# AN ALL SOLID STATE ION-SELECTIVE ELECTRODE FOR LEAD MONITORING IN THE ENVIRONMENT

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## Abstract

Cheap and simple, an all solid state lead ion selective electrode for lead determination is described. The PVC electrode membrane was modified by addition of multiwalled carbon nanotubes and ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate. The electrode with a modified membrane was characterized by a lower detection limit and better selectivity in relation to sodium, potassium, and calcium ions than an electrode having membrane with a classic composition. It also exhibited good potential stability and reproducibility.

**Key words:** lead ion-selective electrode, solid contact, ionic liquid, multiwalled carbon nanotubes

## Introduction

Lead is a very strong poison that is one of the environmental pollutants and tends to accumulate in organisms and ecosystems. Exposure to this element even at a low level causes adverse effects on human health. Lead is an inhibitor of hemoglobin synthesis and shortens the life of erythrocytes, resulting in anemia. It has a detrimental effect on the functioning of the central nervous system, it can lead to brain edema, degeneration of nerve cells and the death of nerve cells. Poisoning with this element can also cause so-called symptoms of psychopathic anxiety, irritability, mental numbness and memory loss, headache or muscle tremors, and in drastic cases even coma and death [1]. Due to the harmful effects of lead, it is very important to monitor its content in the natural environment. It is present in air, soils and natural waters. In the case of marine waters, it is about 10-60 ng/l, and inland surface waters - 200 ng/l [2]. In the environment, lead occurs primarily as inorganic Pb (II) which can be readily detected and quantified potentiometrically with ion-sensitive electrodes (ISEs) sensitive to lead ions. Among different types of construction, ISEs with a solid contact are become more and more popular due to their numerous advantages including small size, simple construction and operation, low cost of production and ability to operate in high pressure environments. Unfortunately in the case of direct connection between polymeric membrane and electronic

conductor, there are often problems with the stability and reproducibility of the potential. Therefore numerous modifications in the electrode construction were introduced including, conducting polymers [3], metal nanoparticles [4], self-assembled redox layer [5] and carbon based nanomaterials [6].

In this paper a new lead ion-selective electrode in all solid state mode is presented. For membrane preparation two additional components, multiwalled carbon nanotubes and ionic liquid, were used.

## Materials and methods

Reagents: Lead ionophore(IV)- Fluka, bis(1-butyl)pentyl adipate (BBPA) – Fluka, polyvinyl chloride (PVC) –Aldrich, multiwalled carbon nanotubes (MWCNTs) –Aldrich, potassium tetrakis(p-chlophenyl)borate (KTpClB)- Fluka, tetrahydrofurane (THF)-POCH. Other reagents were obtained from Fluka.

The ion-selective electrodes were prepared using a glassy carbon (GC) disc of 3 mm diameter as an internal electrode. Before membrane deposition GCEs were polished with alumina powder and rinsed carefully with water and THF. The composition of the membrane mixture was, for electrode 1, 3% (w/w) HMImPF6, 1% (w/w) MWCNT 63% (w/w) BBPA, 33% (w/w) PVC; for electrode 2, 1% (w/w) ionophore, 0,5% (w/w) KTpClPB, 65,75% (w/w) BBPA, 33% (w/w) PVC; for electrode 3, as in electrode 2; for electrode 4, 1% (w/w) ionophore, 3% (w/w) HMImPF6, 1% (w/w) MWCNT, 62% (w/w) BBPA, 33% (w/w) PVC. The membrane components were weighed, dissolved in THF and the mixture was homogenized using an ultrasonic bath for ca. 40 min. Next 50 µL of membrane cocktail was applied on the top of GCE. In the case of electrode 3 the MWCNTs were introduced as an intermediate layer between the membrane and internal GC electrode. The obtained solid contact electrodes were conditioned in $1x10^{-3}$ mol $L^{-1}$ $Pb(NO_3)_2$ for at least 24 h to saturate the PVC membrane with lead ions. All conditioning and sample solutions have the same background $5x10^{-3}$ mol $L^{-1}$ acetate buffer pH=4.8.

