

Recovery of nanomolar detection limit of solid-contact lead (II)-selective electrodes by electrode conditioning

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Abstract Solid-contact Pb^{2+} -selective electrodes (Pb^{2+} -ISEs) were prepared by using polybenzopyrene doped with eriochrome black T as solid contact material and a conventional polyvinyl chloride membrane with lead ionophore IV as selective compound. Nernstian response down to 10^{-9} mol dm^{-3} Pb^{2+} was obtained by careful control of the electrode conditioning process. Furthermore, the response at lowest concentrations was retained by exposing the solid-contact Pb^{2+} -ISEs to a solution containing Na_2EDTA . Finally, the solid-contact Pb^{2+} -ISEs were used in the determination of lead in a synthetic sample ($\text{pPb}^{2+}=7.40$). The analysis of the sample was done with direct potentiometry ($\text{pPb}^{2+}=7.64\pm 0.11$) and single standard addition method ($\text{pPb}^{2+}=7.27\pm 0.07$). These results were in good agreement with those obtained by inductively coupled plasma–mass spectrometry ($\text{pPb}=7.34$). The renewable response of the Pb^{2+} -ISEs at low concentrations opens interesting possibilities when dealing with trace-level measurements of Pb^{2+} .

Introduction

The low detection limit (LDL) is one of the main parameters of potentiometric ion sensors. By new findings on lowering the detection limit of solvent polymeric electrodes, the recommendation for LDL was proposed to be defined as a deviation of the electromotive force (EMF) response by $RT/z_iF \ln 2$ from the extrapolated linear Nernstian part of the calibration curve [1–3].

Early works dealing with the behaviour of electrodes at low analyte concentrations were focused exclusively on solid-state membranes [4–6]. Recently however, a time-dependent adsorption of the analyte on the membrane surface (kinetic calibration) and tuned galvanostatic polarization (chronopotentiometry) method offered possibilities of measurements in the nanomolar concentration range with solid-state membranes [7, 8]. Further possibilities of measurements at ultra low concentrations using ion-selective electrodes appeared with implementation of conventional solvent polymeric membrane electrodes in which the composition of the inner filling solution plays a crucial role in the overall response of ion-selective electrodes (ISEs) as a result of transmembrane ion fluxes [9]. Much study was therefore devoted to optimize the composition of the inner solution as well as the thickness of the ion-selective membrane [10–14], lowering transmembrane ion fluxes by applying various polymeric material–plasticizer ratios and decreasing the quantity of ion exchanger in the membrane [12], covalently binding the ionophore to the polymer backbone or introducing a material other than polyvinyl chloride (PVC) with lower ion diffusion coefficients inside the membrane (e.g. derivatives of polyacrylates) [15–19], and applying galvanostatic polarization of the ion-selective membrane [20–22] to effectively lower the detection limit of ISEs. Above all, for solvent polymeric membranes, a mathematical model was introduced to predict and illustrate

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the detection limit under various conditions. Applying the Nernst–Planck–Poisson model, it was shown that the detection limit of ISEs is concentration- and time-dependent [23].

A number of conducting polymers have been applied either directly as sensing membranes or as solid-contact materials [24]. Lowering the detection limit of conducting polymer used as a sensing material may be difficult to obtain due to e.g. insufficient selectivity, sensitivity to light, pH and dissolved gases [25–29]. More promising in lowering the detection limit are solid-contact ISEs, in which the conducting polymer serves as the ion-to-electron transducer and a plastic membrane is responsible for a sufficiently high selectivity and sensitivity [30–36]. The solid-contact design may significantly help in lowering transmembrane ion fluxes as it replaces the inner reservoir of highly concentrated solution (conventional ISEs) with a solid conducting polymer layer. Additionally, the conducting polymer film may be doped with a compound which complexes the primary ion, thus promoting a supplementary driving force for it to enter the membrane [37, 38]. To improve the low detection limit of solid-contact electrodes, continuous search for novel materials with specific properties, e.g. with lower water uptake, is undertaken. Together with a detailed protocol of measurements and solution handling, the determination of pollutants in real environmental samples with this type of sensor may be very successful [39, 40]. Furthermore, disposable potentiometric sensors based on solid-contact ISEs combined with solid-contact reference electrodes were successfully developed and applied for trace analysis of lead in environmental samples [41].

The response at low concentration for many solid-contact ISEs within first contact with primary ion (adequate for unconditioned membranes) exhibit lower detection limit which is then lost after prolonged contact with the analyte. There is no comprehensive method to deal with this problem. Due to rigorous restrictions, there is a constant need for the development of new sensors with low enough detection limit to measure extremely low concentrations of analyte [42, 43]. The objective of the present work is therefore to develop a solid-contact ISE with renewable response at low concentration of the analyte. For the solid-contact Pb^{2+} -ISEs studied in this work, polybenzopyrene doped with eriochrome black T was chosen as ion-to-electron transducer due to its low hysteresis effect in a wide range of lead activities and also to assure an additional driving force to take up Pb^{2+} due to complex formation of lead (II) with eriochrome black T [28]. The polybenzopyrene-based solid contact was coated with a PVC-based membrane containing Pb^{2+} -selective ionophore. Our design of solid-state Pb^{2+} -selective electrodes together with a measurement protocol assuring recovery of the low detection limit at the nanomolar Pb^{2+} activity range are shown here for the very first time.

Experimental

Reagents

Lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$), sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (NaTFPB), poly(vinyl chloride) (PVC) high molecular weight and tetrahydrofuran (THF) were obtained from Fluka (Buchs, Switzerland). Potassium nitrate (KNO_3), ethylenedinitrilo tetraacetic acid disodium dehydrate (Na_2EDTA) and eriochrome black T (EbT) were obtained from Merck (Darmstadt, Germany). Benzo(*a*)pyrene and acetonitrile were obtained from Sigma-Aldrich (Steinheim, Germany). Nitric acid (HNO_3), 65 %, was purchased from Baker (Deventer, the Netherlands). Chemicals were of analytical grade. Aqueous solutions were prepared with freshly deionized water ($18.2 \text{ M}\Omega \text{ cm}$) obtained with the ELGA purelab ultra water system (High Wycombe, UK).

