

Development of miniature all-solid-state potentiometric sensing system

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ABSTRACT

A procedure for 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.

Keywords: solid-contact electrode, Ion-selective electrode, reference electrode, potentiometry, speciation, water analysis

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 et al [28] and, in particular, a deeper understanding of the instabilities of solid-contact sensors as provided by Fibbioli and co-authors [29]. 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 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 and co-workers [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]. Horvai et al 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 and co-authors 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 microfabrication 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 discs (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 Figure 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 cm² 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 PP on which the polymer films was to be deposited, was 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 Figure 2, a current density of 0.2 mA cm⁻¹ facilitated a uniform and controlled growth of the polymer.

Prior to all polymerizations, electrolyte solutions were deaerated by bubbling nitrogen (N₂) through the solution for at least 30 minutes, 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 Pb^{2+} -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 dried in air, the Pb^{2+} and pH-selective electrodes were first conditioned overnight in 10^{-3}M $\text{Pb}(\text{NO}_3)_2$ solution adjusted to pH 3 with HNO_3 and further in a solution of 10^{-9}M $\text{Pb}(\text{NO}_3)_2$ adjusted to pH 4 with HNO_3 for an additional 24 hours, 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 top of the Au/PEDOT electrode in the centre of the PP 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, 3M KCl, Metrohm, 6.0729.100) with 1M 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 seconds (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, II, 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} = 0.1x10⁻⁹; OH⁻ (log β₁= 6.29; log β₂= 10.88; log β₃= 13.94), SO₄²⁻ (log β₁=2.75; log β₂= 3.47; [SO₄²⁻]_{tot} = 1.55x10⁻⁴); Cl⁻ log β₁= 1.60; log β₂= 1.80; log β₃= 1.70; log β₄= 1.38 [Cl⁻]_{tot} = 1.25x10⁻⁴ M); NO₃⁻ (log β₁= 1.17; log β₂=1.40; [NO₃⁻]_{tot} = 7.20x10⁻⁵); 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 Pb^{2+} - 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 0.1M nitric acid overnight and rinsed with deionised 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 O_2 and CO_2 [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, Pb^{2+} - 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

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

where E_{PB} is the phase boundary potential, k_I , a_I 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 et al [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} M and 10^{-4} M. Figure 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 Figure 3, it can be seen that, after 2 minutes of initial stabilization time, the TBA-TBB RE was insensitive to changes in electrolyte nature and concentration. The observed 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 Pb²⁺-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 [49]. 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(NO₃)₂ and the potential was followed to stabilize for four hours. 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(NO₃)₂ and the potential was monitored for a further four hours. It should be noted that pH of 10^{-3} M Pb(NO₃)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 $K_{\text{Pb,Na}}^{\text{pot}} = -6.3$ [2] and $K_{\text{Pb,H}}^{\text{pot}} = -6.3$ [2] respectively, effect of pH of the used solutions is negligible. Figure 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 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.

Figure 5 shows the response characteristics of the solid-contact pH-selective electrode/SC-RE potentiometric cell. As noted in experimental section, 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 1M NaOH and 1M HNO_3 . A Nernstian response slope of $59.8 \pm 0.1 \text{ mV dec}^{-1}$ 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.

Figure 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 $1 \times 10^{-8} \text{ M}$ (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]:

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

Under these experimental conditions and assuming that ion fluxes originate only from ion exchange at the sample/membrane phase boundary, a detection limit of $a_{Pb} = 1.1 \times 10^{-8}$ M was predicted, using the following values;

selectivity coefficient for protons $\log K_{Pb, H}^{pot} = -3.5$ [2], R_T (the total amount of ionic sites in the membrane) = 0.005 mol/kg, pH = 3.3 (proton activity of $a_H = 5 \times 10^{-4}$ M) and $q = 0.0001$,

The parameter q is expressed as: $q = \frac{D_{org} \delta_{aq}}{D_{aq} \delta_{org}}$ 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} cm²/s) [33], the diffusion coefficient of primary ion-ionophore complex in the membrane (1×10^{-8} cm²/s) [34] and a ten-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 experimental section). The results are shown in Table 1 and presented as the average value obtained with 3 electrodes. The unknown pH values were calculated using the following equation:

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

where E is the observed membrane potential, E_0 is the standard electrode potential, R, T, F, and z_I 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:

$$\Delta (\%) = 100(pH_{\text{meter}} - pH_{\text{ISE}})/pH_{\text{meter}}, \quad (4)$$

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 Δ 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 can not 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.

