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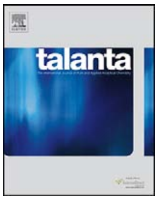

Experimental study on stability of different solid contact arrangements of ion-selective electrodes

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ABSTRACT

Comparison of potentials stability of different types of solid contact lead selective electrodes is presented. Conducting polymer based sensors (hydrophilic and conducting – poly(3,4-ethylenedioxythiophene) or hydrophobic and semiconducting-polyoctylthiophene) were studied in parallel with coated wire and hydrogel (poly(hydroxyethylmethacrylate)) contact electrodes. The within day and between days potential stability was compared, highlighting the effect of sensor storing conditions. The obtained results clearly demonstrate that different conclusions on stability of sensors' potential can be drawn depending on experimental protocol applied. Polyoctylthiophene based contacts show superior within day stability with no influence of dry storage. On the other hand, a chronopotentiometric method of stability evaluation clearly prefers poly(3,4-ethylenedioxythiophene) based sensors, pointing to smallest resistance and polarizability. It is clearly shown that the choice of experimental conditions applied to test stability can favor particular type of contact used.

The inductively coupled plasma mass spectrometry with laser ablation (LA-ICP-MS) experiments conducted for different arrangements tested has shown that for poly(3,4-ethylenedioxythiophene) and poly(hydroxyethylmethacrylate) type contacts longer contact time with lead(II) solution results in changes in the elemental composition of the transducer layer. On the other hand, in line with high stability observed under potentiometric conditions, no changes were seen for polyoctylthiophene based transducer.

1. Introduction

In recent years there is a pronounced interest in solid-state ion-selective electrodes, with clear emphasis on use of conducting polymers (CPs) as solid contacts (ion-to-electron transducer) [1,2]. Coupled ionic and electronic conductivity of CPs resulting in pronounced stability of sensors has attracted much scientific attention leading to sensors of both high stability and optimized analytical parameters. An additional advantage is that conducting polymers are nowadays available commercially in the form of water-based dispersions [3–9] or solid materials that can be dissolved in common solvents [10–17]. They can be cast on substrate electrodes yielding (after drying) a solid contact layer.

Depending on applications envisaged, conducting polymers of different properties can be used as solid contacts, e.g. polymers containing ion-exchangers as doping ions [6,9,18], polymers doped with complexing ligands [19] or those containing dopants forming precipitates with analyte ions [20]. Thus, apart from maintaining charge-transfer equilibrium at the back side of the membrane, additional benefits can arise from lowering free analyte ion activity in the polymer phase, leading to detection limits and selectivities comparable to those of similar systems with tailored internal solution [6,9,18–20].

On the other hand, using more liphophilic, solution processable conducting polymers, e.g. polyoctylthiophene or other alkylthiophenes [10–16], can be also advantageous. These materials, usually applied in neutral, low electronic and ionic conductivity form, are less prone to undergo spontaneous charging/discharging processes [21,22] and thus they do not create significant (undesired) ion-fluxes through ion-selective membranes. Moreover, high liphophilicity of these materials is believed to help to prevent unwanted water layer formation within the sensor [23,24]. On the other hand, the electrical capacitance of this type of layers is significantly lower compared to more oxidized polymers, which can also affect signal stability.

Some benefits of application of CPs in solid contact electrodes are unquestionable and clearly seen when (as usually done) CP based sensors are compared to other arrangements (coated wire or hydrogel [25,26]) in one set of experiments. However, different CP systems are rarely compared to each other. Moreover, different approaches for studying sensor stability have been proposed and are in use. They range from recording potential values in

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different solution activities (or calibrating the sensor) for a couple of days [27,28], recording potential in solutions of constant activity for longer time (water layer tests) [24], using current based electrochemical techniques (impedance spectroscopy and/or chronopotentiometry) [29] or looking at changes in absorption spectra of polymer layers underneath ion-selective membrane [30]. Depending on the method used, and moreover, depending on sensor pretreatment before test, different results can be obtained, making comparison between different systems difficult [18]. Thus, it seemed important to compare different internal solution free sensors under the same experimental conditions (both pretreatment and test set-up) in a parallel experiment. In our opinion, comparison of different sensors and methods used to evaluate stability can add value to the field, it seems also important to check if coherent results are obtained using different experimental approaches. One of the important issues is the effect of polymer capacitance and possible water uptake on sensors stability, thus the experimental conditions were chosen to highlight these effects. It should be stressed that there is not much data in the literature on within day or between days stability of solid-state contact sensors [1,2]. Moreover, results concerning changes of sensors performance with time of its use are still limited. However, both issues are vitally important for practical application of sensors.