Preparation of solid-contact ISEs

The polybenzopyrene films were polymerized on glassy carbon by cycling the potential between 0 and 1.4 V in acetonitrile solution containing 8 mmol dm^{-3} benzo(*a*)pyrene and 10 mmol dm^{-3} eriochrome black T, as described earlier [28]. The PVC-based membranes contained: 0.4 % ($3.80 \text{ mmol kg}^{-1}$) lead ionophore IV, 0.15 % ($1.69 \text{ mmol kg}^{-1}$) NaTFPB, 62.3 % *o*-NPOE and 37.15 % PVC (weight percent). Two hundred milligrams of membrane components was dissolved in 2 mL of THF. When the surface of the polybenzopyrene-based electrodes was visually waterless (2 h after polymerization), the membrane cocktail was applied by drop casting. Portions of $10 \mu\text{L}$ of the membrane components were applied with a 10-min time delay (longer if necessary, till the visual evaporation of the solvent) until a final volume of $60 \mu\text{L}$ of cocktail per electrode. Subsequently, the electrodes were left for overnight evaporation of the residual solvent. Three electrodes were prepared in the same manner.

EMF measurements

For all cases, calibration of Pb^{2+} -ISEs was done by automatic dilution of a stock solution using two Metrohm Dosino 700 instruments equipped with burets of 50-mL capacity (Herisau, Switzerland). The pumps were programmed to dilute the sample solution with freshly deionized water ($18.2 \text{ M}\Omega \text{ cm}$) every 30 min. In all potentiometric measurements, a double-junction electrode Orion (Thermo Scientific Environmental Instruments, Beverly, MA, USA) with $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ | $1 \text{ mol dm}^{-3} \text{ KCl}$ served as a reference electrode. Moreover, potentiometric measurements were carried out in 100-mL disposable polystyrene beakers.

Each beaker was soaked in 10^{-1} mol dm $^{-3}$ HNO $_3$ for 2 days and washed with deionized water. Each solution was stored no longer than 1 week. The data obtained were recorded with an EMF16 Interface (Lawson Labs Inc., Malvern, PA, USA). All experiments were performed at a room temperature (20–21 °C). The activity coefficients were calculated according to the Debye–Hückel approximation. All the EMF data were corrected for liquid junction potentials according to the Henderson equation.

Low detection limit measurements

Lowering of the detection limit of solid-contact electrodes was based on a rigorous protocol of concentration- and time-dependent conditioning. To avoid contamination of the electrodes, a concentrated solution of not more than 10^{-5} mol dm $^{-3}$ was used. Prior to the first potentiometric measurements, the electrodes were kept without contact to any solution. Before the start of the measurement, all the electrodes were preconditioned in 50 mL of 10^{-5} mol dm $^{-3}$ Pb(NO $_3$) $_2$ for 20 min. Subsequently, potentiometric measurement was run from 10^{-5} to 10^{-10} mol dm $^{-3}$ Pb(NO $_3$) $_2$ (the solutions were based on various concentrations of unbuffered: pure lead (II) nitrate or lead(II) nitrate with constant background electrolyte of 10^{-3} mol dm $^{-3}$ KNO $_3$). For each concentration, the electrodes were in the solution for 5 min, continuously stirred. After 5 min, the tenfold dilution of the solution was performed. The whole procedure starting from preconditioning until the final measurement in 10^{-10} mol dm $^{-3}$ Pb $^{2+}$ will be further called conditioning cycle. Every measurement was performed in the same manner. Between the measurements, the electrodes were washed with deionized water and kept in a closed container in contact with air. At the bottom of the container was 20 mL of deionized water. Evaporation of water moistened membranes preventing them from drying and cracking. When electrodes lost the desired low detection limit, they were kept in the solution of 10^{-3} mol dm $^{-3}$ of Na $_2$ EDTA (recovery solution, pH=4.9) for 24 h. Subsequently, the lower detection limit was attained applying the procedure described above for investigation of LDL.

Selectivity measurement

The separate solution method (SSM) was used to determine unbiased selectivity coefficients for lead over the relevant interfering ions. Three solid-contact Pb $^{2+}$ -selective electrodes based on polybenzopyrene doped with eriochrome black T/PVC membrane were first kept in 10^{-3} mol dm $^{-3}$ Na $_2$ EDTA solution for 24 h and subsequently washed with deionized water. Then, the EMF was recorded in the following sequence of cations: Ca $^{2+}$, K $^{+}$, Na $^{+}$, Zn $^{2+}$, Cd $^{2+}$, Cu $^{2+}$ and Pb $^{2+}$. All used salts were chlorides except nitrate salt for Pb $^{2+}$. Additionally, to obtain total free lead concentration, the lead nitrate solutions

contained a constant concentration of 10^{-4} mol dm $^{-3}$ HNO $_3$. By introducing complexation constants of chlorides and nitrates with each investigated interfering ion, the influence of anion on free Pb $^{2+}$ activity was used for slope calculations. The slope of Pb $^{2+}$ -ISEs in lead (II) solutions and the potential of Pb $^{2+}$ -ISEs in primary and interfering ion solutions (close to Nernstian slope and assumption of a constant standard potential of Pb $^{2+}$ -ISEs regardless the measuring solution) were used to calculate selectivity coefficient. The uncertainties of selectivity coefficients were obtained from the measurement done with three identical electrodes.

Lead determination in synthetic sample

The lead determination was done in potentiometric mode with two methods: direct measurement of lead in the sample and single standard addition method. In both cases, the sample consisted of pPb $^{2+}$ =7.40+pKNO $_3$ =3. Before measurements, the electrodes were in contact with 10^{-3} mol dm $^{-3}$ Na $_2$ EDTA solution for 24 h. Subsequently, calibration curves were recorded according to the protocol for low detection limit investigation (for solutions of various lead nitrate concentrations with constant 10^{-3} mol dm $^{-3}$ KNO $_3$ as a background electrolyte). The calibration procedure was repeated until Nernstian response down to 10^{-8} mol dm $^{-3}$ was obtained. The electrodes were rinsed with deionized water and transferred to 50 mL of the sample, and EMF data were recorded for 5 min while stirring. The obtained EMF data for two electrodes were then compared to the previously obtained calibration curve. The uncertainty was calculated from two electrodes out of two measurements. For the single standard addition method, the slope of the calibration curve was obtained in the same manner as for direct determination of Pb $^{2+}$. The slope was used to calculate the concentration of lead in the sample. The determination was done by adding a volume (0.55 mL) of standard solution (10^{-4} Pb(NO $_3$) $_2$) to 50 mL of the sample. The EMF data were recorded for 5 min while stirring. The lead concentration in the sample was calculated from the slope of the calibration curve and the potential difference after addition of the standard. Similarly, the uncertainty was calculated from two electrodes out of two measurements. The potentiometric measurements were compared to the analysis of lead in the synthetic sample done with Perkin Elmer Sciex Elan 6100 DRC plus inductively coupled plasma–mass spectrometer (ICP–MS).

