MINIATURIZED POTENTIOMETRIC SENSORS BASED ON PbS NANOPARTICLES AND A NEWLY SYNTHESIZED IONOPHORE AND THEIR APPLICATION FOR STATIC AND HYDRODYNAMIC MONITORING OF LEAD AS A HAZARDOUS WASTE

Ayman H. Kamel[a,b]*, Fahad M. Al Romian[a], Abdel-Galil E. Amr[c]

New membrane sensors for lead (II) ions are described based on the use of a newly synthesized pyridine carboximide derivatives as neutral ionophore in plasticized PVC membranes (sensor 1) and PbS nanoparticles (NPs) capped in polyvinyl alcohol (PVA) (sensor 2). The sensors exhibited significantly enhanced response towards lead (II) ions over the concentration range 1.0×10^{-7}-1.0×10^{-3} mol L^{-1} at pH 3.0 - /6.5 with a lower detection limit of 7.0-10.0 ng mL^{-1}. The sensors displayed near-Nernstian slope of 28.2-33.5 mV per decade for Pb(II) ions. The sensors showed long life span, good selectivity for Pb(II) over a wide variety of other metal ions, long term stability, high reproducibility, and fast response. Validation of the method by measuring the lower detection limit, range, accuracy, precision, repeatability and between-day-variability revealed good performance characteristics of the proposed sensors. Membrane incorporating the neutral ionophore in a flow detector was used in a two channels flow injection set up for continuous monitoring of Pb^{2+} at a frequency of ca. 48-50 samples h^{-1}. Direct determination of lead in water samples as well as in biological fluids gives results in good agreement with data obtained using standard AAS method.

*Corresponding Authors
     Tel.: +201000743328
     E-Mail: ahkamel76@yahoo.com
[a]   Chemistry Department, College of Science, Qassim
       University, Burayida, KSA.
[b]   Chemistry Department, Faculty of Science, Ain Shams
       University, Abbasia, Cairo, Egypt.
[c]   Pharmaceutical Chemistry Department, College of Pharmacy,
       King Saud University, Riyadh 11451, KSA.

Introduction

Monitoring air, soil and water for hazardous pollutants is important and based on the need to protect the environment and public health from possible distribution of natural and industrial inorganic and organic contaminants. There is a constantly increasing need for online monitoring of contaminants in our environment, driven by new legislation and new technologies.[1] Heavy metals occur naturally in the environment, but, due to industrialization, large amounts of heavy metals bound in fossil fuels and mineral materials have been released into the environment and deposited in trace amounts in nearly every part of the planet. Elevated levels of heavy metals in natural water may have a detrimental effect on both human health and the environment.[1,2]

Lead is the most widely used heavy metal with a number of properties that have made its industrial use increase during recent decades. Lead is an environmental toxicant that affects virtually every system in the body.[3] It is a general metabolic poison and enzyme inhibitor which can cause mental retardation and semi-permanent brain damage with learning and behavior disorders in young children[4]. Moreover, lead has the ability to replace the calcium in bone to form sites for long-term release[5]. Therefore, environmental lead results in a serious and well-known health risk to animals and humans. On the other hand, the presence of trace amounts of lead in many industrial streams is also undesirable, mainly because it may eventually enter the food chain or other products used by people. Hence, the development of analytical methods for the selective and low-level determination of lead ions in natural waterways, potable water, soil, and air is still a challenging task.

In recent years, various techniques for the determination of lead such as spectrophotometric methods,[6] atomic absorption and emission spectroscopy,[7-10] mass spectrometry,[11] and electrochemistry[12-14] have been developed. However, these methods required expensive instruments, well-controlled experimental conditions, frequent maintenance and calibration, and some sample pretreatment. Compared with other analytical methods, potentiometry is an easy and inexpensive technique that has found applications in many clinical, environmental, and toxicological analyses. Most of the reported lead ion-selective electrodes were polymeric membrane electrodes containing neutral carrier ionophores.[15-33]

