



# A highly selective lead-sensitive electrode with solid contact based on ionic liquid

Cecylia Wardak\*

Department of Analytical Chemistry and Instrumental Analysis, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

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## ABSTRACT

A new polyvinylchloride membrane sensor for  $\text{Pb}^{2+}$  with solid contact based on ionic liquid has been prepared. The electrode shows a Nernstian response for lead ions over a wide concentration range ( $1 \times 10^{-8}$  to  $1 \times 10^{-1} \text{ mol L}^{-1}$ ) and the slope of 29.8 mV/decade. The limit of detection is  $4.3 \times 10^{-9} \text{ mol L}^{-1}$ . It has a fast response time of 5–7 s and can be used for 4 months without any divergence in potential. The proposed sensor is not pH sensitive in the range 3.5–7.3 and shows a very good discriminating ability towards  $\text{Pb}^{2+}$  ion in comparison with some alkali, alkaline earth, transition and heavy metal ions. It was successfully applied as an indicator electrode in potentiometric titration of lead ions with  $\text{K}_2\text{CrO}_4$  and for direct determination of  $\text{Pb}^{2+}$  ions in real sample solution.

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## 1. Introduction

In the last few years the need for the determination of lead and other heavy metals has considerably increased because of growing environmental problems. Toxic effects of lead result from its involvement in interactions with enzymes and nucleic acid, where inhibition of biochemical pathways often constitutes the source of symptomatic physiological aberrations [1,2]. Lead causes atmospheric and water pollution due to its application in various industrial products. In the environment it is generally present as inorganic  $\text{Pb}^{2+}$  which can be easily detected and determined by lead ion-selective electrode.

Potentiometric ion selective electrodes (ISEs) are known to offer an excellent low-cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application. The use of ion-selective electrodes in the analysis and monitoring of environmental, clinical, and industrial ions and gases has been continuously expanding [2–5]. Solid internal contact electrodes refer to a type of ISEs in which the internal reference electrode is in direct contact with the electroactive membrane and contains no internal solution. These electrodes will have certain advantages over conventional ones, such as the small size, lower cost of production, and ability to operate in high pressure environments where conventional ISEs might be damaged. Furthermore, this type of electrode allows for low detection limit, which was attributed to the absence of transmembrane ion fluxes [6].

Ionic liquids (ILs) are molten salts with the melting point close to or below room temperature. They are composed entirely of ions and possess unique properties, including low volatility, tunable viscosity, high conductivity, large electrochemical window and low toxicity. These properties make ILs suitable for many applications in chemical analysis [7,8]. Among ILs applications, the use of IL/water two-phase system appears to be very promising for electroanalytical chemistry [9] and extraction [10]. In the literature the application of ILs as extraction solvents for the preconcentration of lead was described successfully [11–13].

The mechanism of the potential formation of ion selective electrodes (ISEs) with a liquid or pseudoliquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases [14–18]. It is known that the nature and amount of the lipophilic additive strongly affect the response of the membrane ion-selective sensors, for instance by reducing the membrane resistance [19,20], improving the response behavior and selectivity [21,22] and in some cases, where the extraction capability is poor, increasing the sensitivity of the membrane sensors [23].

The aim of this research was to create an ion-selective electrode sensitive to lead ions (ISE-s) with solid contact based on a PVC membrane phase containing an ionic liquid as an additional component. Recently it was found out that ILs can replace the commonly used lipophilic ionic additives (phenyl borates) in the membrane phase, which are introduced to the membrane to reduce the anion interference and to lower the membrane resistance. Additionally, chloride ILs keep constant concentration of chloride ions in the membrane phase, which guarantees the potential stability of internal Ag/AgCl electrode [24].

\* Tel.: +48 81 5375655; fax: +48 81 5375553.

E-mail address: [cecylia.wardak@poczta.umcs.lublin.pl](mailto:cecylia.wardak@poczta.umcs.lublin.pl)