Results and discussion

Conditioning in Pb(NO $_3$) $_2$ solutions

The method described here, used to lower the detection limit of solid-contact lead-selective electrode, is based on

concentration- and time-dependent conditioning of the electrodes. The renewable response is based on partially reversing the flux of primary ions from the membrane to the solution. The response of the solid-contact Pb^{2+} -ISE after each conditioning cycle (seven calibrations in total) is shown in Fig. 1. First, the electrodes were kept without stirring in $10^{-5} \text{ mol dm}^{-3}$ unbuffered $\text{Pb}(\text{NO}_3)_2$ solution, then the experiment was run and data were collected every 5 min for each concentration change. The strict protocol of measurement was kept to ensure that the changes of the response are due to the conditioning procedure. To illustrate the changes in the response of ISEs, the calibration curves were aligned from first to seventh conditioning cycle, regardless the standard potential of ion-selective electrodes. The first calibration curve exhibits super Nernstian response between 10^{-6} and $10^{-8} \text{ mol dm}^{-3} \text{ Pb}^{2+}$. This effect is well known for unconditioned membranes, where concentration of analyte at the membrane-sample interface is depleted due to faster uptake of ions inside of the membrane than transport from the bulk of the solution to the membrane surface [14]. Gradually, with each conditioning cycle, the super Nernstian response diminished resulting in Nernstian response after the third conditioning cycle with slope of 30.9 mV dec^{-1} and detection limit down to $\text{pPb}^{2+}=8.7$. However, the optimal conditioning time to lower the detection limit was established after the fourth cycle (in total 80 min conditioning in $10^{-5} \text{ mol dm}^{-3} \text{ Pb}^{2+}$) with slope of 26.6 mV dec^{-1} down to $\text{pPb}^{2+}=9.3$. Further conditioning resulted in increase in detection limit, and finally, the LDL of Pb^{2+} ISE was established at the approximately constant level reported for electrodes based on lead ionophore IV ($\sim 10^{-7} \text{ mol dm}^{-3} \text{ Pb}^{2+}$) [44]. Loss of sensitivity in the lowest concentration range can be attributed

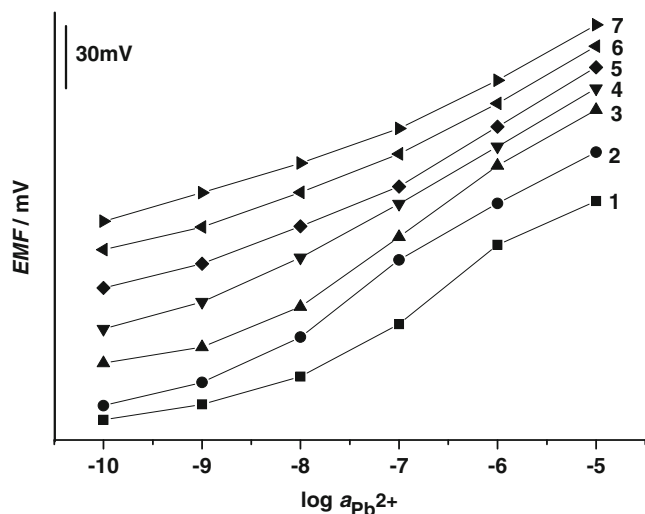


Fig. 1 The response of solid-contact lead-selective electrode when applying conditioning cycles (seven conditioning cycles in total, responses aligned and numbered from first to last). Measurements were done in unbuffered solutions (from 10^{-5} to $10^{-10} \text{ mol dm}^{-3} \text{ Pb}(\text{NO}_3)_2$)

to saturating ion-selective membrane (ISM) with Pb^{2+} . When ISM is in equilibrium with lead ion in the solution, no lowering of the detection limit may be observed. Reaching lower detection limit is possible only when the concentration of primary ion in the ISM is optimized similarly as in the case of conventional solvent polymeric membranes with an internal filling solution [10, 12]. However, due to the lack of an inner filling solution, the optimization of the response is done here by repeating conditioning cycles.

Conditioning in $10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$ solution

When loss of sensitivity between 10^{-7} and $10^{-9} \text{ mol dm}^{-3} \text{ Pb}^{2+}$ occurred, the LDL recovery procedure was applied. Electrodes were placed for 24 h in $10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$. Subsequently, before the measurement the electrodes were washed five times with deionized water, left for 1 hour and finally rinsed with deionized water and applied as previously described in the calibration procedure based on conditioning cycles. In Fig. 2, the response of solid-state Pb^{2+} -ISE is presented after renewing the response by partially reversing the primary ion flux (from the membrane and solid-contact to the recovery solution) and introducing sodium to the membrane. By applying seven conditioning cycles, the low detection limit was investigated. After the first conditioning cycle, the electrode exhibits super Nernstian response between 10^{-6} and $10^{-8} \text{ mol dm}^{-3} \text{ Pb}^{2+}$, similar to the case when the membrane did not have any prior contact with primary ion before the measurement. Soaking the electrode in $10^{-3} \text{ mol dm}^{-3} \text{ Na}_2\text{EDTA}$ caused partial removal of accumulated lead from the membrane, resulting in renewable response (driven by an

