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A Highly Selective Potentiometric Sensor Based on 2,2'-Dithiosalicylic Acid for Sensitive Determination of Pb^{2+} in Aqueous Solution

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ABSTRACT

Here, we report the application of 2,2'-dithiosalicylic acid (DTSA) as a highly selective and sensitive reagent in construction of an efficient sensing element for a durable carbon past electrode for selective potentiometric determination of lead (II) in aqueous solution. This sensor exhibits a Nernstian response for Pb^{2+} ion in a wide concentration range from 8.3×10^{-6} to 3.0×10^{-1} M with a limit of detection 6.7×10^{-6} M. A short response time (~50 s) and the capability of being used without any considerable divergence in measuring potentials for at least four months are distinguished characteristics of this electrode. The proposed electrode was successfully applied to potentiometric determination of Pb^{2+} ion in some different real samples. The merit of data gathered by this electrode was proven by atomic absorption spectrometry as a standard method. The comparison was reasonably acceptable and revealed the good efficiency of the sensor to introduce as a tool with trustworthy qualities for determination of lead (II).

1. Introduction

Electrochemical sensors are well-known tools in analytical chemistry. As we know, the performances of such tools depend on the efficiency of their sensing element, which is incorporated as the heart of the sensor. On the other hand, if the sensor includes robust parts, its applicability will be more useful. Since the discovery of Carbon Paste Electrodes (CPEs) by Adams [1], they have attracted much attention due to their advantages such as ease of preparation, stable response, wide potential windows, and no need for an internal solution. Due to the above-mentioned properties, CPEs found direct applications in a variety of analytical techniques, such as amperometry, voltammetry and potentiometry [2–10]. In addition, CPEs are highly selective, highly sensitive and measuring low detection limits as ion selective electrodes [2–15].

Lead is one of the heavy metals, which are toxic in the environment. Lead may enter the environment through the various industrial products and remain in ecological systems and in the food chain indefinitely because it is not biodegradable. Lead is a neurotoxic metallic element that can be absorbed by the body, accumulated in bones and tissues and greatly threaten human health. For example, excessive Pb^{2+} could result in a wide range of health problems, such as nausea, convulsions, coma, nerve disorders, high blood pressure, cancer and negative effects on metabolism [16]. Thus, determination at low levels of lead in aqueous solution is very important.

There are a number of analytical techniques for measuring trace concentrations of lead, such as spectrophotometry, inductively coupled plasma optical emission spectrometry (ICP OES), atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (MC-ICP-MS) and HPLC [17–29]. These techniques require a good infrastructure development, maintenance and expensive apparatus. Compared to these options, electrochemical methods have the advantages of high sensitivity and selectivity, simplicity and low cost.

In this work, we introduce the design and fabrication of a new CPE based on 2,2'-dithiosalicylic acid (DTSA) for selective determination of Pb(II) by potentiometric method. The results will show that the proposed electrode exhibit an outstanding performance including a wide working concentration range, fast response time and low detection limit.

2. Experimental Methods

2.1 Reagents

The ligand 2,2'-dithiosalicylic acid (DTSA, Fig. 1) was purchased from Merck and used as received. Graphite powder (GP) and paraffin oil (PO) were purchased from Fluka, Switzerland. All nitrate salts of the needed cations were purchased from Merck. Other materials were of the analytical reagent grade (from Fluka). We prepared all required aqueous solutions with double distilled water.

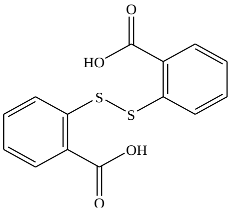

Fig. 1 Chemical structure of 2,2'-dithiosalicylic acid

2.2 Apparatus

Potentiometric and pH measurements were carried out by a pH/mV-Meter Model 3020 (Jenway, UK). The CPE and a saturated calomel electrode (SCE) were used as the indicator and the reference electrode, respectively. All potential measurements were carried out at 25.0 °C.

