



Development of miniature all-solid-state potentiometric sensing system

Salzitsa Anastasova-Ivanova^a, Ulriika Mattinen^b, Aleksandar Radu^{a,*}, Johan Bobacka^b, Andrzej Lewenstam^{b,c}, Jan Migdalski^c, Marek Danielewski^c, Dermot Diamond^{a,*}

^a Adaptive Sensors Group, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

^b Åbo Akademi University, Process Chemistry Centre, Laboratory of Analytical Chemistry, and Centre for Process Analytical Chemistry and Sensor Technology 'ProSens', Biskopsgatan 8, FI-20500, Åbo/Turku, Finland

^c AGH-University of Science and Technology, Al. Mickiewicza 30, PL-30059 Krakow, Poland

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ABSTRACT

A procedure for the development of a pen-like, multi-electrode potentiometric sensing platform is described. The platform comprises a seven-in-one electrode incorporating all-solid-state ion-selective and reference electrodes based on the conductive polymer (poly(3,4-ethylenedioxythiophene) (PEDOT)) as an intermediate layer between the contacts and ion-selective membranes. The ion-selective electrodes are based on traditional, ionophore-based membranes, while the reference electrode is based on a polymer membrane doped with the lipophilic salt tetrabutyl ammonium tetrabutyl borate (TBA-TBB). The electrodes, controlled with a multichannel detector system, were used for simultaneous determination of the concentration of Pb^{2+} and pH in environmental water samples. The results obtained using pH-selective electrodes were compared with data obtained using a conventional pH meter and the average percent difference was 0.3%. Furthermore, the sensing system was successfully used for lead-speciation analysis in environmental water samples.

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1. Introduction

Polymeric membrane based ion-selective electrodes (ISEs) have been very extensively studied over many years, and ISEs for more than 60 analytes have been described so far [1]. In the last decade, the field has undergone a renaissance and the performance of ISEs has dramatically improved in terms of selectivity and detection limit. These improvements have fuelled renewed interest in pursuing application fields that were previously considered unreachable, e.g., environmental analysis. For example, Pb^{2+} -selective electrodes have been successfully used for the determination of lead and lead speciation in Zurich drinking water [2]. More recently, Cs^+ -selective electrodes were applied in the determination of caesium in natural waters [3], while bio-uptake studies were successfully carried out with Pb^{2+} - and Cd^{2+} -selective electrodes [4,5].

The miniaturization of ISEs, while simultaneously preserving their selectivity and sensitivity, is a crucial step in the next phase of ISE evolution. Traditionally, in so-called coated-wire ISEs, the ion-selective membrane is placed directly on a solid electronically conductive support, thereby removing the need for an inner solution [6]. However, in these devices, it was observed that the

long-term potential stability was quite limited, and they were useful only in specific applications such as capillary electrophoresis [7] or in flow-injection analysis [8]. An important breakthrough in ISE design was achieved by application of conducting polymers (CPs) as a solid-contact layer, i.e., a mediating layer between the electronically conducting substrate and ionically conducting ISE membrane, which was possible due to the mixed conductivity of CPs [21]. Various conductive polymers have been examined as possible internal contact materials that could simultaneously stabilize the overall electrode potential and remove the need for an inner filling solution [9–11]. This application of CPs was supported by fundamental theoretical interpretation of signal formation by Lewenstam and co-workers [28] and, in particular, a deeper understanding of the instabilities of solid-contact sensors as provided by Fibbioli and co-workers [12]. In order to avoid the formation of a water layer and to better define the redox potential at the membrane/solid support phase boundary, it was suggested that a lipophilic redox-active layer such as a self-assembled monolayer (SAM) could be introduced between the membrane and the solid support [12].

Despite these advances, deployments of ISEs in new applications are still limited due to the lack of suitable, miniaturized reference electrodes. Like ISEs, conventional reference electrodes (REs) contain an inner reference solution that requires regular maintenance, and a vertical working position [13,14] while also contaminating the sample through leakage of the filling solution. Thus the search for a novel, reliable, stable and low-cost miniature reference

* Corresponding authors.

E-mail addresses: aleksandar.radu@dcu.ie (A. Radu), dermot.diamond@dcu.ie (D. Diamond).

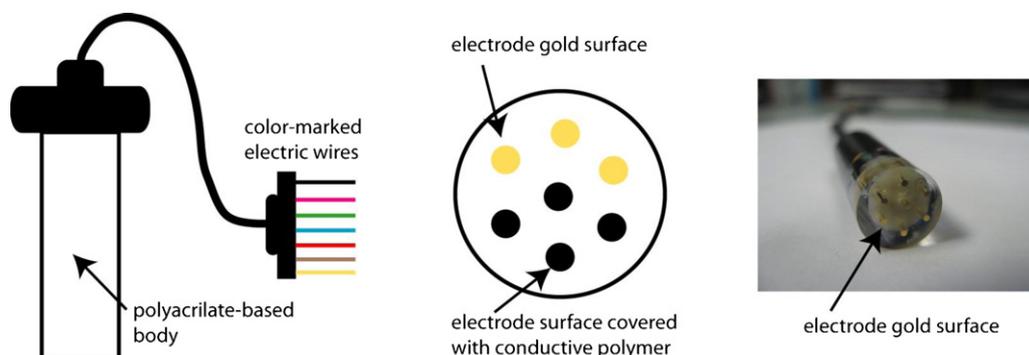


Fig. 1. (Left) Schematic figure of multi-sensor probe. (Middle) Schematic representation of electrodes. (Right) Photo of the multi-sensor probe.

electrode is critical for the realization of practical all-solid-state ion-selective sensors.

Recent progress indicates that solid-contact reference electrodes (SC-REs) based on conducting polymers or ionic liquids may perform this function [15–17]. Nagy et al. [18] proposed two ion-selective electrode membranes connected in parallel could be used as a reference electrode, but this concept is only useful in extremely specialized cases. Lee et al. exploited the fact that various polyurethane membrane materials were found to be essentially nonresponsive when used in ISEs [19]. Vincze and Horvai evaluated traditional plasticized PVC membranes that were doped with various lipophilic electrolytes, e.g., salts of the general class tetraalkylammonium tetrakis(4-chlorophenyl)borate for use as a reference electrodes [20] while Mi et al. investigated the use of a polyion-selective ISE as a RE [21]. The realization of miniaturizable reference electrodes on the basis of hydrophobic membranes is a challenging task, but it is an essential component if integrated potentiometric sensor arrays are to be applied for many potential applications, including remote environmental sensing.