**Table 1**  
Composition of electrode membranes and sensors performance.

No electrode	Membrane composition, wt.%				Limit detection, mol L <sup>-1</sup>	Slope, mV/decade	Measuring range, mol L <sup>-1</sup>
	Ionophore, wt.%	PVC, wt.%	Plasticizer, wt.%	Ionic liquid, wt.%			
1	1	33	TBP, 63	EMImCl, 3	$2.3 \times 10^{-5}$	30.8	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$
2	1	33	TBP, 63	BMImCl, 3	$6.1 \times 10^{-5}$	26.7	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$
3	1	33	TBP, 63	HMImCl, 3	$6.1 \times 10^{-5}$	24.2	$1.0 \times 10^{-4}$ to $1.0 \times 10^{-1}$
4	1	33	NPOE, 63	EMImCl, 3	$2.1 \times 10^{-6}$	23.9	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$
5	1	33	NPOE, 63	BMImCl, 3	$4.8 \times 10^{-7}$	28.8	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-2}$
6	1	33	NPOE, 63	HMImCl, 3	$1.3 \times 10^{-6}$	31.6	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-2}$
7	1	33	NPOE, 63	DMImCl, 3	$6.6 \times 10^{-7}$	26.1	$1.0 \times 10^{-6}$ to $5.0 \times 10^{-4}$
8	1	33	NPOE, 63	NMImCl, 3	$6.6 \times 10^{-7}$	25.7	$1.0 \times 10^{-6}$ to $5.0 \times 10^{-4}$
9	1	33	NPOE, 31.5 BBPA, 31.5	EMImCl, 3	$1.1 \times 10^{-6}$	25.3	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$
10A	1	33	NPOE, 31.5 BBPA, 31.5	BMImCl, 3	$4.8 \times 10^{-7}$	29.0	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$
10B	1	33	NPOE, 31.5 BBPA, 31.5	BMImCl, 3	$3.5 \times 10^{-8}$	28.8	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
10C	1	33	NPOE, 31.5 BBPA, 31.5	BMImCl, 3	$4.3 \times 10^{-9}$	29.8	$1.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$
10D	1	33	NPOE, 31.5 BBPA, 31.5	BMImCl, 3	$5.6 \times 10^{-6}$	28.8	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$
11	1	33	NPOE, 31.5 BBPA, 31.5	HMImCl, 3	$1.8 \times 10^{-6}$	23.9	$1.0 \times 10^{-5}$ to $1.0 \times 10^{-1}$
12	1	33	NPOE, 31.5 BBPA, 31.5	DMImCl, 3	$4.7 \times 10^{-7}$	26.0	$1.0 \times 10^{-6}$ to $1.0 \times 10^{-3}$
13	1	33	NPOE, 31.5 BBPA, 31.5	NMImCl, 3	$3.8 \times 10^{-8}$	23.9	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-3}$

Abbreviations A, B, C, D concern conditioning protocols described in Section 2.3.

## 2. Experimental

### 2.1. Reagents

2-Nitrophenyl octyl ether (NPOE) (Fluka), bis(1-butylpentyl) adipate (BBPA) (Fluka), tributyl phosphate (TBP) (Merck), poly(vinyl chloride) low molecular weight (PVC) (Aldrich), *tert*-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (lead ionophore IV) (Fluka).

The ILs used in this work were: 1-ethyl-3-methylimidazolium chloride (EMImCl), 1-butyl-3-methylimidazolium chloride (BMImCl), 1-hexyl-3-methylimidazolium chloride (HMImCl), 1-decyl-3-methylimidazolium chloride (DMImCl), 1-benzyl-3-methylimidazolium chloride (NMImCl). These ionic liquids are known to be immiscible in water but soluble in plasticizers used for membrane preparation.

All ionic liquids (ILs) (purum;  $\geq 97$ ) and other reagents were purchased from Fluka.

All aqueous solutions were prepared with salts of the highest purity available (pure pro analysis) using freshly deionized water. Buffer solutions pH 2–8 (for the study of effect of pH) were prepared by mixing the corresponding amounts of  $0.02 \text{ mol L}^{-1}$  potassium phthalate monobasic, with  $0.02 \text{ mol L}^{-1}$  HCl or NaOH (pH 2–3.8),  $0.02 \text{ mol L}^{-1}$  CH<sub>3</sub>COOH with  $0.02 \text{ mol L}^{-1}$  NaOH (pH 4–8).

### 2.2. Preparation of the electrode

A clean silver wire was anodized electrochemically for 5 min. in  $4 \text{ mol L}^{-1}$  HCl with constant current 5 V voltage forming an Ag/AgCl electrode. Then the electrode was rinsed with water, dried by tissue-paper and covered by the inner membrane phase.

