Determination of Pb^{2+} ions by a modified carbon paste electrode based on multi-walled carbon nanotubes (MWCNTs) and nanosilica

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ABSTRACT

A novel carbon paste ion selective electrode for determination of trace amount of lead was prepared. Multi-walled carbon nanotubes (MWCNTs) and nanosilica were used for improvement of a lead carbon paste sensor response. MWCNTs have a good conductivity which helps the transduction of the signal in carbon paste electrode. The electrode composition of 20 wt% paraffin oil, 57% graphite powder, 15% ionophore (thiram), 5% MWCNTs, and 3% nanosilica showed the stable potential response to Pb^{2+} ions with the Nernstian slope of 29.8 ($\pm$0.2) mV decade^{-1} over a wide linear concentration range of 10^{-7}–10^{-2} mol L^{-1}. The electrode has fast response time, and long term stability (more than 2 months). The proposed electrode was used to determine the concentration of lead ions in waste water and black tea samples.

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1. Introduction

Lead is the eighty-second element in the periodic table. Lead has a number of uses but many of these are currently being phased out because of growing awareness of its toxicity and of the damage that uncontrolled dispersion in the environment has already caused. Lead is employed in accumulators, ammunitions, piping, paints, in anti-radiation screens and tin-based welding alloys. In the past, lead was added to petrol in the form of tetra-ethyl lead (PbEt$_4$) with an anti-knocking function; however, in developed countries this kind of petrol is currently being phased out for environmental reasons. Lead may also enter the environment as a by-product of mining and of the industrial processing of other metals, such as silver, gold, bismuth, etc.

Lead poisoning is a medical condition caused by increased levels of the metal lead in the blood. Lead may cause irreversible neurological damage as well as renal disease, cardiovascular effects, and reproductive toxicity [1].

Lead ranks second in the list of prioritised hazardous substances issued by the U.S. ATSDR (Agency for Toxic Substances and Disease Registry) in 1999. The noxious effects of this metal have long been well known, especially as regards acute forms of poisoning. How-

ever, as for many other contaminants, the threshold level of safety has been drastically lowered recently. Until approximately 30 years ago, chronic lead poisoning was defined by blood lead levels above 80 (gr/dl, while today a lead level of 30 (gr/dl in blood is considered excessive and levels at or above 10 (gr/dl (0.1 ppm) are considered potentially harmful, particularly in children [2].

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process due to accumulation, exposure and direct contact. These dangers have long been known, though the modern understanding of their full extent and the small amount of lead necessary to produce them is relatively recent; blood lead levels once considered safe are now considered hazardous, with no known threshold.

Now a days, the importance of controlling the level of environmental pollutants in natural waterways and potable water has generated increasing interest in the development of novel sensors for the detection of heavy metals such as lead ions. Lead has toxicity effects to human health. Accordingly, the development of methods for its determination in various biological and environmental samples is both necessary and challenging.

Carbon paste electrodes (CPEs) have attracted attention as ion selective electrodes mainly due to their advantages over membrane electrodes such as renewability, stable response, low ohmic resistance, no need for internal solution [3–7]. The carbon paste usually consists of graphite powder dispersed in a non-conductive mineral oil.

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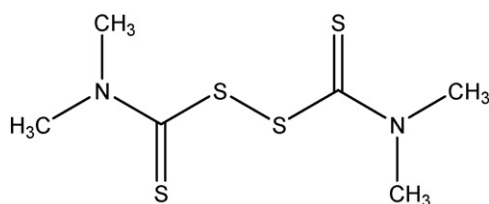
Fig. 1. Chemical structure of tetramethyl thiuram disulfide (thiram) ionophore.

Now a days, carbon nanotubes (CNTs) have also been used in carbon paste electrodes [8–10]. CNTs have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [11]. The facility of electron transfer between the electroactive species and the electrodes offers great promise for fabricating electrochemical sensors and biosensors. The combination of these characteristics make CNTs unique materials with the potential for diverse applications [12–21].

Silica-based materials are of interest for a number of reasons. They are robust inorganic solids displaying both high specific surface area ($200–1500\,m^2\,g^{-1}$) and a three-dimensional structure made of highly open spaces interconnected to each other. This would impart high diffusion rates of selected target analytes to a large number of accessible binding sites, which constitutes definite key factor in designing sensor devices with high sensitivity. On the other hand, a large variety of organic moieties or inorganic layers of defined reactivity can modify the silica surface. When applied in connection to electrochemistry, these properties could be advantageously exploited in electroanalysis by inducing high selectivity (either by specific binding or by preferential recognition), or enabling electrocatalysis at the modified electrode [22].

