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The voltammetric behaviour of lead at a microband screen-printed carbon electrode and its determination in acetate leachates from glazed ceramic plates[☆]

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ABSTRACT

Microband screen-printed carbon electrodes (μBSPCEs) without further modification have been investigated as disposable sensors for the measurement of lead in acetate leachates from ceramic glazed plates. Cyclic voltammetry was employed to elucidate the electrochemical behaviour of Pb^{2+} at these electrodes in a variety of supporting electrolytes. The anodic peaks obtained on the reverse scans, showed that Pb had been deposited as a thin layer on the surface of the μBSPCE. The anodic peak of greatest magnitude was obtained in 0.1 M pH 4.1 acetate buffer containing 13 mM Cl^-. The effect of chromium, copper, phosphate, sulphate and tin was examined and under the conditions employed, no significant change in current was found. The μBSPCEs were evaluated by carrying out lead determinations for acetate leachates from glazed ceramic plates. A highly decorated ornamental plate was found to leach 400 μg Pb^{2+} (%CV = 1.91%). A second plate, designed for dinnerware was found not to leach any detectable levels of Pb^{2+}. However, once fortified with 2.10 μg of Pb (equivalent to 100 ng/ml in the leachate), a mean recovery of 82.08% (%CV = 4.07%) was obtained. The performance characteristics indicate that reliable data has been obtained for this application which could identify potentially toxic sources of lead.

1. Introduction

A number of reports have highlighted that relatively high levels of Pb can be inadvertently consumed as part of our diet via the use of ceramic tableware and cooking utensils containing Pb as part of the decorative pattern or glaze [1–9]. Acidic foods or liquids subsequently used with such products can readily liberate lead from the glazed surface and in some cases result in levels in the high mg/l range [9]. Obviously, in light of the known toxicity of Pb [10], this can be highly detrimental to the individuals that may consume this food or drink and studies have shown a direct correlation with this and lead poisoning [11–14].

Awareness of such problems has generated a demand for methods that are rapid, inexpensive, reproducible, sensitive and accurate. However, the majority of techniques employed, especially in the case of the hyphenated forms necessitate the need for highly trained personnel, the use of explosive gases and an appropriately equipped laboratory to be housed in and are thus relatively expensive. Electrochemical techniques such as anodic stripping voltammetry (ASV) offer a number of advantages both in terms of economics, sensitivity, portability, easy of use, requiring little more than an appropriate low cost potentiostat. It is a non-destructive technique and can be tailored to give a wide dynamic range from extremely low levels to the ppm range, or higher.

However, previously, ASV has suffered from the common use of Hg working electrodes, the use and subsequent disposal of which has lead to its lack of market penetration compared to other techniques. The European Union have now moved to ban Hg in electrical equipment [15] and it should be questioned if we should use a toxic heavy metal such as Hg in the development of new techniques to detect heavy metals. A variety of other electrode materials have been consequently investigated as possible alternatives to Hg [1,16–20]. Recently we have reported on the use of Hg-free screen-printed carbon electrodes (SPCEs) for the determination of Pb [21,22], Cd [23] and Cu [24] in environmental water samples using ASV and in a number of reviews we have reported on a range of applications in which such SPCEs have been utilised [25–28]. The greater part of these have utilised working electrodes with areas in the square millimetre range. However, there are a growing number of reports in which SPCEs in the micrometer (μm) range have been utilised [16,30–38]. Such electrodes exhibit a number of analytically advantageous features, such as, improved signal to noise

