Full Paper

Simultaneous Determination of Thallium and Lead on a Chemically Modified Electrode with Langmuir–Blodgett Film of a *p*-tert-Butylcalix[4]arene Derivative

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Abstract

A new voltammetric sensor, Langmuir–Blodgett (LB) film of a *p-tert*-butylcalix[4]arene derivative modified glassy carbon electrode, was designed and successfully used in simultaneous determination of Tl^+ and Pb^{2+} by square-wave anodic stripping voltammetry. Under the optimum experimental conditions, this newly developed sensor reveal good linear response for Tl^+ and Pb^{2+} in the concentration range of 3×10^{-8} – 4×10^{-6} mol L^{-1} and 2×10^{-7} – 2×10^{-5} mol L^{-1} respectively. The detect limits are 2×10^{-8} mol L^{-1} for Tl^+ and 8×10^{-8} mol L^{-1} for Pb^{2+}. Using proposed method, Tl^+ and Pb^{2+} in environment samples were determined with satisfactory results.

Keywords: Calixarenes, Langmuir–Blodgett, Thallium, Lead, Square-wave anodic stripping voltammetry

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1. Introduction

The determination of heavy metals is of importance due to its wide application to the clinical, environmental and industrial fields [1]. Tl^+ and Pb^{2+} are highly toxic ions, which come into the environment mainly as waste of industrial production. It is reported that Tl^+ and Pb^{2+} have nervous, reproductive and teratogenic toxicity to human being [2–4]. Moreover, the toxicity of Tl^+ is higher than that of Pb^{2+}, Hg^{2+}, Cu^{2+} and Cd^{2+}. The concentrations of Tl^+ and Pb^{2+} in environmental water samples are very low, generally between 10^{-9} g L^{-1} and 10^{-6} g L^{-1} [5]. Therefore, it is essential to develop sufficiently sensitive and reproducible analytical methods for precise determination of these elements at trace levels. Several analytical techniques were used to determine trace thallium and lead in different samples, including inductively coupled plasma mass spectrometry (ICP-MS) [6], flame atomic absorption spectrometry (F-AAS) [7], inductively coupled plasma emission spectrometry [8], laser-induced fluorescence (LIF) [9] and ion chromatography [10]. However, the wide utilization of these techniques is limited for the expensive apparatus or poor sensitivity.

Electrochemical stripping analysis has been widely recognized as a powerful tool for measuring traces of heavy metals due to its remarkable sensitivity, reliability and simplicity of measurement [11–14]. Moreover, in order to avoid the environmental pollution and health hazard caused by traditional mercury (film and drop) electrodes, various mercury-free electrodes have been developed over the past few decades [15–20]. In these works, chemically modified electrodes (CMEs) revealed outstanding performance and wide application prospect. Recently, calixarenes and its derivatives, as a kind of chemical modifier, have received continuous attention for their molecular and ionic recognition ability, versatile modification, outstanding selectivity and high stability [21]. A variety of calixarene derivatives have been successfully used in ion selective electrodes (ISEs) [22–25], chemically modified electrodes for determination of Cd^{2+} [26], Hg^{2+} [27] and Pb^{2+} [28]. Several methods were used for electrode modification in the abovementioned researches, such as chemisorption, covalent binding and polymer film coating. Although these methods are simple in operation, the films obtained in these ways have poor adhesion, inhomogeneous surface, uncontrollable thickness, and low stability, resulting in the poor reproducibility of the determination [29]. Recently, we have proposed a new idea of using LB film technique to modify calixarene derivatives on electrode as voltammetric sensors for recognizing and determining of metal ions. By this idea, we have reported of determining trace of Cu^{2+} [30], Pb^{2+} and Cd^{2+} [31] with p-tert-butylthiacalix[4]arene LB film modifying GCEs and trace of Hg^{2+} [32], Cd^{2+} and Tl^+ [33] with *p*-allylcalix[4]arene LB film modifying GCEs, respectively. All of the detection limits of these metal ions reached below 10^{-8} mol L^{-1}. This is mainly because that the LB technique is a useful way of forming sequential layers of ultrathin organic films and can precisely control the thickness and order of a film at the molecular scale.