In this study, Pb^{2+} carbon paste electrode based on tetramethyl thiuram disulfide (thiram) ionophore, Fig. 1, was constructed in order to determine Pb^{2+} ion concentration. Then the electrode was modified by MWCNTs and nanosilica to achieve the better electrode response. The modified electrode was successfully used in determination of lead content of waste water and black tea samples.

2. Experimental section

2.1. Apparatus

The glass cell, where the Pb^{2+} carbon paste electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as a reference electrode. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at $25.0 \pm 0.1\,°C$.

2.2. Reagents

The graphite powder with a <50 μm particle size (Merck), $2.2\,g/cm^3$ density and about 20–30 g/100 mL bulk density, V_{total} $0.35\,cm^3/g$ and SBET $4.5\,m^2/g$; along with the paraffin oil (Aldrich) was of high purity and was used for the preparation of the carbon pastes. The ionophore thiram was purchased from Fluka Co. The multi-walled carbon nanotubes (MWCNTs) with 10–40 nm diameters, 1–25 μm length, core diameter: 5–10 nm, SBET: $40–600\,m^2/g$, V_{total}: $0.9\,cm^3/g$, bulk density $0.1\,g/cm^3$, true density $2.1\,g/cm^3$ and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran). Nanosilica used is Wacker HDK® H20 with BET surface of the hydrophilic silica of $170–230\,m^2/g$, V_{total}: $0.81\,cm^3/g$ and tamped density 40 g/lit.

2.3. Carbon paste electrode preparation

Different amounts of the ionophore thiram along with appropriate amount of graphite powder, nanosilica and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 24 h by soaking in a $1.0 \times 10^{-3}\,mol\,L^{-1}$ $Pb(NO_3)_3$ solution.

2.4. Emf measurements

The electrochemical cell can be represented as follows:

Ag, AgCl(s), KCl(3 M)||samplesolution|carbonpasteelectrode

Calibration graph was drawn by plotting the potential, E, versus the logarithm of the lead ion concentration.

3. Results and discussions

Selectivity for a certain ion selective sensor is greatly related to the ionophore used [23–25]. Due to the existence of sulfur donor atoms, which is a soft base, in the structure of thiram, its interaction with some mono, di and trivalent metal ions was studied conductometricly in acetonitrile solution [26,27]. The results showed that thiram has special interaction with Pb^{2+} ions, which is a soft acid, in comparison with other cations tested (log $K_f = 5.43 \pm 0.17$) and may act as a suitable ion carrier in fabrication of Pb^{2+} CPE.

3.1. Electrode composition and modification

Different carbon paste compositions, as shown in Table 1, were prepared. As it can be seen, two kind of carbon paste electrode was prepared (modified and unmodified CPEs). The best unmodified CPE, with optimized composition (CPE No. 2), shows a near Nernstian slope about 26.1 mV decade^{-1}.

Using MWCNT in the composition of the carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values. It is clearly seen from Table 1, CPE No. 5.

Using nanosilica in the composition of the carbon paste can also improve the response of the electrode. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode.

3.2. Calibration curve

The measuring range of an ion selective electrode includes the linear part of the calibration graph as shown in Fig. 2. Measurements can be performed in this lower range. According to another definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [28–32]. The applicable measuring range of the

Table 1
The optimization of the carbon paste ingredients.

CPE no.	Paraffin (%)	Thiram (%)	Graphite powder (%)	MWCNTs (%)	Nanosilica (%)	Slope (mV decade^{-1})	DL (mol L^{-1})	Linear range (mol L^{-1})	R^2
1	20	10	75	0	0	16.5 ± 0.3	5.0×10^{-6} to 1.0×10^{-3}	5.0×10^{-6}	0.972
2	20	15	65	0	0	26.1 ± 0.3	5.0×10^{-6} to 5.0×10^{-2}	4.3×10^{-6}	0.992
3	20	20	60	0	0	25.7 ± 0.5	7.0×10^{-6} to 5.0×10^{-2}	5.0×10^{-6}	0.982
4	25	15	60	0	0	24.5 ± 0.3	8.0×10^{-6} to 1.0×10^{-3}	5.5×10^{-6}	0.989
5	20	15	60	5	0	28.2 ± 0.2	7.0×10^{-7} to 5.0×10^{-2}	5.0×10^{-7}	0.994
6	20	15	55	10	0	27.4 ± 0.3	1.5×10^{-6} to 5.0×10^{-2}	3.0×10^{-6}	0.993
7	20	15	59	5	1	28.8 ± 0.3	5.0×10^{-7} to 1.0×10^{-2}	5.0×10^{-7}	0.997
8	20	15	57	5	3	29.8 ± 0.2	1.0×10^{-7} to 1.0×10^{-2}	7.3×10^{-8}	0.998
9	20	15	55	5	5	28.3 ± 0.5	1.0×10^{-7} to 1.0×10^{-2}	1.0×10^{-7}	0.991
10	20	15	62	0	3	20.8 ± 0.3	4.0×10^{-7} to 4.0×10^{-2}	2.0×10^{-7}	0.995

modified sensor as shown in Fig. 2 is between 1.0×10^{-7} and 1.0×10^{-2} mol L^{-1}.