ISEs are attractive for routine monitoring of water samples since they are cost-effective and miniaturizable devices that have very low power demand and can provide unique information on the speciation of analytes [2]. The development of solid-contact ion-selective electrodes (SC-ISEs) and reference electrodes (SC-REs) is in line with current trends in analytical chemistry towards micro-fabrication and mass production of durable chemical sensors.

In this paper, we describe the preparation of a common platform that integrates both SC-ISE and SC-RE and the evaluation of the practical applicability of this platform in environmental analysis.

2. Experimental

2.1. Materials

For membrane preparation, high molecular weight poly(vinylchloride) (PVC), bis(2-ethylhexyl)sebacate (DOS, $\geq 97\%$), 2-nitrophenyl octyl ether (o-NPOE, $>99\%$), tetrahydrofuran (THF), *tert*-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (ionophore Pb IV), sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), 4-nonadecylpyridine, potassium tetrakis(p-chlorophenyl)borate (KTPClPB), tetrabutylammonium tetrabutylborate 98.0% (TBA-TBB) and tetrahydrofuran (THF, $\geq 99.5\%$) were Selectophore grade from Fluka. KCl ($\geq 99\%$), NaCl ($\geq 99.7\%$) from J.T. Baker. 3,4-Ethylenedioxythiophene (EDOT, $>97\%$) was obtained from Sigma–Aldrich. Deionized water obtained with Milli-Q reagent-grade water system was used for all sample solutions.

All the solutions with a concentration lower than 0.01 mol dm^{-3} were prepared immediately prior to use.

2.2. Development of sensor platform

Seven gold disks (1 mm in diameter) were soldered to individual wires and integrated into a polyacrylate-based body of 13 mm diameter. The distal end of the body was finely polished to give an array of 7 integrated electrodes arranged as a multi-sensor probe as shown in Fig. 1.

2.3. Electrodeposition of PEDOT on Au disk electrodes

Poly(3,4-ethylenedioxythiophene) (PEDOT) was chosen to serve as an intermediate layer both in solid-contact ISEs and solid-contact REs because of its low oxidation potential, low band gap (approx. 2 eV) and good stability in the oxidized state [22,23]. Electropolymerization of PEDOT was achieved using an Autolab General Purpose Electrochemical System (AUT20.FRA2–Autolab, Eco Chemie, B.V., and the Netherlands) with galvanostatic electropolymerization, by applying a current of 0.00157 mA onto 0.00785 cm^2 for 714 s. Due to the low solubility of the EDOT-monomer in water (0.01 M), PEDOT was electrodeposited at a low current density (0.2 mA cm^{-2}) [24]. A conventional three-electrode cell was employed, where the auxiliary electrode was a glassy carbon (GC) rod, an Ag/AgCl double junction electrode was the reference, and the Au disk electrodes of the multi-sensor probe on which the polymer films were to be deposited, were the working electrode. The polymerization electrolyte contained 0.01 M EDOT and 0.1 M KCl as the background electrolyte, and the solution was stirred for 2 h to guarantee the dissolution of EDOT-monomer prior to electropolymerization. Optimal conditions for galvanostatic electropolymerization of EDOT in KCl were determined using chronopotentiometry. As shown in Fig. 2, a current density of 0.2 mA cm^{-1} facilitated a uniform and controlled growth of the polymer.

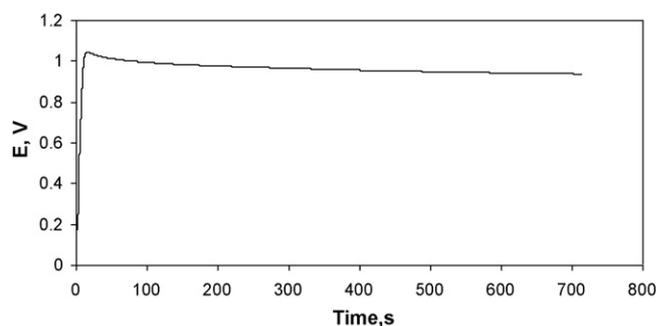


Fig. 2. Chronopotentiometric curves obtained during galvanostatic polymerization of PEDOT onto a 0.00785 cm^2 gold substrate, $I = 0.00157 \text{ mA}$. Solution: 0.1 M KCl + 0.01 M EDOT.

Prior to all polymerizations, electrolyte solutions were deaerated by bubbling nitrogen (N₂) through the solution for at least 30 min, and also allowing N₂ to flow above the solution during the polymerization. The formation of the PEDOT film was monitored using cyclic voltammetry. After polymerization, the Au/PEDOT electrodes were rinsed with H₂O and then air-dried overnight after which the membrane cocktails of desired composition were drop-cast on top of each Au/PEDOT electrode surface.

2.4. Membrane compositions

The cocktail for the Pb²⁺-selective membrane was prepared by dissolving 5 mmol/kg NaTFPB, 15 mmol/kg PbIV, 32 wt% PVC, and 66 wt% of DOS in 3 mL THF. The cocktail for the pH-selective membrane was prepared by dissolving 10 mmol/kg KTpCIPB, 20 mmol/kg H II, 32 wt% PVC and 66 wt% NPOE in 3 mL THF [25]. After the membrane was dried in air, the Pb²⁺ and pH-selective electrodes were first conditioned overnight in 10⁻³ M Pb(NO₃)₂ solution adjusted to pH 3 with HNO₃ and further in a solution of 10⁻⁹ M Pb(NO₃)₂ adjusted to pH 4 with HNO₃ for an additional 24 h, prior to recording calibration curves. Reference electrode membranes were prepared by dissolving TBA-TBB (37.5 mg), o-NPOE (174.9 mg) and PVC (87.5 mg) in 3 mL of THF. This solution was drop-cast on the top of Au/PEDOT electrode in the centre of the multi-sensor probe which had been selected to be reference electrode.

