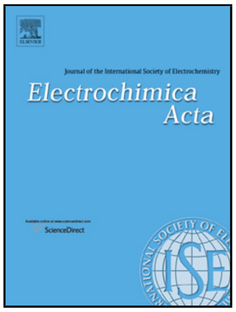

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Disposable Solid-Contact Ion-Selective Electrodes for Environmental Monitoring of Lead with ppb Limit-of-Detection

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Abstract

Solid-contact Pb^{2+}-selective-electrodes and solid contact reference electrodes suitable for use as disposable sensing devices for environmental monitoring of lead have been prepared on screen-printed substrates. Accurate control over the fabrication procedures leads to excellent reproducibility of their calibration characteristics such as slope, offset and limit of detection. In particular, the limit of detection in the nanomolar range opens the possibility of their use for trace analysis of Pb^{2+} in environmental water samples. Significantly, the potentiometric measurements correlate well with data determined using inductively coupled plasma mass spectrometry (ICP-MS) in a number of real samples taken from local rivers. Ways in which these sensors might be employed in autonomous platforms for monitoring water quality in-situ are discussed. The possibility of including arrays of virtually identical sensors is highlighted as a possible route to achieve long-term deployments.

Keywords

Ion-selective electrode; Pb^{2+}, electrochemical sensors; environmental monitoring; wireless sensor networks; screen printing.

1. Introduction

Solid-contact ion-selective-electrodes (SC-ISEs) based on conducting polymers (CPs) have received much interest in recent years thanks to dramatic improvements in their detection limits which opens potential for trace analysis of metal ions [1-5]. For example, it has been demonstrated by comparison with inductively coupled plasma-mass spectrometry (ICP-MS) that ISEs can effectively monitor the concentration of lead down to 0.5 μg L^{-1} in environmental water samples [6,7]. SC-ISEs based on CPs remove transmembrane ion fluxes [8,9], and stabilize the potential at the metal/polymer interface [10-13]. Unlike conventional liquid-filled ISEs, they are also compatible with mass production technologies, which drive down unit cost, while also improving batch to batch reproducibility. Reference electrodes based on solid-contact electrodes can also be prepared using similar approaches [14,15], and these demonstrate insensitivity to changes in electrolyte nature and composition after a short period of stabilization. This is critical, as there is no point in producing low-cost ISEs that have to be used with high-cost conventional reference electrodes.

Screen-printing has been successfully applied to mass production of low-cost and yet highly reproducible and reliable disposable sensors for the determination of a wide range of substances [16,17]. These achievements are a key breakthrough from an analytical point of view as they may allow the realization of disposable potentiometric sensors for the determination of an unknown sample with limited pretreatment [17,18]. Indeed, this approach has been exploited in the past for disposable ISEs used for electrolyte measurements in blood, *e.g.*, Na^+, K^+, Ca^{2+}, but it has not been extended to monitor heavy metals in natural waters, due to the lower concentrations involved.

In this paper we report on the optimised preparation of SC-ISEs and solid contact reference electrodes (SC-REs) using carbon screen-printed substrates. These electrodes are employed for trace analysis of lead in environmental water samples and their analytical performance is validated using ICP-MS. The data obtained show an excellent correlation between the two methods.

2. Experimental

2.1 Materials

For preparation of the ISE membranes, high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl) sebacate (DOS, ≥ 97%), 2-nitrophenyl octyl ether (o-NPOE, > 99%), *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, ≥ 99.5%) were Selectophore grade from Fluka. Poly(3-octylthiophene) (regiorandom) and 3,4-ethylenedioxythiophene (EDOT, > 97%) were obtained from Sigma-Aldrich. Deionised water obtained with Milli-Q reagent-grade water system was used for all aqueous solutions.

2.2 Protocols, Procedures and Equipment

Substrates were prepared using a DEK 248 screen printer as previously reported [19]. The intermediate layer in the solid-contact ISEs (SC-ISEs) was realized using two approaches,

(i) manual drop-casting of poly(3-octylthiophene–2,5 diyl)[19] (POT) (protocol 1), and

(ii) (ii) electrochemical deposition of poly(3,4-ethylenedioxythiophene) (PEDOT) from its monomer [20-23] (protocol 2) using an Autolab potentiostat (AUT20.FRA2-Autolab, Eco Chemie, B.V., The Netherlands).

For the solid-contact reference electrodes (SC-REs) only protocol 2 was followed to produce the solid contact.

The cocktail for the Pb^{2+}-selective membrane was prepared by dissolving 0.4 wt % of NaTFPB, 1.2 wt % of Pb ionophore IV, 32.8 wt % of PVC, and 65.6 wt % of DOS in 3 mL THF. The solution was drop cast on top of the intermediate layer, and after solvent evaporation, the lead (II)-selective electrodes were first conditioned overnight in 10^{-3} M $Pb(NO_3)_2$ solution, followed by 10^{-9} M $Pb(NO_3)_2$ conditioning for 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 PEDOT layer in a manner similar to that used to fabricate the SC-ISEs.