In this study sensors with different solid contacts were compared: polymer layers obtained from different materials including polymers of various oxidation states: (i) aqueous dispersion of semi-oxidized conducting polymer (poly(3,4-ethylenedioxythiophene) – prepared using commercially available water-based dispersion, Baytron, stabilized with poly(4-styrenesulfonate) ions) and (ii) more liphophilic, semi-conductor state, polyoctylthiophene (commercially available polymer – solution cast from chloroform) as well as (iii) poly(hydroxyethylmethacrylate) (pHEMA) contact and (iv) coated wire arrangement. As a model system lead selective electrodes with poly(vinyl chloride) (PCV) based membranes were chosen.

It can be expected that potential instability is related also to changes in the transducer elemental composition occurring as a result of undesired ion-fluxes through ion-selective membrane. Thus, the electrochemical data were supplemented with results of ions-profiles studies performed by ICP-MS measurements coupled with laser ablation (LA-ICP-MS) [9,18,31–36].

2. Experimental

2.1. Apparatus

In the potentiometric experiments a multi-channel data acquisition set-up and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) were used, stable potential readings recorded were used to construct calibration graphs. Pumps systems 700 Dosino and 711 Liquino (Metrohm, Herisau, Switzerland) were used to obtain sequential dilutions of calibrating solutions. In voltammetric experiments galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) and conventional three-electrode cell, with platinum sheet as counter electrode, was used.

An inductively coupled plasma mass spectrometer ELAN 9000 (Perkin-Elmer, Germany) equipped with the laser ablation system LSX-200+ (CETAC, USA), described earlier [9,18,31–36], was used. The applied laser energy was 3.2 mJ/pulse, repetition rate was 5 Hz, spot size was 100 μm. The distribution of selected elements within the ion-selective membrane and transducer thickness were followed and the signal intensities for each element in different sensors were compared. Note that the quantitative analysis of the membranes' components was not aimed.

In potentiometric and voltammetric experiments a double junction Ag/AgCl reference electrode with 1 M lithium acetate in outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used. The recorded potential values were corrected for the liquid junction potential calculated according to Henderson approximation.

2.2. Reagents

Tetrahydrofuran (THF), poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (oNPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), lead ionophore IV tert-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) were from Fluka AG (Buchs, Switzerland), hydroxyethylmethacrylate and 2,2-dimethoxy-2-diphenylacetophenone (DMPP) were from Aldrich (Germany).

Doubly distilled and freshly deionized water (resistance 18.2 MΩcm, Milli-Qplus, Millipore, Austria) was used throughout this work. All measurements were performed in solution of unaltered neutral, pH. All used salts were of analytical grade and were obtained from POCh (Gliwice, Poland). Conducting polymers used were obtained from: poly(3,4-ethylenedioxythiophene) (PEDOT) water dispersion stabilized with poly(4-styrenesulfonate) ions – Baytron P – Bayer AG (Leverkusen, Germany) and polyoctylthiophene (POT) from Aldrich (Germany).

2.3. Preparation of solid contact sensors

Glassy carbon (GC) electrodes of area 0.07 cm^2 were used as substrates. They were polished with Al_2O_3, 0.3 μm and rinsed well in water.

Coated wire (CW) sensors were obtained by covering prepared as described above GC layers with ion-selective membrane cocktail.

Polyoctylthiophene (POT) layers were prepared by applying 20 μl (2 × 10 μl) of polymer solution in chloroform (2.75 mg ml^{-1}) on the GC electrode, prepared as described above placed in upside down position. After drying of CP solvent ion-selective membrane was applied.

Poly(3,4-ethylenedioxythiophene) (PEDOT) layers were obtained by applying 10 μl of as obtained water-based polymer dispersion on top of GC electrode, prepared as described above, placed in upside down position. After drying CP layer was further covered with ion-selective membrane.

Before preparation of poly(hydroxyethylmethacrylate) (pHEMA) layers on prepared as described above GC electrodes, silver layers were deposited (potentiostatically at −0.5 V, reduction charge was equal to 0.05 C), then the silver coated GC electrodes were immersed in 0.1 M $FeCl_3$ solution for 15 min, yielding a Ag/AgCl layer on GC substrate. Then 15 μl of hydroxyethylmethacrylate solution containing 2% (w/w) of DMPP was applied on electrodes placed in upside down position and photopolymerized using UV light for 5 min under nitrogen atmosphere. Thus obtained pHEMA layers were conditioned in 0.1 M KCl for 1.5 h before covering with ion-selective membrane.

2.4. Ion-selective membrane

Lead selective membrane contained (in wt%): 1.5% of lead ionophore IV, 0.8% of NaTFPB, 65.1% oNPOE and 32.6% PVC; total 200 mg of membrane components were dissolved in 2 ml of THF.

20 μl of membrane cocktail were applied on electrode resulting in membrane of thickness ca 200 μm.

2.5. Sensors samples for LA-ICP-MS

Sensor to be targets for LA-ICP-MS elements distributions studies were prepared in the same way as electrochemically tested sensors, but instead of typical supporting electrodes home-made electrodes with exchangeable glassy carbon disks tips were used [34].