The electrode membrane phase consists of two layers placed in a Teflon holder: the inner layer containing plasticized PVC doped with IL in which the Ag/AgCl electrode is placed, and the outer layer containing an ionophore apart from the inner layer components. The outer layer is placed on the inner layer and it is contacted with the tested solution. In order to prepare the inner layer membrane components: IL, PVC and membrane solvents were weighed, mixed thoroughly and the mixture was deaerated by means of vacuum oil pump. The Teflon holder was filled with the mixture so that the silver–silver chloride electrode was immersed in it. Then the mixture was gelled by heating at 80 °C for 30 min. In order to prepare the outer layer, the active substance (ionophore) was dissolved in a plasticizer (the same as the inner layer) with PVC and IL. The mixture was deaerated, placed on the inner layer and

gelled at 80 °C for 10 min. Then the mixture was cooled to room temperature.

The electrode was conditioned before the measurements in appropriate solution. The following conditioning protocols were used: protocol A, 6 h in  $1 \times 10^{-3} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub>, protocol B, 6 h in  $1 \times 10^{-3} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub> followed by 1 day in  $1 \times 10^{-5} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub>, protocol C, 6 h in  $1 \times 10^{-3} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub> followed by 1 day in  $1 \times 10^{-7} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub>, protocol D, 6 h in  $1 \times 10^{-3} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub> followed by 1 day in  $1 \times 10^{-9} \text{ mol L}^{-1}$  Pb(NO<sub>3</sub>)<sub>2</sub>. All conditioning and sample solutions had the same background  $1 \times 10^{-4} \text{ mol L}^{-1}$  HNO<sub>3</sub>. The protocol A was used for all studied electrodes and protocols A, B, C and D were used for the electrode no 10 A.

### 2.3. The measurement of the electromotive force

The measurement of the electromotive force (EMF) of the system: lead electrode – reference electrode Orion 90-02 was carried out at room temperature in a solution stirred with a mechanical stirrer by means of potentiometric system consisting of a 16-channel data acquisition system (Lawson Labs. Inc., USA) and IBM PC computer. A multifunction computer meter CX-741 (Zabrze Mikulczyce Poland) and an Orion 81-72 glass electrode were used for pH measurement. Sequential dilutions of stock solutions were performed using the 700 Dosino and 711 Liquino pump systems (Metrohm, Switzerland).

## 3. Results and discussion

### 3.1. Potential response

The potential response of all membrane sensors was determined in lead nitrate solutions of the concentration  $1 \times 10^{-1}$  to  $1 \times 10^{-10} \text{ mol L}^{-1}$ . The analytical parameters of individual sensors such as the limit of detection, the working concentration range, the slope of the linear section of the response curve and response time were determined from the results of these measurements and are summarized in Table 1.

The detection limit is defined by bulk activity when the measured potential begins to deviate both sides, by  $RT/z_i F \ln 2$  from the linear Nernstian response [25]. This definition has been adopted to determine the detection limit of the studied electrodes.

It is well established that the polarity and chemical structure of the membrane plasticizer can have a significant effect on the selectivity and dynamic response range of ISEs [26]. The kind of

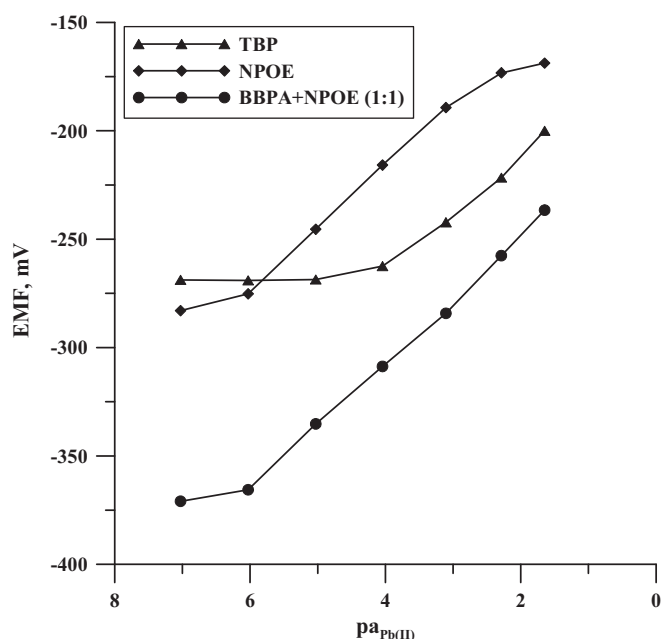


Fig. 1. Effect of plasticizer on lead electrode response.

plasticizer affects both the dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex [23]. The effect of plasticizer on potential response of lead electrodes based on ionic liquid BMImCl is presented in Fig. 1. As can be seen in Fig. 1, a mixture of BBPA and NPOE (1:1) is the best plasticizer for preparation of the membrane.

