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Highly Selective and Sensitive Asymmetric Lead Microsensor Based on 5,5,dithiobis(2-nitrobenzoic acid) as an Excellent Hydrophobic Neutral Carrier for Nano Level Monitoring of Lead in Real Samples

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Solution investigations between 5,5,dithiobis(2-nitrobenzoic acid) (DTBA) and a number of alkali, alkaline earth, transition and heavy metal ions showed a strong tendency of DTBA for lead ions. Then, it was evaluated as neutral ionophore in construction of an asymmetric lead microsensor. The proposed lead microsensor with a membrane composition containing 18% poly(vinyl chloride) (PVC), 74% dibuthyl phthalate (DBP) as solvent mediator, 3% potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) as an anionic additive, and 5% DTBA as an ionophore. The microsensor exhibits a nice Nernstian response of 29.1±0.4 mV per decade of lead activity, and a wide dynamic working range 1.0×10^{-3}-1.0×10^{-9} M. The detection limit of the sensor is 6.0×10^{-10} M and can be used in the pH range of 3.5-9.0. The microsensor has fast response time, and relatively long life time (more than 12 weeks). It was applied for the determination of lead ion contents in water, black tea, hot and black pepper samples.

Keywords: Sensor; Lead Microsensor; Potentiometry; Ion-selective electrode; 5,5,dithiobis(2-nitrobenzoic acid)

1. INTRODUCTION

Lead is the most widely used of the heavy metals. It has a number of properties that has made its industrial use increase during the last decades. Lead is known as a toxic element, which it is accumulative, slow acting and produces a variety of symptoms. The toxic action level of lead is depends on its chemical form. Because of the increased industrial use of lead, and its serious hazardous effect to human health, the importance of controlling the level of this pollutant in natural waterways, potable water, soils, and air has generated increasing interest in the development of methods for its monitoring. Among these methods, potentiometric sensors based on solvent polymeric membranes with incorporated ionophores are well known as very useful and fast tools for clinical, chemical and environmental analyses [1-4]. During the last two decades, a large number of neutral ionophores with different selectivities for lead metal ions have been developed and have found widespread applications for the determination of the lead ions in a variety of real samples [5-27]. This technique in the case of asymmetric state and not in the case of conventional ion-selective electrode is competitive in detection limits with atomic techniques, and also they possess the important advantage of being only sensitive to free ions. This capability makes potentiometric sensors very useful tools in speciation measurements [28-32].

In the conventional ion-selective electrodes, the ion-selective membrane is placed between the sample solution and the internal reference solution, the constant composition of which results in a stable potential at both the inner boundary of the membrane and the interface of the internal Ag/AgCl electrode. This makes the sensors very stable and hence, most of the commercially available potentiometric ion-selective devices are based on the conventional ion-selective electrodes. However, the presence of an internal reference solution causes two disadvantages; the relatively big electrode dimensions and relatively high detection limits. In asymmetric sensors, the internal electrode, being either noble metal wire (platinum, silver, and gold) or even a graphite rod which is directly coated with the ion-selective membrane. In addition, the miniaturization of the working electrode for the in vivo or in vitro determination of the analyte or for using in flow injection system is recently an interesting field of research. Asymmetric sensors exhibit several other attractive possibilities, including exploration of macroscopic domains, detection in micro flow system, time-resolved probing of processes in the single cells and analyses of very small sample volume.

To the best our knowledge this work is the first report on asymmetric lead microsensor based on 5,5,dithiobis(2-nitrobenzoic acid) (DTBA), which exhibits high selectivity and sensitivity for lead ions.

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the lead microsensor was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as a reference electrode. The both indicator and reference electrodes were connected to a Corning ion analyzer with a 250 pH/mV meter with ± 0.1 mV precision .

For the conductivity measurements, a Metrohm 660 conductivity meter and a black platinum dip-type conductivity cell (with a 0.83 cm^{-1} cell constant) were used.

All emf measurements were carried out with the following assembly:

Ag-AgCl (satd.) | sample solution | PVC membrane | gold surface

In all measurements, the ionic strength of the solutions was maintained by using 10^{-4} M of NH_4NO_3.

2.2. Reagents and materials

Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), o-nitrophenyloctylether (NPOE), high relative molecular weight poly vinyl chloride (PVC), potassium tetrakis (p-chlorophenyl) borate (KTpClPB) and tetrahydrofurane (THF) were purchased from Merck and used as received. Nitrate or chloride salts of the cations used (from Merck and Aldrich) were all of the highest purity available and used without any further purification. Distilled deionized water was used throughout. DTBA (Fig. 1) was purchased from Fluka Co.