2.3 Preparation of Carbon Paste Electrode

The needed CPEs were prepared by mixing proper amounts of GP and DTSA. Then, 1 drop of PO was added to the mixture and mixed until a uniform paste was formed. Paste containers, electrode bodies, were made of polypropylene tubes (2 mm id.), the tips of which had been cut off with a sharp cutter. A portion of the carbon paste was packed into one end of a tube. Electrical contact with the carbon paste was made by a copper wire connected to the paste in the inner hole of the tube. The surface of the electrode was smoothed on a filter paper to obtain a fresh surface before use.

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2.4 Potentiometric Measurements

The electrochemical cell system of the electrode was constructed as represented as follows:

CPE | Test Solution | SCE

All potentiometric measurements were directly read from the pH/mV-Meter.

3. Results and Discussion

3.1 Composition and Potential Response Characteristics of the Electrode

The electrode was prepared and used for possible detection of some different cations. The potential measurements were recorded after immersion the electrode assembly into a beaker containing 30 mL of various concentrations of the test ions. We plotted a calibration graph by plotting the potential, E, versus the logarithm of the cation concentration (Fig. 2). As this figure show, among different cations tested, Pb^{2+} with the most sensitive response seem to be suitably determined with the electrode.

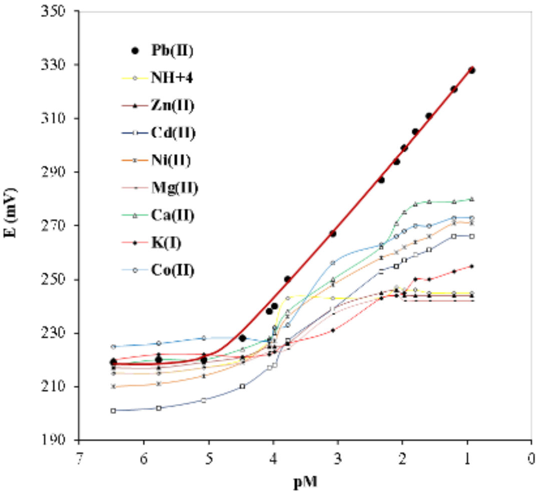

Fig. 2 Calibration graph for the proposed electrode towards different cations in the solution.

Electrode composition has a great effect over the sensitivity, selectivity and stability of the sensor [30, 31]. Thus, different aspects of the composition of the electrode based on DTSA were examined by preparing various electrodes and recording their potential responses to lead (II). The optimized electrode demonstrated a Nernstian response and remarkable selectivity for Pb^{2+}. The results are summarized in Table 1. From this table, the response of the electrode including other components of the electrode composition (without DTSA) was tested ("white electrode"), for which no considerable response was detected (No. 1). The optimum amount of the modifier DTSA was determined through electrodes 2 to 6 (Table 1). We found that the best performance is reachable when the DTSA amount is 6 mg in the presence of 30 mg of PO. Because of the influence of the amount of PO on the electrode function, this effect was tested over two other different electrodes including different amounts of PO (Nos. 7 and 8, Table 1). As can be seen, the electrode function is at its highest value when the PO content is 30 mg. Therefore, the optimum condition, under which the performance of the electrode (slope, detection limit and dynamic range) is at the best situation, is as 100:30:6 mgs of GP:PO:DTSA, respectively (No. 5, Table 1).