In this approach, a new electrochemical voltammetric sensor, based on a *p-tert*-butyl calix[4]arene derivative LB film modified GCE, for simultaneous determination of trace amounts of Tl^+ and Pb^{2+} was designed. This new voltammetric sensor is very stable and has long life. Surprisingly, it is very easy for renewing in determination.

2. Experimental

2.1. Apparatus

LB films were formed and deposited on the surface of GCE (3 mm in diameter) by using a JML-04 LB trough (Shanghai Zhongchen Company, China). The electrochemical measurements were performed with a RST3000 electrochemical system (Suzhou Risetech Instrument Co., Ltd, China) and CHI650 (CH Instruments Company, USA) Electrochemical analyzers. The three electrode system was composed with a GCE, coated LB film of 25,27-Dimethoxy-26-(*N*-trichloroacetyl)carbamoyloxy-*p*-*tert*-butylcalix[4]arene (DCA), a saturated calomel electrode (SCE) and a platinum wire as the working, reference and counter electrodes, respectively. All potentials were reported versus SCE in this paper and all measurements were conducted in solutions (deaerated) by bubbling N_2 for 10 min.

2.2. Chemicals and Reagents

All reagents were of analytical grade and used without further purification. The water used was redistilled water in quartz vessel. DCA (Fig. 1, New Jersey, USA) was dissolved in dichloromethane (distillation before used) to obtain a 1×10^{-4} mol L^{-1} solution. Tl^+ and Pb^{2+} stock solutions (10^{-3} mol L^{-1}) were prepared from Tl_2SO_4 and $Pb(NO_3)_2$, respectively. Acetate buffer solution 0.2 mol L^{-1} (pH 4.4) was employed as supporting electrolyte.

2.3. Preparation of DCA LB Film Modified Electrode

Measurement of $\pi - A$ isotherms and preparation of LB monolayer were performed with a JML-04 LB trough. Before coating, the GCE was polished with 0.1 μm aluminum slurry, rinsed thoroughly with redistilled water and sonicated successively in ethanol and redistilled water, each for 3 min. A sample of DCA in dichloromethane solution was spread onto the subphase (pure water) surface using a syringe, allowing the solvent to evaporate for 30 min before compression with two parallel barriers, which compress or expand symmetrically at the same rate from two sides of the trough. A Wilhelmy balance was used as a surface pressure sensor and situated in the middle of the trough. The Langmuir film was compressed at a rate of 10 mm min^{-1} and then transferred onto GCE at a rate of 5 mm min^{-1} (vertical dipping) under a surface pressure of 25 mN m^{-1}. Sequential monolayer transfer assembled the multilayer films. In the course of deposition, the GCE need to be dried completely (in air for at least 60 min) between every monolayer transfer, so that the following monolayer can be favorably transferred. Then a Z type LB film [34] modified GC electrode (LB_{DCA}-GCE) was gained by this method. The LB_{DCA}-GCE was kept in acetate buffer solution for further using.

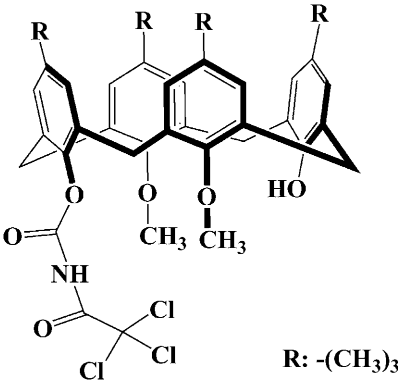

Fig. 1. Chemical structure of DCA.

2.4. Analytical Procedure

Considering the resolution capacity and sensibility, the square wave anodic stripping voltammetry (SWASV) was chosen as detection technique. 10 mL 0.2 mol L^{-1} acetate buffer solution (pH 4.4) was used as blank solution and deaerated with pure nitrogen for 10min before scan. After determining the $i - E$ curve of blank solution, aliquots of Tl^+ and Pb^{2+} solution were added into the cell and accumulated for 90 s at -1.4 V under a magnetic stirring. For a quiescence period of 10 s, the SWASV measurements were performed in the potential range of -1.1 to -0.2 V (vs. SCE). The optimal instrumental parameters were square wave amplitude of 50 mV, square wave frequency of 50 Hz and step height of 3.0 mV. After that, the electrode was cleaned at -0.2 V for 60 s.