After the desired contact time of the sensor with 10^{-3} M $Pb(NO_3)_2$ solution the glassy carbon disks with transducer/supporting electrode and ion-selective membrane were dismounted from the electrode body, well rinsed with water and tissue dried. Then, they were immediately placed in a holder of LA-ICP-MS ablation cell, in upside down position, i.e., the outer PVC membrane was facing the laser beam. Each LA-ICP-MS profile was repeated a few times (at least in triplicate).

2.6. Measurements

Unless otherwise stated, before measurements sensors were conditioned in 10^{-3} M $Pb(NO_3)_2$ for 16 h. All sensors were tested in parallel, the same conditioning and pretreatment were applied for all ion-selective electrodes. Potential vs. log activity dependences were recorded one by one within $Pb(NO_3)_2$ concentration range from 10^{-3} to 10^{-9} M, 7–8 calibrations were recorded daily. All measurements were performed in unbuffered lead ions solutions, however, as all electrodes were tested in parallel, any possible side reactions of Pb^{2+} ions with carbonates or bicarbonates are expected to affect all sensors in the same manner. Between days electrodes were stored dry, following the last calibration of the day the electrodes were well rinsed with water and left in air until the next test day. Before starting measurement on consecutive days, the electrodes were first placed in water for 15 min.

Chronopotentiometric experiments were performed at the end of potentiometric tests in 10^{-3} M $Pb(NO_3)_2$ solution.

3. Results and discussion

For all-solid-state sensors tested, following overnight conditioning in 10^{-3} M $Pb(NO_3)_2$ solution, similar potentiometric responses were recorded. POT, PEDOT and pHEMA based solid contacts sensors were characterized with linear potential responses on logarithm of Pb(II) ions activity with slope close to Nernstian within the activities ranging from 10^{-3} to 10^{-6} (pHEMA solid contact, PEDOT) or 10^{-7} M (POT). The slopes of the second calibration of the first day of tests, for above given activity ranges were: 26.3 ± 0.4 mV dec^{-1} ($R^2 = 0.999$) for pHEMA, 33.1 ± 1.8 mV dec^{-1} ($R^2 = 0.994$) for PEDOT and 30.2 ± 0.6 mV dec^{-1} ($R^2 = 0.999$) for POT based contacts. Detection limits (DLs) of pHEMA and POT contact sensors were quite stable during the day, only small potentials fluctuations – no trend – were observed for the low (10^{-6} and 10^{-9} M) activity of Pb^{2+} ions tested. For pHEMA contact sensor DL was slightly lower than 10^{-6} M (for the second calibration it was equal to $10^{-6.3}$ M), the detection limits of POT contact sensor were close to $10^{-7.5}$ M ($10^{-7.4}$ M for the second calibration of the first day).

For PEDOT contact sensor initially small super-Nernstian potential drop was observed for lead ions activity change form 10^{-6} to 10^{-7} M; however, this effect faded away on third and subsequent calibrations. The detection limit of PEDOT contact sensor was moving towards higher concentrations reaching 10^{-7} M at the end of the first day of tests. This is not unexpected behavior, as it is well known that poly(4-styrenesulfonate) ions present in this polymer bind Pb^{2+} [8,9], leading to change of potential values recorded for low activity of $Pb(NO_3)_2$.

Slightly different responses were obtained for CW type sensors: linear responses were obtained within the Pb^{2+} activities range from 10^{-3} to 10^{-6} M (33.3 ± 2.0 mV dec^{-1}, $R^2 = 0.993$, for the second calibration of the first day) and were followed by super-Nernstian potential drop close to 150 mV observed for activity change from 10^{-6} to 10^{-7} M. The magnitude of potential drop was decreasing in subsequent calibrations – seen as increase of potential recorded for 10^{-9} M solution, reaching only 60 mV at the 8th calibration, the last one of that day.