Table 1 The performance charactrictics of different electrode with various compositions toward Pb^{2+}

No.	Composition (mg)			Slope (mV/dec)	Linear dynamic range (M)	Detection limit (M)
	Graphite	Ligand	Paraffin oil			
1	100	–	30	–	–	–
2	100	3	30	17.8	3.3×10^{-5}–1.2×10^{-1}	2.5×10^{-5}
3	100	4	30	26.4	1.7×10^{-5}–1.2×10^{-1}	1.2×10^{-5}
4	100	5	30	27.0	2.5×10^{-5}–1.2×10^{-1}	2.65×10^{-5}
5	100	6	30	29.9	8.3×10^{-6}–3.0×10^{-1}	6.7×10^{-6}
6	100	7	30	29.4	1.7×10^{-5}–1.2×10^{-1}	9.3×10^{-6}
7	100	6	20	27.3	3.3×10^{-5}–1.2×10^{-1}	2.8×10^{-5}
8	100	6	40	34.6	8.3×10^{-6}–6.25×10^{-2}	9.3×10^{-6}

A clear calibration curve was plotted from the electrode potential responses against various concentrations of Pb^{2+} in the presence of the constructed CPE based on the above optimal conditions (Fig. 3). As this figure shows, the electrode could be used satisfactorily over a linear dynamic concentration range of 8.3×10^{-6} to 3.0×10^{-1} M of Pb^{2+}.

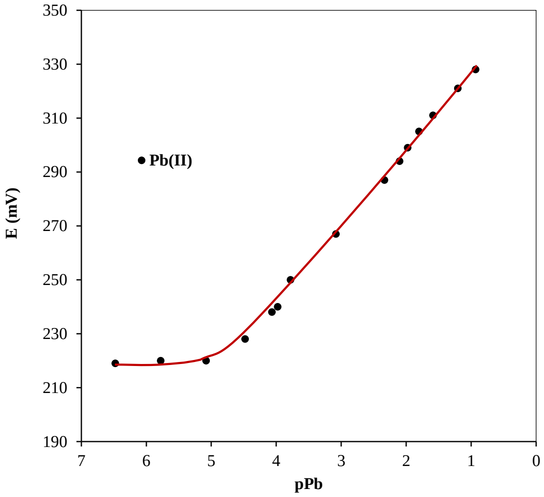

Fig. 3 Calibration graph of the modified CPE for Pb^{2+} in solution.

The detection limit (DL) of the electrode was evaluated from the intersection of the two extrapolated segments of the calibration curve in Fig. 3. Therefore, a detection limit of 6.7×10^{-6} M was evaluated for determination of Pb^{2+} in a solution.

3.2 Effect of pH

In most cases, the solution pH is an important influencing factor on the electrochemical reactions in aqueous media [32]. The influence of the pH on the potential values of the CPE electrode system was investigated in the pH range of 1 – 7 in the presence of 1.6×10^{-3} M of Pb^{2+} in buffer solutions of acetate (0.1 M). The desired pH values were adjusted by adding small amounts of concentrated HCl or NaOH. Representative curves for effect of pH on CPE responses are shown in Fig. 4. This figure shows that the electrode has a better characteristic response about pH of 2.0. Therefore, this pH value was chosen as the optimum pH for the system in subsequent measurements.

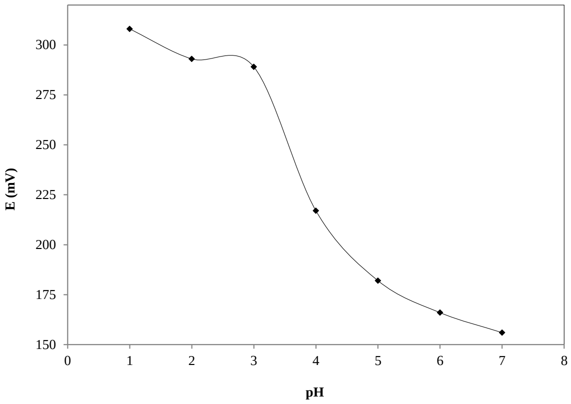

Fig. 4 Effect of the pH of the test solution on the potential response of the CPE (electrode no.5) in the presence of 1.6×10^{-3} M of Pb^{2+} in buffer solutions of acetate (0.1 M).