It is also known that the electrode response depends on the kind and amount of ionic membrane components [19–23]. As a lipophilic additive various ionic liquids with alkylmethyl imidazolium cations and chloride anions were used. The effect of ionic liquid on potential response of lead electrodes based on mixed plasticizer NPOE + BBPA (1:1) is presented in Fig. 2.

It was demonstrated that in the case of solid contact electrodes their conditioning procedure affects both the detection limit and

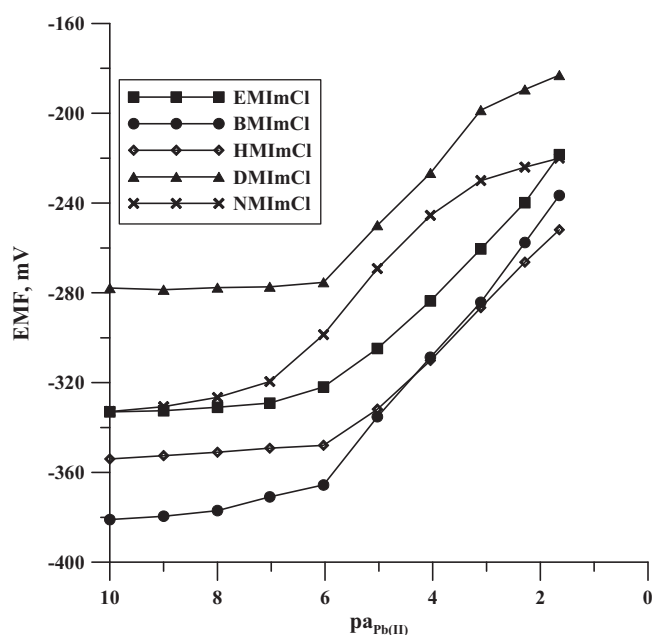


Fig. 2. Effect of ionic liquid on lead electrode response.

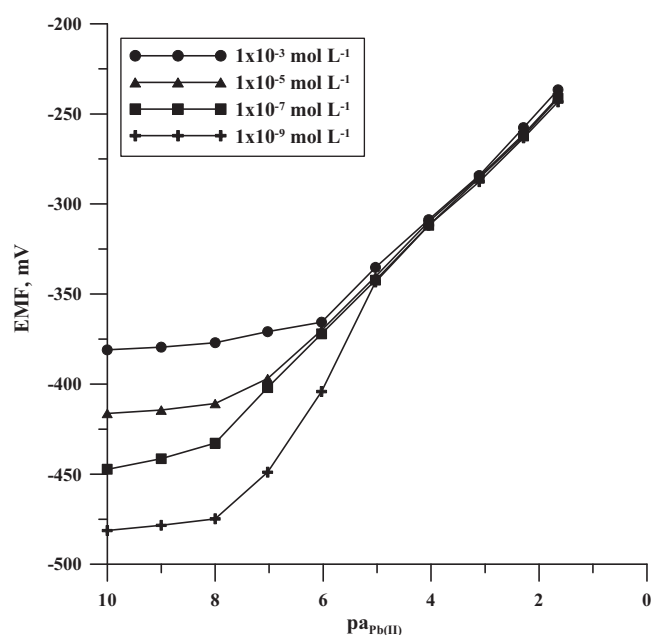


Fig. 3. Effect of lead concentration in conditioning solution on the electrode response.

selectivity coefficients [27,28]. The effect of conditioning solution on the electrode response is shown in Fig. 3.

From the analysis of Table 1 and Figs. 1–3 it is clear that the best response is exhibited by electrode no. 10C incorporating in the membrane ionophore, BMImCl, PVC, NPOE, BBPA in the ratio of 1:3:33:31.5:31.5 (wt.%), respectively, and conditioned in solution containing low concentration of  $Pb^{2+}$  ions  $1 \times 10^{-7} \text{ mol L}^{-1}$ . The characteristic slope of this electrode is 29.8 mV/decade, the limit of detection is  $4.3 \times 10^{-9} \text{ mol L}^{-1}$ , the linearity range is  $1 \times 10^{-1}$  to  $1.0 \times 10^{-8} \text{ mol L}^{-1}$ .

### 3.2. Selectivity

The most important parameter of any ion-selective electrode is its response to the primary ion in the presence of other ions. The selectivity of the studied sensors was evaluated by establishing their selectivity coefficients in reference to interfering ions. The selectivity coefficients were determined by the separate solution method (SSM) (by extrapolating the response functions to  $a_i = a_j = 1 \text{ mol L}^{-1}$ ) [29] as well as by the fixed interference method (FIM) [30] (interfering ions concentration  $1 \times 10^{-1} \text{ mol L}^{-1}$  and  $1 \text{ mol L}^{-1}$ ). The values of selectivity coefficient  $\log K^{Pot}_{Pb/M}$  obtained by both methods for electrode no. 10C are shown in Table 2. As

Table 2  
Selectivity coefficients values for sensor no. 10C.

