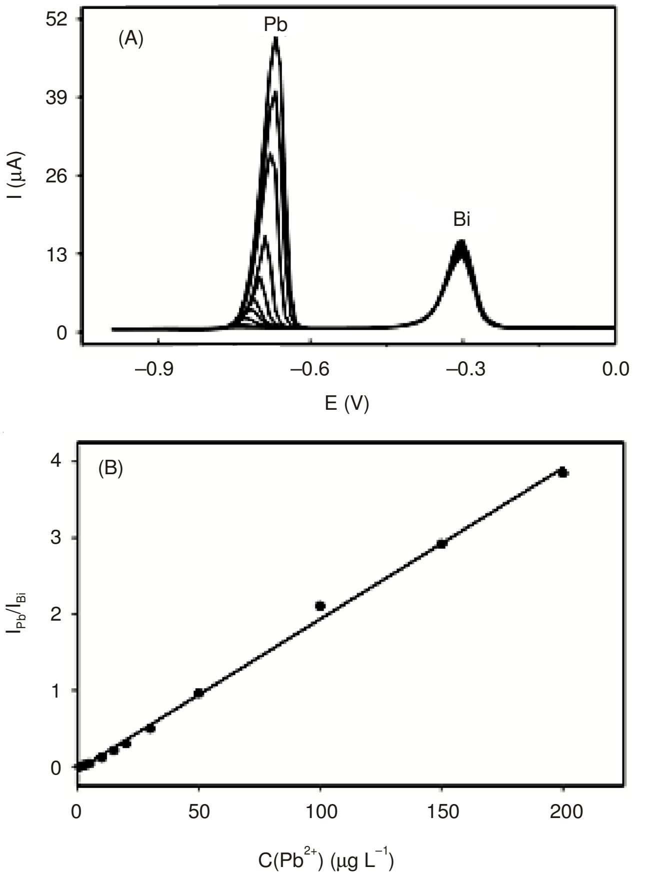

Fig. 4. (A) SWASV for the analysis of lead from 2-200 μg L^{-1} with 120 μg L^{-1} bismuth as internal standard, (B) The corresponding calibration plot using the I_{Pb}/I_{Bi} current ratio as response signal. SWASV parameters were the same as in Fig. 2

Application to river water samples: To further increase the accuracy of anodic stripping analysis, standard addition method together with internal standard method was used to determine Pb^{2+} in two separate river water samples. Fig. 5(A) showed the SWASV responses to lead in Wulong river water sample at SPCEs with bismuth as internal standard. Lead concentrations in river water samples were calculated from Fig. 5(B). These results suggested that under the optimum experimental conditions the combined strategy exhibited low detection limit and high sensitivity towards the determination of Pb^{2+}. Additionally, the results were also compared with those obtained on ICP-MS to prove the accuracy in practical sample analysis. As shown in Table-1, well accordance indicated the suitability of the bismuth as internal standard for trace lead determination in real water samples. More important, the anodic stripping peak current ratio of lead and bismuth can be easily calculated with software and would facilitate the construction of electrochemical platform.

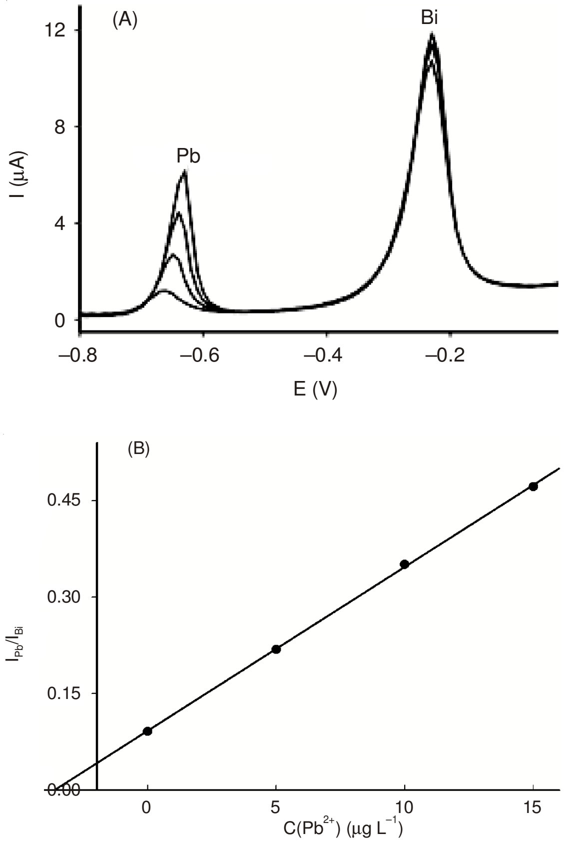

Fig. 5. (A) SWASV for the determination of lead in Wulong river water sample at SPCEs with bismuth as internal standard. From bottom to top: sample and three standard additions of 5 µg L^{-1} Pb^{2+}. (B) The fitting curve of Pb^{2+} measurement obtained from combined standard addition and internal standard. Other parameters were the same as in Fig. 2

TABLE-1
COMPARISON OF SPCEs WITH BISMUTH AS INTERNAL STANDARD AND ICP-MS FOR TRACE LEAD DETERMINATION IN REAL WATER SAMPLES

Samples	Detected by SPCEs	Detected by ICP-MS
Wulong river	7.24 µg L^{-1}	7.40 µg L^{-1}
Wang river	5.36 µg L^{-1}	4.53 µg L^{-1}

Conclusion

Screen-printed carbon electrodes with bismuth as internal standard combined with a portable electrochemical workstation exhibited superior performance in reliable quantitation of trace lead using anodic stripping voltammetry. Herein, bismuth used as internal standard can greatly minimize the variations between batches. To enhance the electrochemical performance of SPCEs, three pretreatment methods were compared. Optimized variables gave low detection concentration in the µg L^{-1} with good reproducibility. The proof-of-concept that the combined internal standard and standard addition method was a rapid and accurate sensing strategy for trace lead determination in river water samples was demonstrated and the results were consistent with those by ICP-MS. The attractive performance of the disposable and low cost carbon strip electrodes, coupled with the highly accurate and efficient method, facilitates the development of portable electrochemical sensing system.

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