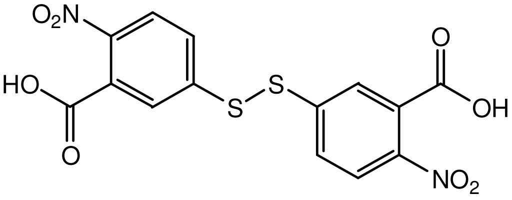

Figure 1. Chemical structure of DTBA

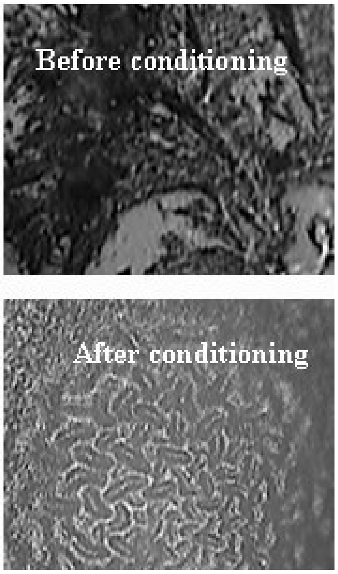

Figure 2. The pictures of membrane sensors before and after conditioning

2.3. Electrode preparation

The general procedure to prepare the PVC membrane was to varying amounts of the ionophore along with appropriate amount of PVC, plasticizer and additive were dissolved in tetrahydrofuran (THF) and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. The gold electrode was prepared by sealing gold micro-wire (Good fellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicular to its length to expose the gold wire. Electrical contact was made using silver epoxy) Johnson Matthey Ltd., UK). Before each experiment the electrode surface was polished for 1 min, using extra fine carborundum paper and then for 10 min with 0.3 μm alumina, sonicated in distilled water and dried in air. The polished gold electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the gold surface and the electrode was allowed to set overnight [29-35]. The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} M of $Pb(NO_3)_2$. The pictures of membrane sensors before and after conditioning are depicted in Fig 2.

2.4. Complexation study procedure

Conductivity measurements can be useful tools to investigate the complexation. In all measurements, the cell should be thermostated at the temperature of 25.0 ºC, using a Phywe immersion thermostat. In typical experiments, 25 mL of an ion solution (1.0×10^{-4} M) are placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, it should be noted that both the starting solution and the titrant have the same ion concentration. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} M) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved.

3. RESULTS AND DISCUSSION

For having a clear clue about the behavior of DTBA with different metal ions, its complexation was studied conductometrically in acetonitrile solution. The formation constants of the 1:1 complexes were calculated using well known equations [36-40]. The resulted formation constants are depicted in Table 1. As it is seen, DTBA has a strong tendency for lead ion respect with other metal ions tested.

Due to the existence of sulfur donor atoms as soft base, in the structure of DTBA and obtained results from solution studies, it seems DTBA can be used as a suitable ionophore for transition and heavy metal ions as soft acids. In preliminary investigations, DTBA was used in construction of a number of microsensors for common alkali, alkaline earth, transition and heavy metal ions and their potential responses were recorded in a wide concentration range of corresponded ions (10^{-2}-10^{-9} M). The potential responses of a number of microsensor are shown in Fig. 3. As it can be seen from Fig. 3

among more than twenty cations tested, except lead microsensors, the responses of all metal ion microsensors were sub-Nernstian or very weak. Thus, ionophore DTBA is very suitable for the fabrication a selective and sensitive asymmetric lead microsensor.

Table 1. The complex formation constants of DTBA with some metal ions

Cations	Log K_f
Li^+	<2.0
Na^+	<2.0
K^+	<2.0
Ag^+	<2.0
Mg^{2+}	<2.0
Ca^{2+}	<2.0
Sr^{2+}	<2.0
Ba^{2+}	<2.0
Cu^{+2}	2.51±0.07
Zn^{+2}	2.25±0.04
Co^{2+}	2.33±0.05
Ni^{2+}	2.40±0.02
Cd^{2+}	2.95±0.03
Hg^{2+}	3.18±0.06
Pb^{2+}	6.22±0.04
Mn^{2+}	2.17±0.03
Fe^{2+}	2.21±0.07