Nanoparticles (NPs) are attracting attention due to their low cost and unique size-dependent properties. The incorporation of NPs into a variety of matrices to form nanocomposite films is attracting much attention. NPs have been used in many electrochemical, electroanalytical and bioelectrochemical applications. The uniqueness of NPs is due to their mechanical, electrical, optical, catalytic and magnetic properties as well as their extremely high surface area per mass. In addition to novel properties, nanomaterials and nanotechnology open up new approaches to manufacture electrodes cost effectively by minimizing the materials needed and waste generation.[34-36] This is especially relevant to expensive materials (e.g., gold and platinum). For example, inexpensive materials (e.g., carbon
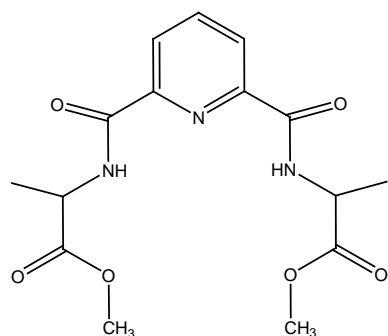
coated by NPs) result in a large ratio of surface area to volume for low-cost sensing electrodes. In recent studies, it was demonstrated that NP electrodes could be obtained with high sensitivity and even with individual NPs giving responses.[37,38] The combination of nanotechnology with modern electrochemical techniques allows the introduction of powerful, reliable electrical devices for effective process and pollution control.

Herein, we investigate the use of a newly synthesized pyridine carboximide derivative (i.e. 2,6-bis((1-(methoxycarbonyl)-N-ethyl)carboxamide)pyridine) as neutral ionophore in plasticized PVC membranes (sensor 1) and PbS nanoparticles (NPs) capped in polyvinyl alcohol (PVA) (sensor 2). The feasibility of employing the above pyridine carboximide derivative as carrier for lead and PbS nanoparticles is examined and their response in terms of detection limit, slope, response time and selectivity over other cations are described. The selectivity behavior, response mechanism, response time and signal stability were evaluated, and found to be superior than most of those previously described. The sensitivity and stability offered by this simple electrode configuration are highly enough to allow accurate determination of low levels of lead in water and biological fluids and the data were compared with atomic absorption spectrometry.

Experimental

Chemicals and reagents

All reagents were of analytical grade and used without further purification. High molecular weight poly(vinyl chloride) (PVC), potassium tetrakis (4-chlorophenylborate) (KTpClPB), *o*-nitrophenyl octyl ether (*o*-NPOE), polyvinyl alcohol (PVA) and dioctyl phthalate (DOP) were obtained from Fluka (Switzerland), dioctyl sebacate (DOS) from BDH Chemical LTD (England) and metal nitrates and tetrahydrofuran (THF) was purchased from Merck (Germany). The ionophore 2,6-bis((1-(methoxycarbonyl)-N-ethyl)carboxamide)pyridine derivative (Fig. 1) was synthesized as described before.[39]

Figure 1. Chemical structure of 2,6-bis((1-(methoxycarbonyl)-N-ethyl)carboxamide)pyridine ionophore

All solutions were prepared with doubly distilled water. A 0.1 mol L^{-1} $Pb(NO_3)_2$ stock solution was prepared and the working solutions of different concentrations were prepared daily by dilution of the stock solution and then by adjusting the ionic strength with 1 mol L^{-1} $LiNO_3$.

Equipments

All potentiometric measurements were made at 25 ± 0.1 ^0C with an Orion pH/mV meter (model SA 720) and Pb^{2+} ion-PVC membrane sensors in conjunction with an Orion Ag/AgCl double junction reference electrode (model 90-02) with 10% (w/v) KNO_3 in the outer compartment. A combination Ross glass pH electrode (Orion 81-02) was used for all pH measurements.

The FIA system consisted of an Ismatech MS-REGLO pump and an Omnifit injection valve (Omnifit, Cambridge, UK) with sample of 100 µL sample. The potential measurements were obtained with a high resolution data logger [Pico Technology limited] (model ADC-16). The flow Tygon tubes were obtained from (AlKEM) (P/N A00349 and P/N A000355), the pump tubes were red/red 0.71 "ID and blue/blue 0.065" ID. The distance between the injection valve and the detector was 40 cm. The end of the tube was placed in a petri dish where a double-junction Ag/AgCl reference electrode was placed downstream from the indicator sensor just before the solution went to waste.