3.3 Response Time and Reversibility

Response time is a significant parameter of the electrode [33]. According to IUPAC recommendations [34], response time may be defined as the time after the addition of the analyte to the sample solution when a limiting potential has been reached. The response time was measured by recording the electromotive force (emf) of the electrode as a function of time when it is immersed in a buffered solution containing 4.6×10^{-3} M $Pb(NO_3)_2$. The results are shown in Fig. 5. The response time of the sensor was obtained about 50 s, which is a short period and is an advantage for this electrode. For this reason, this electrode would be a useful tool for lead (II) determination and can easily be used for routine analyses.

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Another important factor that must be evaluated for the proposed electrode is reversibility of the potentials measured by the electrode [34]. The reversibility of the CPE was evaluated by potential recording of the electrode in the sequence high-to-low from 1.0 × 10^{-2} to 1.0 × 10^{-4} M sample concentrations of Pb^{2+}. The results are shown in Fig. 6. The sensing behavior of the sensor remained unchanged when the potentials were recorded either from the low to the high concentrations or vice versa, a good evidence for reasonable reversibility of the electrode. The evaluated %RSDs were of ±0.2 and ±0.3 ("within group" errors) for the lower and the upper Pb^{2+} concentrations, respectively. Thus, the responses of the electrode are quite repeatable and reversible.

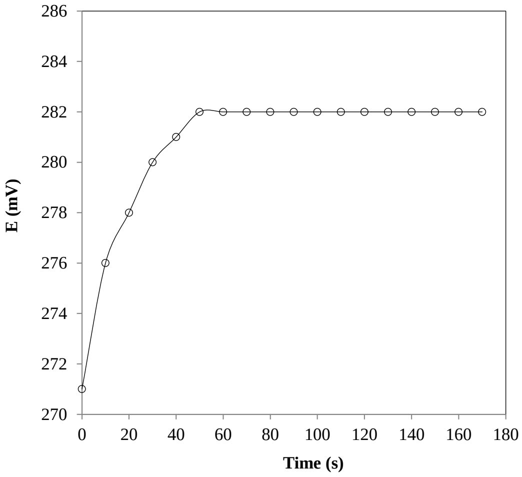

Fig. 5 Practical response time determination by plotting of potential against time, from the moment of addition of Pb^{2+} (4.6×10^{-3} M) solution, for the Pb^{2+} modified CPE, at pH=2.

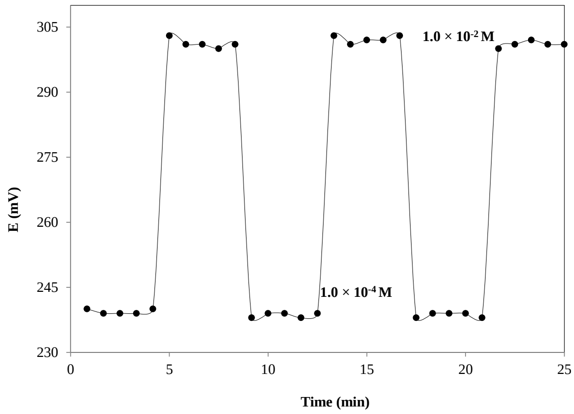

Fig. 6 Dynamic response of the proposed electrode for reversibility with two different concentrations of Pb^{2+}, 1.0×10^{-4} and 1.0×10^{-2} M.

3.4 Potentiometric Selectivity Coefficients

Selectivity of the new electrode toward other common and interfering ions is a major character of the electrode, without which the electrode evaluation would be meaningless [35]. To investigate the potentiometric selectivity coefficients of the CPE over the other common ions, fixed interference ion method (FIM), recommended by IUPAC [34], was used. The emfs of a cell comprising a CPE electrode and a reference electrode (SCE) were measured for solutions of the constant activity of the interfering ion, a_B, and varying activities of the primary ion, a_A. The emf values obtained were plotted vs. the logarithm of the activities of the primary ion, A. The intersection of the extrapolated linear portions of this plot indicates the value of a_A that is to be used to calculate $K_{A,B}^{pot}$ from the following equation:

$$K_{A,B}^{pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

where both z_A and z_B are charges of the primary (A) and the interfering (B) ions.