Ion	$\log K^{Pot}_{Pb/M}$	
	SSM method	FIM method
$Cd^{2+}$	-5.5	-5.1
$Cu^{2+}$	-5.0	-4.8
$Zn^{2+}$	-6.5	-5.7
$Co^{2+}$	-6.4	-6.2
$Ni^{2+}$	-6.2	-6.2
$Ca^{2+}$	-6.0	-6.2
$Ba^{2+}$	-6.4	-5.2
$Mg^{2+}$	-5.1	-6.2
$Sr^{2+}$	-6.1	-6.3
$Li^+$	-5.3	-5.4
$K^+$	-5.6	-5.5
$Na^+$	-5.4	-5.5

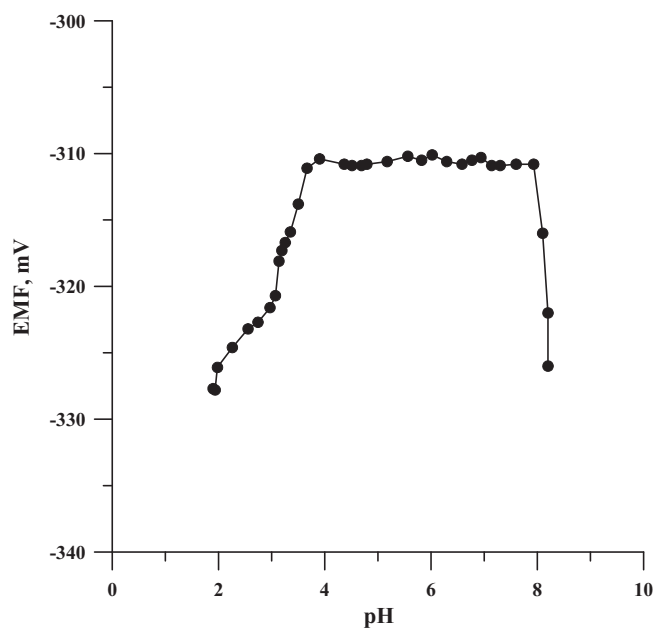


Fig. 4. Effect of pH on the electrode response.

it follows from the analysis of Table 2, the proposed sensor is very selective to lead over all interfering ions ( $\log K^{pot}_{Pb/M} \leq -5$ ). There are some differences between values of selectivity coefficients obtained for the same interfering ion by SSM method and FIM method. Such discrepancies can occur if selectivity coefficient are determined by different methods or under different conditions [30,31].

### 3.3. Dependence of EMF on pH

The dependence of the electrode potential on pH was investigated using  $1 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$  solution over the pH range 2.0–8.0. Adjustment of pH was carried out using universal buffer solutions. From the obtained results the working pH range in which the potential of electrodes is almost constant ( $\pm 2 \text{ mV}$ ) was determined and is presented in Fig. 4, where it can be seen that the potential remains fairly constant in the pH range of 3.5–7.4. Beyond this range, a gradual change in the potential was detected. The decrease of the potential at higher pH values could be caused by the formation of some hydroxy complexes of  $\text{Pb}^{2+}$  in solution and at lower pH by the ionophore protonation.

### 3.4. Response time

The response time of the examined electrodes was established by injecting concentrated standard solutions into a stirred  $\text{Pb}(\text{NO}_3)_2$  solution. Simultaneously, EMF changes of the lead electrode-reference electrode system were recorded. The response time was determined as the time which elapses from the moment when the studied ion-selective electrode and reference electrode are brought into contact with a sample solution at which the activity of the  $\text{Pb}^{2+}$  ions is changed to the first instant when the  $\Delta E/\Delta t$  becomes equal to  $0.4 \text{ mV/min}$  [32]. The response time of the electrode was very short 5–7 s. The dynamic response of the proposed sensor is presented in Fig. 5.