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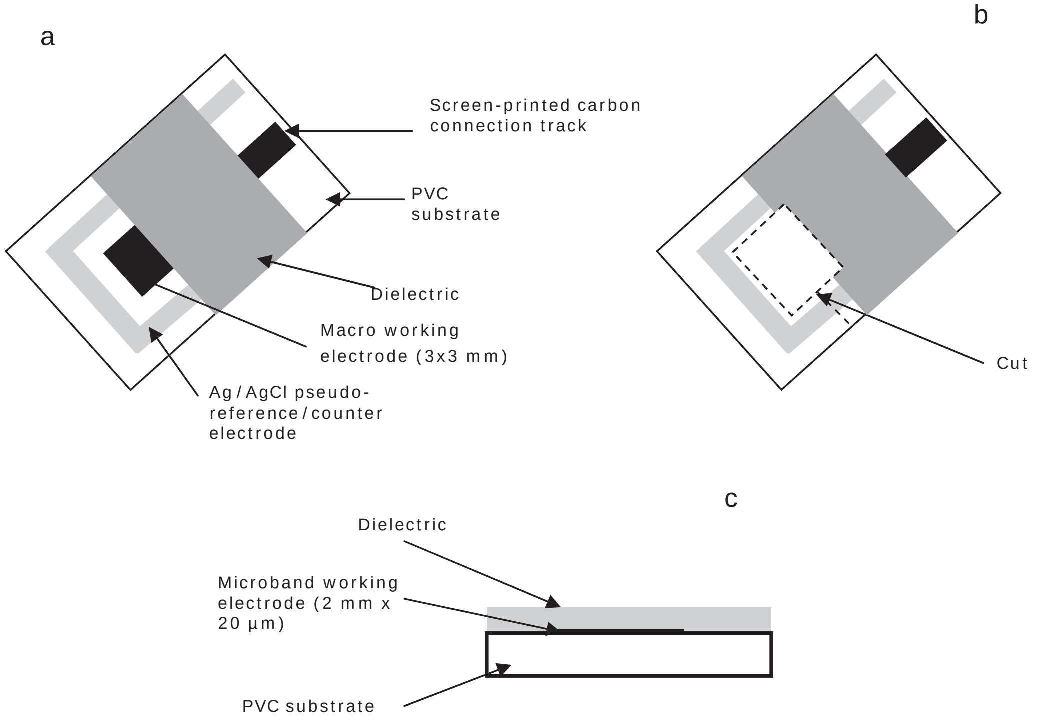

Fig. 1. Diagrammatic representation of our method for the manufacture of microband SPCEs. (a) Plain view of 3 × 3 mm SPCE, (b) and μBSPCE (c) end on view of μBSPCE.

ratios, independence of forced convection and low ohmic drop [39,40].

The manufacture of microelectrodes generally requires a number of relatively involved manufacturing steps, and do not lend themselves to commercialisation. The screen-printing of electrodes has generally elevated such problems, as one of its major strengths is its ability to manufacture highly reproducible sensors in large numbers. However, generally the screen-printing of electrodes in the μm range is considered difficult and not reproducible. Nevertheless, Kadara et al. [29] have shown the possibility of screen-printing shallow recessed microarrays directly with a with reportedly reproducible disc radii of 116 μm for the determination of Mn^{2+} via cathodic stripping voltammetry achieving a limit of detection of 81 nM. Cugnet et al. [41] have used an alternative approach to manufactured microarray electrodes by coating a screen-printed electrode with a polyethylene terephthalate membrane and laser ablating 13 μm wholes through this to form an 8 × 8 microelectrode array. Recently random micro-array electrodes have been formed by spraying screen-printed working with a commercial deodorant [42]. We have recently reported on the application of Hg-free screen-printed microband electrodes (μBSPCEs) for the determination of hydrogen peroxide [34] and lactic acid [35]. The use of such electrodes offers a number of advantages, such as ease of manufacture and renewal of the electrode surface.

Consequently, in this present study we have investigated the possibility of determining trace Pb^{2+} concentrations at unmodified, Hg-free screen-printed microband electrode (μBSPCE). This to our knowledge is the first report on the use of such Hg-free microband electrodes for the determination of Pb.

In the first part of this study, we have utilised cyclic voltammetry to investigate and optimise the voltammetric conditions necessary to determine Pb at our μBSPCEs. In the second section, we then investigate the possibility of utilising these electrodes using anodic stripping voltammetry for the determination of Pb in the leachates from glazed ceramic plates.

2. Experimental

2.1. Chemical and reagents

All chemicals were of Primar grade and supplied from Fisher (Loughborough, UK), unless stated otherwise. Potassium ferrocyanide and lead nitrate was obtained from Sigma–Aldrich (Poole, Dorset, UK). Stock solutions were prepared by dissolving the appropriate mass in deionised water. Working standards, for optimisation of studies, were prepared by dilution of the primary stock solution with deionised water. Deionised water was obtained from a Purite RO200 – Stillplus HP System, (Purite Oxon, UK). Electrolyte solutions for cyclic voltammetric studies were prepared by titrating a 0.2 M acetic acid solution with 0.2 M sodium acetate to give a pH 4.1 solution. This was then fortified with sufficient NaCl to a 26 mM Cl^- solution. A 5.0 ml aliquot of this solution was pipetted directly to the voltammetric cell. To this 5.0 ml of deionised water was then added via pipette, to give a 0.1 M pH 4.1 acetate buffer solution containing 13 mM Cl^-. Ceramic plates were purchased from local commercial outlets.