Potentiometric measurements were performed at room temperature (21 ± 2 ^{o}C) using a Lawson Labs Inc. EMF 16 electrode monitor (3217 Phoenixville Pike Malvern, PA 19355, USA) in a stirred solution employing the SC-RE as reference electrodes. Alternatively to the use of the latter, as comparative study, a conventional Ag/AgCl reference electrode (IFS, 3M KCl**,** Metrohm, 6.0729.100) with 1.0 M LiOAc salt bridge was used. The potential of the SC-RE is ~ -0.340 V against this latter reference electrode. All the potentials are reported against the SC-RE electrode. In this case, the values were corrected for liquid-junction potentials using the Henderson formalism and ion activities were calculated according to the Debye-Hückel approximation [24].

Twelve environmental samples were analyzed: four from the River Liffey, three from the Royal Canal, three from Grand Canal, and two samples from the River Liffey estuary. The samples were collected in sampling containers that were previously soaked in 0.1 M nitric acid overnight, rinsed with deionised water and dried by blowing N_2. Samples were acidified to pH=4 to ensure that all Pb^{2+} was present in the free uncomplexed form. The unknown concentration of lead was determined by a potentiometric measurement using the Pb^{2+} SC-ISEs and SC-RE prepared as described above using the standard additions method. In practice, 100 mL of a sample was spiked with 100 μl aliquots of 10^{-3} M, 10^{-2} M and 0.1 M $Pb(NO_3)_2$ solutions to give final Pb^{2+} concentrations of 10^{-6} M, 10^{-5} M and 10^{-4} M, respectively, neglecting the original Pb^{2+} contribution. The unknown concentration was then estimated by extrapolation of the response line to the *x* axis. The sample concentration of Pb^{2+} was then validated with ICP-MS (Perkin Elmer Sciex, ELAN 6100 DRC Plus) which was calibrated using standard solutions prepared from a commercial multi-standard solution (ULTRA Scientific IMS-102). The detection limit for Pb^{2+} using this instrument is ca. 0.1 ppt.

3. Results and Discussion

In spite of extensive research in the area, it appears that obtaining SC-ISEs with reproducible standard potentials is still a significant challenge [25]. The calibration curves in Figure 1 shows a typical example of this situation for SC-ISEs prepared without careful control during drop casting of the POT layer, *e.g.*, not enough additions to fully cover the carbon disk, and/or using not optimised screen-printed electrodes, *e.g.*, misaligned carbon disk and silver track. These electrodes differ significantly in the baseline, slope and limit of detection (LOD) as reported in Table S1 in the Supporting Information.

Figure 2 depicts the responses of a batch of ISEs produced using the same protocol as employed for the ISEs in the previous figure, but with more reproducible screen-printed electrodes, and more careful deposition of the POT layer to ensure good coverage of the underlying carbon disk, as described previously [19]. Significantly, these electrodes (n=8) have identical slopes, *i.e.*, 23.4 mV and almost identical LODs, *i.e.*, 1.20 ± 0.08 nM but baseline values are more scattered having an average of 46.7 mV and a standard deviation of 18.2 mV (see Table S2 in the Supporting Information). The reason of the latter behaviour most likely arises from the manual drop-casting of the polymer layer, which may result in variable layer thickness and coverage, therefore leading to a variation of the potential at the carbon/POT interface. However, it should be noted that these electrodes would require only *one calibration point* in order to predict the full range of the analytical response, as the response characteristics are very reproducible once the inter-electrode offset value has been established.

If the above explanation is correct, it can be assumed that the inter-electrode offset can be reduced by improving the precision of the conducting polymer layer thickness. This can be achieved using electropolymerization as shown by Vazquez *et al.* [27] who demonstrated that electropolymerized PEDOT-based SC-ISEs had excellent characteristics. We therefore adopted this approach (protocol 2) for deposition of the intermediate solid contact layer. Figure 3 shows that the calibration curves of the sensors prepared using this protocol almost perfectly overlap, with virtually no measureable offset between the curves. Table S3 in the Supporting Information summarizes the values of slope, offset and LOD of the calibration curves obtained with these electrodes (n=6). An increase of the LOD to 10.9 ± 1.1 nM compared to the previous figure (LOD=1.20 ± 0.08 nM) is apparent and this effect may be ascribed to the difference in lipophilicity of PEDOT compared to POT [25]. Batch-to-batch variation in fabrication could be addressed by fine-tuning the protocol or switching to a different calibration model, like standard additions (see below). Overall, these results would suggest that, at least within a particular batch of electrodes, knowledge of a single electrode response may be used to predict unknown sample concentrations using any electrode from the same batch *without further calibration*. This approach is employed very successfully in the clinical area, in which single use disposable sensors are commonplace. However, translation of this approach to the environmental arena remains difficult, due to the lower concentrations of the primary target ions and matrix effects, which require a more complex calibration protocol to enable the low-limit-of-detection capability of ISEs to be exploited.