All potentiometric measurements were performed at room temperature in a solution stirred with magnetic stirrer using a measuring system consisting of a multichannel data potentiometric acquisition system (Lawson Labs. Inc., USA) connected to a PC computer. As a reference electrode the Ag/AgCl electrode Metrohm 6.0750.100 was used.

## Results

The effect of membrane composition on electrode performance was evaluated on the basis of calibration curves determined in $Pb(NO_3)_2$ solution in the range $1x10^{-7}$ – $1x10^{-2}$ mol $L^{-1}$. The obtained results are shown in Figure 1.

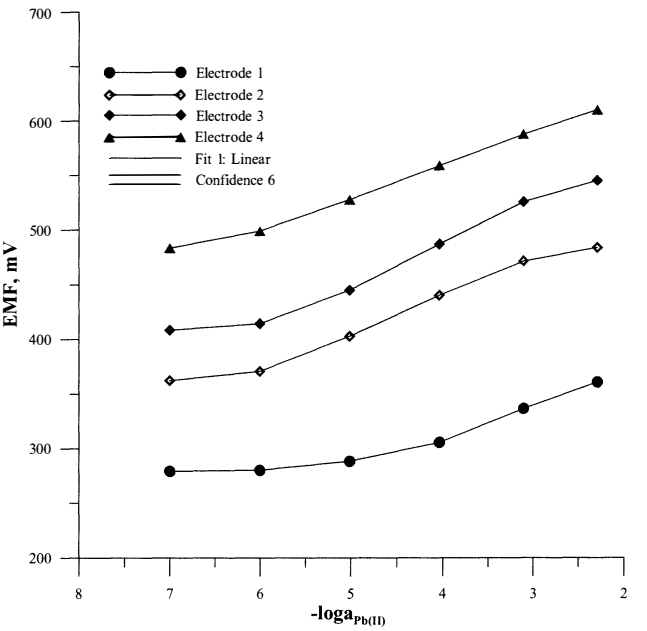


**Figure 1.** Potentiometric response of lead ion-selective electrodes.

On the basis of course the calibration curves basic analytical parameters, such as detection limit, linear range, and characteristic slope were determined. They are summarized in Table 1.

**Table 1.**

| Parameter | Electrode 1 | Electrode 2 | Electrode 3 | Electrode 4 |
|---|---|---|---|---|
| **Characteristic slope mV/ $pa_{Pb(II)}$** | 31.6 | 31.4 | 36.5 | 30.1 |
| **Detection limit, mol $L^{-1}$** | $1.6x10^{-5}$ | $5.6x10^{-7}$ | $4.2x10^{-7}$ | $1.0x10^{-7}$ |
| **Linear range, mol $L^{-1}$** | $1x10^{-4}$ $-1x10^{-2}$ | $1x10^{-6}$ $-1x10^{-3}$ | $1x10^{-6}$ $-1x10^{-3}$ | $1x10^{-6}$ $-1x10^{-2}$ |
| **Potential drift, mV/day** | 0.28 | 3.02 | 2.86 | 0.13 |
| **Potential reversibility, mV** | 2.39 | 1.54 | 1.32 | 0.78 |
| **Potential reproducibility, mV** | 7.34 | 42.93 | 55.13 | 1.09 |

The selectivity of studied electrodes toward interfering ions such as: ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$) was evaluated. To this purpose the selectivity coefficients values were determined using a separate solution method [7]. The obtained results are listed in Table 2.