2.5. Potentiometric measurements

Potentiometric measurements were performed at room temperature (21 °C) using a Lawson Labs Inc. (3217 Phoenixville Pike Malvern, PA 19355, USA) EMF 16 electrode monitor. EMF measurements were conducted in stirred solutions using a stirring plate. For comparative measurements, a conventional Ag/AgCl reference electrode (IFS, 3 M KCl, Metrohm, 6.0729.100) with 1 M LiOAc as bridge electrolyte was used. All values were corrected for liquid junction potentials using the Henderson formalism and ion activities were calculated according to the Debye-Hückel approximation [26].

The stability of the solid-contact reference electrodes was studied using protocols described by Mattinen et al. [27]. Briefly, the electrodes were immersed in 0.1 M and 0.01 M KCl for 10 min at a time and rinsed with deionized water between solutions (Protocol I). Then the effects of larger concentration differences and changes in the mobility of electrolyte salt were studied by immersing electrodes in 0.1 M KCl, 10⁻⁴ M KCl, 10⁻⁴ M NaCl, 0.1 M NaCl and 0.1 M KCl (Protocol II). The measurement time in each solution was 10 min, and electrodes were rinsed with deionized water between subsequent measurements in electrolyte solutions. The stabilization time of the electrodes was studied by changing electrolyte solution between 0.01 and 0.1 M KCl every 30 s (Protocol III). After this the electrodes were kept dry for at least one day, and Protocol I was repeated followed directly by 18 h soaking in 0.01 M KCl during which the potential was recorded (Protocol IV). After the soaking, the whole set of measurements (Protocols I–III), was repeated in order to observe possible changes.

The theoretical curves for determination of speciation of lead were calculated with Visual Minteq software by taking into account the equilibria of Pb²⁺ with the following species: CO₃²⁻ (log β₁ = 6.20; log β₂ = 8.85; [CO₃²⁻]_{tot, min} = 0.1 × 10⁻⁹; OH⁻ (log β₁ = 6.29; log β₂ = 10.88; log β₃ = 13.94); SO₄²⁻ (log β₁ = 2.75; log β₂ = 3.47; [SO₄²⁻]_{tot} = 1.55 × 10⁻⁴); Cl⁻ (log β₁ = 1.60; log β₂ = 1.80; log β₃ = 1.70; log β₄ = 1.38 [Cl⁻]_{tot} = 1.25 × 10⁻⁴ M); NO₃⁻ (log β₁ = 1.17; log β₂ = 1.40; [NO₃⁻]_{tot} = 7.20 × 10⁻⁵); HCO₃⁻ (log β₁ = 3.20); HSO₄⁻ (log β₁ = 2.10) The logarithmic equilibrium constants for the protonation of CO₃²⁻ were log β₁ = 10.33 and log β₂ = 16.35 [14].

Calibration data and measurements in environmental water samples are presented as the average value of 3 pH and 3 Pb²⁺ ISE measurements taken simultaneously using the sensor arrays. Lead speciation was done using the multi-sensor probe where one electrode had the role of RE, while the remaining six were divided equally between three Pb²⁺- and three H⁺-selective electrodes.

2.6. Measurements in environmental water samples

Eight samples were analyzed: deionized water, tap water from the laboratory at Dublin City University (DCU), Tolka River (Dublin's Botanic garden), 4 samples from Royal Canal taken within Dublin city limits (Charleville Mall, Shandon gardens, Portland Plaza and Royal Canal Av.) and a sample of rainwater. Map of the sampling location is shown in [supplementary info](#). The samples were collected in sampling containers that were previously soaked in 0.1 M nitric acid overnight and rinsed with deionized water. Measurements of pH were validated using a portable pH instrument (EDT Instr. LTD, RE 357 Microprocessor).

3. Results and discussion

The use of conductive polymers as intermediate layers in solid-state ISEs is relatively common practice these days and in this work we used PEDOT due to its stability and low sensitivity to O₂ and CO₂ [28,29]. Furthermore, it is one of the most studied conductive polymers and it has been used in both reference electrodes [14,15] and other sensor applications [9]. In this research, we have evaluated the performance of RE, Pb²⁺- and pH-selective ISEs individually, and in an integrated sensor platform for the determination of speciation of lead in water samples.

3.1. Stability of solid-contact reference electrode

For the development of solid-contact RE, we have adopted Horvai's approach [20] of doping the polymeric membrane with a lipophilic salt. In this approach it is important to choose a salt that exhibits medium lipophilicity and allows limited partitioning of the salt into the aqueous sample. This partitioning renders the membrane responsive to these ions according to the traditional phase boundary potential equation:

$$E_{PB} = \frac{RT}{zF} \ln \left(\frac{k_1 a_1}{[I^+]} \right) \quad (1)$$

where E_{PB} is the phase boundary potential, k_1 , a_1 and $[I^+]$ are the phase transfer energy, activity in the aqueous phase and the concentration of the ion I in the membrane phase, respectively. In our case, the equitransferent ions TBA⁺ and TBB⁻ can behave as the ion I rendering the membrane responsive only to these ions. Since the membrane is the only source of the ions, its potential is stable and insensitive to any other ions from the sample. The use of the TBA-TBB salt in a solid-contact reference electrode was suggested and evaluated previously by Mattinen [27].