The excellent reproducibility of the sensors in Figure 3 implies that variations of the thickness of the drop-casting of the ion-selective membrane do not have a significant effect on the overall response (as this is deposited manually). This behaviour agrees with the extended Nickolsky-Eisemann equation, as described by Ceresa *et al*., [28] which predicts that an increase in the membrane thickness results in a decrease in electrode potential at concentrations where inner membrane fluxes are important, *i.e.*, around the LOD. However, a 20 % change in membrane thickness causes a decrease in the zero-point of only ~ 1 mV. Therefore, variations in membrane thickness originating from manual drop-casting have virtually no influence on the entire response of ISEs.

While the inter-batch reproducibility of the PEDOT SC-ISEs is striking, it is important to establish the timescale over which these results remain valid in order to extend their use from single shot measurements to a continuous monitoring mode of operation. The electrodes were tested for a period of 8 days, with the sensors stored in a 10 nM $Pb(NO_3)_2$ conditioning solution acidified to pH 4 with HNO_3. The results are shown in Figure 4 and the summarised characteristics are reported in Table S4 in the Supporting Information. After 4 days the average slope and the average zero point had decreased slightly, *i.e.*, 2.5 % and 1.2 %, respectively, while there was virtually no change in the average LOD, ca. 11 nM. After 8 days, the average slope and zero point decreased overall by 5.9 % and 9.7 % , respectively, while the LOD increased to 37 nM. These results suggest that the electrodes do retain their initial response characteristics to within a few % points error for a period of several days, which could be useful for applications for which such errors are acceptable.

In this regard the PEDOT SC-ISEs could offer significant advantages for the field of autonomous environmental monitoring, as they are very low-cost, have virtually no power demand, are highly reproducible and are capable of measuring lead down to nanomolar levels. In order to test the feasibility of analytical monitoring in real samples, the PEDOT SC-ISEs were employed to determine lead concentrations in a number of environmental water samples taken from local waterways.

In the literature, one of the most influential papers describing the application of ISEs to the determination of lead in water samples at nano-molar concentrations was published by Pretsch *et al.* in 2001 [6]. This paper was a demonstration of the practical application of ground-breaking developments in ISE theory by Pretsch and others during the previous decade, that had successfully shown ways by which the limit-of-detection of these sensors could be reduced by orders of magnitude. In this work, the ISEs were conventional liquid-filled devices, and careful attention to calibration procedures and conditioning suggested that detection limits in the nM region were practically possible. This was applied to the analysis of nine samples drawn from local rivers and lakes, and from tap water, and ICP-MS was used as the reference method to establish the ‘true’ lead concentrations in the samples. The results showed rather poor correlation and large errors between the two methods. This was ascribed to the very low concentration of lead in some of the samples, which was below the improved limit of detection of the ISEs, but still within the linear range of the ICP-MS method. Despite this, the conclusion was that the ISEs could be reliably used to determine samples that were above the EPA action limit (7.2×10^{-9} M or 1.5 ppb) and for the first time, these sensors could be considered for use as threshold detectors for lead in natural waters and domestic water supplies. This was an important development, as prior to this, it was understood that it would not be possible to use ISEs to detect thresholds in the low nM /ppb region.

However, to our knowledge, since this ground-breaking work progress in establishing the low limit of detection approach with ISEs as a practical tool has been disappointing, and there have been no convincing demonstrations of the application of

ISEs to determine lead at nM levels in real environmental samples. In this study, we seek to address this situation, through the use of recent advances in screen-printed SC-ISEs and SC-REs. Therefore, we have borrowed some of the methodology employed in this earlier study, such as the use of ICP-MS as the reference method, and standard additions calibration in the samples with extrapolation to determine the unknown concentrations. However, unlike the previous study, we are not using liquid-filled ISEs, and each sensor is used only once, and then discarded. This latter strategy is only possible due to the very low-cost and inherently disposable nature of the screen-printed SC-ISEs.

Table 1 compares the results obtained using the SC-ISEs and ICP-MS methods for the 13 samples, and the % relative error (%RE) for each sample, assuming the ICP-MS value to be the true concentration of lead in the unknown samples. A number of features are apparent from these data;

- The two sets of data track each other closely over the full range of samples, even though for 11 out of 12 results, the lead concentration is below 50 nM (10 ppb) according to both methods, well below the conventional limit-of-detection of ISEs;
- According to both methods, sample L shows a lead concentration that is approximately two orders of magnitude higher (ca. 200 ppb) than the average of the other samples. This location is near the city centre and within the tidal reach of the river.
- The %RE at first glance may appear relatively high in some cases, for example B (-29.4%), G (-34.1%), H (+22.0%) and particularly A (-62.5%). However, it should be appreciated that, with the exception of L, the concentration of Pb^{2+} in every case is < 50 nM, well below the normal dynamic range of ISEs.

Figure 5 shows the data from Table 1 plotted, excepting L, as this point behaves like a statistical outlier from the rest of the data and distorts the statistics. The plot shows the data to be highly correlated ($R^2 = 0.989$) with almost unity slope and intercept (low bias). Comparison with the ideal fit shows a slight positive bias for the SC-ISE method compared to the ICP-MS method. These results are a dramatic improvement on the data presented in the earlier study referred to above, in terms of correlation and accuracy. This is probably due to a number of factors, partly arising from the use of solid-state as opposed to liquid-filled ISEs, the highly reproducible nature of the sensors and the ability to use them essentially as single-shot devices, and the fact that the average Pb^{2+} concentration in our samples (2.88 μg/L, n = 11; sample L neglected) was ca. 2.5 times higher than that found by Pretsch *et al.* (1.13 μg/L, n = 9), which makes the analytical task somewhat easier.