**Table 2.**

| Ion | Electrode 1 | Electrode 2 | Electrode 3 | Electrode 4 |
|---|---|---|---|---|
| $Na^+$ | -2,2 | -1,5 | -2,5 | -4,3 |
| $K^+$ | -1,1 | -3,3 | -3,8 | -5,3 |
| $Ca^{2+}$ | -3,7 | -2,2 | -3,7 | -3,8 |
| $Mg^{2+}$ | -3,6 | -6,9 | -6,8 | -6,5 |
| $Co^{2+}$ | -3,4 | -6,9 | -6,8 | -5,9 |
| $Ni^{2+}$ | -1,4 | -6,7 | -6,6 | -5,6 |
| $Cu^{2+}$ | 0,39 | -6,7 | -6,6 | -5,3 |
| $Zn^{2+}$ | -1,5 | -6,9 | -6,8 | -5,9 |
| $Cd^{2+}$ | -2,8 | -3,5 | -4,4 | -3,4 |

## Discussion

In this research the effect of membrane modification on electrode properties was studied. Four kinds of ion selective electrodes were constructed and studied. As can be seen in Figure 1 all electrodes exhibited theoretical sensitivity to lead ions but the detection limit and the linear range were different for particular electrodes. Electrode 2 with membrane containing commonly used components responds linear to $Pb^{2+}$ ions in the activity range $1x10^{-6}$ – $1x10^{-3}$ mol $L^{-1}$. The linear range and the detection limit were improved by introduction to the membrane phase IL and MWCNTs. Electrode 4 whose membrane contained these components exhibited the lowest detection limit $1x10^{-7}$ and a linear response in the activity $1x10^{-6}$ -$1x10^{-2}$ mol $L^{-1}$. Electrode 4 also had better parameters in comparison to electrode 3 with classic membrane composition and carbon nanotubes used as a separate inner layer between the ion-selective membrane and internal electrode. The modification of the membrane by MWCNTs and IL results in essential improvement of potential stability, reversibility, and reproducibility. These parameters determined for electrode 4 were significantly better than for the remaining electrodes (Table 1) .

Selectivity is one of the most important electrode parameters. From the analysis of the values of selectivity coefficients given in Table 2 it can be concluded that all electrodes were characterized by good selectivity coefficients towards interfering ions. Electrode 4 with modified membrane exhibited better selectivity in relation to sodium, potassium, and calcium ions in comparison to electrodes 2 and 3. This is a beneficial effect, from a practical point of view in the case of sample analysis, for instance of natural water where the content of these ions is higher than the lead concentration. On the other hand slightly worse values of selectivity coefficients were observed in relation to cobalt, nickel, copper and zinc ions. This change is not important because the values obtained were still very good and interference from these ions can be negligible.

## Conclusions

As a result of the conducted tests, it was found that modification of the membrane with carbon nanotubes and ionic liquid has a positive effect on the parameters of the electrode. Electrode no 4 with a modified membrane exhibits better parameters than electrode 2 with a classic membrane composition and electrode 3 with classic membrane composition, carbon nanotubes used as a separate inner layer between the ion-selective membrane and an internal electrode. The electrode is characterized by a lower limit of detection and better selectivity in relation to sodium, potassium and calcium ions. It also demonstrates good stability and reproducibility of the potential. An additional advantage is the fact that its preparation, usage and service are very simple.

## References:

1. Manahan, S. E. Toksykologia środowiska. Aspekty chemiczne i biochemiczne. 1st edn. Warsaw, Wydawnictwo Naukowe PWN, 2010: 168 pp.
2. Naumczyk J., Chemia środowiska, 1st edn. Warsaw, Wydawnictwo Naukowe PWN, 2017: 191 pp.
3. Bobacka J. (2006) Conducting polymer-based solid-state ion-selective electrodes. Electroanalysis, 18: 7-18.
4. Paczosa-Bator B., Cabaj L., Piech R., Skupień K. (2012) Platinum nanoparticles intermediate layer in solid-state selective electrodes. Analyst, 137: 5272-5277.
5. Grygolowicz-Pawlak e., Plachecka K., Brzózka Z., Malinowska E. (2007) Further studies on the role of redox-active monolayer as intermediate phase of solid-state sensors. Sensor and Actuators B-Chem., 123: 480-487.
6. Ping J., Wang Y., Wu J., Ying Y. (2011) Development of an all-solid-state potassium ion-selective electrode using graphene as the solid-contact transducer. Electrochemical Communications, 13: 1529-1532.
7. Bakker E., Pretsch E., Bühlman P. (2000) Selectivity of potentiometric ion sensors. Analytical Chemistry, 72: 1127-1133.