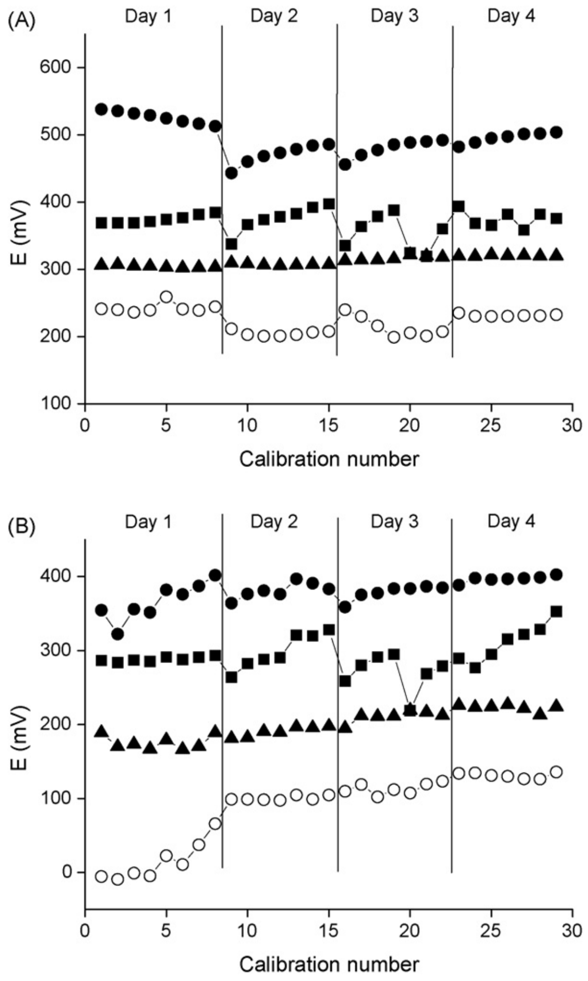

Fig. 1. Open circuit potentials recorded for tested all-solid-state sensor during repeated calibrations in $Pb(NO_3)_2$ solutions over 4 days in: (A) 10^{-3} M and (B) 10^{-9} M lead nitrate solutions, (■) pHEMA contact sensor, (●) PEDOT contact sensor, (▲) POT contact sensor, and (○) coated wire type sensor.

3.1. Short-term potential stability

Fig. 1 presents changes of potential values in time recorded for different activities (10^{-3} and 10^{-9} M) of lead ions in solution, for all sensors tested during experiment in which sensors were repeatedly calibrated. As it can be seen from Fig. 1, POT contact sensor is clearly characterized with the highest stability – both within all days as well as between them. POT contact based sensor, as only one among tested, is not sensitive to dry storage. Nevertheless, for low activities of Pb^{2+} in solutions a gradual increase of potential values recorded is observed, pointing to gradual increase of DL of the sensor. This can be effect of stepwise accumulation of analyte ions in the membrane or at the membrane/CP interface. This conclusion is supported by high stability of potential values recorded for higher activity solutions, where leakage of previously accumulated analyte ions from the sensor phases does not affect potential values recorded. The high stability of potential values recorded in high activity range both between test days and within test day is a clear advantage of high liphophilicity of the applied contact material. It should be stressed that high stability was observed despite the fact that sensors were not protected from light, which in prin-

Table 1
Mean values of potentials obtained for given sensor type and $Pb(NO_3)_2$ activity ± SD during 29 calibrations conducted during 4 days.

Log a_{Pb}	Solid contact type/potential value (mV)			
	pHEMA	PEDOT	POT	Coated wire
−3	369.6 ± 19.2	494.2 ± 24.5	311.7 ± 7.0	223.8 ± 17.2
−4	348.4 ± 19.2	467.5 ± 23.2	284.5 ± 7.5	198.0 ± 15.6
−5	326.6 ± 21.2	443.3 ± 20.4	259.6 ± 9.8	171.7 ± 14.5
−6	305.2 ± 21.8	416.9 ± 17.2	231.3 ± 12.4	142.6 ± 13.5
−7	293.9 ± 22.8	394.7 ± 11.1	211.4 ± 15.5	112.7 ± 26.3
−8	292.4 ± 23.4	383.0 ± 14.8	203.4 ± 18.8	96.7 ± 41.1
−9	292.0 ± 25.9	379.8 ± 18.3	198.1 ± 19.8	85.6 ± 49.1

ciple can adversely effect stability of semiconductor polymer based transducer sensors [26].

For PEDOT, hydrophilic polymer obtained by casting from aqueous dispersion, a significant effect of dry storage was observed. At each of test days, potentials recorded at the beginning of tests were lower than those recorded at the end of the day, this effect is clearly seen even for the highest activity tested, Fig. 1. Most probably, CP layer dries out during storage and upon contact with electrolyte solution accumulates water again within solid contact material. It should be stressed that once the solid contact layer was rehydrated (about 4th calibration on the day), more stable potentials were recorded.

As expected, a significant effect of dry storage was observed also for pHEMA based contact sensor. In this case changes of potential values recorded were even more pronounced that in the case of PEDOT contact; moreover, they were quite random especially on the 3th and 4th day of test. Comparison of results obtained for PEDOT and pHEMA based contact electrodes clearly shows the superiority of the conducting polymer, in accordance with earlier reports [26]. However, it should be stressed that the volume of the conducting polymer layer (and water accumulation capacitance) is significantly smaller for PEDOT compared to pHEMA layer.

Surprisingly, potentials recorded for coated wire based sensor were, especially for higher activities, more stable than those of pHEMA contact electrode. Although the effect of dry storage was clearly seen – the potential values recorded following storage were shifted compared to those obtained on the previous day, potentials recorded within days were (except the day 3) quite stable. Similarly, as for PEDOT and POT based sensors, gradual increase of potential values obtained for 10^{-9} M solution was observed.

The comparison of data obtained for tested sensors during the first day points out that observed changes in potential readings can be attributed to different effects. At low concentrations potential changes observed can reflect a binding process occurring in the contact phase [8,9] (as seen for PEDOT doped with poly(4-styrenesulfonate) ions), i.e., they can reflect methathesis – a chemical change of the contact layer. It should be stressed that this process is accompanied by drift (not random changes) of potentials recorded for higher activities. It is also expected that due to limited amount of transducer material any chemical process will be predominantly observed rather at the beginning of the sensor use.