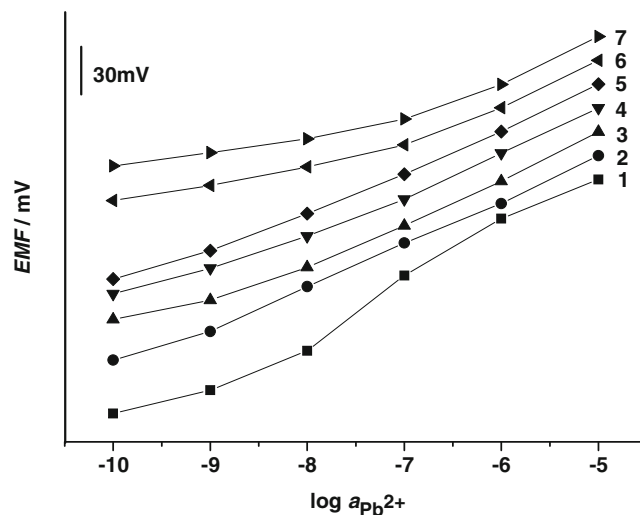


Fig. 2 The response of solid-contact lead-selective electrode when applying each conditioning cycle (seven conditioning cycles in total, responses aligned and numbered from first to last). Measurements were done in unbuffered solutions (from 10^{-5} to $10^{-10} \text{ mol dm}^{-3} \text{ Pb}(\text{NO}_3)_2$) after the recovery process was applied

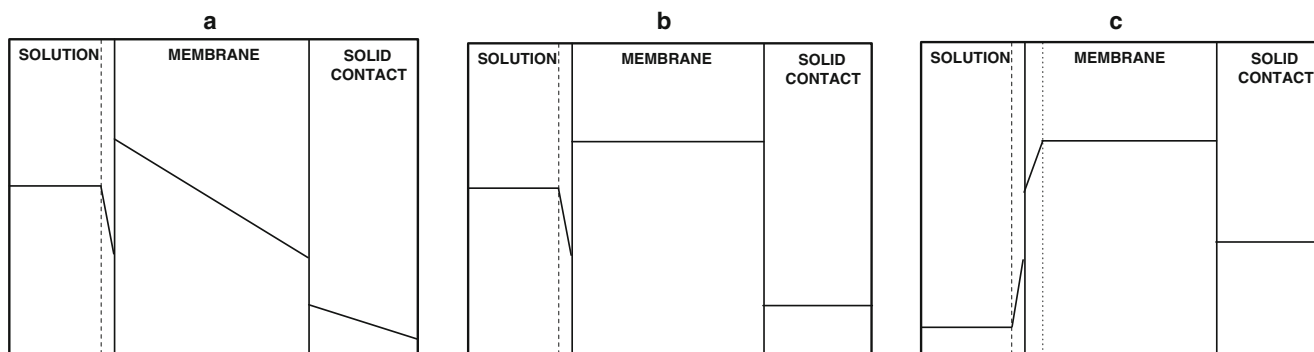


Fig. 3 Simplified concentration profiles for solid-contact (GC/polybenzopyrene(EbT)/PVC membrane) Pb^{2+} -selective electrode for: **a** unconditioned membrane, **b** well-conditioned membrane and **c** when partially reversing primary ion flux by applying recovery process

ion uptake) in the diluted solutions. By applying a ligand (EDTA) which complexes strongly lead ion (stability constants, $\log K_{\text{PbL}}^{\text{Pb,L}} = 18.0$, $\log K_{\text{PbL}_2}^{\text{Pb,L}} = 2.9$ [45]) and simultaneously introduces Na^+ to the membrane [33], a flux of Pb^{2+} from the membrane to the solution was achieved. The EDTA is too large to enter the membrane, and any possible surface accumulation of that component was washed off with deionized water after soaking in the recovery solution; thus, the response at nanomolar concentrations is attributed to the partial removal of lead from the membrane/solid-contact layer. The new established state of the membrane allows lowering the detection limit to approximately $\text{pPb}^{2+} = 9$ already after the second conditioning cycle (retaining up to four conditioning cycles), which indicates that only a small fraction of lead was removed. From the sixth cycle, the LDL was established at around $10^{-7} \text{ mol dm}^{-3} \text{ Pb}^{2+}$. The mechanism behind the renewable response is schematically illustrated by the simplified concentration profiles in Fig. 3. When the membrane has not been in contact with a primary ion, rapid uptake of Pb^{2+} occurs and the flux of Pb^{2+} is realized from the solution to the membrane. An additional driving force for uptake of Pb^{2+} from the solution is realized by the ion-to-electron transducer layer. In our case, the doping ion used for electrosynthesis of the polybenzopyrene film was eriochrome black T which strongly binds ionized lead ($\log K_{\text{PbL}}^{\text{Pb,L}} = 13.19$ [46]). It was previously stated that eriochrome black T retains its complexation properties toward lead inside the membrane [28] (Fig. 3a). Subsequently, when the membrane is saturated with Pb^{2+} , the concentration of primary ion inside the membrane is approximately constant. The driving force for lowering of the detection limit is then eliminated; thus, no significant improvements in the response at low concentrations are obtained (Fig. 3b). Our approach to partially reverse the Pb^{2+} flux creates possibility to renew the response at extremely low concentrations. By applying a strong complexing agent in the solution that also may introduce Na^+ to the membrane, the flux of ions was reversed resulting in partial removal of Pb^{2+} from the membrane as well as removal of all ionic

impurities and traces of lead by complexation with EDTA (Fig. 3c). The process is effective enough to retain lower detection limit up to a few measurements.

