

Determination of Lead Ions Using an Diantipyrylmethane-Based Electrode

S. D. Tataeva*, V. S. Magomedova, and K. E. Magomedov

Dagestan State University, Makhachkala, 367000 Russia

*e-mail: anchemist@yandex.ru

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Abstract—The possibility of using diantipyrylmethane as an ionophore component of a lead-selective electrode membrane was assessed. Membrane composition (wt %) was optimized: polyvinyl chloride (31.89), dioctyl sebacate (63.81), diantipyrylmethane (2.50), and oleic acid (1.80). The proposed model of the electrode works in the concentration range of 1×10^{-5} –0.1 M with a detection limit of 2 mg/L. A slope of the electrode function of the diantipyrylmethane-based electrode is 29.4 ± 0.5 mV/pPb. Concentration of Pb(II) ions in various samples was determined.

Keywords: potentiometry with ISE, potential, membrane ionophore component, lead, response, selectivity, electrode, determination, samples

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Heavy metals belong to the most important biosphere pollutants. This is largely because of the biological activity of many of them. In the choice of a method of analysis, analysts take into account rapidity, accuracy, cost, and ease of measurement implementation. Ion-selective electrodes (ISE) are the most needed [1]. Insufficiently low detection limits and short electrode life should be assigned to the disadvantages of potentiometry with ISE. In this connection, a search for new ionophore components of ISE membranes and their comprehensive certification are of great importance [2, 3].

One of the trends in present-day science is a search for new low-cost and available materials with useful physicochemical properties. From this point of view, various lipophilic analytical reagents used both for the extraction [4] and direct photometric determination of different elements are of interest for potentiometry with ISE.

The aim of this work was the approbation of a diantipyrylmethane-based ISE for the determination of Pb(II) ions in different samples. Three water samples taken from different sources (Samur river located in southern Dagestan and Azerbaijan, Pakhra river located in Moscow Oblast, and wastewater of “Hajiyev Plant,” Dagestan) and also blue household paints of the Decor brand were used as test samples.

EXPERIMENTAL

Reagents. 4,4-Methylenebis(1,2-dihydro-1,5-dimethyl-2-phenyl-3-pyrazolone) (DAM), dibutyl

phthalate (DBP), dioctyl sebacate (DOS), dioctyl phthalate (DOP), tributyl phosphate (TBP), oleic acid (OA) of reagent grade, polyvinyl chloride (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), sodium tetraphenylborate (NaTPB) (Fluka Selectophore grade, Switzerland), tetrahydrofuran, and cyclohexanone (CH) (Vekton, SPb.) were used.

Equipment. Potential was measured using an Ekotest-120 8-channel high-precision computerized potentiometric station (“Izmeritel’naya tekhnika,” Moscow) with a ESr-10101 two-key reference electrode (3.5 M KCl). PVC-tubes of the size 12 × 90 mm with plasticized PVC-membranes and DAM as an ionophore were used. The internal reference electrode of the ISE was silver wire coated with an AgCl layer according to the procedure described in [5]. Single-channel BLEK dispensers of varied volume (Thermo Fisher Scientific) were used to set precise volumes of membrane compositions.

Procedure. To prepare Pb-SE, DAM was used as an ionophore component. Because of the lack of accurate calculation methods of the selection of membrane thickness at a precise molar concentration of ionophore components, an iteration equation was derived:

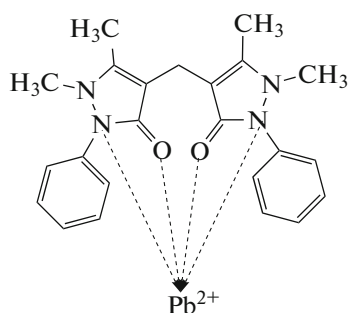
$$m_{\text{PI}_{i+1}} = \frac{n+m}{n/\rho_{\text{Poi}} + m/\rho_{\text{PI}}} \pi r^2 h - \frac{m_{\text{PI}_i} n}{m} - c_{\text{I}} M_{\text{I}} \frac{m_{\text{PI}_i}}{\rho_{\text{PI}}} - c_{\text{IE}} M_{\text{IE}} \frac{m_{\text{PI}_i}}{\rho_{\text{PI}}} - c_{\text{LS}} M_{\text{LS}} \frac{m_{\text{PI}_i}}{\rho_{\text{PI}}}, \quad (1)$$

where i is iteration step; n/m is polyvinyl chloride-to-plasticizer weight ratio; r is membrane radius; h is

membrane height; c_1 , c_{IE} , and c_{LS} are concentrations of ionophore, ion exchanger, and lipophilic salt; M_1 , M_{IE} , and M_{LS} are molar weights of ionophore, ion exchanger, and lipophilic salt; and ρ_{Pol} and ρ_{Pl} are densities of polymer and plasticizer, respectively.