To enable numerical comparison of the data gathered, Table 1 gives the mean values obtained for each type of sensors and each concentration tested for the whole study described above ($n = 29$) with standard deviation. The data presented in Table 1 clearly show that within higher activities the most stable potentials were recorded for POT contact type sensor. As expected, a liphophilic conducting polymer in semiconductor form, resistive to spontaneous charging/discharging processes [21], is excellent choice for solid-state potentiometric sensors transducers. Nervertheless, with decreasing sample activity more pronounced changes in potential values recorded were observed. The increase of SD value in this range can result from irreproducible leakage of primary ions from the sensor (which is negligible for higher activities).

An increase in SD value, which is a measure of stability of potentials readings, with decreasing activity of solution, seems to be a rule also for other sensors tested with exception of PEDOT contact. However, for pHEMA type contact the SD increase is rather small (couple of mV) compared to coated wire type sensors (about 30 mV). For PEDOT type contact a few mV decrease in SD value was observed for decreasing lead(II) activity in solutions. This effect can be related to presence of high reservoir of lead ions at the back side of the membrane due to presence of ion-exchanger poly(4-styrenesulfonate) ions in the conducting polymer. It can be expected that leakage of Pb^{2+} ions from the sensor at low sample activities stabilizes the potential values recorded.

Summarizing this part of experiments, it is clear that periodical testing with intervals of dry storage should be avoided in the case of contact layers prone to accumulate water. Moreover, the above presented results point out that stability of the solid contact sensor is dependent on the activity of tested solution.

3.2. *Long-term potential stability – continuous test*

Other potentiometric tests applied were based on recording sensors potential changes in 10^{-3} M solutions of $Pb(NO_3)_2$ or KNO_3, i.e., experiments similar to water layer test [24]; however, used with some modification and with numerical representation of the data obtained. During this test electrodes were in continuous contact with electrolyte solution, the potential changes were recorded and results – to enable comparison of different sensors – were expressed as rate of potential changes, Table 2. The pretreatment for this test included 2 h conditioning in deionized water, then the electrodes were placed in lead ions solutions and the potentials were recorded. The initial (with respect to sensor lifetime) contact of lead(II) sensors with $Pb(NO_3)_2$ solutions was in fact eager saturation of the membranes with lead(II) ions and equilibration with electrolyte solution, potential changes recorded during this time were not used for calculations. For all sensors tested, except for pHEMA contact ones, potential increase was observed during this time; whereas for pHEMA based sensor significant decrease of potential was observed.

Table 2
The rate of potential vs. time changes ± SD for continuous monitoring of long-term potential changes for sensors with different contact types.

Electrolyte/time	Solid contact type/potential vs. time changes ($mV\,min^{-1}$)			
	pHEMA	PEDOT	POT	Coated wire
10^{-3} M $Pb(NO_3)_2$ (2–9 h)[a]	−0.160 ± 0.0009	−0.043 ± 0.0012	−0.023 ± 0.0004	−0.057 ± 0.0006
10^{-3} M KNO_3 (12–18 h)[b]	−0.038 ± 0.0004	0.066 ± 0.0013	0.056 ± 0.0007	0.049 ± 0.0005
10^{-3} M $Pb(NO_3)_2$ (18–50 h)[c]	0.032 ± 0.0006	−0.0210 ± 0.0001	−0.031 ± 0.0002	−0.026 ± 0.0002
10^{-3} M KNO_3 (50–62 h)[c]	0.015 ± 0.0004	0.0003 ± 0.0001	−0.014 ± 0.0001	−0.017 ± 0.0004

[a] For calculations potentials recorded after initial significant changes: increase (PEDOT, POT and coated wire) or decrease (pHEMA) were used.

[b] For calculations potentials recorded after initial significant changes – decrease, lasting for about 2 h after changing the electrolyte solutions, were used.

[c] Potential changes are linear for the stated electrolyte and all data were used for calculations.

As it can be seen from results presented in Table 2, during following 7 h, potentials of all sensors tested were decreasing with time. This is most probably still the effect of saturation of the membrane and/or contact with Pb^2 ions from solution. The smallest change, corresponding to about 1.5 mV h^{-1}, was observed for POT contact sensor. Electrodes using PEDOT as solid contact layer were characterized with nearly two times higher potential change, even more pronounced changes were observed for coated wire type sensors (close to 3.5 mV h^{-1}). The most pronounced changes in potential values, close to 10 mV h^{-1}, were recorded for pHEMA contact sensor. Summarizing, clearly higher changes were observed for sensors with a contact able to participate in ion exchange (pHEMA and PEDOT) and (as expected) for coated wire one.