Conditioning in $\text{Pb}(\text{NO}_3)_2$ solutions + $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ background electrolyte

To this point, conditions were simplified to pure, unbuffered solutions. However, measurements in environmental samples are performed at higher ionic strength. Subsequently, the influence of background electrolyte was investigated. After the recovery process was applied to ISEs, the conditioning and the response of the electrodes were investigated in solutions consisting of various concentrations of $\text{Pb}(\text{NO}_3)_2$ and constant concentration of $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$. The results from the

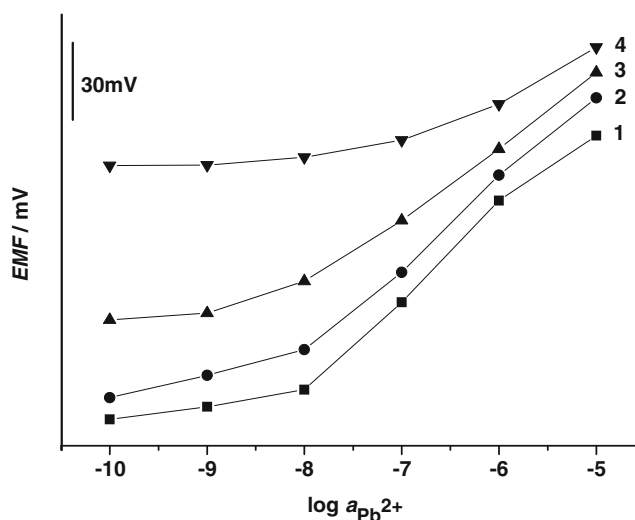


Fig. 4 The response of solid-contact lead-selective electrode when applying each conditioning cycle (four conditioning cycles in total, responses aligned and numbered from first to last). Measurements were done in unbuffered solutions (from 10^{-5} to $10^{-10} \text{ mol dm}^{-3} \text{ Pb}(\text{NO}_3)_2$ with constant background electrolyte $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$) after the recovery process was applied

conditioning procedure are shown in Fig. 4. As previously shown, the first conditioning cycle resulted in super Nernstian response between 10^{-6} and 10^{-8} mol dm $^{-3}$ Pb $^{2+}$. With the next two conditioning cycles, the linearization of the response occurred down to pPb $^{2+}$ ~8. Further conditioning cycles negatively influenced the response at the lowest concentrations. By introducing the background electrolyte, the lower detection limit was one order of magnitude higher in comparison to pure lead (II) nitrate solutions. The change in LDL is primarily dictated by the selectivity coefficient for Pb $^{2+}$ over K $^{+}$ for Pb $^{2+}$ -ISEs ($\log K_{\text{Pb}^{2+}, \text{K}^{+}}^{\text{pot}} = -5.7 \pm 0.6$). Nevertheless, the useful concentration range was broad enough to consider the sensor in measurements of lead in diluted samples. Figure 5

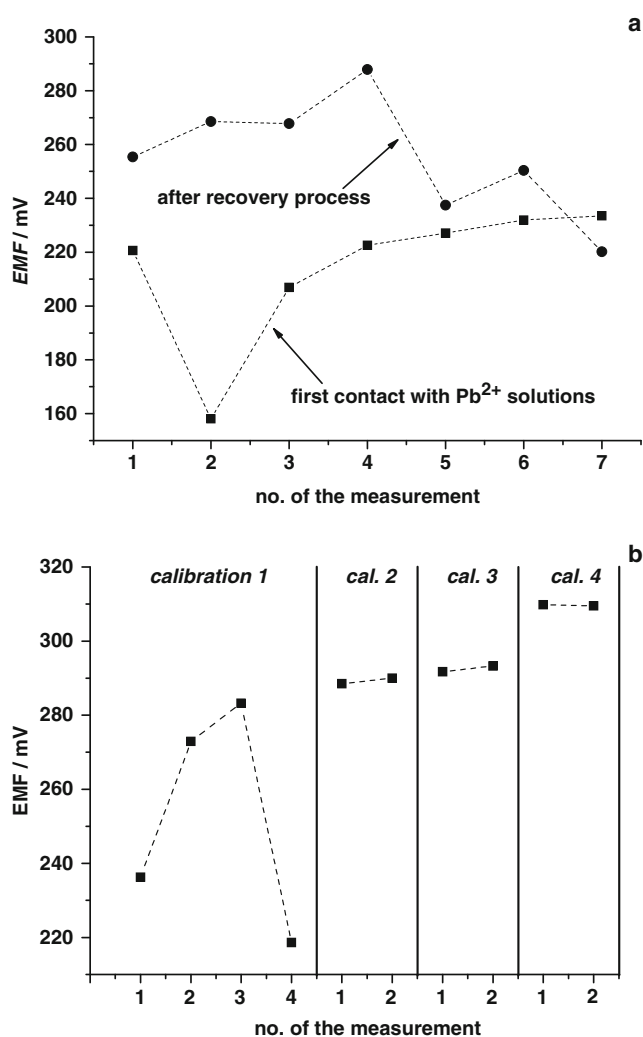


Fig. 5 Changes of open circuit potential values (E°) in 10^{-5} mol dm $^{-3}$ Pb $^{2+}$ after each conditioning cycle: **a** for pure, unbuffered solutions of lead (II) nitrate (black squares first contact with lead solutions and black circles after the recovery process) and **b** for lead (II) nitrate with constant potassium nitrate background electrolyte (including up to four recovery cycles called calibration1, cal.2, cal.3, cal.4; vertical lines are as an indication of performed recovery process)

presents changes of standard potential at open circuit in 10^{-5} mol dm $^{-3}$ Pb $^{2+}$ after each conditioning cycle: (a) for pure, unbuffered solutions of lead (II) nitrate and (b) for lead (II) nitrate with constant potassium nitrate background electrolyte (including up to four recovery cycles). After the second cycle when the electrode was first time in contact with Pb $^{2+}$, the potential at pPb $^{2+}$ =5 significantly dropped. With the next cycles, the potential gradually increased to an approximately constant value when no effect of lowering of the detection limit was anymore observed (Fig. 5a, black squares). It is clear that unconditioned membranes exhibit deviation in standard potential, and only when the membrane is well conditioned is the E° ought to be stable. After the recovery process in pure solution, irregular deviation of potential at pPb $^{2+}$ =5 was observed. It can be attributed to the exchange of Na $^{+}$ that has accumulated in the PVC membrane during the recovery process to Pb $^{2+}$ from the solution. However, more interesting is the fact that after the fifth cycle, the potential of the electrode was established to be approximately the same potential as in the previous case (Fig. 5a, black circles). It indicates that the membrane was again well conditioned and showed no lowering of the detection limit. Figure 5b presents consecutive measurements consisting of conditioning cycles to obtain response at low concentrations (LDL ~ 10^{-8} mol dm $^{-3}$ Pb $^{2+}$). When the response was lost at the lowest concentration of Pb $^{2+}$, the recovery process was applied, and the measurement was run again (four in total). Although with each recovery process an upward change of E° was observed, the standard potential of the electrodes when reaching the desired low detection limit within one measurement was not significantly changing, lasting for at least two conditioning cycles. From three consecutive

