

## New lead-sensitive ion selective electrode with low detection limit

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**Abstract.** A new polyvinylchloride membrane sensor for  $\text{Pb}^{2+}$  with solid contact has been prepared. The electrode membrane phase contains 1-hexyl-3-methylimidazolium hexafluorophosphate (HMImPF<sub>6</sub>) as lipophilic ionic additive. The electrode shows a Nernstian response for lead ions over a wide concentration range ( $1 \times 10^{-8}$ - $1 \times 10^{-1}$  mol L<sup>-1</sup>) and the slope of 28.1 mV/decade. The limit of detection is  $2.3 \times 10^{-9}$  mol L<sup>-1</sup>. It has a fast response time of 5-7 s and can be used more than 2 months without any divergence in potential. The proposed sensor is not pH sensitive in the range 4.0-6.9 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.

**Key words:** lead-selective electrode, solid contact, heavy metals, potentiometry

### Introduction

Determination of lead is very important because it is highly toxic element. 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 (ISE).

The mechanism of the potential formation of ion selective electrodes with a liquid or pseudoliquid (polymeric) membrane depends strongly on extraction and ion-exchange processes between the aqueous and organic phases [Sandblom 1967, Morf 1999]. 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, improving the response behavior and selectivity and in some cases, where the extraction capability is poor, increasing the sensitivity of the membrane sensors [Bakker 1997]. Recently it was found that ionic liquid can replace the commonly used lipophilic ionic additives (phenyl botates) in the membrane phase [Wardak 2009, 2012].

The aim of this research was to create an ion-selective electrode sensitive to lead ions (ISE-s) with PVC membrane phase containing an ionic liquid: 1-hexyl-3-methylimidazolium hexafluorophosphate (HMImPF<sub>6</sub>) as a new lipophilic ionic component.

Recently Abulhassani et al. [2010] have successfully used this ionic liquid as extraction solvents for the preconcentration of lead from environmental and biological samples.

### Materials and Methods

#### Preparation of the electrode

The composition of the lead ion-selective membrane was as follows (% wt.): 33% PVC, 61 % BBPA, 3% (HMImPF<sub>6</sub>) and 3% ionophore (*tetr*-butylcalix [4] arene-tetrakis (N,N-dimethylthio-acetamide); 100 mg of mixture of membrane components was dissolved in 1 ml of THF to give the membrane cocktail. The internal electrode was a glassy carbon disk. Before the electrode preparation the glassy carbon electrode was polished with 0.3  $\mu\text{m}$   $\text{Al}_2\text{O}_3$  powder and well rinsed with water and THF. Next poly(n-octyl)thiophene (POT) was applied on the electrode surface by drop-casting 10  $\mu\text{l}$  of 25 mM chloroform solution (respective monomer). The film was left to dry for at least 1 hour. Then an average amount of 2 x 25  $\mu\text{l}$  of the membrane cocktail was cast on the top of the POT layer and left to dry. After overnight THF evaporation, the obtained solid contact electrode was conditioned for at least 24 hours in  $1 \times 10^{-3}$  mol L<sup>-1</sup>  $\text{Pb}(\text{NO}_3)_2$  to saturate PVC membrane in the primary ions and then for at least 24 hours in the appropriate

conditioning solution before potentiometric measurements. Concentrations of conditioning solutions were as follows:  $1 \times 10^{-3}$  mol L<sup>-1</sup>,  $1 \times 10^{-5}$  mol L<sup>-1</sup>,  $1 \times 10^{-7}$  mol L<sup>-1</sup> and  $1 \times 10^{-9}$  mol L<sup>-1</sup>. The electrode construction is shown in Figure 1.

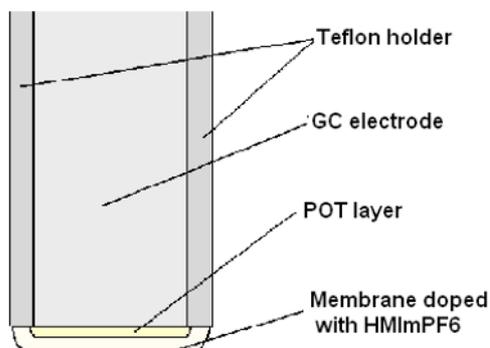


Fig. 1 Construction of lead solid contact electrode.

The measurement of the electromotive force

The measurement of the electromotive force (EMF) of the system: ion-selective 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)

## Results and Discussion

The potential response of membrane sensor was determined in lead nitrate solutions of the concentration  $1 \times 10^{-1}$ – $1 \times 10^{-10}$  mol L<sup>-1</sup>. The analytical parameters of sensor 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 selectivity of the examined electrode was evaluated by establishing its selectivity coefficients in reference to interfering ions. The selectivity coefficients were determined by the separate solution method (by extrapolating the response functions to  $a_i = a_j = 1$  mol L<sup>-1</sup>) as well as FIM method. The obtained results are presented in Fig. 2. As it follows from the analysis of Fig. 2, the proposed sensor is very selective to lead over all interfering ions ( $\log K_{Pb/M}^{pot} \leq -5$ ).

Practical usefulness of the membrane sensor was shown by its use as an end point indicator electrode for the potentiometric titration of 50mL 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 50mL 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 four replicate samples was 1.2% and 1.5% 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. 3. As can be seen, the amount of lead ions in the solution can be accurately determined with the proposed electrode.