In this work, the stability of the solid-contact reference electrodes was investigated via potentiometric measurements in salt solutions of KCl and NaCl, in concentrations 10⁻¹ and 10⁻⁴ M. Fig. 3 shows the behaviour of the TBA-TBB-based RE studied using Protocol II compared to the conventional double junction RE. It should be noted that in these measurements one conventional RE is used as reference electrode while the TBA-TBB RE and a second conventional RE were connected as working electrodes. Therefore, the ideal result is that minimal/no change in signal will happen regardless of sample composition. From Fig. 3, it can be seen that, after 2 min of initial stabilization time, the TBA-TBB RE was insensitive to changes in electrolyte nature and concentration. The observed

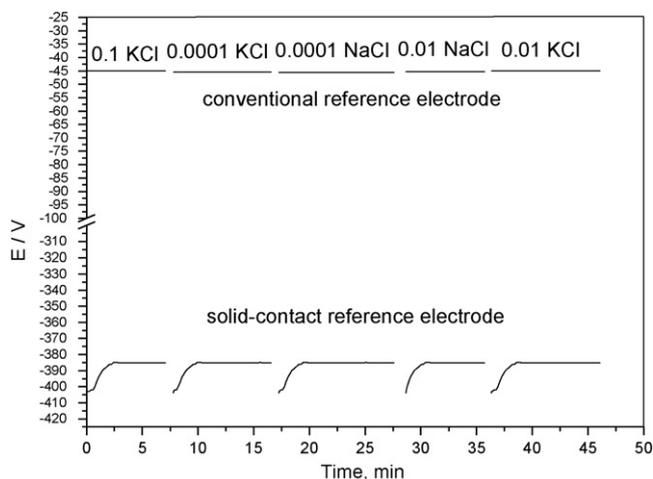


Fig. 3. Potential response of conventional reference electrode and solid-contact reference electrode to salt solutions (0.1 M KCl, 0.0001 M KCl, 0.0001 M NaCl, 0.01 M NaCl, 0.01 M KCl) during 10 min measurement.

initial slow response has been associated previously with kinetic hindrance due to surface ion-exchange processes [27]. Furthermore, the long-term stability and reproducibility was excellent (electrodes did not show any significant deviation in response after 3 months of constant use while preserving the response time of ca. 2 min).

3.2. pH- and Pb^{2+} -selective solid-contact ISEs

The SC-ISEs were produced and evaluated according to recently published recommendations [30]. We placed particular attention to unintentional formation of a thin aqueous layer between the solid contact and the membrane. Since SC-ISEs do not possess an inner solution, it is reasonable to expect that they would not show bias due to zero current fluxes and therefore they should exhibit improved detection limits. However, recent studies have shown that detection limits in SC-ISEs are biased by the same leaching processes as those occurring in liquid-contact ISEs [10,12]. In general, ion exchange at both membrane surfaces (outer-facing the sample and inner-facing internal contact) generate fluxes leading to biased detection limits [30]. The presence of a hydrophobic conductive polymer has been shown to be important not only for the ion-to-electron transduction process but also for inhibiting the formation of water layer at the electrode substrate/sensing membrane interface that degrades the response of the ISE [31].

In our work, the electrodes were tested for the presence of an internal water layer using the lead-selective ISEs according to the following protocol. The electrodes were first immersed in a solution of 10^{-3} M $Pb(NO_3)_2$ and the potential was followed to stabilize for 4 h. The electrodes were then transferred in 10^{-3} M NaCl and the potential monitored overnight. The electrodes were then re-immersed in 10^{-3} M $Pb(NO_3)_2$ and the potential was monitored for a further 4 h. It should be noted that pH of 10^{-3} M $Pb(NO_3)_2$ and 10^{-3} M NaCl solutions were 4.6 and 7.2. Considering selectivity coefficients of Pb IV ionophore to Na^+ and H^+ of $K_{Pb,Na}^{pot} = -6.3$ [2] and $K_{Pb,H}^{pot} = -6.3$ [2], respectively, effect of pH of the used solutions is negligible. Fig. 4 compares the results obtained with an electrode that contains PEDOT as inner contact (electrode A) and an electrode having no conductive polymer at the inner contact, i.e., ion-selective membrane deposited directly on the gold surface (electrode B). An almost instantaneous emf shift of ca. 70 mV reflects the change in the outer phase boundary potential as a consequence of membrane selectivity. A strong potential drift in the case of electrode B is evidence of the formation of water layer

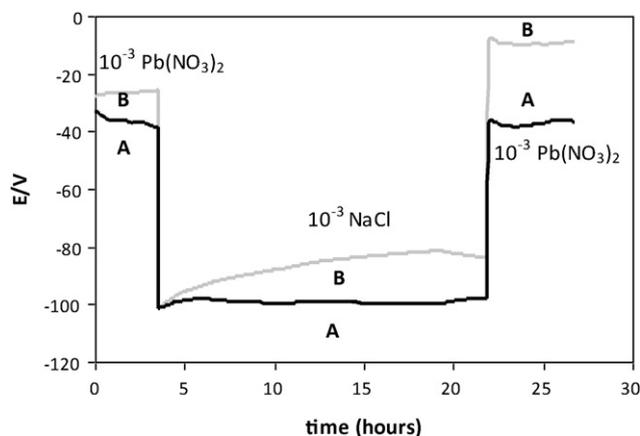


Fig. 4. Potentiometric response of Pb^{2+} -selective electrodes using solid-contact reference electrode with (A) and without (B) PEDOT as the inner contact. Electrode A—Au/PEDOT/PVC. Electrode B—Au/PVC.

between the membrane and the Au support [29]. The positive drift which occurs when the electrode is exposed to interfering ions (in this case Na^+) arises from exchange of Pb^{2+} with the interfering ion (Na^+) at the inner membrane phase boundary (membrane/water layer), as reported previously by Sutter et al. [11,32]. This confirms the benefit of using PEDOT as an intermediate layer and its effectiveness as a water layer suppressant.

Fig. 5 shows the response characteristics of the solid-contact pH-selective electrode/SC-RE potentiometric cell. As noted in Section 2, calibration was carried out in a 1 mM universal buffer solution of citric acid, boric acid and KH_2PO_4 . The pH was adjusted using 1 M NaOH and 1 M HNO_3 . A Nernstian response slope of 59.8 ± 0.1 mV dec^{-1} was obtained for the range pH 2–9, confirming excellent potential of this ISE for environmental applications, since the pH of most environmentally important samples typically fall in this range. Furthermore, the long-term stability of the pH-electrodes was excellent, with no change in the working range and slope observed after 6 months use.