Overall, we regard these results as very promising, considering that the European Water Framework Directive recommends a concentration of 7.2 μg L^{-1} for Pb^{2+} as the upper limit for surface waters, and 10/12 of the samples had concentrations below this level, as determined by both methods. The ability of the SC-ISEs to track changes in Pb^{2+} at low ppb levels in real samples (11/12 samples in Table 1 were below 10 ppb) is a striking result, as these low cost disposable sensors could be used for in-situ measurements, in contrast to ICP-MS. Clearly therefore, these results suggest that the sensors may be suitable for use as a very low cost, early stage alarm in autonomous sensing platforms.

However, applying these sensors for measuring Pb^{2+} at very low concentrations in real environmental samples with reasonable accuracy needs a careful consideration of the methods used and the limitations of the sensors. A key restriction is the deterioration of the sensors characteristics over a period of several days to a point wherein they are no longer useful. In this regard, it may be possible to extend the useful lifetime of the sensors by incorporating them into microfluidic platforms [29], within which it is possible to control the sensor conditioning, perform simple calibration, and restrict the exposure time to real samples. Devices with extended useful lifetimes are critical for the creation of chemical sensing deployments widely distributed over large geographical areas [30,31]. Indeed, as the sensors proved to have reasonably stable and almost identical characteristics for a period of up to 4 days, it may be possible to significantly extend the operability of the deployed platforms using an array of SC-ISEs [32,33].

Therefore, while the goal of using these sensors in an autonomous manner for distributed environmental monitoring appears tantalisingly close, significant restrictions do apply, and each analytical strategy raises its own issues in terms of complexity (and therefore cost) of the resulting analytical instrument. For instance, an array of sensors, each of which is used once, or for a restricted period of days, implies that a series of valves must be incorporated in a microfluidic platform to allow sensor selection. Furthermore, accurate measurements in the nano-molar region requires a more complex analytical approach, like standard additions, and the resulting instrument must therefore house the standards, as well as conditioning solution and any waste generated. Consequently, even though an array of these sensors could be integrated with a fluidic platform relatively easily, the platform would also have to employ totally new approaches to control fluid movement, as conventional valves are too big (and must be housed off-platform), consume too much power, and are too costly [34]. Therefore, breakthroughs in liquid movement control, through for example, photo-actuating polymer valves are absolutely vital to progress this area [29,35]. If low-cost multiple sensing and valving functions can be integrated successfully into a microfluidic platform, then the vision of widely distributed environmental chemo/bio-sensing may become a reality.

4. Conclusions

The fabrication of Pb^{2+}-SC-ISEs on screen-printed electrodes with almost identical response characteristics is possible provided the conditions for deposition for each layer are carefully optimised, and manual procedures are avoided. These sensors have been successfully applied to the determination of nano-molar Pb^{2+} in local river water samples and the results validated using ICP-MS. Coupling appropriate SC-ISEs with screen-printed solid-contact reference electrodes (SC-REs) [23] in principle opens the way to practical low-cost analytical devices capable of performing analytical measurements at low nano-molar concentrations for a number of environmentally important target ions.

Acknowledgements

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Supporting Information Available

Table S1 reports baseline, slope and LOD of the calibration curves obtained with the SC-ISEs of Figure 1; Table S2 reports baseline, slope and LOD of the calibration curves obtained with the SC-ISEs of Figure 2; Table S3 reports baseline, slope and LOD of the calibration curves obtained with the SC-ISEs of Figure 3; Table S4 reports baseline, slope and LOD of the calibration curves obtained over a period of eight days with the same SC-ISEs in Table S3.

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FIGURE CAPTIONS

Figure 1. Calibration curves of SC-ISEs electrodes produced without careful control of the screen-printed electrodes features and/or POT drop casting step.