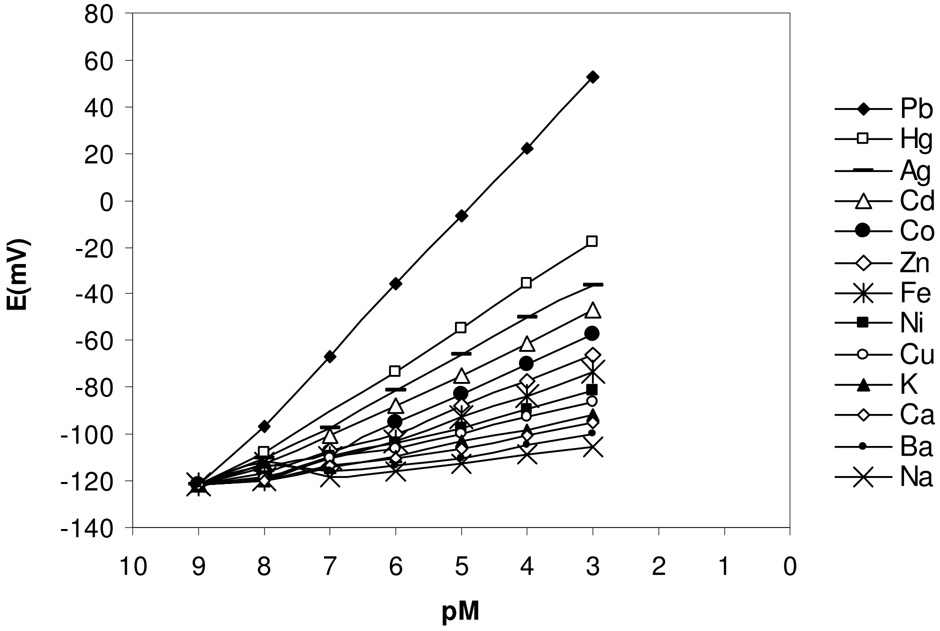

Figure 3. The potential responses of a number microsensors

3.1. Membrane composition effect on the potential response of the microsensor

It is well understood the degree of sensitivity and selectivity for a certain ionophore is greatly related to the membrane compositions. In this study, the effect of different membrane compositions on the response of the lead microsensor was studied and the obtained results are given in Table 2. As can be seen, the membrane with the composition of 18% PVC, 5% DTBA, 3% KTpClPB and 74% DBP (no. 10) is the optimum composition in the preparation of this sensor. This membrane composition was selected for further considerations.

Table 2 shows the effect of the DTBA amounts on the sensitivity of the microsensor. As it is seen, the best response is obtained in the presence of 5% of DTBA. Addition of more 5% to the membrane reduces its sensitivity (no. 6). This is due to the some inhomogeneity in the membrane. From Table 2, it was obvious that in the absence of DTBA in the membrane, while other components are in the membrane (no. 14) the sensitivity is very poor. This is due to the high tendency of DTBA for lead ion.

Table 2 shows among three plasticizers used (NB, NPOE and DBP), DBP with lower dielectric constant increases the sensitivity of the microsensor. This is most probably due to the relatively low charge density of lead ion, which will increase its extraction from aqueous solution to the membrane as an organic phase within a low dielectric plasticizer,

The presence of anionic additive in the response of the lead microsensor was also evaluated. As can be seen from Table 2, addition of 3% of KTpClPB to the membrane increases the slope of the microsensoe from 16.2 to 29.1 mV per decade.

Table 2. Membrane composition effect on the potential response of the microsensor

No.	PVC (%wt)	Plasticizer (%wt)	DTBA (%wt)	KTpClPB (%wt)	Slop (mV/decade)
1	20	DBP, 77	3	-	12.3±0.2
2	20	DBP, 76	4	-	14.7±0.4
3	20	DBP, 75	5	-	15.8±0.3
4	20	DBP, 74	6	-	15.5±0.2
5	19	DBP, 76	5	-	16.1±0.4
6	18	DBP, 77	5	-	16.2±0.3
7	17	DBP, 78	5	-	16.1±0.2
8	18	DBP, 76	5	1	22.7±0.4
9	18	DBP, 75	5	2	25.6±0.3
10	18	DBP, 74	5	3	29.1±0.4
11	18	DBP, 73	5	4	29.0±0.3
12	18	NPOE,74	5	3	25.3±0.2
13	18	NB, 74	5	3	25.7±0.3
14	18	DBP, 79	-	3	3.9±0.2