Fig. 6 shows the response of the solid-contact lead-selective electrode vs. SC-RE in a background of pH 3.3. A detection limit of 1×10^{-8} M (2 ppb) is estimated from the intersection of the two linear segments according to IUPAC recommendations. The experimental detection limit corresponds closely to theoretically predicted value according to the equation developed elsewhere [2]:

$$\log a_{Pb,LDL} = \left(\frac{1}{3}\right) \log \left[K_{Pb,H}^{pot} \left(\frac{a_H q R T}{2}\right)^2 \right] \quad (2)$$

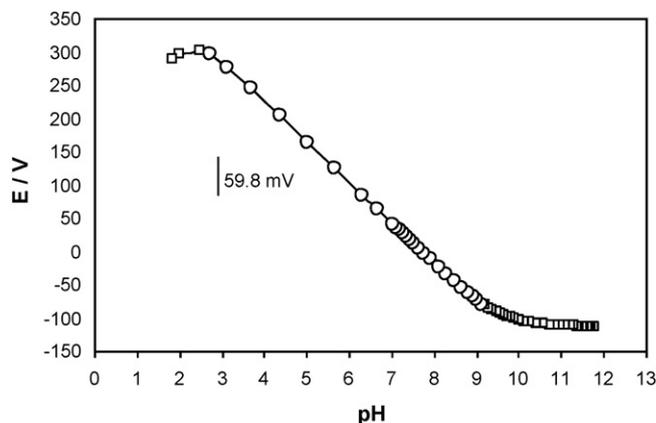


Fig. 5. Response of solid-contact pH ISEs vs. SC-RE. Nernstian response slope at room temperature (59.8 mV dec^{-1}) in the range between pH 2 and pH 9.

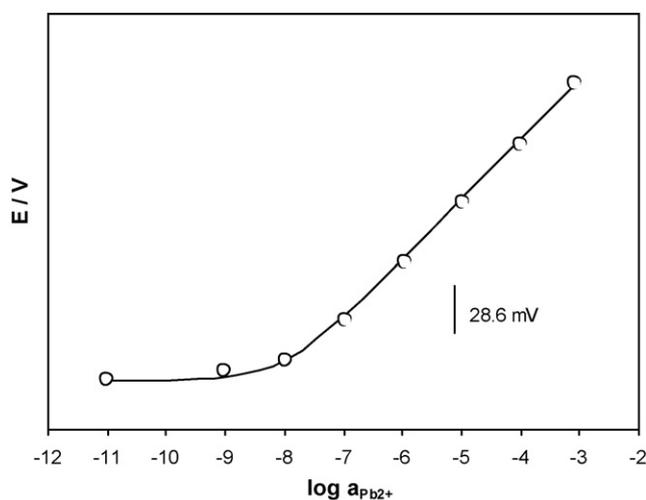


Fig. 6. Response of solid-contact Pb^{2+} ISEs vs. SC-RE. The LOD (10^{-8} M) is determined from the intersection of the horizontal low-concentration segment of the calibration plot and the extrapolation of the Nernstian segment of the calibration curve.

Under these experimental conditions and assuming that ion fluxes originate only from ion exchange at the sample/membrane phase boundary, a detection limit of $a_{\text{pb}} = 1.1 \times 10^{-8}$ M was predicted, using the following values; selectivity coefficient for protons $\log K_{\text{pb,H}}^{\text{pot}} = -3.5$ [2], R_T (the total amount of ionic sites in the membrane) = 0.005 mol/kg, $\text{pH} = 3.3$ (proton activity of $a_{\text{H}} = 5 \times 10^{-4}$ M) and $q = 0.0001$. The parameter q is expressed as $q = D_{\text{org}}\delta_{\text{aq}}/D_{\text{aq}}\delta_{\text{org}}$ where D and d are the diffusion coefficients and diffusion layer thicknesses of the organic (org) and aqueous (aq) phases, respectively. The parameter q was estimated using the diffusion coefficient of lead in water (1.35×10^{-5} cm^2/s) [33], the diffusion coefficient of primary ion-ionophore complex in the membrane (1×10^{-8} cm^2/s) [34] and a 10-fold smaller thicknesses of the aqueous compared to organic layer, which is a reasonable assumption based on a fast stirring rate [35].

Over a period of three days continuous use of the electrodes, no significant change in detection limit and slope was observed. It is important to note that this excellent detection limit was achieved using the TBA-TBB-based RE, which reinforced the excellent overall stability of the solid-state ISE-RE combination potentiometric cell.

3.3. Measurements in real samples

The combination of pH-RE potentiometric cell was used for estimation of pH in deionized water, rain water and tap water, and *in situ* measurements of pH values Tolka River and 4 Royal Canal samples (as noted in Section 2). The results are shown in Table 1 and presented as the average value obtained with 3 electrodes. The

Table 1

Comparison of reference pH values measured with pH meter (pH_{meter}) and values from the SC-ISEs (pH_{ISE}), using the multi-sensor probe, and the relative (R) % error.

Samples	pH_{meter}	pH_{ISE}	R (%)
Deionized water	4.30	4.28 ± 0.05	0.52
Rain water	5.85	5.82 ± 0.02	0.52
Tap water	7.94	7.92 ± 0.04	0.25
Tolka river (Botanic garden)	7.50	7.49 ± 0.02	0.19
Royal Canal 1 (Charleville Mall)	7.52	7.50 ± 0.03	0.21
Royal Canal 2 (Portland Plaza)	7.95	7.93 ± 0.01	0.22
Royal Canal 3 (Shandon gardens)	7.53	7.50 ± 0.03	0.35
Royal Canal 4 (Royal Canal Av.)	7.95	7.94 ± 0.04	0.17

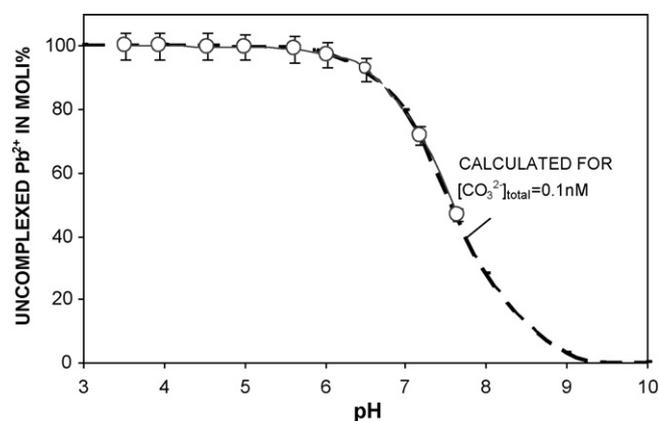


Fig. 7. Direct potentiometric speciation of Pb^{2+} in deionized water spiked with 9.1 ppb Pb^{2+} as a function of pH. Circles: experimental data; solid line: fraction of uncomplexed Pb^{2+} calculated based on complexation of Pb^{2+} and CO_3^{2-} as dominant complexing anion present in the sample.

unknown pH values were calculated using the following equation:

$$\text{pH} = \frac{(E_0 - E)z_1F}{2.303RT} \quad (3)$$

where E is the observed membrane potential, E_0 is the standard electrode potential, R , T , F , and z_1 are the gas constant, the absolute temperature, the Faraday constant, and charge of the primary ions I, respectively.