2.2. Apparatus

Cyclic voltammetry and linear sweep anodic stripping voltammetry (LSASV) were performed with a Pstat10 potentiostat interfaced to a PC for data acquisition via the General Purpose Electrochemical System Software Package (GPES) version 3.4 (Autolab, Windsor Scientific Limited, Slough Berkshire UK). The 3 × 3 mm based SPCE senor was printed from C10903P14 ink and supplied by Gwent Electronic Materials (GEM) (Pontypool, UK) (Fig. 1a) and are similar in design to that we have reported in earlier reports [21–24]. The end of this working electrode was cut-off perpendicular to the screen-printed carbon track to expose a 2 mm wide section of the screen-printed carbon connection strip (Fig. 1b), sandwiched between the dielectric (insulting tape) and the PVC substrate, hence forming the microband electrode (2 mm × 20 μm)

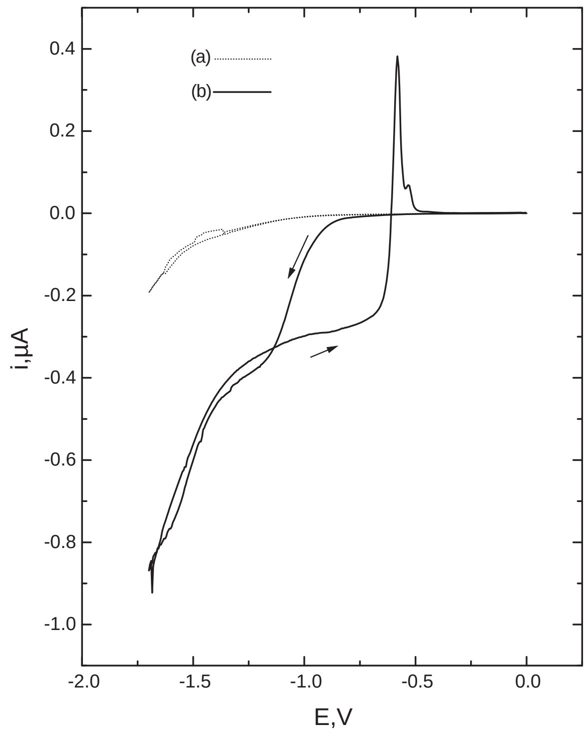

Fig. 2. Typical cyclic voltammograms obtained with a microband SPCE for 0.1 M pH 4.1 acetate buffer/13 mM NaCl, (a) in the absence of and (b) the presence of 0.1 mM Pb. Initial and finial potential: 0.0 V; switching potential −1.7 V; scan rate 50 mV/s.

(Fig. 1c). The microband working and pseudo-reference/counter electrodes were then connected to the potentiostat using a gold clip attached to coaxial cable inserted into the appropriate sockets. New microband electrodes were readily formed by removing a further small portion of the working electrode in order to produce new carbon surface. The cell used for the voltammetric measurements was obtained from Metrohm (Switzerland). Energy dispersive X-ray spectroscopy (EDXS) was undertaken using an Oxford Link ISIS system fitted to a Phillips XL30 ESEM.

Cyclic voltammograms were recorded in plain solutions (0.1 M) of the supporting electrolyte and then in the same solution containing 0.1 mM of Pb^{2+}. All solutions were purged with oxygen free nitrogen to eliminate oxygen reduction waves. The voltammetric conditions were as follows: starting and finial potential, 0.0 V with a switching potential −1.7 V using a scan rate 50 mV/s. Cyclic voltammetric investigations of a 5.1 mM potassium ferrocyanide in 0.1 M KCl solution were undertaken using a starting and final potential of −0.25 V, initial switching potential of +1.0 V, with a second switching potential of −0.5 V. The effect of scan rate was explored over range 5–100 mV/s.

LSASV was carried out using a deposition time of either 15 s or 1500 s with an applied potential of −1.3 V (vs. Ag/AgCl) in quiescence. All LSASV measurements were undertaken without prior purging with nitrogen. The measurement step was undertaken using a starting potential of −1.3 V and an end potential of 0.0 V with a scan rate of 50 mV/s.