3.2. Effect of pH on the microsensor response

For understanding the influence of pH on the microresponse response, the potential responses of the lead microsensor were measured at two particular concentrations of the Lead ion solution (1.0×10^{-5} M and 1.0×10^{-7} M) in the pH range of 2.0-11.0 (concentrated NaOH or HCl solutions were used for the pH adjustment) and the resulted data are shown in Fig. 4. As seen, the potential response of the microsensor remained constant in the pH range of 3.5-9.5, which indicating the applicability of this microsensor in the specific pH range. The observed fluctuations above the pH value of 9.0 might be justified by the formation of the soluble and insoluble lead hydroxy complexes in the solution ($Pb(OH)^+$ and $Pb(OH)_2$). On the other hand, the fluctuations below the pH value of 4.0 were attributed to the partial protonation of the employed ionophore.

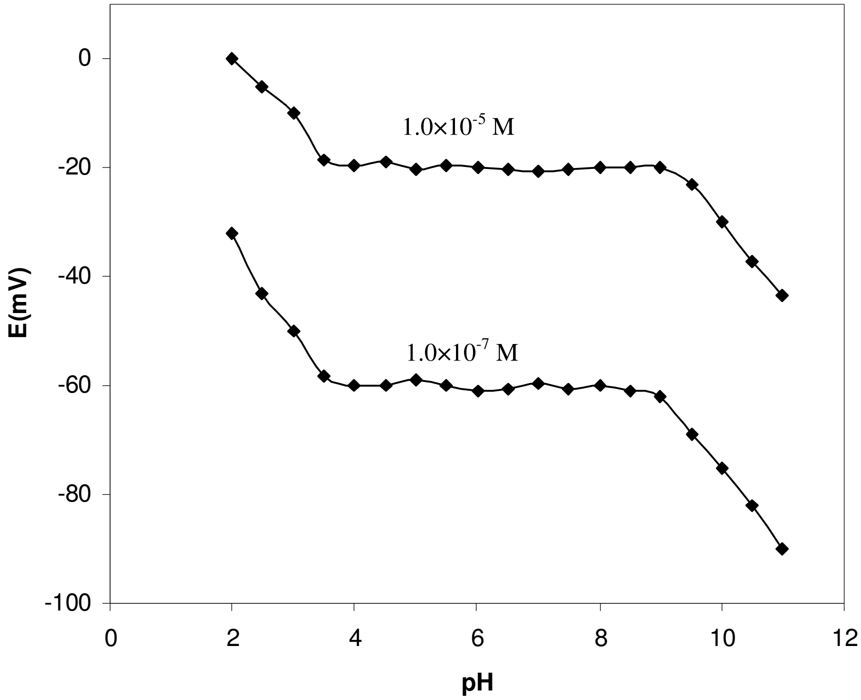

Figure 4. Effect of pH on the microsensor response

3.3. Evaluation of lead microsensor

The performance of any ion-selective electrode is characterized by Measuring rang, detection limit, Response time, Selectivity and Lifetime.

3.3.1. Measuring range and detection limit

The measuring range of the proposed lead microsensor (linear part of the calibration graph) was evaluated by measuring the response of the sensor in a wide concentration range (1.0×10^{-10}–

1.0×10^{-2} M). The obtained results are shown in Fig. 5. As it is seen, the applicable measuring range of the proposed microsensor is between 1×10^{-9} and 1×10^{-3} M.

Detection limit can be calculated by extrapolating the linear parts of the ion-selective calibration curve (Fig. 5). In this work the detection limit of the proposed microsensor was 6.0×10^{-10} M which was calculated by extrapolating the two segments of the calibration curve.