A conventional pH meter was used to validate results. The difference between measured pH value and the conventional pH meter is expressed as

$$R(\%) = \frac{100(\text{pH}_{\text{meter}} - \text{pH}_{\text{ISE}})}{\text{pH}_{\text{meter}}} \quad (4)$$

where pH_{meter} is the value from measured with the conventional pH meter and pH_{ISE} is the pH value measured using SC-ISEs. The values of R are between 0.17 and 0.52%.

In addition to the determination of pH values we wanted to demonstrate the potential of the multi-sensor probe as a sensor array. To this end we prepared a RE on one of the seven available gold contacts while the remaining six electrodes were used to prepare three pH- and three Pb^{2+} -selective electrodes. This configuration allowed us to determine speciation of lead by simultaneously measuring the concentrations of Pb^{2+} and pH in triplicate. It is well-known that lead in water complexes with a variety of anions and this complexation depends strongly on pH. Since ISEs measure free ion activity rather than total ion concentration, the tracking the potential of the Pb^{2+} -selective electrodes while the pH is varied allows a very simple determination of lead speciation. A simple sensing system with this capability has a great advantage over other classical lab-based instrumental techniques such as Atomic Absorption Spectrometry (AAS), which cannot be used for this measurement as it determines only the total concentration of ions, and special sample treatment is needed in order to determine the speciation.

Fig. 7 illustrates the results of the lead-speciation analysis wherein the ISEs were used to determine the Pb^{2+} activity in one of the samples (deionized water, spiked with 9.1 ppb Pb^{2+}) at various pH values. The open circles are the experimental results obtained by calculating the fraction of uncomplexed lead based on the sample pH, and the dotted line represents theoretically calculated values, taking into account lead complexation with sample anions. For simplicity, we used deionized water as a model sample. In this, Pb^{2+} is complexed by carbonate ions so the theoretical calculation took into account three different carbonate forms (H_2CO_3 , HCO_3^- and CO_3^{2-}). The determination of the concentration of CO_3^{2-} , HCO_3^- ,

H₂CO₃, CO₂ was achieved by measuring the pH of samples that were left overnight open to the air. In order to calculate the concentration of each species, account must be taken of the acid–base carbonate equilibria, the hydration equilibrium between dissolved CO₂ and H₂CO₃ with constant $k_H = [\text{H}_2\text{CO}_3]/[\text{CO}_2]$ and the equilibrium between dissolved CO₂ and gaseous CO₂ above the solution given as



with $[\text{CO}_2]/p_{\text{CO}_2} = 1/k_H$, where $k_H = 29.76 \text{ atm}(\text{mol/L})$ at 25 °C (Henry constant) and p_{CO_2} is partial pressure of CO₂. The corresponding equilibrium equations together with the

$$[\text{H}^+][\text{OH}^-] = 10^{-14} \quad (6)$$

relation and the neutrality condition

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (7)$$

result in six equations for the six unknowns [CO₂], [H₂CO₃], [H⁺], [OH⁻], [HCO₃⁻], [CO₃²⁻]. Solving these equations yields values for the pH and the concentration of different species. From the experimental data we obtained the value of 0.1 nM CO₃²⁻ concentration in deionized water. This value was used for the theoretical determination of the fraction of uncomplexed lead in Fig. 7. As can be seen, we observed excellent agreement between the experimental measurements and theoretical calculations. Therefore, the multi-sensor probe consisting of solid-contact ISEs and a solid-contact RE can be used to very accurately determine lead speciation using direct potentiometric measurements.

4. Conclusions

The results demonstrated in this work show that solid-contact ion-selective electrodes and solid-contact liquid junction-free polymer-based reference electrode can be successfully integrated in a single platform, and successfully applied in environmental analysis. Using this solid-state multi-sensor probe we have successfully determined the pH of environmental sample, and shown that Pb²⁺ can be measured down to very low levels (2 ppb). Finally, using integrated array consisting of an all-solid-contact RE, three Pb²⁺ electrodes and three pH-selective ISEs, we have successfully determined speciation of lead using direct potentiometry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2010.02.044.

References

- [1] E. Bakker, P. Buhlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, *Chem. Rev.* 97 (1997) 3083–3132.
- [2] A. Ceresa, E. Bakker, B. Hattendorf, D. Gunther, E. Pretsch, Potentiometric polymeric membrane electrodes for measurement of environmental samples at trace levels: new requirements for selectivities and measuring protocols, and comparison with ICPMS, *Anal. Chem.* 73 (2001) 343–351.