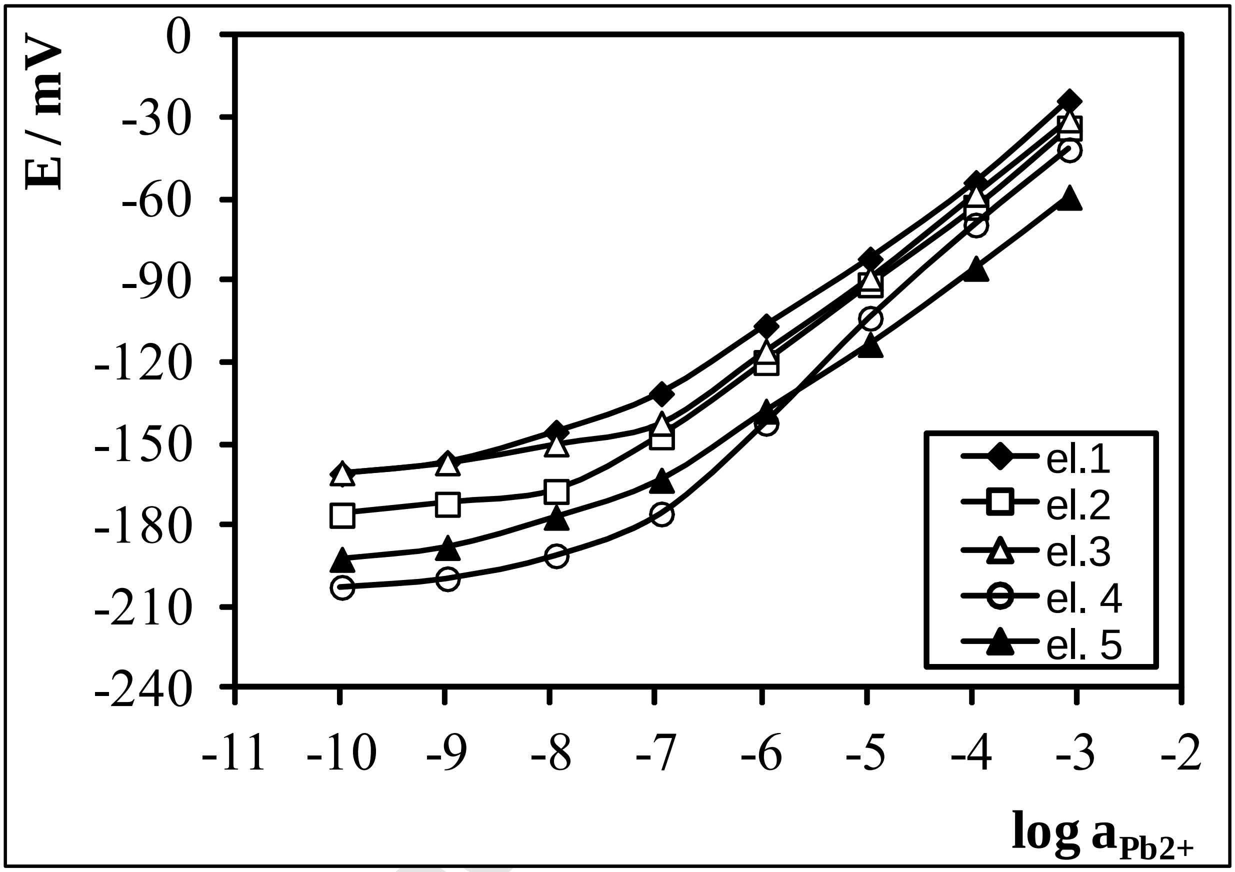
Figure 2. Calibration curves for eight SC-ISEs vs. SC-RE using optimised screen-printed electrodes with the intermediate solid contact layer provided by manually drop cast POT.

Figure 3. Superimposed calibration curves for six SC-ISEs vs. SC-RE using optimised screen-printed electrodes with the intermediate solid contact layer provided by electrochemically deposited PEDOT according to protocol 2.

Figure 4. Calibration curves of mean responses (n = 6) obtained with SC-ISEs prepared according to protocol 2 vs. SC-RE after 0, 4 and 8 days of storage in a 1 nM $Pb(NO_3)_2$ solution adjusted to pH 4.

Figure 5. Correlation of Pb^{2+} concentrations in environmental water samples A-K (Table 1) obtained by ICP-MS and direct potentiometry using SC-ISEs and SC-RE. The experimental lead concentrations in the samples are indicated with (●) while the solid line (—) represents the linear regression fit, and the dashed line gives the ideal fit for two methods. The European Water Framework Directive recommended upper threshold level for Pb^{2+} in surface waters is indicated by the arrow on the 'X' axis.

Figure 1.