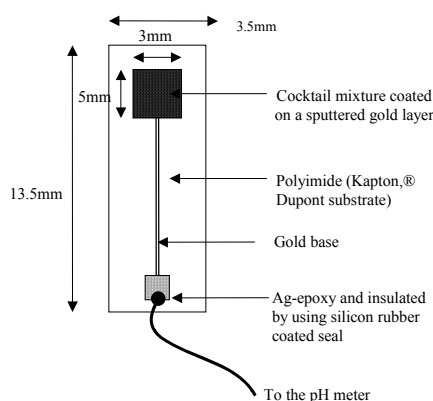### Preparation of PbS nanoparticles

The PbS nanoparticles is prepared by the method proposed by Badr and Mahmoud.[40] Lead acetate $(Pb(CH_3COO)_2.2H_2O)$, 50 mmol L^{-1}, with different volumes (1, 4, 8, 12, and 16 mL) was added to 2.2 g PVA (13,000 g/mol) and the volume of each solution was completed to 50 mL by bidistilled water. Each solution was left for 24 h at room temperature to swell, and then the solutions were warmed up to 60 ^{o}C and stirred for 4 h until viscous transparent solutions were obtained. One milliliter Na_2S (50 mmol L^{-1}) was dropped to each solution with gentle stirring. Each solution was cast on flat glass plate dishes. After the solvent evaporation, a thin film containing PVA-capped PbS NPs was obtained. The films were washed with deionized water to remove other soluble salts.

Sensors fabrication

The membrane cocktail was prepared by adding three milligrams of 2,6-bis((1-(methoxycarbonyl)-N-ethyl)-carboxamide)pyridine derivative ionophore to 124 mg of *o*-NPOE plasticizer, 66 mg PVC and 1mg KTpClPB. All are dissolved in ca. 3 mL of THF.

A planar gold base electrode (3mm×5 mm) was sputtered on a (13.5mm×3.5 mm) flexible polyimide (Kapton®, DuPont) substrate (125 µm thick), as shown in Fig. 2; single site electrode (area = 0.06 cm^2) (used for all the optimization and characterization studies), and used as previously described.[41] An electrical wire was connected to the electrode by means of Ag-epoxy (Epoxy Technology). Insulation of the electrical contact was made using silicon rubber coating seal (Dow Corning 3140 RTV).

The membrane cocktail mixture was directly coated to the sputtered gold layer using micro-syringe to apply few microliters of the sensing solution (typically 10µL of membrane cocktail is dispersed), left to dry in the air for 1 min before repeating further addition (i.e. four times of the sensing solution).

Figure 2. Planar-chip sensor

For sensors based on PbS NPs, the resulting membrane containing PVA-capped PbS NPs was peeled off from the glass mould and disks of 9-mm i.d. were cut out and glued onto a 7-mm i.d. PVC body (2 cm long) using THF. The tube was filled with 1×10^{-3} mol L^{-1} Pb^{2+} solution of pH 4.5. An Ag/AgCl coated wire was used as an internal reference electrode.

Potentiometric procedures

All electrodes were placed in a convenient support over a magnetic stirrer with an Ag/AgCl double junction reference electrode into a 25 mL beaker containing 9.0 mL of 10^{-2} mol L^{-1} acetate buffer solution pH 4. Portions (1.0 mL) of 10^{-6} to 10^{-1} mol L^{-1} standard pb^{2+} solutions were successively added and the potential response of stirred solutions was measured after stabilization to ±0.2 mV. A calibration graph was constructed by plotting the emf readings against the logarithm of Pb^{2+} concentrations. The plot was used for subsequent determination of unknown pb^{2+} ions.

The influence of pH on the electrode potential response of was investigated using 1×10^{-3} and 1×10^{-4} mol L^{-1} of Pb^{2+} solution over the pH range 2–8. Adjustment of pH was carried out using nitric acid or sodium hydroxide solution.

For FIA measurements, a series of 100 µL portions of Pb^{2+} test solutions spanning the concentration range from 1.0×10^{-2} to 1.0×10^{-6} mol L^{-1} were injected into a flow stream of 1.0×10^{-2} mol L^{-1} acetate buffer of pH 4.5, flowing at a rate of 3.5 mL min^{-1}. The lead sensor was used as a working sensor against Ag/AgCl double junction reference electrode. Each solution was measured in triplicate. The average potentials at maximum heights were plotted against log $[Pb^{2+}]$.

Analytical applications

Water samples were spiked by Pb^{2+} at a concentration of 0.5, 1.0, 2.0 and 5.0 µg mL^{-1}. These samples do not need pretreatment before potentiometric determination of Pb^{2+} ions by these sensors using the calibration curve method.