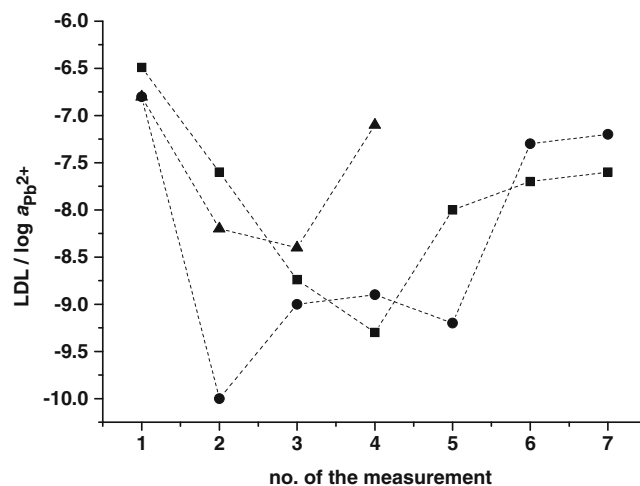


Fig. 6 Low detection limit of solid-contact Pb $^{2+}$ -selective electrode as a function of the number of conditioning cycles performed (black squares pure, unbuffered solutions of Pb(NO $_3$) $_2$, black circles pure, unbuffered solutions of Pb(NO $_3$) $_2$ after the recovery process and black triangles unbuffered solutions of Pb(NO $_3$) $_2$ with constant background electrolyte 10^{-3} mol dm $^{-3}$ KNO $_3$)

Table 1 Low detection limits (LDL) and slopes of the responses of solid-contact Pb²⁺-ISEs when applying conditioning protocol to lower the detection limit (three cases investigated: pure, unbuffered solutions of Pb(NO₃)₂ (first time in contact with primary ion), pure, unbuffered solutions of Pb(NO₃)₂ after recovery process and unbuffered solutions of Pb(NO₃)₂ with constant background electrolyte 10⁻³ mol dm⁻³ KNO₃)

No.	LDL/ log a _{Pb²⁺}	Slope/mV dec ⁻¹
Pure, unbuffered Pb(NO ₃) ₂ solutions (Fig. 1)		
1 ^a	-6.5	20.7
2 ^a	-7.6	25.5
3	-8.7	30.9
4	-9.3	26.6
5	-8.0	28.1
6	-7.7	27.1
7	-7.6	26.1
After recovery process (Fig. 2)		
1 ^a	-6.8	24.7
2	-10.0	27.7
3	-9.0	26.5
4	-8.9	26.9
5	-9.2	26.2
6	-7.3	26.6
7	-7.2	26.0
Unbuffered Pb(NO ₃) ₂ solutions, const. 10 ⁻³ mol dm ⁻³ KNO ₃ (Fig. 4)		
1 ^a	-6.8	25.7
2 ^a	-8.2	33.0
3	-8.4	27.5
4	-7.1	22.5

^a Super Nernstian response occurred

measurements, the standard potential shift between two calibration procedures based on concentration- and time-dependent conditioning was determined to be 1.1±0.6 mV. This allowed preparation of the calibration curve and immediate analysis of the sample. The effects of conditioning of the ion-selective membrane on the low detection limit are

Table 2 Observed electrode slopes and selectivity coefficient obtained according to separate solution method for solid-contact Pb²⁺-ISE; the slope between log a_{Pb(II)} 2.3 and 4.0 was 29.2±1.9 mV dec⁻¹ (the standard deviation from the measurement was obtained from three identical electrodes)

<i>j</i>	Slope/mV dec ⁻¹	log <i>a_j</i> range for slope calculation	log <i>K_{Pb²⁺,j^{pot}}</i>
Ca ²⁺	30.5±1.3	1.5–3.1	-4.9±0.9
K ⁺	42.6±0.7	1.1–3.0	-5.7±0.6
Na ⁺	33.9±0.7	1.1–3.0	-5.4±0.5
Zn ²⁺	27.1±1.6	2.3–4.0	-7.4±0.7
Cd ²⁺	26.1±1.0	2.3–4.0	-3.0±0.3
Cu ²⁺	26.8±0.6	2.3–4.0	-2.5±0.4

summarized in Fig. 6. Obtaining a low detection limit by controlled conditioning of the membrane depends not only on the membrane but also on the conditioning solution. When using solutions with higher ionic strength, the lower detection limit was obtained faster, but it lasted shorter than in the case of pure solutions of Pb(NO₃)₂. Nevertheless, the system is limited by concentration and time of conditioning, and the lowering of the detection limit was obtained only for unconditioned membranes. When membranes were saturated with Pb²⁺, the sensitivity toward primary ion was much worse. All the LDLs and slope values calculated from measurements done using the conditioning protocol are collected in Table 1.