2.3. Sample preparation

Two plates were selected as representative of the range that would be expected. Plate A, a highly decorated ornamental plate, and plate B designed as tableware. Plates were first washed with deionised water and left to dry. An aliquot (20 ml) of 0.1 M pH 4.1 acetate buffer containing 13 mM NaCl was then pipetted onto the surface of the plate. This was then left for 24 h in the dark at room temperature; covered to protect it from atmospheric deposition. The resulting solution was then transferred to a glass vial and the volume adjusted to 20 ml. A 4 ml aliquot of this was then transferred to the voltammetric cell and the concentration of Pb determined using the optimised LSASV conditions. The concentration of Pb present in the leachate was determined using the method of multiple standard additions.

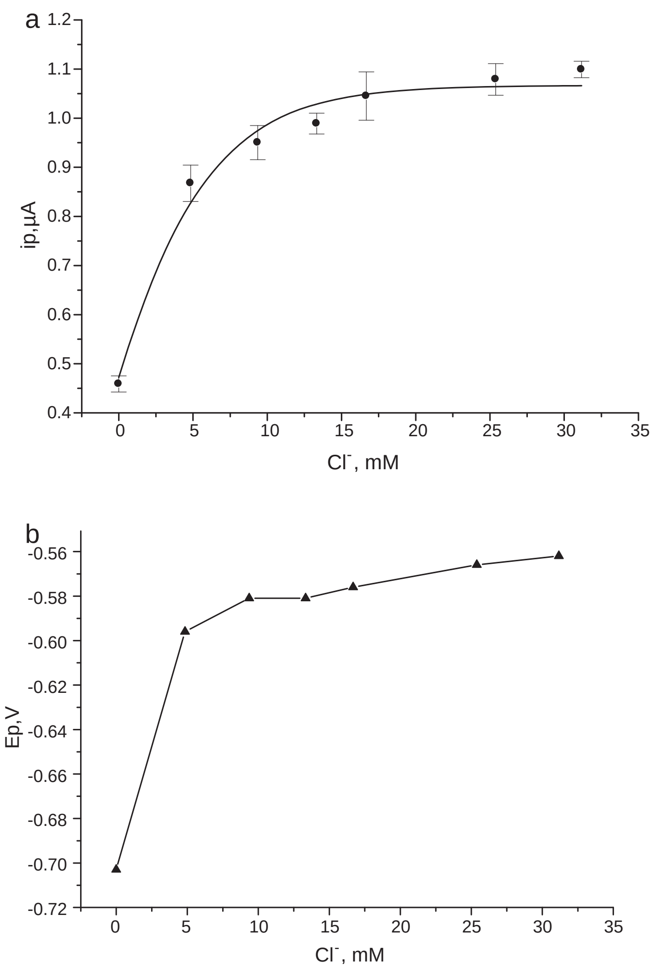

Fig. 3. Effect of Cl^- ions on the LSASV behaviour for 0.1 M acetate buffer pH 4.1 solution containing 0.1 mM Pb^{2+}. (a) Peak current and (b) peak potential. Voltammetric conditions: accumulation time 60 s, accumulation potential −1.3 V.

3. Results and discussion

3.1. Cyclic voltammetric investigations using microband SPCEs with potassium ferrocyanide

Initial investigations were made on the cyclic voltammetric behaviour of our µBSPCEs with 5 mM potassium ferrocyanide in 1.0 M KNO_3. This resulted in the sigmoidal behaviour expected for this species at a microelectrode. A current density of 9.072 A m^{-2} was obtained, compared to only 0.030 A m^{-2} at a 3 × 3 mm SPCE. The large increase in current density showing the elevated mass transport that occurs at the microband electrodes is due to radial diffusion. However, the µBSPCE show some degree of hysteresis, showing some small contribution of planar diffusion was occurring. Similarly, investigations into the effect of scan rate (2–100 mV/s) showed this to be generally independent of i_p with a very shallow slope of 3.5 nA/mV/s.

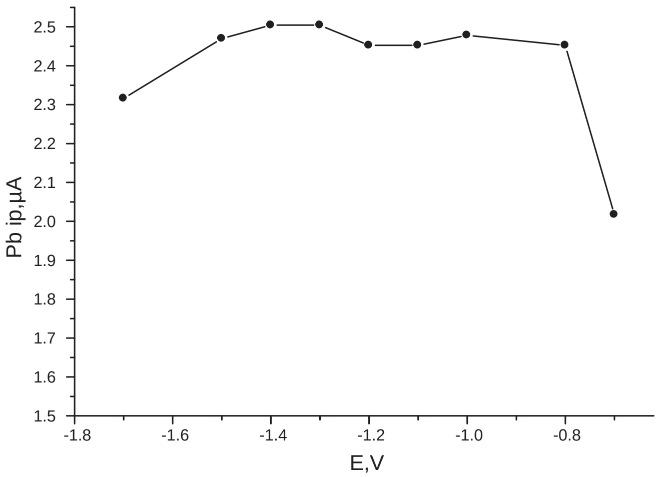

Fig. 4. Effect of deposition potential on the LSASVs for a 0.1 mM Pb in 0.1 M pH 4.1 acetate buffer containing 13 mM Cl^- at a microband SPCE. Accumulation time 60 s.