For the determination of lead in human serum, aliquots of human blood were obtained from some volunteers and analyzed within 3 h of extraction. Blood was collected in tubes and then 9 mL portion of absolute ethyl alcohol was added, thoroughly mixed and left for 10 min before being centrifuged at 4000 rpm. The supernatant liquid was without removal of any particulate matter to a 20 mL beaker and then evaporated at 50 °C on a hot plate till dryness before being reconstituted in de-ionized water. A 9 mL of 10^{-2} mol L^{-1} acetate buffer solution of pH 4.5 was added. The extracts were transferred to 25 mL measuring flask and complete to the mark. A 10 mL aliquot of the sample solution was transferred to a 25 mL beaker. The working and reference electrode were immersed, and the potential readings were recorded after reaching the equilibrium response (10–20s). The concentration of lead, expressed as $[Pb^{2+}]$, was calculated using a calibration graph.

For flow injection analysis (FIA), a flow stream of the carrier solution (10^{-2} mol L^{-1} acetate buffer of pH 4.5) was allowed to pass through the flow cell at a flow rate 3.5 mL min^{-1}. Successive 100 µL aliquots of standard 10^{-2} to 10^{-6} mol L^{-1} Pb^{2+} and unknown test sample solutions were injected into the flowing stream. The corresponding potential change was measured and recorded versus time. A typical calibration plot was made used to determine the concentration of the unknown samples.

Result and discussion

Potentiometric characteristics of sensors incorporating 2,6-bis((1-(methoxycarbonyl)-N-ethyl)carboxamide)pyridine derivative ionophore and PbS NPs revealed strong response for Pb^{2+} ions. Results from replicate studies indicated near-Nernstian slope of 22.1±0.6, and 33.5±0.3 mV per decade, with lower detection limits of 0.05 and 0.007 µg mL^{-1} for sensors based on the neutral ionophore and PbS NPs, respectively. Addition of 0.5 wt. % KTpClPB to the ionophore significantly improved the sub-Nernstian calibration slope from 22.1±0.6 to 28.2±0.2 mV per decade and decreased the limit of detection from 0.05 to 0.01 µg mL^{-1}. Typical calibration curves of these sensors are shown in Fig. 3 and their general response characteristics are presented in Table 1.

Replicate measurements (n=10) of an internal quality control (IQS) sample (2.0 µg mL^{-1}, 9.66×10^{-6} mol L^{-1} of certified reference Pb^{2+}) gave an average results of 1.8±0.2 µg mL^{-1}. Calculation of the student's (*t*) value at 95% confidence level was made using Eqn 1:
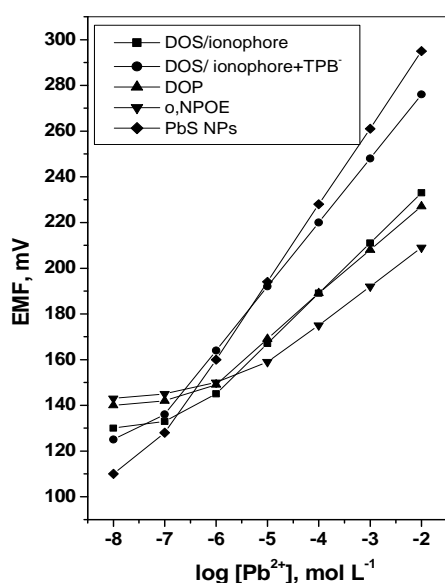
$$t_{exp} = \frac{(\mu - x)n^{0.5}}{S} \tag{1}$$

where

μ is the concentration of the initial internal quality control sample,

x is the average concentration found, n is the number of replicates analyzed and *s* is the standard deviation of measurements.

Table 1. Response characteristics of lead membrane sensors in 0.01 mol L^{-1} acetate buffer of pH 4.5.

Parameter	Ionophore DOS	Ionophore DOS+TPB$^-$	Ionophore DOP	Ionophore o,NPOE	PbS NPs
Slope (mV decade^{-1})	22.1±0.6	28.2±0.2	19.5±0.6	16.7±0.9	33.5±0.3
Correlation coefficient, r (n=5)	0.999	0.999	0.998	0.998	0.999
Linear range, mol L^{-1}	1.0x10^{-6}	1.0x10^{-7}	1.0x10^{-6}	1.0x10^{-5}	1.0x10^{-7}
Detection limit, μg mL^{-1}	0.05	0.01	0.16	0.65	0.007
Working range, (pH)	3.5-6.0	3.5-6.0	3.5-6.0	3.5-6.0	3.0-6.5
Response time, (s)	<10	<10	<10	<10	<20
Standard deviation σ$_v$ (mv)	2.1	1.6	1.4	1.7	1.5
Repeatability, Cv_w (%)	1.3	0.8	0.9	1.1	0.9
Accuracy (%)	99.1	98.6	99.3	99.6	99.4