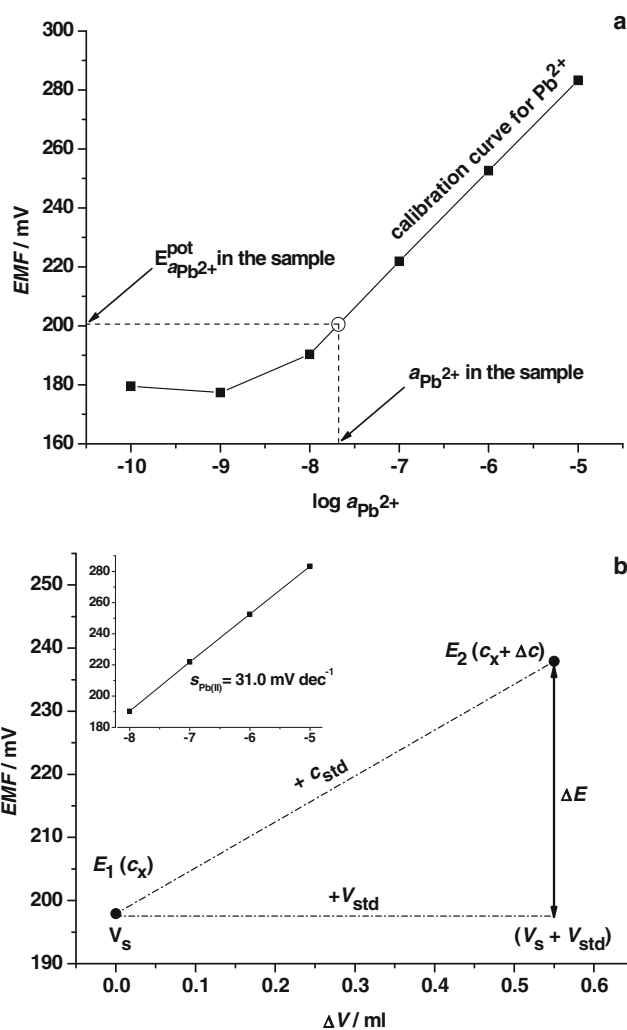


Fig. 7 Analytical procedure of lead determination in synthetic sample (4.0×10⁻⁸ mol dm⁻³ Pb(NO₃)₂, 10⁻³ mol dm⁻³ KNO₃) for solid-contact lead-selective electrodes: **a** direct ionized lead determination from Pb²⁺ calibration curve and **b** single standard addition method (SAM), where *E*₁(*c*_X) potential of the solid-contact electrode in the synthetic sample, *E*₂(*c*_X + Δ*c*) potential of the solid-state electrode after standard addition, *c*_{std} concentration of the standard solution, *V*_s volume of the sample, *V*_{std} volume of the standard. *Insert*: Pb²⁺ calibration curve done prior to the determination, slope used to calculate ionized lead concentration in the synthetic sample

Selectivity and synthetic sample analysis with ISEs validated by ICP–MS

When considering measurements in the samples, it is important that the membrane exhibits high selectivity toward the primary ion. The selectivity for solid-contact electrodes was determined using SSM and presented as selectivity coefficients in Table 2. Significantly better selectivity coefficients for Pb^{2+} over K^+ , Na^+ and Zn^{2+} were attained than in the previously inspected conventional type of Pb^{2+} -ISEs based on lead ionophore IV [47]. Moreover, the obtained selectivity indicates that the electrodes are more selective to lead than to any of the inspected interfering ions. Together with the small shifts of E° , it indicates possibility to apply this sensor in the determination of lead in various samples. The analysis of the synthetic Pb^{2+} sample ($4.0 \times 10^{-8} \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ with $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$) was performed. The analysis was done at non-equilibrium conditions by two potentiometric methods: direct determination taking readout from the calibration curve (Fig. 7a) and the single standard addition method (Fig. 7b). The results were validated by ICP–MS. Taking into account that the synthetic sample was indeed within the analytical range of the electrode and the selectivity of Pb^{2+} -ISEs was sufficient enough, after the recovery process the determination could be performed. When applying the conditioning-based calibration, solid-contact lead-selective electrodes obeyed the Nernst equation down to $\text{pPb}^{2+}=8$ with a slope 30.5 mV dec^{-1} . Subsequently, electrodes were immersed in synthetic sample solution and the potential readout after 5 min while stirring was used to calculate the activity of Pb^{2+} in the synthetic sample. The uncertainty was calculated for two electrodes out of two measurements. The Pb^{2+} activity was determined to be $\text{pPb}^{2+}=7.64 \pm 0.11$. Additionally, the single standard addition method was performed. This method has significant advantages, e.g. elimination of standard potential of the electrode (E°) [48]. As it was reported, E° of the solid-state Pb^{2+} -selective electrode shifts with every measurement; thus, the application of this method is convincingly justified. Knowing the slope of the calibration curve (newly prepared calibration curve, 31.0 mV dec^{-1}) and that the concentration of the synthetic sample was within the response range of the electrode, the determination was performed. The EMF of the electrode was measured in 50 mL of the sample (stirred solution), and the potential readout ($E_1(c_x)$) was taken after 5 min. When adding 0.55 mL (V_{std}) of $8.7 \times 10^{-5} \text{ mol dm}^{-3} \text{ Pb(NO}_3)_2$ (c_{std}) to 50 mL (V_s) of synthetic sample, the EMF data were recorded (stirred solution) for another 5 min ($E_2(c_x + \Delta c)$). Knowing the slope of the Pb^{2+} -calibration curve ($s_{\text{Pb(II)}}$), volume ($V_s + V_{\text{std}}$) and concentration of Pb^{2+} standard solution, and the potential difference (ΔE) after addition of standard solution, the Pb^{2+} activity in the synthetic sample was calculated. The uncertainty was obtained

for two electrodes out of two measurements. The Pb^{2+} activity was determined to be $\text{pPb}^{2+}=7.27 \pm 0.07$. The activity of lead in the synthetic sample done in potentiometric modes was compared with inductively coupled plasma–mass spectrometry. The value of the total lead concentration obtained by ICP–MS measurement was $\text{pPb}=7.34$. Although the determination was performed at non-equilibrium conditions, the single standard addition method was performed with satisfactory accuracy in comparison to the ICP–MS analysis.

Conclusions

The renewable response was obtained with solid-contact Pb^{2+} -ISEs by using a strict protocol of electrode conditioning allowing determination of concentrations which are not usually reachable for ISEs without any modifications. Together with the measurement protocol, the solid-state design of the electrode allowed partially reversing the ion flux (from the membrane to the recovery solution) which resulted in renewable response at extremely low concentrations of primary ion. By applying a fairly diluted conditioning solution containing Na_2EDTA , the release of Pb^{2+} from the membrane was possible (recovery process). Additionally, solid-contact lead-selective electrodes based on polybenzopyrene doped with eriochrome black T and PVC membrane (lead ionophore IV) were successfully applied in the determination of Pb^{2+} in synthetic sample and favourably compared to analysis done with ICP–MS. The result obtained for single standard addition method was closer to the assumed value of concentration when preparing the sample as well as when measuring with ICP–MS. Although the result obtained during direct determination did not differ much from the one obtained with ICP–MS, a more reliable way when measuring with solid-contact Pb^{2+} -electrode is to apply single standard addition method to eliminate any possible drift in E° . The parameters of the membrane, e.g. thickness, membrane composition (ionophore, ionophore–ionic additive ratio, polymeric material, plasticizer), as well as the protocol of the measurement (time exposure and composition of conditioning and recovery solutions), may be adjusted for the specific needs of the particular determination.