3.2. Cyclic voltammetric behaviour of lead at microband SPCEs

Fig. 2 shows a typical cyclic voltammogram obtained for 0.1 mM Pb solution at our μBSPCE. Generally, the resulting voltammograms exhibited one cathodic peak on the forward negative going scan and two sharp symmetrical anodic peaks on the return positive scan with a notable degree of hysteresis. We believe that these peaks result from similar processes we have reported previously for the ASV behaviour of Pb at 3 × 3 mm SPCE manufactured from the same ink [22]. The cathodic peak results from the deposition of Pb ions from solution to the electrode surface. The two subsequent anodic peaks result from the stripping of mono and multi-layers of Pb metal adsorbed at the electrode; the different Ep reflecting the difference in adsorption energies the different layers of metal exhibit.

The formation of such adsorbed layers is necessary for the accumulation step in anodic stripping voltammetry; these studies suggest the possibility of using these microband electrodes for the determination Pb using ASV.

3.3. Effect of chloride ion concentration

In order to explore the voltammetric behaviour and optimise the conditions for electrochemical determination of Pb^{2+} at a microband SPCE, studies were made to ascertain the optimum supporting electrolyte. In recent studies we have shown that the addition of halide ions, such as Cl^- [43] and I^- [21] gave superior voltammetric behaviour for the determination of metal ions at our SPCEs. In light of this, and the improvement in i_p reported at Hg electrodes [44], we believe that the addition of such anions could improve the voltammetric behaviour of Pb at our μBSPCEs. It can be seen from Fig. 3a that with increasing Cl^- concentration a notable increase the resulting i_p obtained, with a maximum seen between 13 mM and 33 mM Cl^-. The magnitude of the Pb anodic stripping peak was greater than that obtained in either hydrochloric acid or nitric acid (not shown). As a result, an electrolyte of 0.1 M pH 4.1 acetate buffer, containing 13 mM Cl^- was used in further studies. Fig. 3b shows how the Ep values were found to shift with by 100 mV with the addition of 5 mM Cl^- then become constant at Cl^- concentrations above 10 mM.

Recently, cyclic voltammetric investigations at Pb electrodes have shown that Cl^- ions passivate the oxidation potential of Pb [45]. This effect can stabilise the deposited Pb film on the surface of the SPCE. The effects of this are possibly evident from the observed increased i_p and positive shifts in Ep seen for the Pb stripping peak with increasing Cl^- concentrations (Fig. 3a and b).

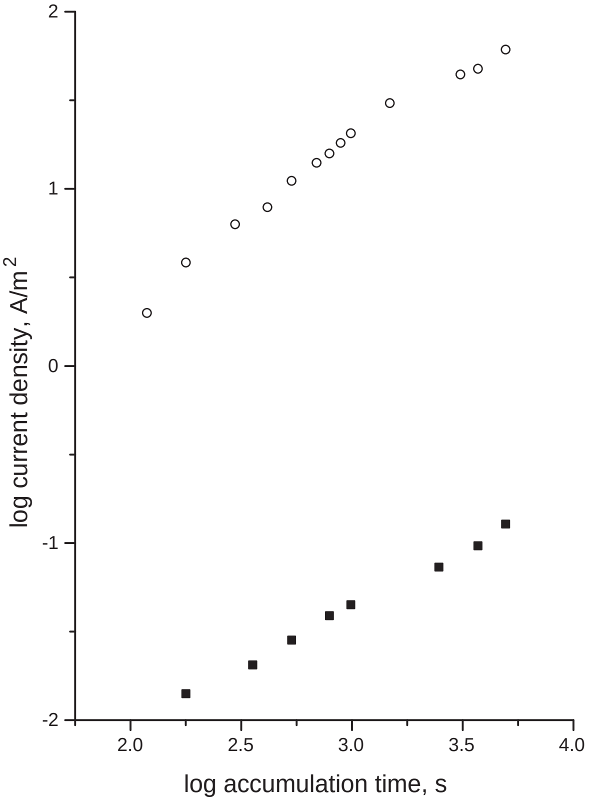

Fig. 5. Effect of accumulation time on the current density gained at a μBSPCE (open circle) and a 3 × 3 mm SPCE (closed square) for a 2.11 μg/ml Pb^{2+} solution. Voltammetric conditions as for Fig. 4, but accumulation potential set at −1.3 V.