3. Results and Discussion

3.1. $\pi - A$ Isotherms

The $\pi - A$ isotherm of DCA is presented in Figure 2. It exhibits a typical characteristic of condensed monolayer where only a vertical condensed phase is observed. The stable monolayer reveals the collapse pressure of 49 mN m^{-1} and extrapolated molecular area of 0.8 nm^2 per molecule.

3.2. Characterization of LB_{DCA}-GCE

3.2.1. Cyclic Voltammetry

When the DCA was modifying on the GCE surface, the surface structure and electrochemical characters of elec-

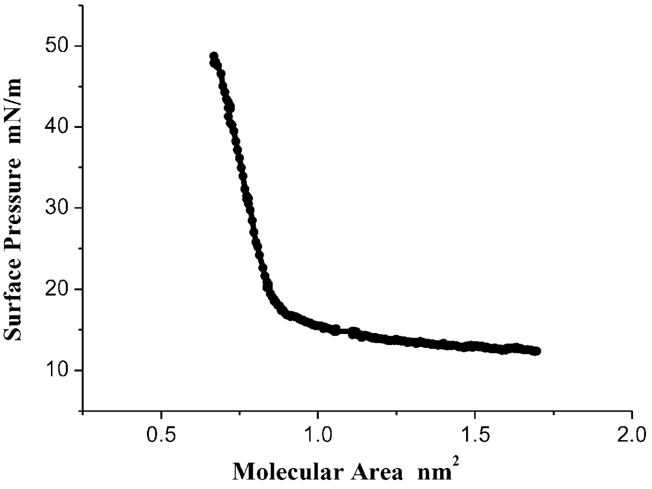

Fig. 2. Pressure-area isotherms of DCA.

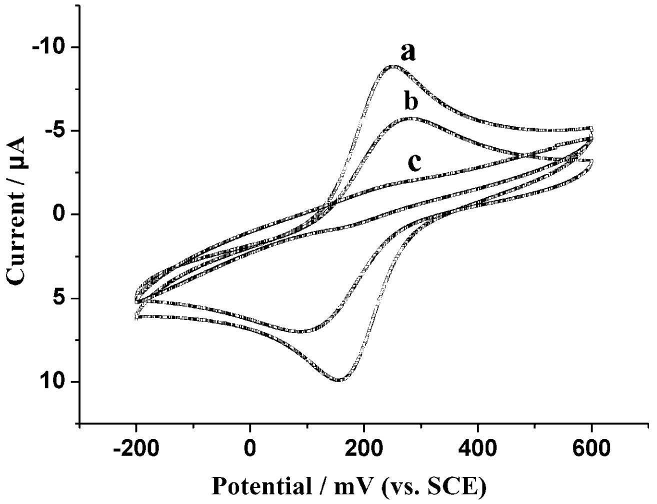

Fig. 3. Cyclic voltammograms of $Fe(CN)_6^{3-}$ (1×10^{-3} mol L^{-1}) at a clean, freshly polished bare GCE (a); one layer LB_{DCA}-GCE (b) and two layers LB_{DCA}-GCE (c) with scan rate $v = 0.10$ V s^{-1}.