Upon transfer to interferent (KNO_3) solution initially (ca 2 h) relatively fast potential decrease was observed (but not potential overshoots) for all sensors. This effect is in accordance with earlier reports describing similar experiment – water layer test [24]. The rate of potential changes vs. time was calculated for following 6 h sensors contact time with interferent, 10^{-3} M KNO_3, solution. The values gathered in Table 2 show that except pHEMA based sensors, similar – within the range of experimental error – potential changes were observed for all tested electrodes. All potentials were increasing with the rate of about 3 mV h^{-1}. The same effects were observed for PEDOT and POT contact sensors as well as for coated wire ones, suggesting that potential changes are related to ion-selective membrane properties. A different picture was obtained for pHEMA based contact, where potential decrease was observed, however, the rate of potential changes was smaller than observed for other sensors tested in parallel. It should be stressed that potential changes observed for 6 h test in interferent solution were in all cases quite small, suggesting high stability of all sensors under experiment conditions.

Then the sensors were transferred into a new portion of 10^{-3} M $Pb(NO_3)_2$ solution and their potentials were followed for next 32 h. Potential changes observed in time were similar (pHEMA contact) or even smaller (POT, PEDOT contact and coated wire sensor) than those recorded for KNO_3 solution, Table 2. It should be stressed that the absolute values of potential vs. time dependence were similar within the range of experimental error and not bigger than 2 mV h^{-1}; pointing to high stability of potential. For POT and PEDOT based contact, as well as the coated wire sensors, potential decrease was observed, whereas for pHEMA contact potential increase was recorded. The smallest rate of potential vs. time changes was observed for PEDOT based contact.

Upon repeated transfer into KNO_3, potential changes in time, Table 2, were small compared to those observed in $Pb(NO_3)_2$. Potential changes observed for POT or pHEMA based contact sensors and coated wire electrode were close to 1 mV h^{-1}. Again the PEDOT based contact sensor was characterized with the most stable potential.

The above results clearly point out that stability of the sensor potential is dependent not only on contact type applied but also on electrolyte used or on membrane/contact saturation with primary ions. Generally, the stability of potential readings increases with time, reaching ultimately similar values for all contacts tested. The results presented in Table 2 show that the most stable, under this test, were sensors with PEDOT based contact. The contradiction of the results of this test and of repeatable calibrations can be explained by different experimental conditions applied, which favors one of the conducting polymer applied.

3.3. Chronopotentiometric tests

The above described results were supplemented by chronopotentiometric tests, useful for fast estimation of ion-selective sensors stability [29]. Fig. 2 presents chronopotentiometric plots recorded for cathodic and then anodic galvanostatic polarization using current 1 nA. The results are highly dependent on the presence and kind of the solid contact material. For coated wire electrode and the electrode with PEDOT contact, the potential jump accompanying current direction change, corresponding to ohmic drop, is below 1 mV. This denotes that the ion-selective membrane resistance is lower than 500 kΩ and resistance of the solid contact is low. It should be stressed that chronopotentiometric test was conducted after the repeated potentiometric calibrations – thus it can be expected that PEDOT contact is well saturated with mobile ions (Pb^{2+}) contributing to low resistance. On the other hand, for the electrode with POT contact a small potential jump was recorded pointing to resistance close to 2 MΩ. Because the same membrane was used as in previous cases, this result should be related to POT layer – this polymer was applied in the neutral form of relatively low conductivity. The highest potential jump and thus the highest resistance was observed for the sensor with pHEMA layer, Fig. 2 – inset.

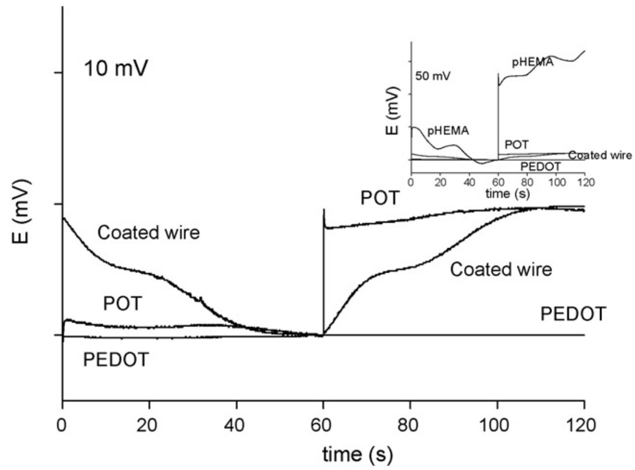

Fig. 2. Chronpotentiometric test of solid contact electrodes, passing current: $\pm 10^{-9}$ A in 10^{-3} M $Pb(NO_3)_2$ (inset: chronopotentiometric responses in the scale showing also pHEMA contact sensor).

For the electrodes with either POT or PEDOT contacts, potentials changes accompanying cathodic or anodic polarization were small, confirming the earlier conclusions of stabilizing influence of the above mentioned contacts on the potentiometric responses. Thus, both polymers assure high quality contact with ion-selective membrane, independently of different conductivity and hydrophobicity of the polymer (PEDOT: hydrophilic and conducting, POT: hydrophobic and semiconducting). For the coated wire arrangement significant potential changes, both in cathodic and anodic polarization mode were observed, confirming low stability of potentiometric response, similar instability was also observed for the sensor with pHEMA.