No statistical difference was detected between the practically obtained (t_{exp}= 1.63) and the theoretically tabulated (t_{tab}=1.833) values. Thus the null hypothesis is retained and the method accuracy is acceptable.

o,NPOE plasticizers. Selectivity for Pb^{2+} in the presence of many common cations such as Ni^{2+}, Co^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+} and Hg^{2+} was significantly improved with sensor incorporating DOS. All subsequent measurements were made with membranes plasticized with DOS.

Table 2. Selectivity coefficient values using lead based membrane sensors

Interferent	Ionophore				PbS NPs
	DOS	DOS+TPB$^-$	DOP	o,NPOE	
Pb^{2+}	0	0	0	0	0
Hg^{2+}	-2.6	-2.7	-2.5	-1.9	-3.1
Zn^{2+}	-3.1	-3.2	-3.1	-2.5	-0.9
Mg^{2+}	-4.1	-4.2	-4.0	-4.0	-4.1
Ca^{2+}	-3.8	-3.9	-3.9	-3.7	-4.0
Cu^{2+}	-0.05	-0.03	-0.05	-0.02	-0.5
Co^{2+}	-3.0	-2.9	-2.9	-2.8	-3.4
Ni^{2+}	-3.1	-3.0	-3.2	-2.9	-1.1
Cd^{2+}	-1.8	-1.9	-1.7	-1.6	-2.6
Ba^{2+}	-4.2	-4.05	-4.0	-3.9	-1.3
K$^+$	-4.5	-3.9	-4.3	-4.4	-0.8
I$^-$	-4.6	-4.5	-4.3	-4.4	-1.3
SCN$^-$	-4.5	-4.6	-4.3	-4.5	-1.1
S^{2-}	-4.3	-4.4	-4.2	-4.2	0

Figure 3. Potentiometric response of lead membrane sensors using 0.01mol L^{-1} acetate buffer of pH 4.5.

Effect of plasticizer

Potentiometric response of sensor based on the neutral ionophore was greatly influenced by the polarity of the membrane medium. Lead PVC matrix membrane sensor incorporating the ionophore with (DOS), (DOP) and (o,NPOE) plasticizers were prepared and tested. The calibration slope and lower limit of detection were declined from 22.1±0.6 to 19.5±0.6 and 16.7±0.9 mV decade^{-1} and from 0.05 to 0.16 and 0.65 mg mL^{-1} upon using DOS instead of DOP and o,NPOE, respectively. It can be seen that membranes incorporating DOP plasticizer gave more favorable slope than those containing o,NPOE plasticizer. Table 2 shows the selectivity coefficients of membrane sensor incorporating the ionophore with DOS, DOP and

Effect of pH and response time

The effect of pH on the response of the sensors based on either the ionophore (sensor 1) or PbS nanoparticles (sensor 2) were studied over the pH range of 2 to 8 at 10^{-4} and 10^{-3} mol L^{-1} of Pb^{2+} solution. The pH of solutions was adjusted with either HNO$_3$ or NaOH solutions. The potential remained constant at pH range of 3 to 6.5 and 4 to 6 for both sensors 1 and 2, respectively. Below pH 3, the change in the potential is due to co fluxing of hydrogen ions and above pH 6.5, the variation of potential may be due to formation of some hydroxyl complex of the Pb^{2+} ions in the solution. The response time of the sensors, tested by measuring the time required to achieve a steady potential (within ±3 mV), was less than 10 s for sensor 1 but exceeds to be less than 20 s for sensor 2. The detection system was very stable, and after a period of 8 weeks, calibration sensitivity decreased about 1.5 mV without any considerable change in its linear range.

The reproducibility of the slope of calibration graphs was within ±1.5 mV per decade over a period of 8 weeks (*n*=6).

The ruggedness of the potentiometric method was also evaluated by carrying out the analysis using four different sensors and two different instruments on different days. A relative standard deviation (RSD) of less than 1.0 % was observed for repetitive measurements during three different days (*n*=10). The results indicate that the method is capable of producing results with high precision and stability.