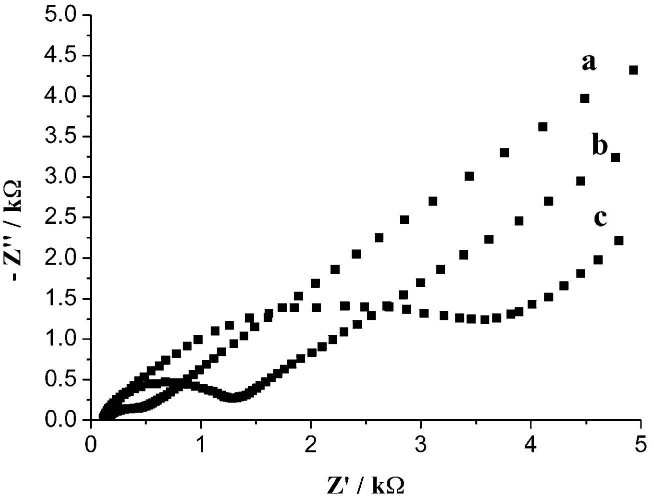

Fig. 4. Electrochemical impedance spectroscopy (EIS) of a clean, freshly polished bare GCE (a); one layer LB_{DCA}-GCE (b) and two layers LB_{DCA}-GCE (c) in 1.0×10^{-3} mol L^{-1} $Fe(CN)_6^{3-/4-}$.

trode were token. Ferricyanide, a well-known electrochemical probe, was used as a convenient tool to monitor the characters (density and defects) of the LB_{DCA}-GCE. Figure 3 shows the cyclic voltammograms of $Fe(CN)_6^{3-}$ (1×10^{-3} mol L^{-1}) recorded at a bare GCE (clean, freshly polished) and LB_{DCA}-GCE (1 layer and 2 layers). It is clear that the CV curve of the $Fe(CN)_6^{3-}$ show a typical reversible shape at the bare GC electrode (Fig. 3, curve a). The peak current decreased sharply and the peak potentials shifted bidirectional (Fig. 3, curve b) when one layer DCA was employed on electrode surface, and there was no redox peak apparent with two layers (Fig. 3, curve c). This means that LB_{DCA} can act as barrier for blocking the electron and mass transfer, and it hinders the diffusion of ferricyanide toward to the electrode surface. It seems that the two layers LB_{DCA} film is more compact than one layer LB_{DCA} film.

3.2.2. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is also a powerful technique to study the interface properties of surface modified electrodes. If the Nyquist plot of impedance spectra includes a semicircle portion and a linear portion, the semicircle portion at higher frequencies corresponded to the electron transfer limited process and the linear portion at lower frequencies corresponded to the diffusion process. The semicircle diameter of EIS equals the R_{et}, called reaction resistance, which can be used to describe electron transfer resistance at the electrode surface. Nyquist diagrams of samples were recorded at 0.246 V vs. SCE from 100 KHz to 0.05 Hz with perturbation amplitude of 5 mV. Figure 4 exhibits the EIS of the bare GC electrode (curve a) and LB_{DCA} modified electrodes (curve b for 1 layer and curve c for 2 layers) in the solution of equimolar 1.0×10^{-3} mol L^{-1} $Fe(CN)_6^{3-/4-}$ ions, respectively. The Nyquist plot present as an almost straight line at bare GCE while the LB_{DCA}-GCE Nyquist plots consist of a semicircle portion and a linear part. It can be seen from Figure 4 that the diameter of the semicircle increases along with the increasing layer numbers of DCA film modified on the electrode surface. After fitting suitable circuit and calculation, R_{ct} obtained is about 0.31 kΩ, 1.07 kΩ and 3.02 kΩ for 0 layer, 1 layer and 2 layers (Fig. 4, lines a–c) DCA film, respectively. This suggests that LB_{DCA} acted as the blocking layer for electron and mass transfer that hinders the diffusion of ferricyanide toward the electrode surface. This result obviously also prove that LB_{DCA} film is successfully immobilized on the GCE surface.

3.2.3. Atomic Force Microscope

Morphology of LB_{DCA} film on GCE surface was also examined by using Atomic force microscope (AFM) imaging. Silicon was used as substrates to substitute GCEs. These