E / mV
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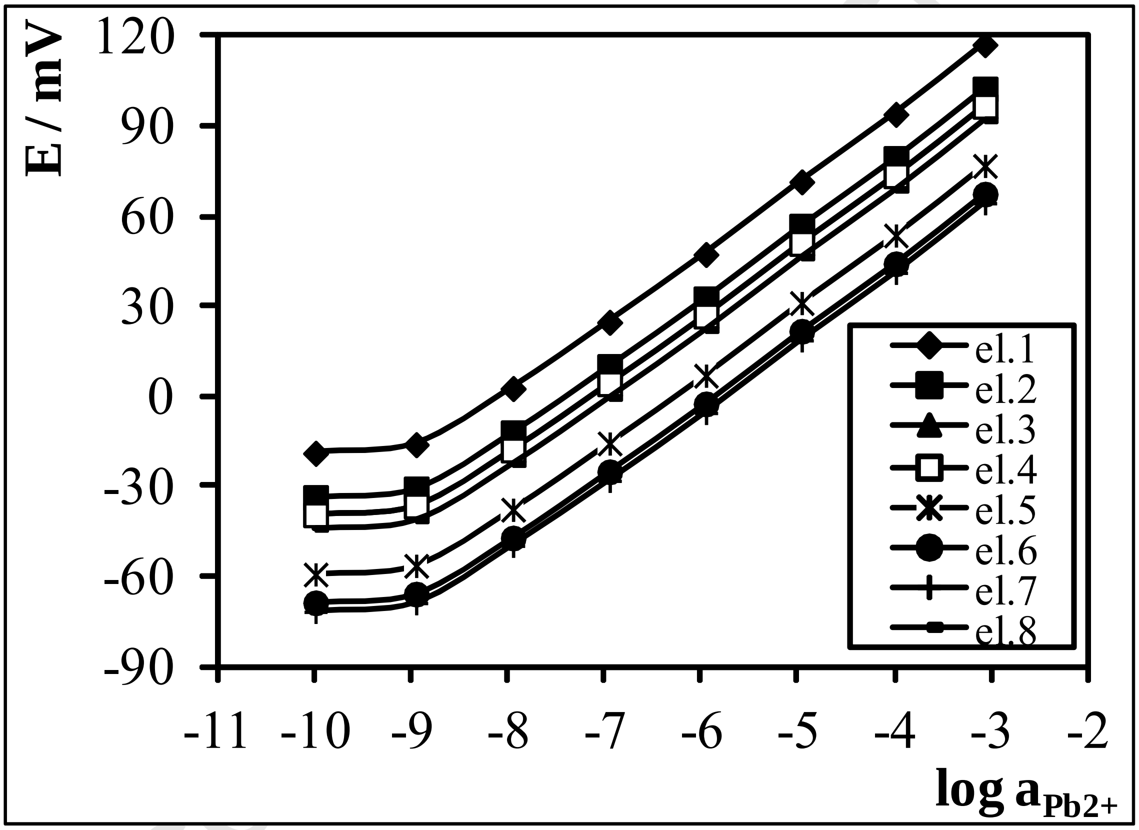
-30
-60
-90
-120
-150
-180
-210
-240
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
log a_{Pb2+}
el.1
el.2
el.3
el. 4
el. 5

Figure 2.


E / mV
120
90
60
30
0
-30
-60
-90
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
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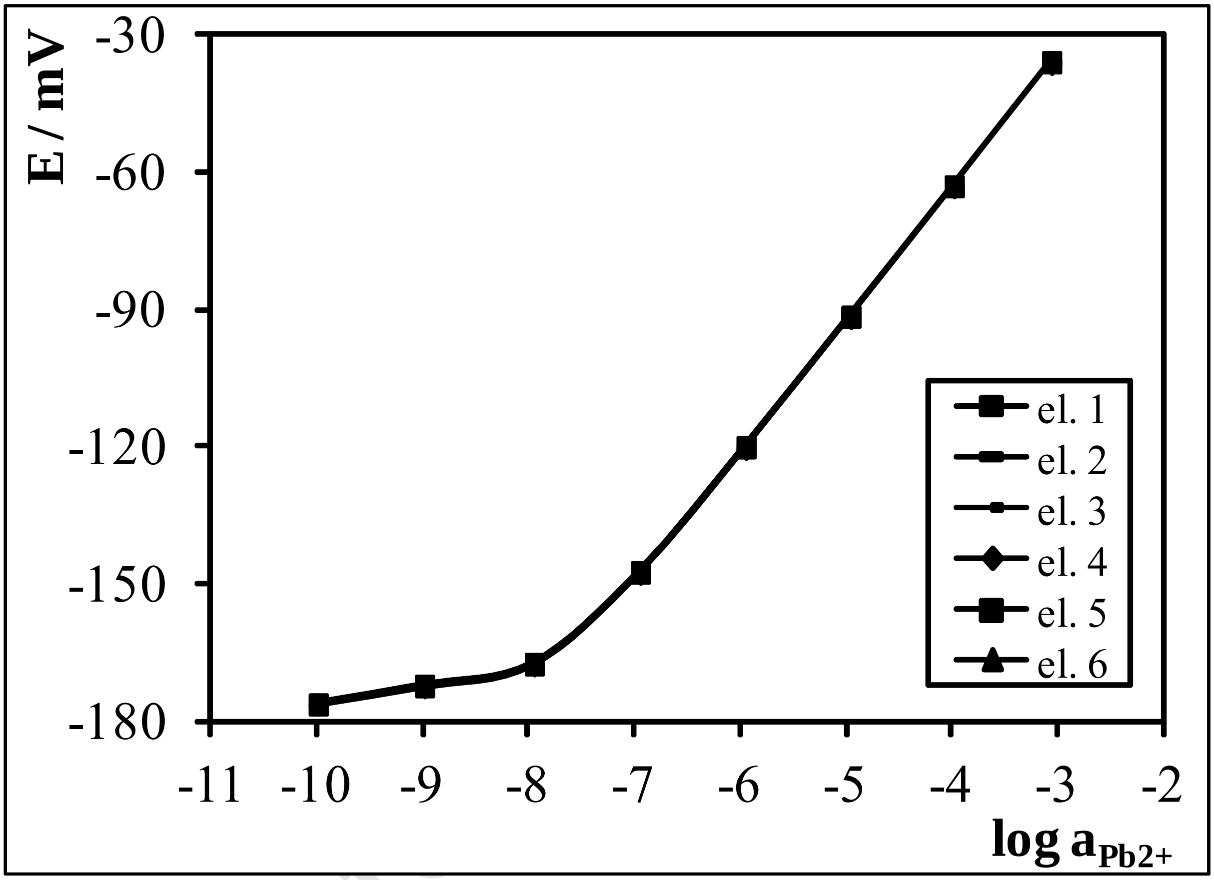
el.1
el.2
el.3
el.4
el.5
el.6
el.7
el.8

Figure 3.