Similar improvements in i_p response were found for the addition of I^-. However, these were found to have a detrimental effect on the half cell reaction of the Ag/AgCl reference electrode, causing notable shifts in the Ep of the Pb stripping peak from −0.52 V to −0.12 V for an addition of 15 mM I^-.

Further studies were also performed on the effect of F^- on the same 2.11 mg/l Pb^{2+} solution by LSASV. No changes in either Ep or i_p were seen for F^- concentrations up to 18.5 mM. However, above this the i_p of the Pb stripping peak was seen to decrease with increasing F^- concentration; in agreement with that shown in earlier studies at Hg electrodes [46]. In such studies, Pb^{2+} and Cd^{2+} showed very little tendency to adsorb on Hg electrodes when they are present with non-adsorbing anions such as fluoride or anions such as nitrate, perchlorate or sulphate. However, in the presence of iodide, Cd^{2+} adsorption was shown to increase at the Hg electrode, with these iodide anions, being depicted as acting as “bridges”, holding the Cd^{2+} at the electrode surface. We believe that similar effects could also explain the increase in Pb^{2+} adsorption we have found in this present study.

Another factor which may partly explain the improvement seen with Cl^- ions is the effect this anion has on the competing reactions occurring at the anode. The electrochemical deposition of Pb^{2+} as lead dioxide (PbO_2) at a suitable anode has been utilised as a method for the determination of Pb for some time [47]. In such determinations, the presence of Cl^- is particularly deleterious, as it is oxidised at potentials much lower than Pb^{2+} (+1.358 V compared to +1.456 V) [47].

As these reactions occurring at the anode can be seen to be in competition to that occurring at the cathode, *i.e.* the accumulation step in ASV. Any process that will decrease the rate that these occur