Figure 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 deionised 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^- , H_2CO_3 , CO_2 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 CO_2 and H_2CO_3 with constant $K_h = [\text{H}_2\text{CO}_3]/[\text{CO}_2]$ and the equilibrium between dissolved CO_2 and gaseous CO_2 above the solution given as:



with $[\text{CO}_2]/p_{\text{CO}_2} = 1/k_H$, where $k_H = 29.76 \text{ atm (mol/L)}$ at 25°C (Henry constant) and p_{CO_2} is partial pressure of CO_2 . 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 $[\text{CO}_2]$, $[\text{H}_2\text{CO}_3]$, $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$. 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 CO_3^{2-} concentration in deionized water. This value was used for the theoretical determination of the fraction of uncomplexed lead in Figure 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 Pb^{2+} can be measured down to very low levels (2ppb). Finally, using integrated array consisting of an all-solid contact RE, three Pb^{2+} electrodes and three pH-selective ISEs, we have successfully determined speciation of lead using direct potentiometry.

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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 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.

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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.

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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 Dep't 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.

Prof. Dermot Diamond

Dermot Diamond received his Ph.D. and D.Sc. 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

FIGURE CAPTIONS

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

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

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.

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 .

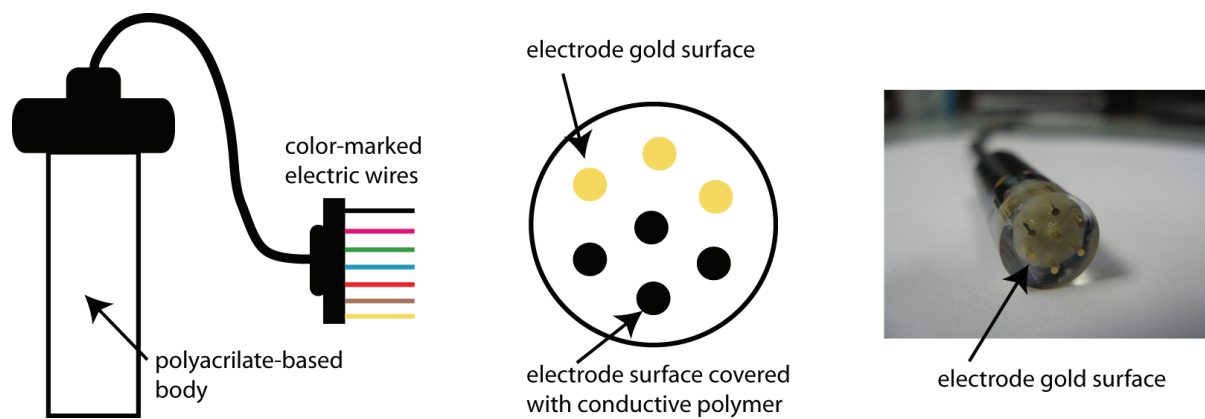
Fig. 5. Response of solid-contact pH ISEs vs. SC-RE. Nernstian response slope at room temperature (59.8 mV dec^{-1}) in the range between pH 2 and pH 9.

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.

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.

Figure 1.