The membranes were prepared according to the procedure described in [6]. A portion of the resulting membrane composition of the volume 1.45 mL was poured into fluoroplastic cups ($d = 30$ mm), covered with filter paper to prevent the rapid evaporation of the solvent, and allowed to stand for one day or more. After the evaporation of the solvent, membranes with a thickness of 500 μm were obtained; they used for the preparation of ISE. A membrane with a diameter of 12 mm was cut and glued to ends of a PVC tube using a 13 wt % solution of PVC in CH.

Structural formula of an ionophore complex with the lead ion is shown below:



Possible structural formula of the 4,4-methylenebis(1,2-dihydro-1,5-dimethyl-2-phenyl-3-pyrazolone) complex of the lead ion at pH 4.

Ag/AgCl,
KCl (3.5 M)

Calibration
solution

Electrode
membrane

0.005 M $\text{Pb}(\text{NO}_3)_2$
and 0.01 M KCl
(internal solution)

AgCl/Ag

RESULTS AND DISCUSSION

It is known that sensitivity and selectivity of an ionophore substantially depend on the composition of the membrane and the nature of the solvent and additives. Table 1 presents data on the study of the effect of membrane composition, nature and amount of plasticizer, and also ionic additive on the potential of the Pb-SE.

The effect of such plasticizers as *o*-NPOE, DBP, DOS, DOP, and TBP was studied. The analysis of the results showed that, in the presence of DOS, the membrane became more elastic, the results were more reproducible (RSD = 10%), and the nature of the plasticizer did not significantly affect linearity range in the determination of the concentration of Pb(II) ions.

Water sample was filtered through a membrane filter with a pore size of 0.45 μm purified by boiling for 10 min in 1% HNO_3 and double boiling in twice-distilled water, then pH 3–5 was adjusted using 0.1 M NaOH and HCl solutions, depending on the medium of the test sample.

While determining the concentration of Pb(II) ions in water, we used the added–found method. To do this, 20.00 mL of a test solution was placed in a dry beaker, electrodes were put into it, and potential was measured before and after the introduction of 1 mL of a standard 0.1 M Pb(II) solution into it. The solution was stirred with a magnetic stirrer without touching the surface of the membrane to avoid its damage. E was measured by detecting change not less than 30 mV relative to the test solution. The results were calculated by the following equation:

$$c_x = c_{st} \frac{V_{st}}{V_x + V_{st}} \left(10^{\frac{\Delta E}{S}} - \frac{V_x}{V_x + V_{st}} \right)^{-1}, \quad (2)$$

where ΔE is the observed change in the potential, mV; S is a slope of the electrode function found from the diagram; V_{st} and V_x are volumes of the standard and analyzed solution; and c_{st} and c_x are Pb(II) concentrations in the standard and analyzed solution, respectively [7].

Sample pretreatment of household paints was carried out in a TOPwave microwave oven at 200°C and pressure of 10 bar for 35 min. Then 50 mg of a paint were placed in a fluoroplastic reaction vessel and 7 mL of conc. HNO_3 and 1 mL of 33% H_2O_2 were added.

The composition of the electrochemical cell was as follows:

To improve electrode functions of membranes, we used NaTPB and OA anionic additives. The best results were obtained with an additive of 1.80 wt % of OA; this is, most likely, because of hydrophobization and a decrease in the acidity of the reaction mass.

A Pb-SE was constructed based on a membrane containing polyvinyl chloride (31.89 wt %), dioctyl sebacate (63.81 wt %), diantipyrylmethane (2.50 wt %), and oleic acid (1.80 wt %) and its potentiometric characteristics were determined (Fig. 1).

The membrane function is linear in the range from 1×10^{-5} M to 0.1 M (the slope equals to 29.4 ± 0.5 mV/pc). The reproducibility of the potential values (RSD) was 10%.