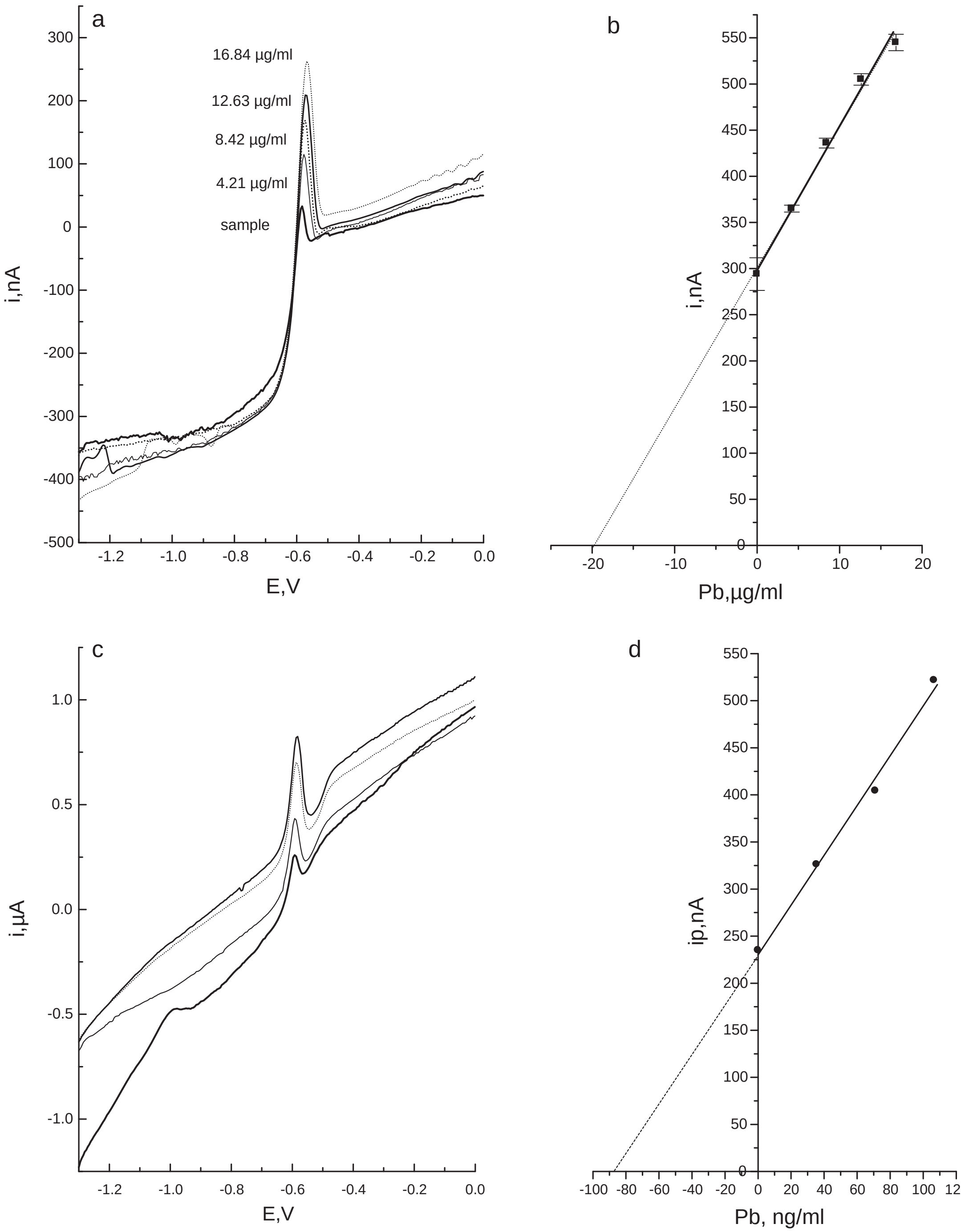

Fig. 6. LSASVs of plate sample leachate (a) and (b) plate A and (c) and (d) plate B. (a) Added concentrations of Pb 0.00 µg/ml 4.21 µg/ml, 8.42 µg/ml, 12.63 µg/ml, and 16.84 µg/ml Pb. Accumulation time: 15 s, deposition potential −1.3 V (vs. Ag/AgCl). (c) Added concentrations of Pb 0.00 µg/ml 35.5 ng/ml, 71.1 ng/ml, 106.6 ng/ml Pb. Accumulation time: 1500 s, deposition potential −1.3 V (vs. Ag/AgCl). (b) and (d) resulting standard addition plots.

will allow for more Pb^{2+} to be available for reduction at the SPCE surface. This would tend to lead to increases in the number of moles of Pb^0 reduced and accumulated at the SPCE and hence the overall efficiency of the assay.

3.4. Effect of applied potential

The effect of applied potential was studied for a 0.1 mM Pb^{2+} solution over the range −0.7 V to −1.7 V (vs. Ag/AgCl) using an accumulation time of 60 s (Fig. 4). Under these conditions, the magnitude of the stripping peak was found to increase with increasing negative potential, until forming a plateau between −1.0 V and −1.6 V (vs. Ag/AgCl). Consequently, further investigations were made using an applied potential of −1.3 V (vs. Ag/AgCl).

3.5. Effect of accumulation time

As we were particularly interested in determination low concentrations of Pb^{2+} studies were undertaken to ascertain the effect of accumulation time using an applied potential −1.3 V (vs. Ag/AgCl) for a 2.11 mg/l Pb^{2+} solution in the optimised electrolyte. Under quiescent conditions, peak current for the anodic Pb stripping were found to increase linearly with time up to 1500 s, (1.20 nA/s, $R^2 = 0.999$) becoming independent of time beyond this point.

As shown in Fig. 5 a comparison between the μBSPCE and a 3 × 3 mm SPCE shows a dramatic increase in current density for the former. This result confirms our simple method of miniaturisation of the SPCE results in microband behaviour. For a 2.11 mg/l Pb^{2+} solution at 180 s, a current density of 3.78 A m^{-2} was obtained, compared to only 0.0139 A m^{-2} for a 3 × 3 mm SPCE.

3.6. Effect of Pb concentration

Using an accumulation time of 1500 s in quiescence at an applied potential of −1.3 V (vs. Ag/AgCl), a linear relationship with Pb concentration and i_p was obtained from 50 μg/l to 1.70 mg/l ($R^2 = 0.999$, 1.04 nA/ng/ml). Based on a signal-to-noise ratio of three, a theoretical detection limit of 2.3 ng/ml was calculated. Using a shorter accumulation time of 15 s, a linear range of between 2 mg/l and 50 mg/l Pb was obtained.