### 3.5. Lifetime and long-term stability

The usefulness of analytical time of the prepared electrode was tested over a period of 6 months. During that period the electrode

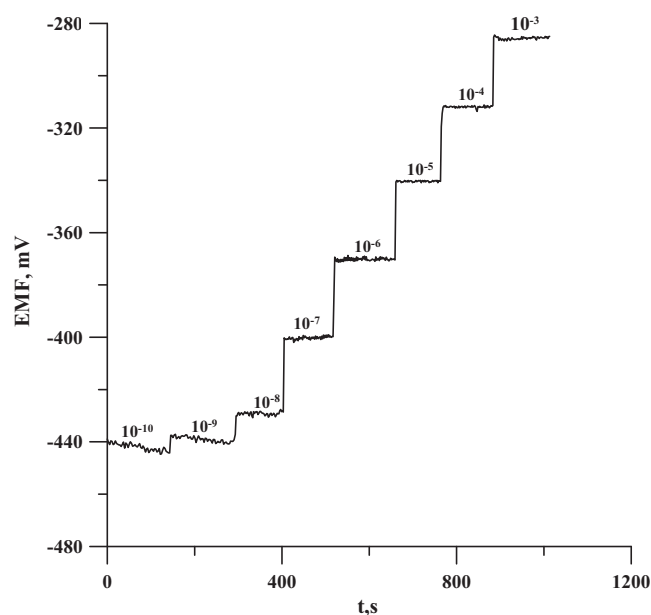


Fig. 5. Dynamic response of the proposed lead electrode no. 10C.

was exposed to weekly use for 5 h and the slopes and detection limits were measured in freshly prepared  $\text{Pb}(\text{NO}_3)_2$  solutions. Based on the obtained results the lifetime of electrode was estimated. The proposed sensor works correctly over a period of four months without observing any significant variation in the detection limit, working concentration range, or the slope. After that period a slight change in the slope and detection limit was observed. The electrode potential was stable in time. The determined drift of potential for electrode no. 10C was  $0.1 \text{ mV}$  per day.

### 3.6. Analytical application of electrode

Practical usefulness of the membrane sensor was shown by its use as an end point indicator electrode for the potentiometric

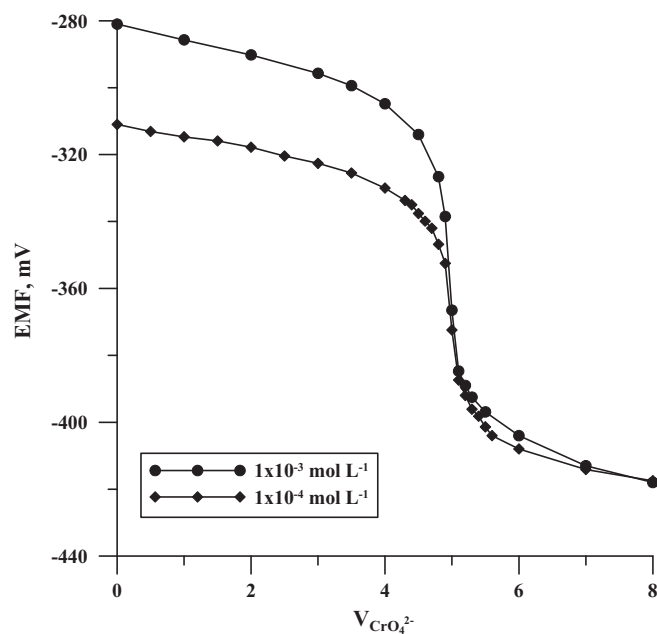


Fig. 6. Potentiometric titration curve of  $50 \text{ mL}$  of  $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$  solution (pH 4.8 acetate buffer) with  $1.0 \times 10^{-2} \text{ mol L}^{-1} \text{ K}_2\text{CrO}_4$  solution and  $50 \text{ mL}$  of  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$  solution (pH 4.8 acetate buffer) with  $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_2\text{CrO}_4$  using the proposed sensor as an indicator electrode.

**Table 3**  
Determination of Pb<sup>2+</sup> by the proposed electrode in the real samples.

Sample	Added lead, mg L <sup>-1</sup>	Found lead by ISE <sup>a</sup> , mg L <sup>-1</sup>	Recovery, %	Found lead by ASV, mg L <sup>-1</sup>
Tap water	0.041	0.039 ± 0.001	95.1	0.040
	0.104	0.109 ± 0.002	104.8	0.106
	0.166	0.164 ± 0.002	98.8	0.167
	0.207	0.209 ± 0.003	101.0	0.207
	0.414	0.414 ± 0.003	100.0	0.413
River water	0.041	0.038 ± 0.002	92.7	0.039
	0.104	0.105 ± 0.003	101.0	0.105
	0.166	0.166 ± 0.003	100.0	0.166
	0.207	0.206 ± 0.005	99.5	0.208
	0.414	0.411 ± 0.005	99.3	0.415
Waste water	–	0.021 ± 0.003	–	0.022
	0.041	0.064 ± 0.003	104.8	0.063
	0.104	0.123 ± 0.005	98.1	0.126
	0.166	0.186 ± 0.005	99.4	0.187
	0.207	0.229 ± 0.007	100.5	0.227
	0.414	0.434 ± 0.007	99.8	0.434