By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated [33–35].

In this work the detection limit of the modified CPE was 7.3×10^{-8} mol L^{-1} which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 2.

3.3. pH effect on the electrode response

In order to investigate the pH effect on the potential response of the electrode, the potentials were measured for a fixed concentration of Pb^{2+} solution (1.0×10^{-4} mol L^{-1}) having different pH values. The pH varied from (2–10) by addition of HNO$_3$ or KOH. The potential variation as a function of pH is plotted in Fig. 3. The composition of the electrode was kept constant during all experiments. The results showed the potential of electrode is constant between pH (4–8). Thus the electrode works satisfactorily in the pH range 4–8, as no interference from H$^+$ or OH$^-$ is observed in the range. The fluctuations above the pH value of 8.0 might be justified by the formation of the soluble and insoluble Pb^{2+} ion hydroxy complexes in the solution. And the fluctuations below the pH value of 4.0 were attributed to the partial protonation of the employed ligand [36,37].
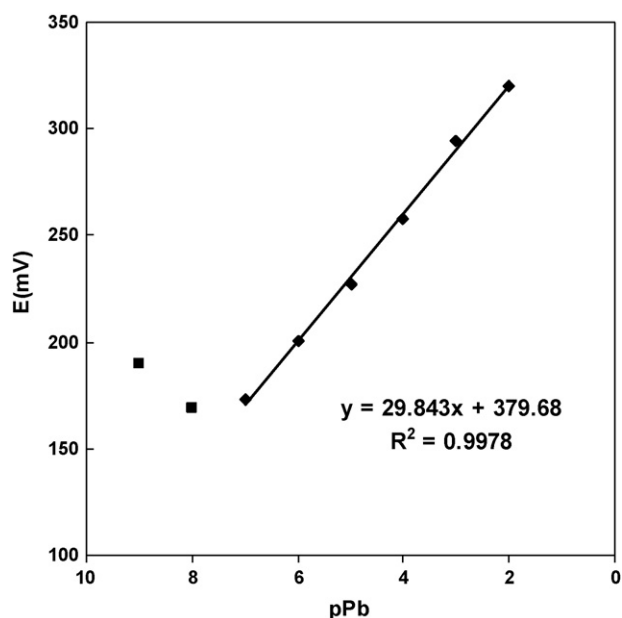
3.4. Response time

The response time of an ion-selective electrode is also an important factor for any analytical application. In the case of all electrodes, the average response time was defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference [38–41]. The resulting potential–time responses for the mentioned electrode were obtained upon changing the Pb^{2+} concentration from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} (by fast injection of μL-amounts of a concentrated solution of Pb^{2+}). Results showed that the potentiometric response time of the electrode was about 10 s.

3.5. Interference studies

The potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the lead ion, Pb^{2+}, were determined by the matched potential method (MPM). The MPM is recommended by IUPAC [42] to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation [43].

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (1.0×10^{-7} mol L^{-1} lead nitrate, in this case) and the potential is measured. In a separation experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient,
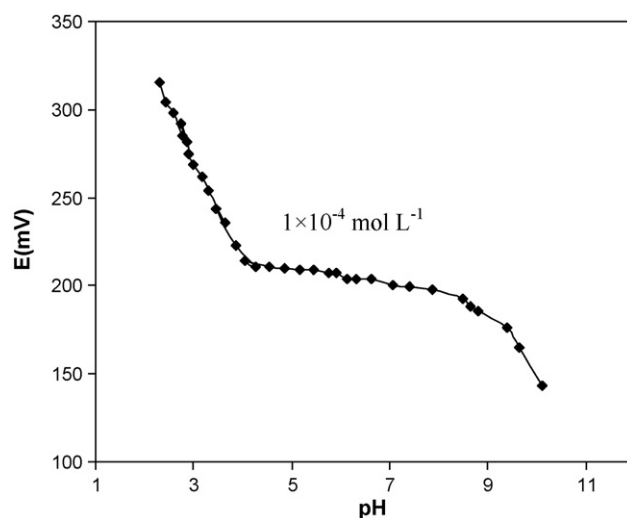

Fig. 2. The calibration curve of the Pb^{2+} modified CPE (electrode no. 8).

y = 29.843x + 379.68
R^2 = 0.9978

1×10^{-4} mol L^{-1}

Fig. 3. pH effect on the potential response of the Pb^{2+} modified CPE (electrode no. 8).

Table 2
The selectivity coefficients of various interfering cations for the electrode no. 8.