E / mV
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-60
-90
-120
-150
-180
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
log a_{Pb2+}
el. 1
el. 2
el. 3
el. 4
el. 5
el. 6

Figure 4

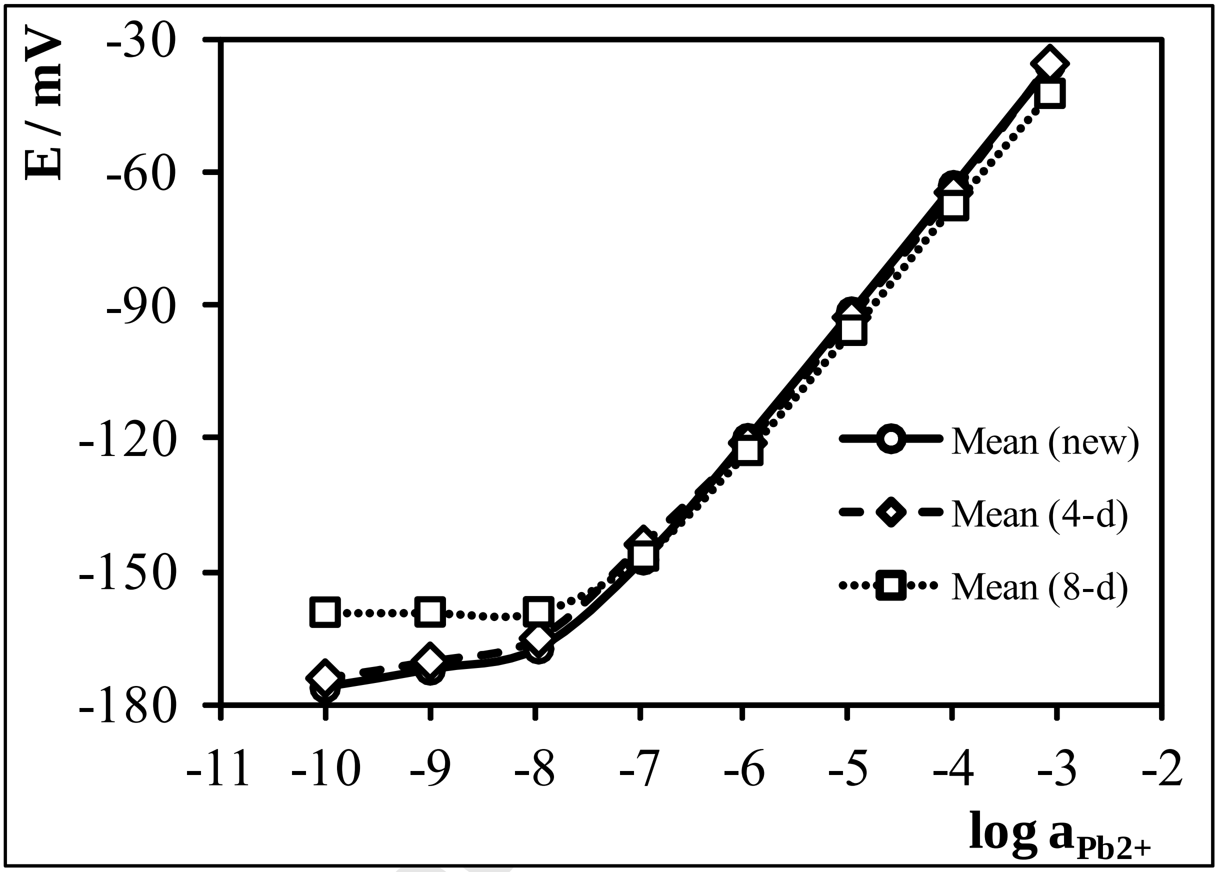
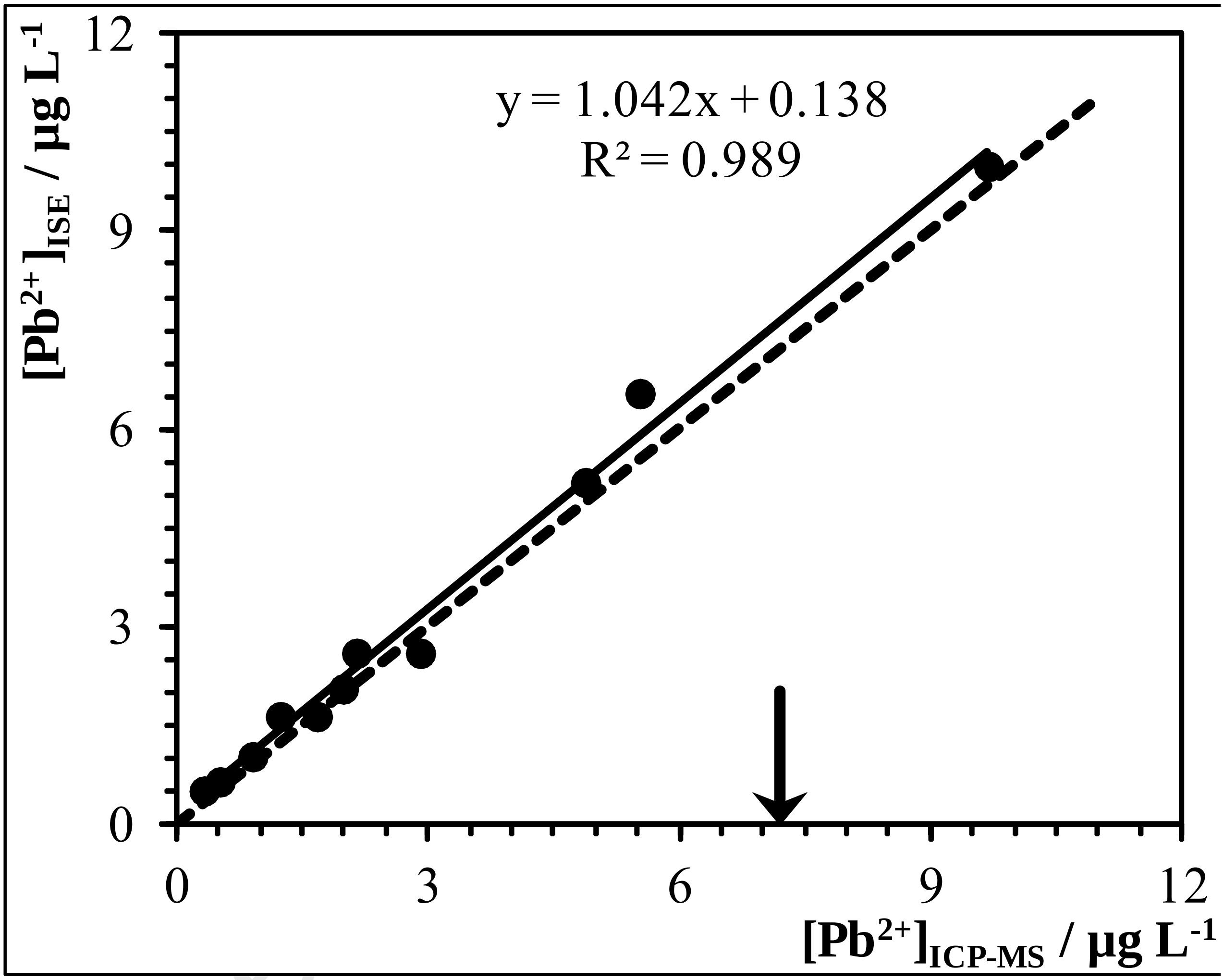