<sup>a</sup> Result are based on four measurements.

titration of 50 mL of  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution (pH 4.8 acetate buffer) with  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> K<sub>2</sub>CrO<sub>4</sub> solution and 50 mL of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solution (pH 4.8 acetate buffer) with  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> K<sub>2</sub>CrO<sub>4</sub> solution. The end point of the titration was determined using the first derivative method. The relative standard deviation in the determination of five replicate samples was 1.1% and 1.4% for  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> and  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> lead concentration, respectively. The obtained potentiometric titration curves are shown in Fig. 6. As can be seen, the amount of lead ions in the solution can be accurately determined with the electrode no. 10C.

To assess the practical applicability of the sensor in real samples, an attempt was made to obtain recoveries of lead in tap water and river water samples. Furthermore, the electrode was used for determination of lead ions in waste water samples. The analysis was performed by the standard addition technique. The results are summarized in Table 3. As can be seen, the obtained results are comparable with those obtained by the anodic stripping voltammetry (ASV) analysis. Thus the electrode provides a good alternative for the determination of Pb<sup>2+</sup> in real samples.

#### 4. Conclusion

A new composition of the membrane phase of lead ion selective electrode with solid contact is proposed. The presented electrode is characterized by good analytical parameters: low detection limit, wide measuring range, wide pH range and excellent selectivity. The application of an ionic liquid instead of a conventional lipophilic additive results in a decrease of membrane resistance and short response time. Furthermore the ionic liquid keeps constant concentration of chloride ions in the membrane phase, which guarantees the potential stability of internal Ag/AgCl electrode, which in turn results in a small potential drift of 0.1 mV per day. The presented electrode has no internal solution, so it is simple to construct, easy to transport and more convenient in use because it does not have to work in a vertical position and does not need to operate with the internal solution. The electrode may be used for lead determination in the range  $1 \times 10^{-1}$  to  $1 \times 10^{-8}$  mol L<sup>-1</sup>.