3.4. LA-ICP-MS studies

The results of electrochemical tests presented above suggest that in some cases metathesis of the transducer layer can occur. To verify this hypothesis LA-ICP-MS, used successfully before for testing all-solid-state sensors' transducer layers, was applied [9,33]. Before measurements all targets: transducer/support electrode covered with ion-selective membrane were conditioned for either 4 or 14 h in 10^{-3} M $Pb(NO_3)_2$ solution. Results of LA-ICP-MS studies are presented in Fig. 3. For PEDOT, POT or pHEMA transduc-

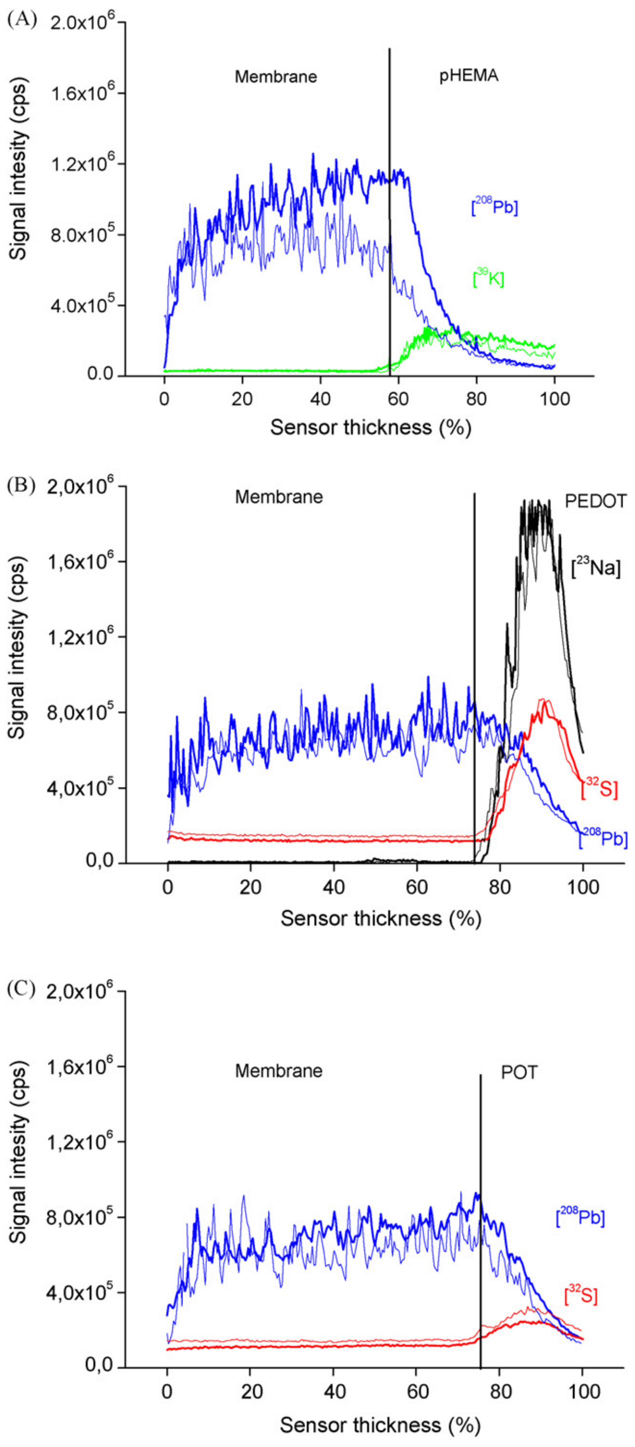

Fig. 3. Intensity of the measured signal as a function of laser ablation penetration depth obtained for tested lead selective electrode: (A) pHEMA contact sensor, (B) PEDOT contact sensor, and (C) POT contact sensor. Black lines corresponds to sodium signal, red lines to sulfur signal, blue lines to lead signal and green to potassium signal. Vertical line visualizes approximated interface between lead selective membrane and underlying conducting polymer. Thin lines corresponds to sensors conditioned for 4 h in 10^{-3} M $Pb(NO_3)_2$ and thick lines to sensors conditioned for 14 h in 10^{-3} M $Pb(NO_3)_2$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ers' based sensors the onset of sulfur signal (PEDOT or POT) or potassium signal (pHEMA) was considered as a beginning of the transducer phase. For all sensors tested, following 4 h conditioning in 10^{-3} M $Pb(NO_3)_2$ solution, membranes were saturated with lead ions which can be seen as lack of major lead signal intensity changes within the membrane thickness [34]. Following 4 h contact with lead(II) solution the lead signal intensity in all membranes was similar and was close to 8×10^5 cps.