Interference (x)	$k_{Pb,X}^{MPM}$
Mg^{2+}	5.3×10^{-4}
Hg^{2+}	1.5×10^{-2}
Co^{2+}	1.3×10^{-3}
Ba^{2+}	8.2×10^{-4}
Ca^{2+}	6.7×10^{-4}
Zn^{2+}	2.5×10^{-3}
Ag^+	8.0×10^{-4}
Na^+	2.3×10^{-4}
K^+	1.1×10^{-3}
Cd^{2+}	7.5×10^{-3}
Cu^{2+}	1.6×10^{-3}
Ni^{2+}	1.4×10^{-3}
Fe^{3+}	5.1×10^{-4}

$k_{Pb,X}^{MPM}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $k_{Pb,X}^{MPM} = \Delta \frac{a_{Pb}}{a_X}$ [44–48]. The resulting values for the Pb^{2+} CPE are listed in Table 2. The selectivity sequence of the employed modified CPE for different inorganic cations more or less obeys the order:

$$Hg^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > K^+ > Ba^{2+}$$
$$> Ag^+ > Ca^{2+} > Fe^{3+} > Mg^{2+} > Na^+$$
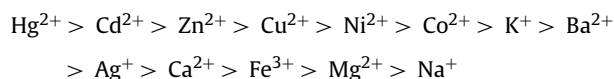
3.6. Lifetime

The lifetime of the modified electrode was studied by periodically recalibrating the potentiometric response to Pb^{2+} ion in standard lead nitrate solutions. After the conditioning step the electrode repeatedly calibrated three times during a period of 1 month, no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about 2 months.

3.7. Analytical application

3.7.1. Waste water samples
To assess the applicability of proposed electrode in real samples an attempt was made to determine lead ions in waste water samples. The analysis was performed by using the standard addition method and direct potentiometry using calibration curve method. The results are given in Table 3. The results obtained by the modified electrode in combination with those obtained by certified inductively coupled plasma (ICP) method. These results demonstrated the applicability of the developed sensor with the employment of the nanosilica and nanotubes for interference-free determination of lead traces in the analyzed environmental samples.

3.7.2. Black tea samples
The proposed method was also applied to the determination of lead ion in three black tea samples. The procedure used for the extraction of these metals from tea samples was similar to that

Table 3
Determination of Pb^{2+} in waste water samples.

Sample	Concentration of Pb^{2+} (mol L^{-1})		
	Modified CPE* (standard addition method)	Modified CPE* (direct determination)	ICP
A	$4.2(\pm0.2) \times 10^{-6}$	$4.4(\pm0.3) \times 10^{-6}$	$4.1(\pm0.3) \times 10^{-6}$
B	$5.3(\pm0.2) \times 10^{-6}$	$5.7(\pm0.3) \times 10^{-6}$	$5.0(\pm0.2) \times 10^{-6}$
C	$4.7(\pm0.3) \times 10^{-6}$	$5.2(\pm0.4) \times 10^{-6}$	$4.5(\pm0.4) \times 10^{-6}$

* The results are based on triplicates measurements.

Table 4
Determination of Pb^{2+} in black tea samples.

Sample	Concentration of Pb^{2+} (mol L^{-1})	
	Modified CPE (ppm)*	ICP (ppm)
Iraninan black tea-Lahijan (sample 1)	$0.91(\pm0.22)$	$0.80(\pm0.12)$
Iraninan black tea-Lahijan (sample 2)	$1.23(\pm0.43)$	$0.85(\pm0.35)$
Indian black tea-Seylan (sample 3)	$1.23(\pm0.43)$	$0.85(\pm0.35)$

* The results are based on triplicates measurements.

reported in the literature [49]. One gram of the dry tea sample (dried at 110 °C) was placed in a 50 mL beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a watch glass. The beaker was allowed to stand overnight, than the contents were heated (150 °C), for 15 min. The sample was cooled, 8 mL of perchloric acid was added, and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The watch glass was removed and the acid evaporated to dryness at 150 °C. The residue was completely dissolved in 5 mL of 1 mol L^{-1} nitric acid and the solution was transferred to a 100 mL volumetric flask. The solution was neutralized with NaOH solution and diluted to the mark, and the Pb^{2+} content was determined by the proposed electrode with calibration method. The results are shown in Table 4. As it can be seen, the amounts of lead, in black tea samples can be accurately determined with the proposed method.

4. Conclusion

The results of this study show that the potentiometric method using modified carbon paste electrode provides an attractive alternative for the determination of Pb^{2+} ion. The electrode exhibited linear response over a wide concentration range with a Nernstian slope, fast response time, selective to lead ion, and is easy to prepare. Another unique feature of the present sensor for lead is its good long term stability (more than 2 months). The proposed electrode can be successfully applied for determination of trace amount of Pb^{2+} ions in real samples.

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