Table 1. Electrochemical characteristics of PVC-plasticized membranes

Membrane composition, wt %									Electrode characteristics*		
DAM	PVC	plasticizer					ionic additive		<i>S</i> , mV/pc	τ , s	RSD, %
		DBP	TBP	DOP	DOS	NPOE	NaTPB	OA			
2.35	31.94	63.94	—	—	—	—	1.77	—	29.95	60	12.5
2.54	31.55	—	63.73	—	—	—	2.18	—	28.83	20	1.1
2.51	31.26	—	—	63.40	—	—	2.83	—	28.29	35	4.2
2.72	31.77	—	—	—	63.54	—	1.97	—	22.45	20	7.0
2.46	31.78	—	—	—	—	63.58	2.18	—	25.44	50	6.6
2.50	31.89	—	—	—	63.81	—	—	1.80	29.40	20	1.0
2.39	31.95	—	—	—	—	63.92	—	1.74	10.98	45	10.7
2.84	32.45	—	—	—	64.71	—	—	—	22.03	30	7

* Linearity range 10^{-5} –0.1 M for all membranes.

The effect of medium acidity on the response of the Pb-SE was studied (Fig. 2). In the range of pH 3–5, the potential of the Pb-SE was stable with a drift not of more than 2 mV. Further measurements were performed at the optimum pH 3–4.

The potentiometric selectivity coefficients of lead ions relative to some d-elements, hydrogen sulfide group metals, and also alkali and alkaline-earth metals were determined by the method of biionic potentials. The response of membranes was strongly affected by metal ions of hydrogen sulfide group, and also by Cu(II) ions; therefore, it was necessary to use masking reagents. To increase the selectivity of the membrane

to Pb(II) ions, 0.1 M NH_3 was introduced into the test solution to fix Cu(II), Zn(II), Hg(II), and Cd(II) ions into ammonia complexes, which were more stable than DAM complexes (Fig. 3). From the values of selectivity factors one can see that heavy metal ions after masking with 0.1 M NH_3 do not substantially affect the electrode response.

Table 2 presents comparative potentiometric characteristics of Pb-SE, close in technical solution to the proposed electrode. One can see that electrode functions (slope, linearity range, and response) of the considered electrodes are close, but the DAM-based electrode favorably differs in reproducibility and selectivity and ensures the determination of Pb(II) ions in more acidic media. Therefore, the DAM-based electrode may be used as an alternative to other Pb-SE [8–14].

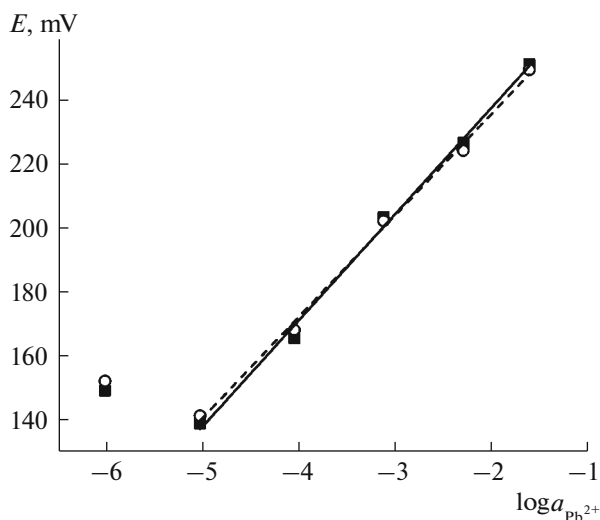


Fig. 1. Calibration curves of the dependence of *E* values on the logarithm of activity of lead ions, where ■ is direct calibration, and ○ is inverse calibration. Solid and dashed lines are functions of direct and inverse Pb-SE calibrations, respectively.

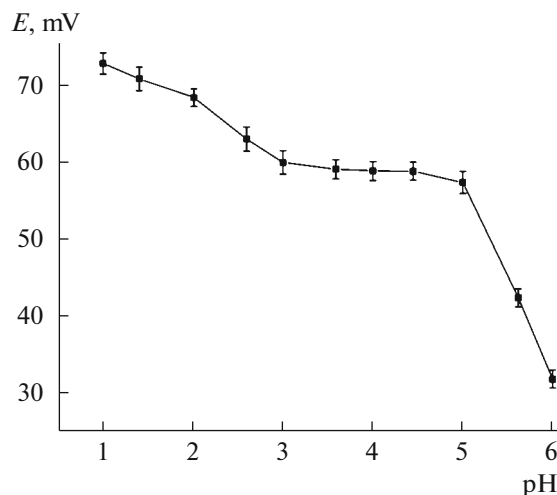


Fig. 2. Effect of pH on the electrode potential of the DAM-based Pb-SE.