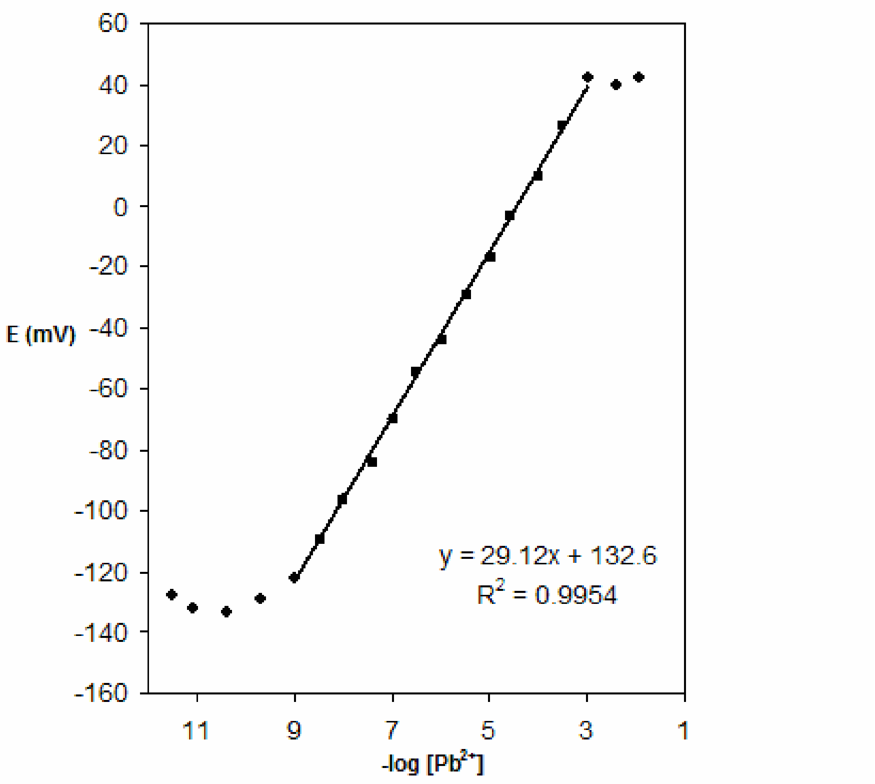

Figure 5. The microsensor calibration curve based on ionophore

3.3.2. Response time

The static response time for any sensor is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. It is notable that the experimental conditions-like the stirring or flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before experiment measurement was performed, any previous usages or preconditioning of the electrode, and the testing temperature have an effort on the experimental response time of a sensor [41-45]. In this work, less than 7 s response time was obtained for the microsensor in the concentration range of 1.0×10^{-6} - 1.0×10^{-3} M, and about 10s for lower concentrations than 1.0×10^{-6} M.

3.3.3. Selectivity

Selectivity, which describes an ion-selective electrode's specificity toward the target ion in the presence of interfering ions, is the most important characteristic of these devices, especially when they applied for concentration determination of target ion in a complexed solution. The matched potential method (MPM) [46-50] was used for the evaluation of potentiometric selectivity coefficients of the lead microsensor. The resulting values of the selectivity coefficients and the conditions are depicted in Table 3. As it is seen, for common alkali and alkaline earth metal ions the selectivity coefficients are lower than 10^{-4}. For common transition metal ions are also smaller than 2.5×10^{-2}, which seems to indicate negligible interferences in the performance of the microsensor assembly.

Table 3. The selectivity coefficients of various interfering cations for the electrode no. 10

Ion	**Log K_{MPM}**
Na^+	-3.5
Mg^{2+}	-3.3
Hg^{2+}	-1.6
Co^{2+}	-2.3
Ba^{2+}	-3.1
Ca^{2+}	-3.1
Zn^{2+}	-2.4
Ag^+	-2.0
K^+	-3.0
Cd^{2+}	-2.1
Cu^{2+}	-2.8
Ni^{2+}	-2.7
Fe^{3+}	-2.6

3.3.4. Lifetime

The lifetime is one of the most important factor for any sensors. The average life time of the reported ion-selective sensors is in the range of 4–10 weeks. Usually, after this periode the slope and detection limit of the sensor will drastically change (decreasing in slope and increasing in detection limit) [51-58]. The life time of the proposed lead microsensor was evaluated tested for 15 weeks, while during this periode the microsensors were used extensively (one hour per day). The obtained results are given in Table 4. As it obvious, the significant changes in the slope and detection limit of the lead microsensor were happen after 12 weeks. Thus, the proposed lead microsensor can be used for at least twelve weeks. During this time a slight gradual decrease in the slopes (from 29.1 to 24.3 mV per decade) and, an increase in the detection limit (from 6.0×10^{-10} M to 5.0×10^{-9} M) will be observed. It is well known the loss of plasticizer, carrier, or ionic site from the pol ymeric film due to leaching into the sample is a primary reason for the limited lifetimes of the sensors.