Assuming diffusion coefficient of Pb^{2+} ions in the membrane plasticized with oNPOE, $D = 5 \times 10^{-8}$ cm^{-1}/s [37] and the membrane thickness $d = 200$ μm, the calculated time needed to saturate the membrane $t = d^2/D$ is below 3 h, i.e., it is shorter than applied in herein described experiments. Also applying simple diffusion model of Pb^{2+} ions transport from solution to the membrane [34] it was found that the concentration of lead ions in solution was sufficient to saturate the membrane.

Stable and low intensity of sodium signals within the membrane were recorded (not shown, for POT, PEDOT and coated wire type sensor). The results obtained for pHEMA transducer sensor (Fig. 3A) clearly show that for shorter conditioning time lead ions do not enter the pHEMA layer, the decreasing signal of lead within this layer is related to broadening of the membrane crater while penetrating underlying polymer transducer layer. Significantly different picture was obtained for longer conditioning time applied. Results presented in Fig. 3A indicate that lead enters pHEMA transducer layer, the onset of the decrease of lead signal intensities is moved into the pHEMA layer. Interestingly, the potassium signals corresponding to pHEMA layer were not affected. It should also be stressed that only for pHEMA transducer based sensor the intensity of lead signals for longer conditioning time applied was significantly increased compared to 4 h sensor contact time with Pb^{2+} solution. This effect can be visualization of the exchange of K^+ ions from pHEMA layer for Pb^{2+}, which can be additionally complicated by $PbCl_2$ precipitate formation (enhanced by relatively high Cl^- concentration) close to the membrane/pHEMA interface. The results obtained using LA-ICP-MS technique indicate that in course of longer contact of pHEMA transducer based sensor changes in composition of the pHEMA layer occur, which contribute to lower stability of this type sensor, apart from effects related to drying of the hydrogel layer.

Taking into account ion-exchanging properties of PEDOT doping anions, it can be expected that lead is incorporated within this transducer layer during sensor contact with Pb^{2+} containing solution. In fact, as it can be seen from Fig. 3B, both for short and longer contact sensor time with $Pb(NO_3)_2$ solution, lead signals were seen not only within the membrane but also in the transducer phase (it should be stressed that the thickness of PEDOT or POT layer was significantly smaller than the thickness of pHEMA layer). Extended conditioning time in $Pb(NO_3)_2$ solution had little effect on the lead penetration of PEDOT layer. The outcome of LA-ICP-MS studies clearly corresponds to results of potentiometric stability testing – the initial period of sensor contact with Pb^{2+} solution results in major changes in the transducer composition. Interestingly, similarly as in the case of pHEMA sensor, signals corresponding to the mobile cation of the transducer phase – sodium signals for PEDOT layer were not much affected when extending sensor conditioning time. It should be also stressed that in contrary to pHEMA layer, poly(4-styrenesulfonate) anions present in the PEDOT layer can bind Pb^{2+} ions – therefore the activity of free lead(II) ions in PEDOT was most probably kept low and constant during the time of this experiment. Thus, different effects were observed under potentiometric conditions for PEDOT and pHEMA transducer layers.

According to expectation based on result of electrochemical studies, the sensor with POT layer was less affected by extending the conditioning time. The lead penetration depth was not much affected by conditioning time, moreover as seen in Fig. 3C lead is not incorporated within transducer phase – in contrary to pHEMA or PEDOT transducers. Thus LA-ICP-MS results obtained clearly confirm that no methathesis of POT transducer occurs upon conditioning of these sensors in $Pb(NO_3)_2$ solution.

4. Conclusions

The results presented clearly highlight the benefits of using conducting polymer contact. Potentiometric and chronopotentiometric tests showed that stability of these type of sensors is superior over hygrogel and coated wire type one, both in longer (between days stability) and shorter (within day) time scale. Generally, higher stability of potential values recorded was observed for higher activities range compared to lower ones. Nevertheless, the choice of conducting polymer applied is important factor affecting the stability of ion-selective electrodes. As it can be expected, the hydrophilic and conducting polymer doped with ion-exchanger (PEDOT) contact is characterized with the lowest electrical resistance and high stability; however, it is very sensitive to dry storage conditions. Moreover, ions accumulation in the solid contact layer can affect the initial stability of the sensor and during this time it affects its detection limit. On the other hand, hydrophobic and semiconducting-polyoctylthiophene is an excellent contact material characterized with high resistance to dry storage; nevertheless, its resistance is higher. It should be stressed that experimental conditions of stability testing can affect the result obtained. Thus, it seems that a define protocol should be used whenever a comparison is made.

Hence, to obtain high stability potentiometric sensor is seems important to choose the right contact for the applications envisaged and concentrations range in which its use is expected.

The results of LA-ICP-MS studies are fully complimentary with electrochemical studies. No changes of lead contents were seen for POT transducer based sensor with extending conditioning time. In contrary, for PEDOT and especially for pHEMA based transducer significant changes in lead signals intensities, corresponding to lead contents within solid contact phase were recorded.

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