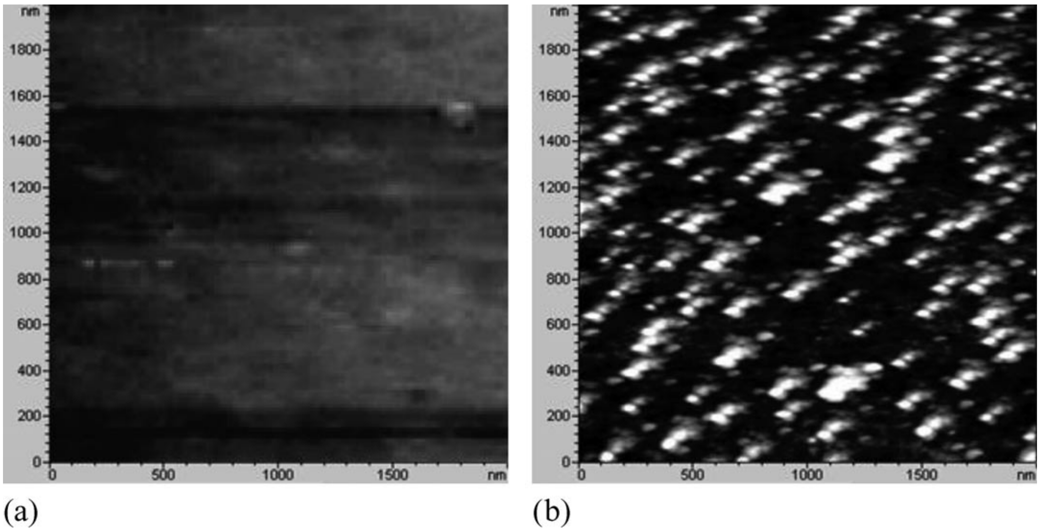

Fig. 5. AFM images of (a) bare silicon surface and (b) modified surface of silicon with LB_{DCA} film, scan size 2 μm × 2 μm.

silicon substrates were ultrasonic cleaned with ethanol and redistilled water for 10 minutes, respectively. Then the substrates were dipped in Piranha solution (1:3 mixtures of H_2O_2 and H_2SO_4) for 20 minutes. Later, they were again ultrasonic cleaned in redistilled water for 5 minutes. Finally, the pretreated silicon were kept in redistilled water for further using. The surfaces of samples were scanned in air using 5500 Atomic Force Microscopy (Agilent, United States) by contact mode at a scan of about 0.500 Hz and 2 μm × 2 μm of size. Figure 5 shows AFM images of the bare silicon surface (a) and the modified surface with LB_{DCA} film (b). The bare silicon has no impurity on its surface and shows very even surface (Fig. 5a). From Figure 5b, we can see that DCA is nearly well-proportioned on the silicon surface, indicating successful immobilization of LB_{DCA} film on the substrate surface [35].

3.3. Electrochemical Behavior of Tl^+ and Pb^{2+} on LB_{DCA}-GCE

The ability of the LB_{DCA}-GCE for recognition of Tl^+ and Pb^{2+} was studied. The method was described in Section 2.4. Figure 6 shows the SWASV i ~ E curves of 5×10^{-7} mol L^{-1} Tl^+ and Pb^{2+} in 0.2 mol L^{-1} acetate buffer (pH 4.4) at bare GCE (a); two layers LB_{DCA}-GCE (b) and one layer LB_{DCA}-GCE (c). It is noticed from Figure 6 that the LB_{DCA}-GCE exhibited a well-defined response for trace of Tl^+ and Pb^{2+}, while no obvious peaks appeared at the bare GCE. The peaks, which appear at − 0.84 V and − 0.54 V (vs. SCE), are related to the oxidation of Tl and Pb, respectively. In addition, the peak currents at one layer LB_{DCA}-GCE are larger than that of two layers LB_{DCA}-GCE. The reason is easily understand from the results of cyclic voltammetry and electrochemical impedance spectroscopy. That is the LB_{DCA} acts as a bulwark and the R_{et} of two layers LB_{DCA} (3.02 kΩ) is larger than that of one layer (1.07 kΩ). Therefore, the peak currents of Tl^+ and Pb^{2+} are larger at one layer LB_{DCA}.