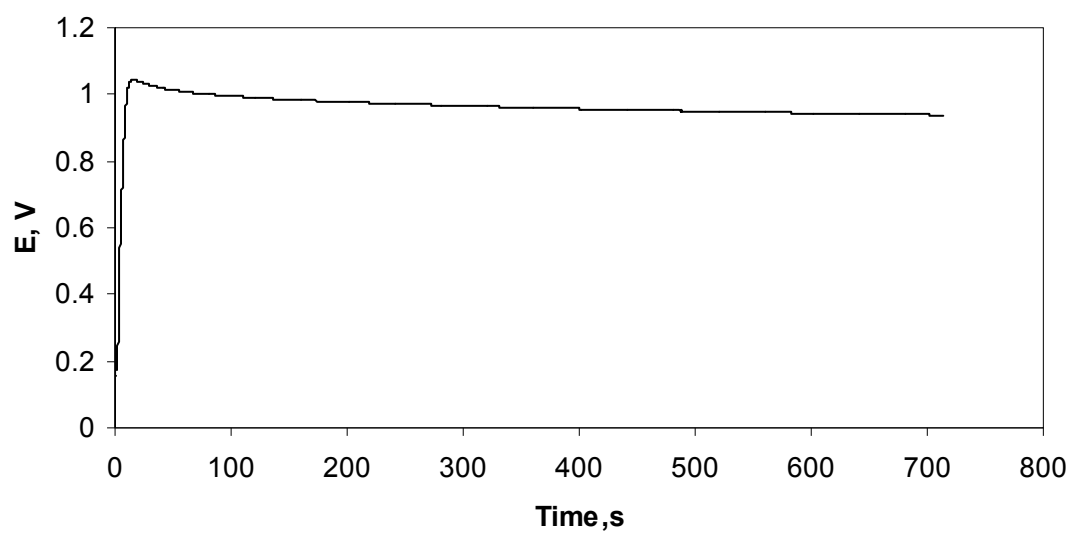


Figure 2.

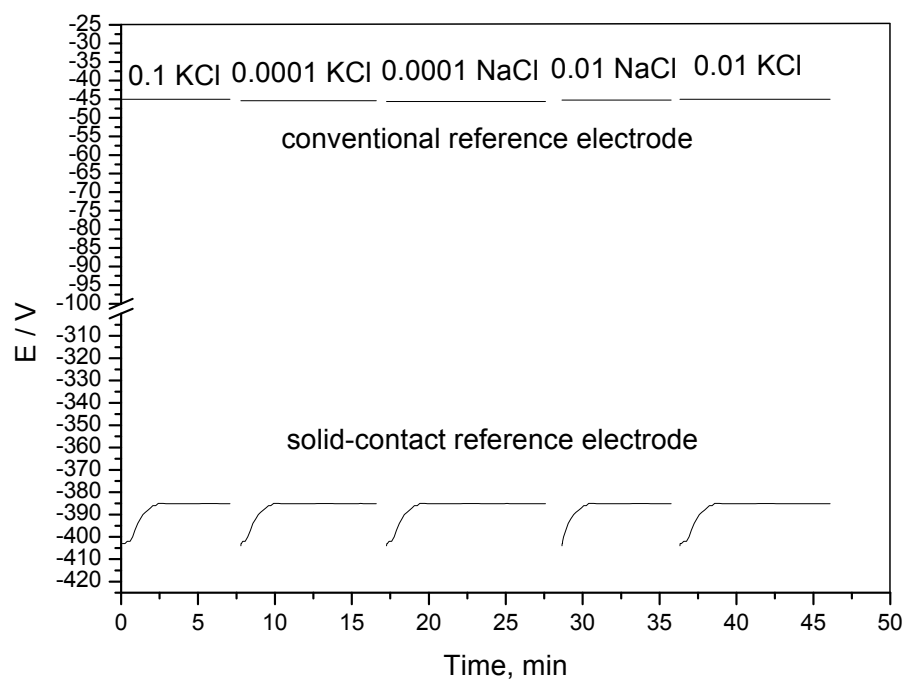


Figure 3.

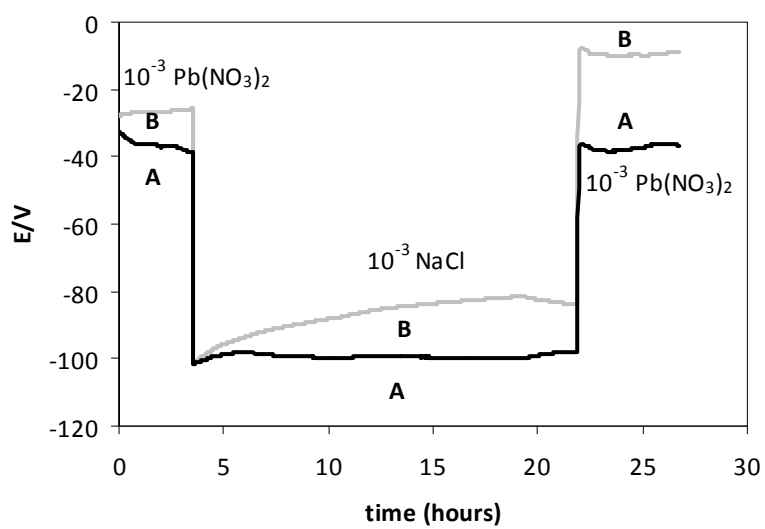


Figure 4.