E / mV
-30
-60
-90
-120
-150
-180
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
log a_{Pb2+}
Mean (new)
Mean (4-d)
Mean (8-d)

Figure 5.


y = 1.042x + 0.138
R² = 0.989
[Pb2+]ISE / µg L-1
[Pb2+]ICP-MS / µg L-1
0
3
6
9
12
0
3
6
9
12

TABLES

X^{T} **Table 1.** Total lead concentrations of environmental water samples determined by ICP-MS analysis *vs.* SC-ISE using the standard addition method. %RE is the % relative error between the two methods calculated using $\%RE = \frac{\left(X^{*} - X^{T}\right)}{X^{T}}$, where X^* is the ISE value, and X^T is the reference value (ICP-MS) which is assumed to be the 'true' value. Molar concentrations can be obtained by dividing by the atomic mass of Pb^{2+} (207.2).

Location name	Water type	Pb (ICP-MS) µg/L	Pb (ISE) µg/L	%RE
(A) - Royal Canal Ave	canal	0.32 ± 0.02	0.52 ± 0.06	-62.5
(B) – Withworth Rd	canal	0.51 ± 0.04	0.66 ± 0.08	-29.4
(C) – Charleville Mall	canal	1.67 ± 0.08	1.65 ± 0.09	-15.6
(D) – North Wall	estuary	1.98 ± 0.07	2.07 ± 0.09	1.2
(E) – N Wall Quay	estuary	4.87 ± 0.11	5.20 ± 0.14	-4.5
(F) – Wilton Terrace	canal	1.23 ± 0.08	1.65 ± 0.09	-6.8
(G) – Windsor Terrace	canal	0.90 ± 0.03	1.04 ± 0.05	-34.1
(H) – Dolphin Rd	canal	2.14 ± 0.07	2.61 ± 0.09	22.0
(I) – S Circular Rd	river	9.68 ± 0.25	10.00 ± 0.10	-3.3
(J) – Lower Rd	river	2.90 ± 0.11	2.61 ± 0.30	10.0
(K) – Lower Lucan Rd	river	5.52 ± 0.18	6.55 ± 0.05	-18.7
(L) – Inns Quay	river	172.35 ± 12.15	207.20 ± 0.14	-20.2