3.7. Interference studies

The effects of a $PO_4{}^{3-}$, $SO_4{}^{2-}$, Cr^{3+} and Cu^{2+} were investigated as possible interferences in the proposed DPASV assay for Pb^{2+}. No effects were observable for $PO_4{}^{3-}$ concentrations up to 2.1 mg/l, $SO_4{}^{2-}$ up to 210 mg/l, Cu^{2+} up to 2.5 mg/l and Cr^{3+} up to 5.2 mg/l. However, additions of K_2CrO_4 were found to result in a marked decrease in the Pb stripping peak current, presumably due to the formation of insoluble lead chromate [48].

Analysis of plate A by energy depressive X-ray spectroscopy (EDXS) showed strong signals for both Pb and Sn. Tin is known to be often utilised in the form of stannic oxide in both glaze and as decoration [49]. The element would hence be a possible interference for the determination of Pb, as it is known to exhibit very similar voltammetric behaviour [50]. However, the solubility of stannic oxide in the pH 4.1 acetate buffer employed here is relatively low and would not be expected to be extracted. Similarly, in electrolytes more basic than pH 3 the voltammetric behaviour of Sn is rather poor as it undergoes hydrolysis and subsequent precipitation [50]. For a 13 mg/l solution of Sn^{2+} under the optimised conditions using a 15 s accumulation time, no stripping peaks were observable. However, a peak with an Ep of −0.473 V was obtained for 38.7 mg/l Sn^{2+}; this was found not interfere with the stripping peak gained for a 0.605 mg/l addition of Pb^{2+}.

3.8. Analytical application

The proposed method was evaluated by carrying out Pb^{2+} determinations on two different glazed ceramic plates; one highly decorated ornamental (plate A) and a plain form, designed as tableware (plate B). Both were leached in 0.1 M pH 4.1 acetate buffer for 24 h at room temperature. Fig. 6a shows a representative set of voltammograms obtained for the leachate from plate A, with the corresponding standard addition plot shown in Fig. 6b. The leachate from the decorated ornamental plate A was found to contain a mean concentration of 20.01 mg/l Pb (%CV = 1.91%), a relative high concentration, as would be expected as the plate was designed for ornamental purposes only. Under the same conditions, the tableware plate B showed no detectable native leachable Pb. Plate B was then fortified with 2.10 μg Pb, and leached for a second 24 h period as before. Fig. 6c and d shows the resulting voltammograms and standard addition plot. Table 1 summaries the concentration leached into the acetate buffer. These data demonstrate that the proposed method has promise for the determination of Pb^{2+} in such samples.

Table 1
Precision data for the LSASV determination of Pb^{2+} leached from ceramic plate B fortified with 2.10 μg Pb^{2+}.

	Original concentration μg	Added μg	Found μg	% Recovery
1	ND	2.10	1.68	80.22
2	ND	2.10	1.64	78.25
3	ND	2.10	1.80	85.72
4	ND	2.10	1.70	80.72
5	ND	2.10	1.79	85.47

ND = none detected. Mean recovery = 82.08%; coefficient of variation = 4.07%.

4. Conclusions

We have investigated the redox behaviour of Pb at Hg-free microband SPCEs prepared from a commercial ink preparation (C10903P14) and found that well-defined anodic peaks could be obtained utilising an electrolyte comprising of 0.1 M pH 4.1 acetate buffer containing 13 mM Cl^- using LSASV. By using a deposition potential of −1.3 V, it was demonstrated that a microband screen-printed carbon electrode could be used in conjunction with LSASV for the trace determination of Pb without the need for any modification of the μBSPCE or degassing of the sample.

This is the first report on the determination of Pb by LSASV at a Hg-free microband SPCE and the first report on the use of such unmodified μBSPCEs for the determination of Pb in glazed ceramic leachates.

The use of a μBSPCE in this present report offers several advantages over our previous reported investigations into the determination of Pb^{2+} by ASV using a 3 × 3 mm SPCE [22]. Firstly, utilising a microband working electrode we able to dispense with the need for forced convection, so making the method more amenable for onsite analysis. Secondly, we were also able to gain a lower detection limit, a reflection of the improved signal to noise ratios that can be gained with μBSPCEs compared to macro size electrodes. Consequently, the proposed microband SPCE in conjunction with LSASV could have a wide application in identifying potential toxic sources of lead. It is envisaged that further work will be performed to develop microband SPCEs for trace detection of Pb and other metal pollutants in consumer products such as paint [51], toys [52] and jewellery [53]. We feel that the method could also be readily adapted to the rapid measurement of Pb in other important areas such as biological, environmental and forensic investigations such as for serum and water analysis.

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