#### References

- [1] I. Pais, J.B. Jones Jr., The Handbook of Trace Elements, St. Lucie Press, Florida, 1997.
- [2] J. Palca, Get-the-lead-out guru challenged, Science 253 (1991) 842–843.
- [3] E. Bakker, E. Pretsch, The new wave of ion-selective electrodes, Anal. Chem. 72 (2002) 420A–426A.
- [4] E. Bakker, E. Pretsch, Potentiometry at trace levels, Trends Anal. Chem. 20 (2001) 11–19.
- [5] R. De Marco, G. Clarke, B. Pejic, Ion-selective electrode potentiometry in environmental analysis, Electroanalysis 19 (2007) 1987–2001.
- [6] J. Sutter, A. Radu, S. Peper, E. Bakker, E. Pretsch, Solid-contact polymeric membrane electrodes with detection limits in the subnanomolar range, Anal. Chim. Acta 523 (2004) 53–59.
- [7] R.J. Soukup-Hein, M.M. Warnke, D.W. Armstrong, Ionic liquids in analytical chemistry, Annu. Rev. Anal. Chem. 2 (2009) 145–168.
- [8] P. Sun, D.W. Armstrong, Ionic liquids in analytical chemistry, Anal. Chim. Acta 661 (2010) 1–16.
- [9] D. Wei, A. Ivaska, Applications of ionic liquids in electrochemical sensors, Anal. Chim. Acta 607 (2008) 126–135.
- [10] R. Liu, J.F. Liu, Y.G. Yin, X.L. Hu, G.B. Jiang, Ionic liquids in sample preparation, Anal. Bioanal. Chem. 393 (2009) 871–883.
- [11] S. Haixia, L. Zajun, L. Ming, Ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate as a solvent for extraction of lead in environmental water samples with detection by graphite furnace atomic absorption spectrometry, Microchim. Acta 159 (2007) 95–100.
- [12] J. Abulhassani, J.L. Manzoori, M. Amjadi, Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry, J. Hazard. Mater. 176 (2010) 481–486.
- [13] E.M. Martinis, P. Berton, J.C. Altamirano, U. Hakala, R.G. Wuilloud, Tetradecyl (trihexyl)phosphonium chloride ionic liquid single-drop microextraction for electrothermal atomic absorption spectrometric determination of lead in water samples, Talanta 80 (2010) 2034–2040.
- [14] J. Sandblom, G. Eisenman, J.L. Walker, Electrical phenomena associated with the transport of ions and ion pairs in liquid ion-exchange membranes. I. Zero current properties, J. Phys. Chem. 71 (1967) 3862–3870.
- [15] R. Dumkiewicz, Mechanisms of the origins of membrane potentials for pseudo-liquid poly(vinyl chloride) matrix membranes incorporating coordinatively solvated complexes, Analyst 118 (1993) 1533–1536.
- [16] W.E. Morf, M. Badertscher, T. Zwickl, N.F. de Rooij, E. Pretsch, Effects of ion transport on the potential response of ionophore-based membrane electrodes: a theoretical approach, J. Phys. Chem. B 103 (1999) 11346–11356.
- [17] Y. Yoshida, M. Matsui, K. Maeda, S. Kihara, Physicochemical understanding of the selectivity at an ion selective electrode of the liquid membrane type and relation between the selectivity and distribution ratios in the ion-pair extraction, Anal. Chim. Acta 374 (1998) 269–281.
- [18] R. Dumkiewicz, K. Sykut, C. Wardak, Sequence of characteristics of the ion-selective electrode with the pseudoliquid membrane as a function of active substance concentration, Chem. Anal. 45 (2000) 383–394.
- [19] M. Oehme, W. Simon, Microelectrode for potassium ions based on a neutral carrier and comparison of its characteristics with a cation exchanger sensor, Anal. Chim. Acta 86 (1976) 21–25.
- [20] T.A. Nieman, G. Horvai, Neutral carrier potassium-selective electrodes with low resistances, Anal. Chim. Acta 170 (1985) 359–363.
- [21] U. Schaller, E. Bakker, U.E. Spichiger, E. Pretsch, Ionic additives for ion-selective electrodes based on electrically charged carriers, Anal. Chem. 66 (1994) 391–398.
- [22] S. Amemiya, P. Bühlmann, E. Pretsch, B. Rusterholz, Y. Umezawa, Cationic or anionic sites? Selectivity optimization of ion-selective electrodes based on charged ionophores, Anal. Chem. 72 (2000) 1618–1631.
- [23] E. Bakker, P. Bühlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, Chem. Rev. 97 (1997) 3083–3132.
- [24] C. Wardak, Ionic liquids as new lipophilic additives to the membrane of lead ion-selective electrodes with solid contact, Int. J. Environ. Anal. Chem. 89 (2009) 735–748.
- [25] T. Sokalski, T. Zwickl, E. Bakker, E. Pretsch, Lowering the detection limit of solvent polymeric ion-selective electrodes. 1. Modeling the influence of steady-state ion fluxes, Anal. Chem. 71 (1999) 1204–1209.
- [26] I. Bedlechowicz, M. Maj-Zurawska, T. Sokalski, A. Hulanicki, Effect of a plasticizer on the detection limit of calcium-selective electrodes, J. Electroanal. Chem. 537 (2002) 111–118.
- [27] A. Konopka, T. Sokalski, A. Lewenstam, M. Maj-Zurawska, The influence of the conditioning procedure on potentiometric characteristics of solid contact calcium-selective electrodes in nanomolar concentration solutions, Electroanalysis 18 (2006) 2232–2242.
- [28] K.Y. Chumbimuni Torres, N. Rubinova, A. Radu, L.T. Kubota, E. Bakker, Solid contact potentiometric sensors for trace level measurements, Anal. Chem. 78 (2006) 1318–1322.
- [29] E. Bakker, E. Pretsch, P. Bühlmann, Selectivity of potentiometric ion sensors, Anal. Chem. 72 (2000) 1127–1133.
- [30] Y. Umezawa, K. Umezawa, H. Sato, Selectivity coefficients for ion-selective electrodes—recommended methods for reporting  $K_{A,B}^{pot}$  values, Pure Appl. Chem. 67 (1995) 507–518.
- [31] C. Macca, The current usage of selectivity coefficients for the characterization of ion-selective electrodes. A critical survey of the 2000/2001 literature, Electroanalysis 15 (2003) 997–1010.
- [32] R.P. Buck, E. Lindner, Recommendations for nomenclature of ionselective electrodes, Pure Appl. Chem. 66 (1994) 2527–2536.