Effect of diverse ions

The influences of different cation and anion ions on the response of Pb^{2+} sensors were investigated. The selectivity coefficients $K^{pot}_{Pb2+,J}$ were evaluated according to IUPAC recommendations using the matched potential method (MPM) [42] in 0.01 mol L^{-1} acetate buffer at pH 4.5. In this method, the potentiometric selectivity coefficient is defined as the activity ratio of primary ion and interfering ions that give the same potential under identical conditions. At first, a known activity (a_A) of the primary ion solution is added into a reference solution that contains a fixed activity ($a_A = 10^{-4}$ mol L^{-1}) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of an interfering ion (a_B) is added to the reference solution until the same potential change (ΔE) is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases. The selectivity coefficient is calculated from the Eqn. (2):

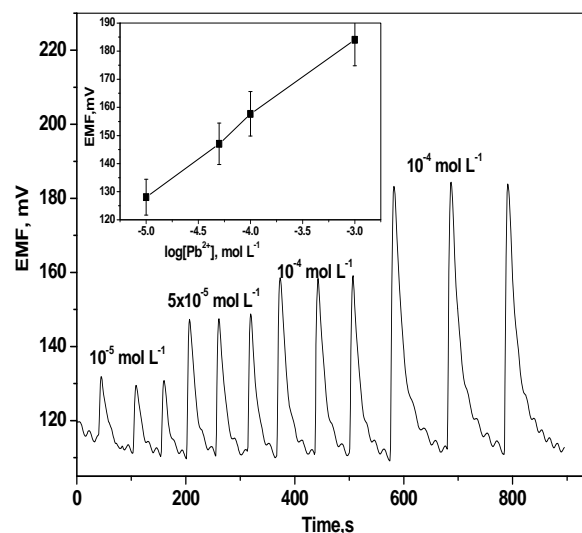$$K^{POT}_{A,B} = \frac{(a_A - a_A')}{a_B} \qquad (2)$$

The results given in Table 2 revealed reasonable selectivity for lead ion in presence of many related substances.

Flow Injection Set Up

A planar-chip detector incorporating the ionophore+TPB⁻/DOS based membrane sensor was prepared and used under hydrodynamic mode of operation for continuous Pb^{+2} quantification. A linear relationship between Pb^{+2} concentrations and FIA signals was obtained over a concentration range of 10^{-5} to 10^{-3} mol L^{-1} using 10^{-2} mol L^{-1} acetate buffer, pH 4.7. The flow rate was chosen to be 3.5 mL min^{-1} (Fig. 4). The slope of the calibration plot was near Nernstian (28.2±0.2 mV decade^{-1}). The limit of detection was 8.0x10^{-6} mol L^{-1}. The sampling frequency is ca. 48-50 samples per hour.

Lead assessment

Lead(II) was determined in drinking as well as in biological fluids under both the static and the hydrodynamic mode of operations. The use of the sensors in a FIA mode of operation shorten the assay time, allow the use of little sample quantities for lead detection. The samples analyzed by the proposed method using both the ionophore and PbS

Figure 4. Typical FIA signal obtained by injecting Pb^{2+} standard solutions using ionophore I membrane based sensor.

nanoparticles membrane based sensors. Their content in lead is presented in Table 3.

A blank sample was used to control and ascertain the accuracy of the analytical results. This blank sample was marketed bottled water that had no lead on its content. Standard additions were carried out over this sample. For this, the blank sample was spiked with 0.5, 1.0, 2.0 and 5.0 μg mL^{-1}; the lead found was 0.47 (±0.05); 0.95 (±0.04), 1.94 (±0.06) and 4.82 (±0.03) μg mL^{-1}. The corresponding coefficient variation was 6.0%, 5.0%, 3% and 3.6%, respectively, attesting for the precision of the flow-potentiometric method. Thus, the analytical data support the application of the proposed potentiometric method for the routine control of lead.

Another application of the present method for determining Pb^{2+} in biological fluids was tested by spiking aliquots of human plasma samples with a known concentration of standard Pb^{2+} in 10^{-2} mol L^{-1} acetate buffer of pH 4.5. Internal QC samples containing 0.5–5 μg mL^{-1} Pb^{+2} were spiked into human plasma test solutions to evaluate the effect of matrix and the method recovery (φ, %) were using Eqn 3.

$$\varphi = \frac{X_s - X}{X_{add}} 100 \qquad (3)$$

where

X_s, X and X_{add} are the results of spiked sample, mean results of un-spiked sample and of added (spiked) reference, respectively.