- [3] A. Radu, S. Peper, C. Gonczy, W. Runde, D. Diamond, Trace-level determination of Cs⁺ using membrane-based ion-selective electrodes, *Electroanalysis* 18 (2006) 1379–1388.
- [4] S. Plaza, Z. Szigeti, M. Geisler, E. Martinoia, B. Aeschlimann, D. Gunther, E. Pretsch, Potentiometric sensor for the measurement of Cd²⁺ transport in yeast and plants, *Anal. Biochem.* 347 (2005) 10–16.
- [5] V.I. Slaveykova, K.J. Wilkinson, A. Ceresa, E. Pretsch, Role of fulvic acid on lead bioaccumulation by *Chlorella kesslerii*, *Environ. Sci. Technol.* 37 (2003) 1114–1121.
- [6] R.W. Cattrall, H. Freiser, Coated wire ion selective electrodes, *Anal. Chem.* 43 (1971) 1905.
- [7] P. Schnierle, T. Kappes, P.C. Hauser, Capillary electrophoretic determination of different classes of organic ions by potentiometric detection with coated-wire ion-selective electrodes, *Anal. Chem.* 70 (1998) 3585–3589.
- [8] T. Dimitrakopoulos, J.R. Farrell, P.J. Iles, A photo-cured calcium ion-selective electrode for use in flow injection potentiometry that tolerates high perchlorate levels, *Electroanalysis* 8 (1996) 391–395.
- [9] J. Bobacka, Conducting polymer-based solid-state ion-selective electrodes, *Electroanalysis* 18 (2006) 7–18.
- [10] A. Michalska, A. Konopka, M. Maj-Zurawska, All-solid-state calcium solvent polymeric membrane electrode for low-level concentration measurements, *Anal. Chem.* 75 (2003) 141–144.
- [11] J. Sutter, E. Pretsch, Response behavior of poly(vinyl chloride)- and polyurethane-based Ca²⁺-selective membrane electrodes with polypyrrole- and poly(3-octylthiophene)-mediated internal solid contact, *Electroanalysis* 18 (2006) 19–25.
- [12] M. Fibbioli, W.E. Morf, M. Badertscher, N.F. de Rooij, E. Pretsch, Potential drifts of solid-contact ion-selective electrodes due to zero-current ion fluxes through the sensor membrane, *Electroanalysis* 12 (2000) 1286–1292.
- [13] R. Maminska, A. Dybko, W. Wroblewski, All-solid-state miniaturised planar reference electrodes based on ionic liquids, *Sens. Actuators B* 115 (2006) 552–557.
- [14] A. Kisiel, H. Marcisz, A. Michalska, K. Maksymiuk, All-solid-state reference electrodes based on conducting polymers, *Analyst* 130 (2005) 1655–1662.
- [15] T. Blaz, J. Migdalski, A. Lewenstam, Junction-less reference electrode for potentiometric measurements obtained by buffering pH in a conducting polymer matrix, *Analyst* 130 (2005) 637–643.
- [16] J. Ghilane, P. Hapiot, A.J. Bard, Metal/polypyrrole quasi-reference electrode for voltammetry in nonaqueous and aqueous solutions, *Anal. Chem.* 78 (2006) 6868–6872.
- [17] T. Kakiuchi, T. Yoshimatsu, N. Nishi, New class of Ag/AgCl electrodes based on hydrophobic ionic liquid saturated with AgCl, *Anal. Chem.* 79 (2007) 7187–7191.
- [18] K. Nagy, K. Eine, K. Syverud, O. Aune, Promising new solid-state reference electrode, *J. Electrochem. Soc.* 144 (1997) L1–L2.
- [19] H.J. Lee, U.S. Hong, D.K. Lee, J.H. Shin, H. Nam, G.S. Cha, Solvent-processible polymer membrane-based liquid junction-free reference electrode, *Anal. Chem.* 70 (1998) 3377–3383.
- [20] A. Vincze, G. Horvai, The design of reference electrodes without liquid junction, in: *Proceedings of the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods*, 97, 1997, pp. 550–555.
- [21] Y.M. Mi, S. Mathison, E. Bakker, Polyion sensors as liquid junction-free reference electrodes, *Electrochem. Solid State Lett.* 2 (1999) 198–200.
- [22] B.L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, Poly(3,4-ethylenedioxythiophene) and its derivatives: past, present, and future, *Adv. Mater.* 12 (2000) 481–494.
- [23] G. Heywang, F. Jonas, Poly(alkylenedioxythiophene)S—new, very stable conducting polymers, *Adv. Mater.* 4 (1992) 116–118.
- [24] J. Bobacka, Potential stability of all-solid-state ion-selective electrodes using conducting polymers as ion-to-electron transducers, *Anal. Chem.* 71 (1999) 4932–4937.
- [25] E. Bakker, A.P. Xu, E. Pretsch, Optimum composition of neutral carrier based pH electrodes, *Anal. Chim. Acta* 295 (1994) 253–262.
- [26] E. Bakker, E. Pretsch, P. Buhlmann, Selectivity of potentiometric ion sensors, *Anal. Chem.* 72 (2000) 1127–1133.
- [27] U. Mattinen, J. Bobacka, A. Lewenstam, Solid-contact reference electrodes based on lipophilic salts, *Electroanalysis* 21 (2009) 1955–1960.
- [28] M. Vazquez, P. Danielsson, J. Bobacka, A. Lewenstam, A. Ivaska, Solution-cast films of poly(3,4-ethylenedioxythiophene) as ion-to-electron transducers in all-solid-state ion-selective electrodes, *Sens. Actuators B* 97 (2004) 182–189.
- [29] M. Vazquez, J. Bobacka, A. Ivaska, A. Lewenstam, Influence of oxygen and carbon dioxide on the electrochemical stability of poly(3,4-ethylenedioxythiophene) used as ion-to-electron transducer in all-solid-state ion-selective electrodes, *Sens. Actuators B* 82 (2002) 7–13.
- [30] E. Lindner, R.E. Gyurcsanyi, Quality control criteria for solid-contact, solvent polymeric membrane ion-selective electrodes, *J. Solid State Electrochem.* 13 (2009) 51–68.
- [31] J.P. Veder, R. De Marco, G. Clarke, R. Chester, A. Nelson, K. Prince, E. Pretsch, E. Bakker, Elimination of undesirable water layers in solid-contact polymeric ion-selective electrodes, *Anal. Chem.* 80 (2008) 6731–6740.
- [32] J. Sutter, A. Radu, S. Peper, E. Bakker, E. Pretsch, Solid-contact polymeric membrane electrodes with detection limits in the subnanomolar range, *Anal. Chim. Acta* 523 (2004) 53–59.
- [33] A.J.M. Valente, A.C.F. Ribeiro, V.M.M. Lobo, A. Jimenez, Diffusion coefficients of lead (II) nitrate in nitric acid aqueous solutions at 298 K, *J. Mol. Liquids* 111 (2004) 33–38.