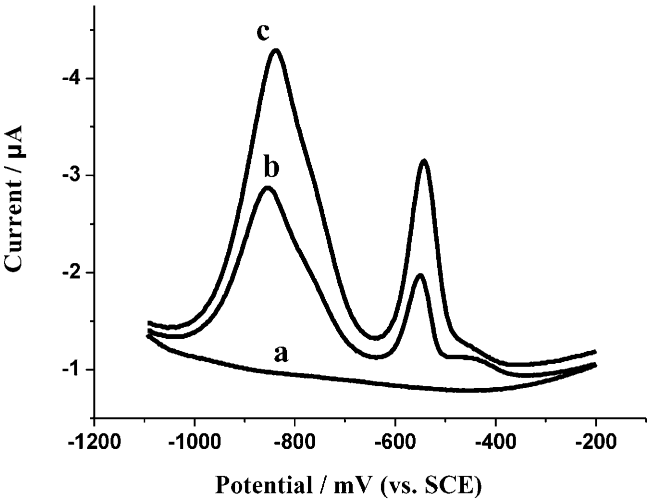

Fig. 6. Square-wave stripping voltammograms of 5×10^{-7} mol L^{-1} Tl^+ and Pb^{2+} at different electrodes: (a) Bare GCE, (b) 2 layers LB_{DCA}-GCE, (c) 1 layer LB_{DCA}-GCE. Supporting electrolyte: 0.2 mol L^{-1} acetate buffer solution; Accumulation time: 90 s; Accumulation potential: − 1.4 V.

3.4. The Reaction Process of Tl^+ and Pb^{2+} on LB_{DCA}-GCE

Our previous works [30 – 33] reported calixarene LB film modified electrode as voltammetric sensors for recognition and determination of metal ions. In those works, the metal ions were complexation with calixarene during the accumulation step under open circuit condition. However, in this work, the Tl^+ and Pb^{2+} could not be so. They could be accumulated only under comparative negative potentials. That is, Tl^+ and Pb^{2+} are not complexation with DCA. The LB_{DCA} only provide a site for Tl^+ and Pb^{2+} reduction, and its function is just as a new electrode material. So the mechanism of electrode reaction can be described as two steps:

Reduction step (accumulation):

$$\mathrm{LB_{DCA}(surface)} + \mathrm{M}^{n+}\mathrm{(solution)} + n\ \mathrm{e} \rightarrow \mathrm{LB_{DCA}} - \mathrm{M^0(surface)}$$

Oxidation step (stripping):

$$\mathrm{LB_{DCA}} - \mathrm{M^0(surface)} \rightarrow \mathrm{LB_{DCA}(surface)} + \mathrm{M^{n+}(solution)} + n\ \mathrm{e}$$

3.5. Optimum Operation Conditions of Determination

The influences of supporting electrolytes on stripping peak currents were investigated in KCl-HCl, acetate buffer solution, phosphate buffer solution and B-R buffer solution respectively. The results showed that voltammetric peaks were observed in all these electrolyte solutions, while the best peak shape and largest stripping peak current was obtained in 0.2 mol L^{-1} acetate buffer (pH 4.4) solution. Therefore, 0.2 mol L^{-1} acetate buffer (pH 4.4) solution was employed as blank solution in following experiments.

Accumulation (Reduction) potential and accumulation time are very important parameters in stripping techniques and have significant effect on the detection sensitivity. Accumulation potentials were investigated between -1.5 and -1.1 V. The anodic peak current of Tl^+ increased with the reduction potential shift from -1.5 to -1.1 V, while the anodic peak current of Pb^{2+} showed contrary trend. Finally, -1.4 V was chosen as the reduction potential for the two well-separated stripping peak and well-defined peak currents. The influence of accumulation time on the anodic peak currents of Tl^+ and Pb^{2+} (10^{-6} mol L^{-1}) were studied from 60 to 240 s. Under the fixed accumulation potential of -1.4 V, the peak current of Tl^+ increased with increasing accumulation time all the while. However, the peak current of Pb^{2+} increased in the initial period and decreased from 150 s. This indicated that there was competitive reduction between Tl^+ and Pb^{2+} on the surface of LB_{DCA}-GCE. For all we known, the longer accumulation time, the lower detect limit will be. However, the linear range is also narrower for prolonging the accumulation time. Considering the sensitivity and the efficiency, accumulation time of 90 s was used in following experiments.