In this manner, the CPE and the reference electrodes were placed in a 30.0 ml of 1.0 × 10^{-2} M of the interfering ion, B, solution and various volumes of $Pb(NO_3)_2$ solution were added to obtain various concentrations of lead(II). After each addition, the cell potential was recorded. The results are summarized in Table 2. This table show that the electrode exhibited high selectivity for lead (II) over some common cations. Some minor interference could be expected for monovalent ions in this table. This unwanted results come from the nature of the evaluation method, FIM, in which the resulted values are apparently higher than the real effect of the corresponding ion for monovalent cations in the solution.

Table 2 Potentiometric selectivity coefficients of the proposed electrode with respect some diverse cations

Cation	$K_{A,B}^{pot}$
Ni^{2+}	1.4×10^{-3}
Al^{3+}	1.9×10^{-3}
Mg^{2+}	2.2×10^{-3}
Co^{2+}	2.9×10^{-3}
Cr^{3+}	6.3×10^{-3}
Cu^{2+}	6.2×10^{-1}
Na^{+}	6.7×10^{-2}
K^{+}	9.3×10^{-2}
NH_4^{+}	2.1×10^{-1}

3.5 Stability and Lifetime

The stability and lifetime [34] of the proposed sensor were tested on a period of 4 months. During this period, no significant change (<3%) observed on the optimized response characteristics of the electrode. This shows that the electrode has a good lifetime and is durable for using at practical situations.

3.6 Analytical Applications

The electrode was employed for the determination of lead (II) ion in some real samples by using standard addition method.

3.6.1 Lipstick Sample

Exactly 1 g of a lipstick sample was placed in a beaker and digested in 5 mL mixture of concentrated nitric and perchloric acids (in a ratio of 3:1). Then the mixture was heated until a white color residue appeared (about 3 h). The digested sample was completely dissolved in 10 mL of double distilled water, filtered and diluted to 25.0 mL.

3.6.2 Solder Alloy

A sample 0.1 g was put in a beaker and a mixture of 10 mL of double distilled water and 5 mL of concentrated nitric acid was added, then it was heated until the alloy was dissolved, followed by reduction of the volume until a light color precipitate appeared. The solution was finally diluted to 50 mL after filtering.

3.6.3 Water Sample

The water sample was first boiled for about 5 min to remove Cl_2. The pH values of the water sample were adjusted to around 2.0 by HNO_3.

The concentrations of Pb^{2+} ion in these samples were determined by the proposed CPE. In addition, the lead (II) contents of the sample solutions were examined by AAS as a standard method. The results of four repeated measurements are given in Table 3. As it can be seen, the amounts of lead (II) in the environmental samples can accurately be determined by the proposed method and reasonably, there are good agreements between the results obtained by the two methods.

Table 3 The concentrations of Pb^{2+} ion in some real samples, determined by the new carbon paste electrode and atomic absorption spectroscopy as a standard method (for four repeated measurements)

Sample	New electrode (ppm)	AAS (ppm)
lipstick	3.5 ± 0.1	3.4 ± 0.1
solder alloy	242.5 ± 0.2	246.1 ± 0.1
water sample	6.7 ± 0.1	6.3 ± 0.1

4. Conclusion

In the present work, a modified carbon paste electrode based on 2,2'-dithiosalicylic acid for determination of Pb(II) was prepared. The results of this study indicated that the electrode has good operating characteristics such as high sensitivity, good stability, fast response time, low detection limit and a wide linear working range. The proposed electrode was successfully applied for determination of trace amount of Pb^{2+} ion concentration in real samples.

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