- [34] M. Puntener, M. Fibbioli, E. Bakker, E. Pretsch, Response and diffusion behavior of mobile and covalently immobilized H⁺-ionophores in polymeric membrane ion-selective electrodes, *Electroanalysis* 14 (2002) 1329–1338.
- [35] A. Radu, S. Peper, E. Bakker, D. Diamond, Guidelines for improving the lower detection limit of ion-selective electrodes: a systematic approach, *Electroanalysis* 19 (2007) 144–154.

Biographies

Salzitsa Anastasova Salzitsa Anastasova-Ivanova received her BSc in analytical chemistry in 2002 and obtained PhD in inorganic and analytical chemistry in 2008 from University of Sofia, Bulgaria. The PhD thesis entitled “SiO₂-based Ru(II)-containing films as oxygen sensors” was performed under the supervision of Professor Dimitar Todorovsky and Assoc. Professor Maria Milanova. In 2008 she moved to Germany to work as a research scientist at University of Regensburg and later she moved to Ireland to become a postdoctoral researcher at Dublin City University. Her research interests involve studying and development of potentiometric and optical sensors for environmental and biomedical applications. She is currently working on a multinational FP6-MATERA-ERA-NET project with the goal of development miniaturized potentiometric sensing system for the detection of analytes important for health and environment.

Ulriika Mattinen Ulriika Mattinen graduated as Master of Science in chemistry from Åbo Akademi University in 2008. The topic of her thesis was “Solid-state reference electrode”, and it was done under the supervision of Professors Johan Bobacka and Andrzej Lewenstam. She is now a PhD student at the Laboratory of Analytical Chemistry at Åbo Akademi University, and a member of the Graduate School of Chemical Sensors and Microanalytical Systems (CHEMSEM). She is working with conducting polymers, solid-state ion-selective electrodes and solid-state reference electrodes.

Aleksandar Radu Aleksandar Radu received BSc in physical chemistry in 1997 from Belgrade University, Serbia. He then worked for three years in Occupational health and Environmental Protection Co. in Belgrade before commencing postgraduate studies at Auburn University, USA. He obtained his PhD in analytical chemistry in 2005 and moved to Ireland to become a postdoc at Dublin City University. His research interests are wide and converge around ionophore-based chemical sensors and their utilization in a range of environmental and biomedical applications. He is currently working on a multinational FP6-MATERA-ERA-NET project with the goal of development miniaturized potentiometric sensing system for the detection of analytes important for health and environment. In 2008 Aleksandar was awarded DCU Research Career Start allowing him to study the utilization of variety of intelligent materials in chemical sensing.

Johan Bobacka Johan Bobacka received his PhD degree in analytical chemistry in 1993 from Åbo Akademi University. During the years 1994–1997, Johan Bobacka worked as a research scientist at Kone Instruments Corporation (now Thermo Fisher Scientific), and since 1997, he is a Docent in electroanalytical chemistry at Åbo Akademi University. He was a senior researcher (1997–2001) and Academy of Finland Research Fellow (2001–2006) at the Laboratory of Analytical Chemistry, which is part of the Åbo Akademi Process Chemistry Centre (Finnish Centre of Excellence

2000–2001). Currently, Johan Bobacka is Professor (pro tem) of Analytical Chemistry at Åbo Akademi University (2006–2010). His current fields of interest include electroanalytical chemistry, process analytical chemistry, chemical sensors, conducting polymers, and electrochemical impedance spectroscopy, with special emphasis on the development of potentiometric ion sensors based on conducting polymers. Johan Bobacka has published over 80 peer-reviewed papers in international scientific journals.

Andrzej Lewenstam Andrzej Lewenstam obtained his PhD (1977) and his DSc (1987) from Warsaw University and since 1990 he has been a Professor. Currently he is Professor of Sensor Technology at Åbo Akademi University and Director of the Center for Process Analytical Chemistry and Sensor Technology ‘ProSens’ at this University, Professor in Chemistry, AGH University of Science and Technology, Cracow, and Adjunct Professor in Chemical Engineering, Laval University, Quebec, Canada. Since 2006, he is a chairman of the Working Group on Selective Electrodes and Biosensors of the International Federation of Clinical Chemistry (IFCC). His current fields of interest are chemical sensors and biosensors, clinical chemistry, membrane potential and biomimetics, conducting polymers, hydrometallurgy, and mathematical modelling, as well as methodology of chemistry and philosophy of Science. He is the author of approximately 200 papers in chemistry and philosophy of Science and 20 patents and is a member of the editorial board of 4 international journals.

Jan Migdalski Jan Migdalski received his PhD in 1980 (title of PhD work “Chemical properties of reduced silicomolybdic acids”, supervisor prof. Z. Kowalski) and his DSc in 1992 (title of DSc work “Modern electrochemical sensors”), both from University of Science and Technology in Krakow. At present, he is the University Professor at AGH University of Science and Technology, Krakow, Poland. His current fields of interest include electroanalytical chemistry, chemical sensors, ion sensors based on conducting polymers, voltammetry, trace analysis as well as designing of instruments devoted for electroanalytical applications.

Marek Danielewski Marek Danielewski received his PhD from AGH Univ. of Sci. & Technology (1978) and DSc in 1985. He published over 200 papers in international journals and is author in 18 patents. At present he is the Head of the Dept. of Solid State Chemistry and member of the Interdisciplinary Centre for Materials Modeling. He is a member of the editorial advisory boards of the international journals: *Materials Transactions*, *Computer Methods in Materials Sci.* and *Defect and Diffusion Forum*. His current activity is focused on mechano and electro-chemistry where he combines the bi-velocity method with linear irreversible thermodynamics.

Dermot Diamond Dermot Diamond received his PhD and DSc from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was VP for Research at Dublin City University (2002–2004). He has published over 200 peer-reviewed papers in international journals, is a named inventor in 13 patents, and is co-author and editor of three books. He is currently director of the National Centre for Sensor Research (www.ncsr.ie) at Dublin City university, and a Principle Investigator in CLARITY (www.clarity-centre.com), a major research initiative focused on wireless sensor networks. In 2002 he was awarded the inaugural silver medal for Sensor Research by the Royal Society of Chemistry, London and in 2006 he received the DCU President's Award for research excellence. Details of his research can be found at www.dcu.ie/chemistry/asg.