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References

1. Bobacka J, Ivaska A, Lewenstam A (2008) *Chem Rev* 108:329–351
2. Sokalski T, Ceresa A, Zwickl T, Pretsch E (1997) *J Am Chem Soc* 119:11347–11348
3. Sokalski T, Zwickl Z, Bakker E, Pretsch E (1999) *Anal Chem* 71:1204–1209
4. Morf WE, Kahr G, Simon W (1974) *Anal Chem* 46:1538–1543
5. Hulanicki A, Lewenstam A (1976) *Talanta* 23:661–665
6. Hulanicki A, Lewenstam A, Maj-Zurawska M (1979) *Anal Chim Acta* 107:121–128
7. Lisak G, Sokalski T, Bobacka J, Harju L, Lewenstam A (2010) *Talanta* 83:436–440
8. Lisak G, Sokalski T, Bobacka J, Harju L, Mikhelson K, Lewenstam A (2011) *Anal Chim Acta* 707:1–6
9. Gyurcsányi R, Pergel É, Nagy R, Kapui I, Lan BTT, Tóth K, Bitter I, Lindner E (2001) *Anal Chem* 73:2104–2111
10. Sokalski T, Ceresa A, Fibbioli M, Zwickl T, Bakker E, Pretsch E (1999) *Anal Chem* 71:1210–1214
11. Qin W, Zwickl T, Pretsch E (2000) *Anal Chem* 72:3236–3240
12. Ceresa A, Sokalski T, Pretsch E (2001) *J Electroanal Chem* 501:70–76
13. Malon A, Radu A, Qin W, Qin Y, Ceresa A, Maj-Zurawska M, Bakker E, Pretsch E (2003) *Anal Chem* 75:3865–3871
14. Szigeti Z, Vigassy T, Bakker E, Pretsch E (2006) *Electroanalysis* 18:1254–1265
15. Püntener M, Vigassy T, Baier E, Ceresa A, Pretsch E (2004) *Anal Chim Acta* 503:187–194
16. Heng LY, Hall EAH (2000) *Anal Chem* 72:42–51
17. Qin Y, Peper S, Radu A, Ceresa A, Bakker E (2003) *Anal Chem* 75:3038–3045
18. Heng LY, Tóth K, Hall EAH (2004) *Talanta* 63:73–87
19. Lisak G, Grygoliowicz-Pawlak E, Mazurkiewicz M, Malinowska E, Sokalski T, Bobacka J, Lewenstam A (2009) *Microchim Acta* 164:293–297
20. Pergel É, Gyurcsányi R, Tóth K, Lindner E (2001) *Anal Chem* 73:4249–4253
21. Peshkova MA, Sokalski T, Mikhelson KN, Lewenstam A (2008) *Anal Chem* 80:9181–9187
22. Peshkova MA, Sokalski T, Mikhelson KN, Lewenstam A (2010) *Currier of St Petersburg Univ* 4:106–118 (Russ)
23. Sokalski T, Kucza W, Danielewski M, Lewenstam A (2009) *Anal Chem* 81:5016–5022
24. Bobacka J (2006) *Electroanalysis* 18:7–18
25. Hulanicki A, Michalska A, Lewenstam A (1994) *Talanta* 41:323–325
26. Migdalski J, Blaz T, Lewenstam A (1996) *Anal Chim Acta* 322:141–149
27. Michalska A, Lewenstam A (2000) *Anal Chim Acta* 406:159–169
28. Lisak G, Wagner M, Kvamström C, Bobacka J, Ivaska A, Lewenstam A (2010) *Electroanalysis* 22:2794–2800
29. Lindfors T (2009) *J Solid State Electrochem* 13:77–89
30. Sutter J, Lindner E, Gyurcsányi R, Pretsch E (2004) *Anal Bioanal Chem* 380:7–14
31. Sutter J, Radu A, Peper S, Bakker E, Pretsch E (2004) *Anal Chim Acta* 523:53–59
32. Konopka A, Sokalski T, Lewenstam A, Maj-Zurawska M (2006) *Electroanalysis* 18:2232–2242
33. Chumbimuni-Torres KY, Rubinova N, Radu A, Kubota LT, Bakker E (2006) *Anal Chem* 78:1318–1322
34. Yu S, Li F, Qin W (2011) *Sens and Actuat B* 155:919–922
35. Yu S, Li F, Yin T, Liu Y, Pan D, Qin W (2011) *Anal Chim Acta* 702:195–198
36. Yin T, Pan D, Qin W (2012) *J Solid State Electrochem* 16:499–504
37. Michalska A, Konopka A, Maj-Zurawska M (2003) *Anal Chem* 75:141–144
38. Konopka A, Sokalski T, Michalska A, Maj-Zurawska M (2004) *Anal Chem* 76:6410–6418
39. Lindfors T, Szücs J, Sundfors F, Gyurcsányi R (2010) *Anal Chem* 82:9425–9432
40. Mikhelson KN (2010) *J Anal Chem* 65:112–116
41. Anastasova S, Radu A, Matzeu G, Zuliani C, Mattinen U, Bobacka J, Diamond D (2011) Disposable solid-contact ion-selective electrodes for environmental monitoring of lead with ppb limit-of-detection. *Electrochim Acta*. doi:10.1016/j.electacta.2011.10.089
42. Ceresa A, Bakker E, Hattendorf B, Günther D, Pretsch E (2001) *Anal Chem* 73:343–351
43. Directive 2006/118/EC (27.12.2006) Offi J of the European Union 372:19–31
44. McGraw CM, Radu T, Radu A, Diamond D (2008) *Electroanalysis* 20:340–346
45. Schwarzenbach G, Gut R, Anderegg G (1954) *Helv Chim Acta* 7:937–957
46. Kodama M, Sasaki C (1968) *Bull Chem Soc Japan* 41:127–130
47. Malinowska M, Brzozka Z, Kasiura K, Egberink RJM, Reinhoudt DN (1994) *Anal Chim Acta* 298:253–258
48. Bader M (1980) *J Chem Educ* 57:703–706