The results show average recoveries (accuracy) of 97.4±1.1% and 98.2±1.5% and 96.5± 1.8% and 96.4±1.4% in plasma samples using batch and FIA techniques, respectively (Table 3). This confirms the applicability of the method for accurate routine analysis of Pb^{2+} in biological fluids.

Table 3. Potentiometric determination of Pb^{2+} in spiked water and human plasma samples using lead based membrane sensors.

Matrix	Spiked concentration, $(\mu g\ mL^{-1})$	Recovery found* (%)				
		Sensor (I)		Sensor (II)		AAS
		Batch	FIA	Batch	FIA	
Water						
	0.5	0.47±0.002	0.45±0.003	0.48±0.002	0.46±0.002	0.48±0.003
	1.0	0.95±0.007	0.93±0.006	0.97±0.004	0.95±0.003	0.97±0.002
	2.0	1.94±0.06	1.91±0.03	1.97±0.07	1.93±0.08	1.97±0.02
	5.0	4.82±0.08	4.77±0.07	4.79±0.03	4.69±0.05	4.81±0.01
Human serum						
	0.5	0.48±0.003	0.46±0.005	0.47±0.01	0.46±0.007	0.45±0.001
	1.0	0.98±0.005	0.97±0.004	0.95±0.008	0.93±0.007	0.94±0.004
	2.0	1.93±0.07	1.91±0.04	1.91±0.09	1.88±0.06	1.93±0.03
	5.0	4.82±0.06	4.75±0.02	4.77±0.07	4.73±0.09	4.76±0.02

*Average of 5 measurements

Conclusion

New lead sensors based on synthesized 2,6-bis((1-(methoxycarbonyl)-N-ethyl)carboxamide)pyridine as neutral ionophore in plasticized PVC membranes and PbS nanoparticles (NPs) capped in polyvinyl alcohol (PVA) were prepared, characterized and used for Pb^{2+} measurements. The sensors offered the advantages of fast response, reasonable selectivity, low cost and possible interfacings with computerized and automated systems. Interfacing the sensors in a FIA system offers adequate analysis speed, good reproducibility, high sample throughputs and excellent response characteristics. The sensors were useful to perform the analysis of lead in water and biological fluids samples. The potentiometric devices are simple, of low cost and easy to manipulate. The overall procedure is precise, accurate and inexpensive regarding reagent consumption and equipment involved.

Acknowledgements

References

[1]Huang, X., Sillanpaa, M., Gjessing, E. T., Peraniemi, S., Vogt, R. D., *River Res. Appl.*, **2011**, *27*, 113-121.

[2]Huang, X., Sillanpaa, M., Gjessing, E. T., Vogt, R. D., *Sci. Total Environ.* **2009,** *407*, 6242-6254.

[3]Needleman, H. L., Gatsonis, C. A., *J. Am. Med. Assoc.*, **1990**, *263*, 673-678.

[4]McMichael, A. J., Baghurst, P. A., Wigg, N. R., Vimpani, G. V., Robertson, E. F., Roberts, R. J., *N. Engl. J. Med.*, **1988**, *319*, 468-475.

[5]Volesky, B., *Biosorption of heavy metals,* CRC, Boca Raton, **1990**.

[6]Klamtet, J., Sanguthai, S., Sriprang, *NU Sci J.*, **2007**, *4*, 122.

[7]Chen, J., Xiao, S., Wu, X., Fang, K., Liu, W., *Talanta*, **2005**, *67*, 992-996.

[8]Talebi, S. M., Safigholi, H., *J. Serb. Chem. Soc.*, **2007**, *72*, 585-590.

[9]Mattos, J. C. P. D., Nunes, A. M., Martins, A. F, Dressler, V. L., Flores, E. M. D. M., *Spectrochim Acta*, **2005**, *60*, 687-692.

[10]Campos, R. C. D., Santos, H. R. D., Grinberg, P., *Spectrochim Acta B,* **2002**, *57*, 15-28.

[11]Bhandari, S. A., Amarasiriwardena, D., *Microchim. J.,* **2000**, *64*, 73-84.

[12]Kamel, A. H., *Electroanalysis*, **2007**, *19*, 2419-2427.

[13]Li, G., Ji, Z., Wu, K., *Anal. Chim. Acta*, **2006**, *577*,178-182.