**Table 1.** Change of the analytical parameters of the lead electrode in time

Parameter	LIFE TIME		
	3 days	14 days	60 days
S (mV/pa <sub>Cd</sub> )	28.1	28.1	28.0
Measuring range (M)	$1 \times 10^{-1} - 1 \times 10^{-8}$	$10^{-1} - 1 \times 10^{-8}$	$10^{-1} - 1.1 \times 10^{-8}$
Range of pH	-	4.0 – 6.9	-
Response time (s)	5	5	5
Life time (month)			>60days
Detection limit (M)	$2.3 \times 10^{-9}$	$2.3 \times 10^{-8}$	$5.2 \times 10^{-9}$
Intercept, mV	257.6	256.8	251.4
Resistance, MΩ	2.5	-	-

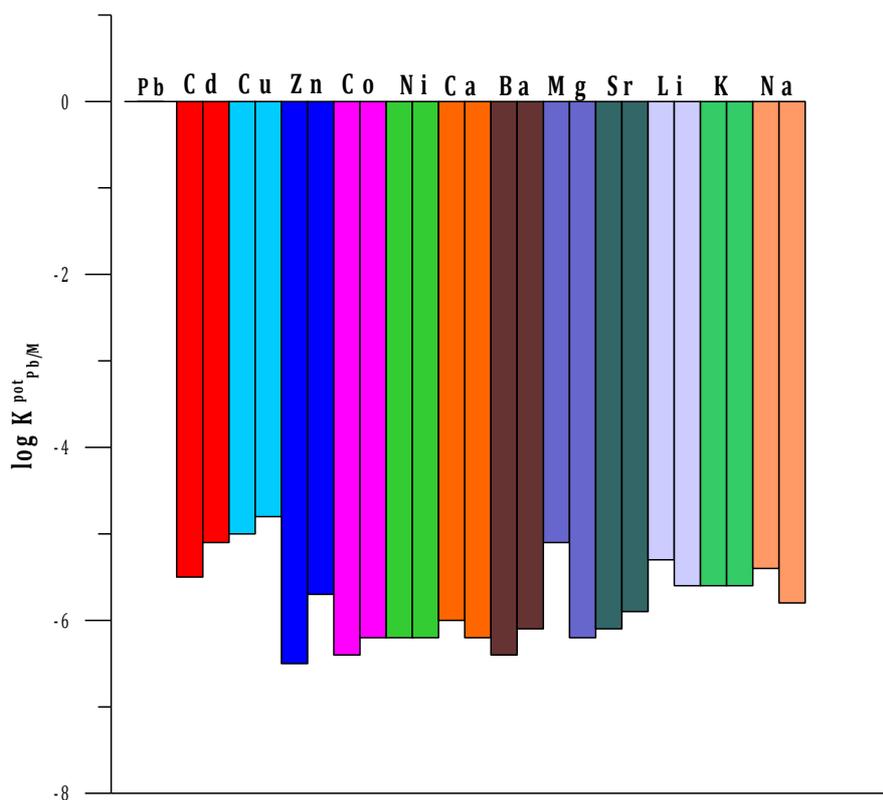


Fig. 2. Selectivity coefficients values for studied sensor determined by SSM method(1<sup>st</sup> column) and FIM method (2<sup>nd</sup> column).

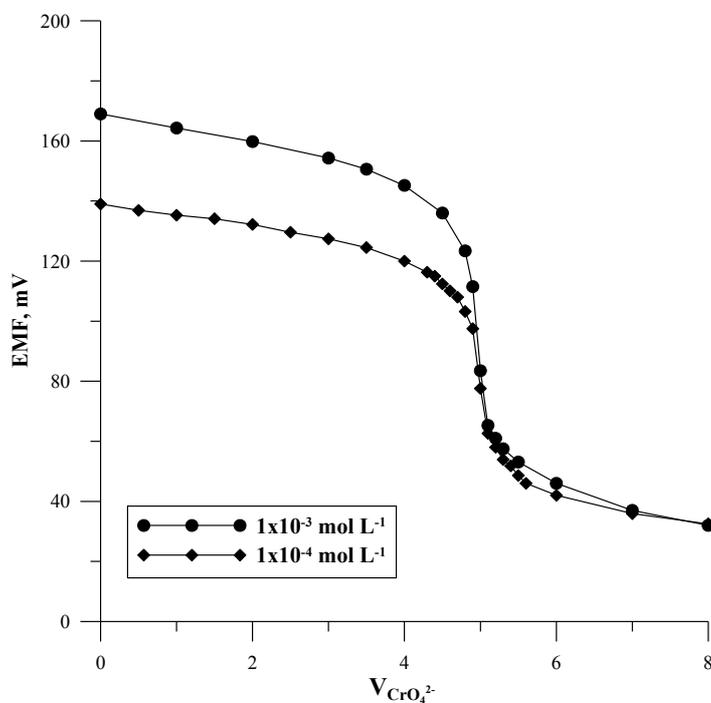


Fig. 3. Potentiometric titration curve of 50mL of  $1.0 \times 10^{-3} \text{ mol L}^{-1}$   $\text{Pb}(\text{NO}_3)_2$  solution (pH = 4.8 acetate buffer) with  $1.0 \times 10^{-2} \text{ mol L}^{-1}$   $\text{K}_2\text{CrO}_4$  solution and 50mL of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$   $\text{Pb}(\text{NO}_3)_2$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

## Conclusion

A new composition of the membrane phase of lead ion selective electrode is proposed. The application of new membrane component ionic liquid: 1-hexyl-3-methylimidazolium hexafluorophosphate instead of conventional lipophilic additive results in obtaining excellent lead sensor. The proposed electrode is characterized by good analytical parameters: low detection limit, wide measuring range, wide pH range, high potential stability and excellent selectivity. Presented electrode has not internal solution so it is simple to construct, easy to transport and more convenient in use because it have not to work in vertical position and doesn't need operation with internal solution. The electrode may be used for lead determination in the range  $10^{-1} - 1.0 \times 10^{-8} \text{ mol L}^{-1}$ .

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