Table 4. The life time of the proposed lead microsensor

Week	Slope (mV/decade)	Detection Limit (M)
First	29.1 ± 0.3	6.0×10^{-10}
Second	29.2 ± 0.3	6.0×10^{-10}
Third	29.1 ± 0.2	7.3×10^{-10}
Fourth	29.3 ± 0.2	8.1×10^{-10}
Fifth	29.2 ± 0.3	8.3×10^{-10}
Sixth	29.0 ± 0.5	8.7×10^{-10}
Seventh	28.2 ± 0.2	9.0×10^{-10}
Eighth	28.3 ± 0.4	9.5×10^{-10}
Ninth	28.0 ± 0.2	9.8×10^{-10}
Tenth	27.8 ± 0.4	1.0×10^{-9}
Eleventh	27.5 ± 0.3	1.8×10^{-9}
Twelfth	27.2 ± 0.4	2.3×10^{-9}
Thirteenth	26.2 ± 0.3	3.1×10^{-9}
Fourteenth	25.6 ± 0.2	3.7×10^{-9}
Fifteenth	24.3 ± 0.2	5.0×10^{-9}

3.3.5. Comparison study

Literature survey revealed that there is no report on Pb(II) asymmetric potentiometric membrane sensor. The proposed Pb(II) sensor is the first reported Pb(II) sensor. There are more than 30 reports on Pb(II) symmetric potentiometric membrane sensors [5-27]. The proposed sensor because of the different response mechanism and lack of internal filling solution show lower detection limit respect to the previously reported sensors.

3.4. Analytical application

To assess the applicability of proposed electrode in real samples an attempt was made to determine lead ions in water samples. The electrode was applied to the direct measurement of lead ion in local spring waters from the Calsimine lead and zinc mines (Dandi, Zanjan, Iran). The water samples were adjusted to pH of about 5.5 using 0.01 M ammonium nitrate buffer and their potentials were measured by direct potentiometry. The results obtained were compared with those from inductive coupled plasma atomic emission spectrometry (ICP-AES) analysis (Table 5). As seen, the agreement is good and we conclude that the membrane electrode may have applications in the environmental monitoring of lead ions. The proposed sensor was also applied to determination of lead in black tea and pepper samples. One gram of the dry tea sample (dried at 110 ºC) 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 ºC), for 15 min. The sample was cooled, 8 mL of perchloric acid was added, and the mixture was heated again at 200 ºC until the solution became clear (about 1 h). The watch glass was removed and the acid evaporated to dryness at 150 ºC. 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 5. As it can be seen, the amounts of lead, in black tea samples can be accurately determined with the proposed method.

A 100 mg pepper was taken in a beaker and dissolved in concentrated nitric acid (5 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 ml with water in a calibrated flask. An aliquot (10-20 mL) of the sample solution was taken and lead was determined by the calibration procedure. The results are given in Table 5. As seen the results obtained by the proposed method and ICP-AES are in satisfactory agreement.

Table 5. Determination of lead in black tea, hot and black pepper samples

Sample	Pb (μg/g) (Microsnsor)	Pb (μg/g) (ICP-AES)
Water sample 1	1.4 (0.3)	1.1 (0.3)
Water sample 2	1.5 (0.3)	1.3 (0.2)
Iranian black tea (Lahijan)	25.5 (1.4)	26.0 (1.0)
Indian black tea (Seylon)	18.5 (1.2)	18.7 (1.0)
Black pepper	405.5 (1.1)	402.9 (1.6)
Hot pepper	0.05 (1.2)	0.05 (0.9)

4. CONCLUSIONS

1. In this work, the first Pb(II) microsensor was introduced based on 5,5,dithiobis(2-nitrobenzoic acid) (DTBA) as a sensing material.
2. The proposed lead microsensor with a membrane composition containing 18% poly(vinyl chloride) (PVC), 74% dibuthyl phthalate (DBP) as solvent mediator, 3% potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) as an anionic additive, and 5% DTBA as an ionophore.
3. The microsensor exhibits a nice Nernstian response of 29.1±0.4 mV per decade of lead activity, and a wide dynamic working range 1.0×10^{-3}-1.0×10^{-9} M. The detection limit of the sensor is 6.0×10^{-10} M and can be used in the pH range of 3.5-9.0. The microsensor has fast response time, and relatively long life time (more than 12 weeks).
4. It was applied for the determination of lead ion contents in water, black tea, hot and black pepper samples.

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