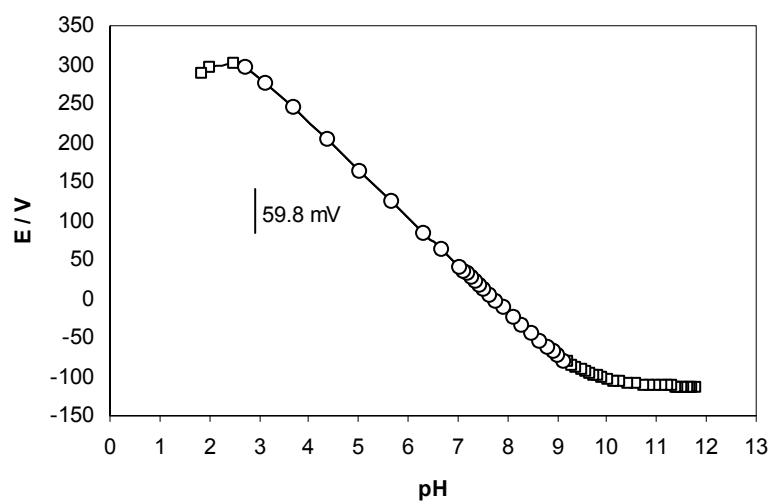


Figure 5.

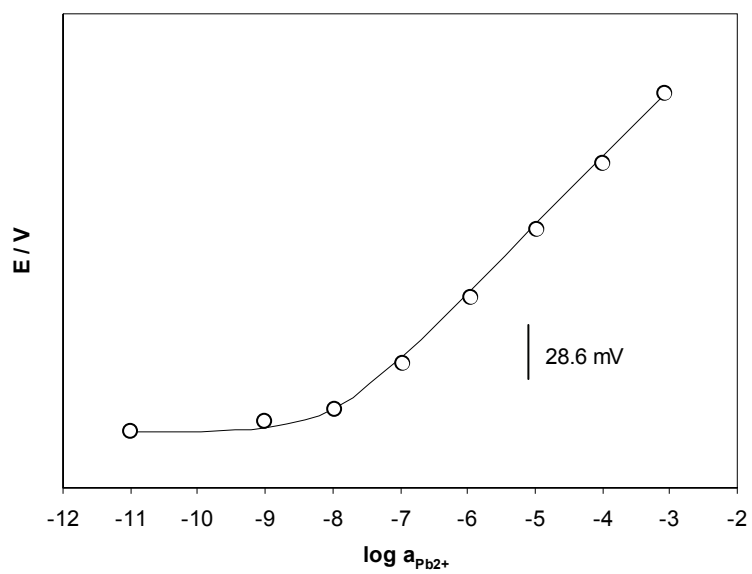


Figure 6.

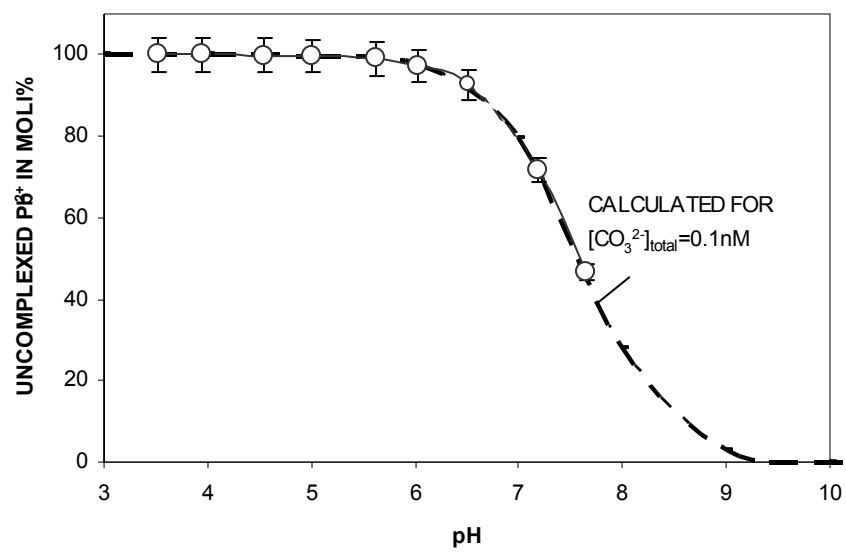


Figure 7.

TABLES

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