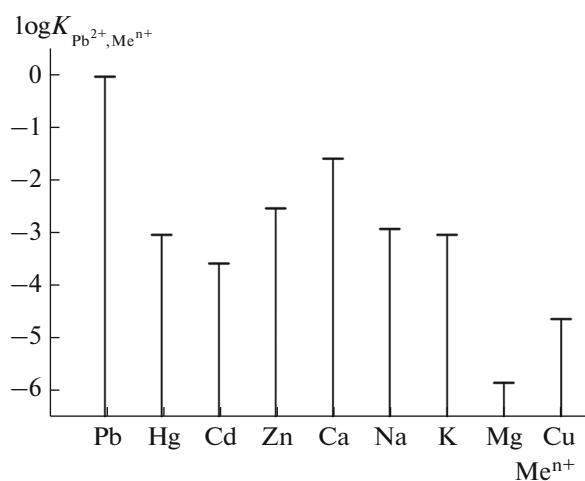


Fig. 3. Potentiometric selectivity coefficients of the DAM-based Pb-SE.

The possibility of using a DAM-based Pb-SE for the determination of Pb(II) ions in water samples and household paint was tested (Table 3). The results were compared with the data obtained using a commercial ELIS – $131Pb^{2+}$ electrode and also with the data of atomic absorption spectrometry (AAS) and stripping voltammetry (SVA). The concentration of Pb(II) ions found with the DAM-based Pb-SE is close to the results obtained using a commercial electrode and by AAS and SVA. Thus, the DAM-based electrode can be used as an alternative to ELIS – $131Pb^{2+}$ for the determination of Pb(II) ions in various samples.

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Table 2. Comparison of electrochemical characteristics and selectivity coefficients of different Pb-SE

Ionophore	Concentration range, M	pH range	c_{min} , M	S , mV/pc	Reference
3,15,21-Triazo-4,5;13,14-dibenzene-6,9,12-trioxobicyclogenecoza-1,17,19-trien-2,16-dion	1.3×10^{-2} – 3.6×10^{-6}	3.7–6.5	2.0×10^{-6}	31.2	[8]
1,5-Diphenylthiocarbazone (dithizon)	5.0×10^{-6} – 1.0×10^{-2}	8–10	3.4×10^{-6}	29 ± 2	[9]
1,10-Dibenzyl-1,10-diaza-18-crown-6	5.0×10^{-5} – 1.0×10^{-2}	–	2.8×10^{-5}	29.3 ± 0.7	[10]
N^d -dipicolinoil-bis(L-leucyl-DL-norvalil methyl ester)	5.8×10^{-5} – 1.0×10^{-2}	4.5–7	1.8×10^{-5}	33.1	[11]
Cyclo-(N^d -dipicolinoil)bis(L-leucyl-DL-norvalil)-L-lysine methyl ester	4.0×10^{-6} – 1.0×10^{-2}	4.5–7	2.1×10^{-6}	25	[12]
Lead sulfide nanoparticles	1.0×10^{-5} – 1.0×10^{-2}	3–7	–	–	[13]
N,N' -bis(2-hydroxy-1-naphthalene)-2,6-pyridiamine	3.2×10^{-6} –0.1	3.5–7.5	–	29.1 ± 0.1	[14]
4,4-Methylenebis(1,2-dihydro-1,5-dimethyl-2-phenyl-3-pyrazolone)	1.0×10^{-5} –0.1	3–5	1.0×10^{-5}	29.4 ± 0.5	This study

Table 3. Results of analyses of water samples and Decor household paint for the concentration of lead ions ($n = 3$, $P = 0.95$)

Method	Pb concentration in water samples, $\mu\text{g/L}$						Pb concentration in Decor paint, mg/L	RSD, %
	Samur river	RSD, %	Pakhra river	RSD, %	“Hajiyev Plant”	RSD, %		
Potentiometry with ISE commercial electrode	2.93	4	1.15	8	1.08	6	9.60	4
Potentiometry with ISE DAM-based electrode	2.84	5	1.12	9	1.10	7	9.61	3
AAS	2.61	3	1.08	5	1.03	1	9.57	1
SVA	3.70	31	1.36	40	1.21	20	–	–

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