[14]Mhammedi, M. A. E., Achak, M., Bakasse, M., Chtaini, A., Chemosphere, **2009**, *76*, 1130-1134.

[15]Mousavi, M. F., Sahari, S., Alizadeh, N., Shamsipur, M., *Anal. Chim. Acta*, **2000**, *414*, 189–194.

[16]Ganjali, M. R., Rouhollahi, A., Mardan, A. R., Hamzeloo, M., Mogimi, A., Shamsipur, M., *Microchem. J.,* **1998**, *60*, 122–133.

[17]Ganjali, M. R., Hosseini, M., Basiripour, F., Javanbakht, M., Hashemi, O. R., Rastegar, M. F., Shamsipur, M., Buchanen, G.W., Anal. Chim. Acta, **2002**, *464,*181–186.

[18]Chen, L., Zhang, J., Zhao, W., He, X., Liu, Y., *J. Electroanal.Chem.* **2006**, *589*, 106 –111.

[19]Bhat, V. S., Ijeri, V. S., Srivastava, A. K., *Sens. Actuators B*, **2004**, *99*, 98–105.

[20]Bochenska, M., Guzinski, M., Kulesza, J., *Electroanalysis*, **2009**, *21*, 2054–2060.

[21]Vassilev, V., K. Tomova, K., Boycheva, S., *J. Non-Cryst. Solids*, **2007**, *353*, 2779–2784.

[22]Ardakani, M. M., Kashani, M. K., Niasari, S. M., Enasfi, A. A., *Sens. Actu. B*, **2005**, *107*, 438–445.

[23]Jeong, T., Lee, H. K., Jeong, D. C., Jeon, S., *Talanta*, **2005**, *65*, 543–548.

[24]Lee, H. K., Song, K., Seo, H. R., Choi, Y. K., Jeon, S., *Sens. Actu. B*, **2004**, *99* 323–329.

[25]Barzegar, M., Mousavi, M. F., Khajehsharifi, H., Shamsipur, M., Sharghi, H., *IEEE Sens. J.*, **2005**, *5*, 392–397.

[26]Xu, D. F., Katsu, T., *Anal. Chim. Acta*, **1999**, *401*, 111–115.

[27]Hassan, S. S. M., Ghalia, M. H. A., Amr, A. G. E., Mohamed, A. H. K. , *Talanta*, **2003**, *60*, 81–91.

[28]Abbaspour, A., Tavakol, F., *Anal. Chim. Acta*, **1999**, *378*, 145–149.

[29]Sadeghi, S., Dashti, G. R., Shamsipur, M., *Sens. Actu. B*, **2002**, *81*, 223–228.

[30]Xu, D. F., Katsu, T., Talanta, **2000**, *51*, 365–371.

[31]Mousavi, M. F., Barzegar, M. B., Sahari, S., *Sens. Actu. B*, **2001**, *73*, 199–204.

[32]Lu, X. Q., Chen, Z. L., Hall, S. B., Yang, X. H., *Anal. Chim. Acta*, **2000**, *418,* 205–212.

[33]Wilson, D., Arada, M. D., Alegret, S., del Valle, D., *J. Hazard. Mater.,* **2010**, *181*, 140–146.

[34]Welch, C.M., Compton, R.G., Anal. Bioanal. Chem., **2006**, *384*, 601.

[35]Campbell, F. W., Compton, R.G., *Anal. Bioanal. Chem.*, **2010**, *396*, 241.

[36]Ward Jones, S. E., Compton, R. G., *Curr. Anal. Chem.*, **2008**, *4*, 177.

[37]Belding, S. R., Dickinson, E. J. F., Compton, R. G., *J. Phys. Chem. C*, **2009**, *113* 11149.

[38]Zhou, H. J., Fan, F. R. F., Bard, A. J., *J. Phys. Lett.*, **2010**, *1*, 2671.

[39]Abounassif, M. A., Al-Omar, M. A., Amr A.G. E., Mostafa, G. A. E., *Drug Test. Analysis,* **2011**, *3*, 373–379.

[40]Badr, Y., Mahmoud, M. A., *Physica B*, **2005**, *369*, 278–286.

[41]Kamel, A. H., *J. Pharm. & Biomed. Anal.,* **2007**, *45*, 341–348.

[42]Umezawa, Y., Batlmann, P., K. Umezawa, K., Tohda, K., Amemiya, S., *Pure Appl. Chem.*, **2000**, *72*, 1851.