3.6. The Relationship between Peak Currents and Tl^+/ Pb^{2+} Concentrations

A series of determination of Tl^+ and Pb^{2+} co-exist with different concentration were performed under the optimized working conditions described above. The results showed that the peak currents were linearly proportional to the concentrations of Tl^+ and Pb^{2+} in the range of 3×10^{-8} to 4×10^{-6} mol L^{-1} (Tl^+) and 2×10^{-7} to 2×10^{-5} mol L^{-1} (Pb^{2+}).

The linear regression equations and linear correlation coefficients are:

$$i_p = 0.033 + 0.282\ C_{Tl} \qquad r = 0.996$$

$$i_p = 0.120 + 0.313\ C_{Pb} \qquad r = 0.996$$

The lowest detectable concentrations of Tl^+ and Pb^{2+} at 90 s accumulation time were estimated to be 2×10^{-8} and 8×10^{-8} mol L^{-1} respectively. The repeatability experiment was employed in parallel for 10 times determination of 10^{-6} mol L^{-1} Tl^+ and Pb^{2+}, and the relative standard deviations were 1.57% and 4.42% for Tl^+ and Pb^{2+} respectively. The results demonstrate that the LB_{DCA}-GCE has good repeatability for response of Tl^+ and Pb^{2+}. Moreover, the response of Tl^+ and Pb^{2+} on LB_{DCA}-GCE did not change remarkably after 30 days. This means that the LB_{DCA}-GCE is a very stable and long life voltammetric sensor for Tl^+ and Pb^{2+}.

3.7. Interferences

Interference effect of coexisting metal ions was investigated by adding various excess amounts of the species to a 10^{-6} mol L^{-1} solution of Tl^+ and Pb^{2+}. The result showed that 10^2-fold of alkali metal ions and same concentration of Fe^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} did not significantly influence the strength of the peak currents. However, same concentration of Hg^{2+} and Cd^{2+} were found to increase the response currents of Tl^+ and Pb^{2+} about 5%. This may be explained as Hg^{2+} ions were reduced simultaneously to form a thin mercury film, which increased the accumulation efficiency of Tl^+ and Pb^{2+}. For the Cd^{2+} ion, its relevant signals are close to that of Tl^+ in the electroanalysis, which lead to superposition of the response signals.

3.8. Analysis of Real Samples

Unfortunately, the suitable real sample was not found in our area. To investigate the applicability of the proposed method described above, tap water and lake water samples were employed for determining Tl^+ and Pb^{2+} by standard addition technique. The standard Tl^+ and Pb^{2+} solutions were added in sample solution before analysis and the recovery was detected for proving the detection accuracy. The results are listed in Table 1.

4. Conclusions

A new electrochemical voltammetric sensor, based on a calixarene derivative LB film modified electrode, for simultaneous determination of trace amounts of Tl^+ and Pb^{2+} was designed. The recognition mechanism of this electrode for Tl^+ and Pb^{2+} and the optimized working conditions were optimized. By using this LB_{DCA}-GCE, Tl^+ and Pb^{2+} could be determined simultaneously with detection limit of 2×10^{-8} and 8×10^{-8} mol L^{-1} respectively under accumulation time of 90s. Using the proposed method, Tl^+ and Pb^{2+} in natural water samples were determined with high accuracy and good recovery. This LB_{DCA}-GCE pos-

Table 1. Recovery and precision data for Tl^+ and Pb^{2+} obtained on tape and lake water samples ND: none detected. The measurements were repeated three times.

Sample	Ions	Original concentration (mol L^{-1})	Added (1.0×10^{-7} mol L^{-1})	Found (1.0×10^{-7} mol L^{-1})	Recovery (%)
Tap water	Tl^+	ND	5.00	4.90	98.1
	Pb^{2+}	ND	5.00	4.81	96.3
Lake water	Tl^+	ND	5.00	5.13	102.5
	Pb^{2+}	ND	5.00	4.65	93.0

sesses high stability and long life. In view of its environmental friendly characteristics, it adds diversity to the application of mercury-free electrode in trace metal ions analysis. More importantly, it is very easy to be renewed.

5. Acknowledgements

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6. References

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