

University of the West of England

# The Voltammetric Behaviour of Lead at a Microband Screen-Printed Carbon Electrode and its Determination in Acetate Leachates from Glazed Ceramic Plates Kevin C. Honeychurch and John P. Hart\*

Effect of Chloride Ion Concentration

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## Introduction

Relatively high levels of Pb can be readily consumed as part of our diet from ceramic glazed tableware containing Pb as part of the decorative pattern or glaze. Awareness of such problems has generated a demand for methods that are rapid, inexpensive, reproducible, sensitive and accurate. Electrochemical techniques such as anodic stripping voltammetry (ASV) offer a number of advantages both in terms of economics, sensitivity, portability and easy of use,

requiring little more than an appropriate power supply for such applications. Coupled to these advantages, the technique of ASV can also be tailored to give a wide dynamic range from these 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. However, there are a growing number of reports in which Hg-free SPCEs with working electrodes in the micrometer (µm) range have been utilised, the radial diffusion inherent with these divises allows for complicits lob made utilised to be greated and the formed penetration. with these devices allows for analysis to be made without the need for forced convection. In this present study we have investigated the possibility of determining trace Pb concentrations at a screen-printed microband electrode ( $\mu$ BSPCE). This to our knowledge is the first report on the use of such microband electrodes (pbb) dc), that of an interlog of the matrix due to the use of such microband electrodes for this application. In the first part of this study, we have used cyclic voltammetry to 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 (ASV) for the determination of Pb in the leachates from glazed ceramic plates



Figure 1. Schematic diagram demonstrating the method for the manufacture of microband SPCEs from C10903P14. (a) \$25 mm SPCE working electrode, with screen-printed Ag/AgCI pseudoreference/counter electrode. (b) Microband SPCE (plan view). (c) Microband SPCE (cross section).

Voltammetric Conditions Cyclic voltammetric Conditions Cyclic voltammetric conditions voltammetric conditions were accorded in plain solutions (0.1 M) of the supporting electrolyte and then in the same solution voltammetric conditions were as follows: starting and finial potential, 0.0 w with a switching potential -1.7 V using a scan rate S0 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. AgAC) in quiescence. Al 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. S0 mV/s. Beapter and the solution are fortuned to the wave for two mode with deviced were and left for using a classification of the scan rate of 50 mV/s. S0 mV/s. Beapter and the deviced as representative of the range that would be expected. Plate A a highly decorated commental to the and only diverse and the deviced as representative of the trange that would be expected. Plate A a highly decorated commental to the and only diverse and the deviced as the deviced of the transpected of the device and left for the and the deviced with deviced and the deviced of the device and left for the A and the deviced of the transpected of the device and left for the A and the deviced of the device and left for the A and the deviced of the deviced

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

### Results & Discussion

### Cyclic voltammetric behaviour of Lead at Microband SPCEs

Figure 2 shows a typical cyclic voltammogram obtained for 0.1 mM Pb solution at our µSPCE. 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.



Figure 2. Typical cyclic voltammograms obtained with a microband SPCE for 0.1 M pH 4.1 acetate buffer13 mM NaCl, (a) in the absence of and (b) the presence of 0.1 mM Pb. Initial and final potentials: 0.0V; switching potential -1.7 V; scan rate 50 mV/s.

Figure 3. 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 NaCl at a microband SPCE. Accumulation time

The effect of applied potential was studied for a 0.1 mM Pb solution over the range -0.7 V to -1.7 V (vs. Ag/AgCl) using an accumulation time of 60 s (Figure 5). 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).

In order to explore the voltammetric behaviour and optimize the conditions for the ASV determination of Pb at a microband SPCE, studies were made to ascertain the optimum supporting electrolyte. For a 0.1 M pH 4.1 acetate buffer, it can be seen from Figure 4 that with appending to a concentration on a notable increase the resulting in for the Pb stripping peak is obtained, with a maximum seen between 10 mM and 33 mM NaCl. Consequently, a 0.1 M pH 4.1 acetate buffer containing 13 mM NaCl was used in further investigations.



Figure 4. Effect of CI ions on the LSASV Peak current for 0.1 M acetate buffer pH 4.1 solution containing 0.1 mM Pb. Voltammetric conditions: accumulation time 60 s, accumulation potential -1.3 V.

Figure 5. Effect of accumulation time on the current density gained at a microband SPCE and a 3x3 mm SPCE for a 2.11 mg/l Pb solution in quiescence.

As can be seen from figure 5, much greater current densities can be gained from the µBSPCE compared to the 3x3 mm SPCE under quiescent conditions. Pb stripping peaks were found to increase linearly with time up to 1500 s (1.20 nA/s) becoming independent of time beyond this point.

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 ip was obtained from 50 µg/l to 1.70 mg/l (R<sup>2</sup> = 0.999, 1.04 nA/ng/m). 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.

### Interference Studies

Tin is often utilised in the form of stannic oxide in both glaze and as decoration. A peak at -0.473 V was obtained for 38.7 mg/l Sn. However, this was found not interfere with the stripping peak gained for Pb at a concentration of only 0.605 mg/l in the same solution (Figure 6).





Figure 7. LSASVs of plate sample leachate at µBSPCEs (a) and (b) example voltammograms for added concentrations of Pb. Accumulation time: 15 s for plate A and 1500 s for plate B, deposition potential -1.3 V (vs. Ag/AgCl) (b) and (d) resulting standard addition plots

Figure 7a and 7b show a representative voltammograms obtained for the leachate from plates A and B, Figure 7 a flat 75 show a representative voltation goal in Source of the resolution for the resolution for the resolution of the resolution for the resolution of the resolut

## Conclusions

We have successfully demonstrated a relative quick and economic approach for the manufacture of microband screen-printed carbon electrodes. We have investigated the redox behaviour of Pb at these microband SPCEs prepared from a commercial ink preparation (C1000SP14) and found that well-defined anodic peaks could be obtained in 0.1 M pH 4.1 acetate buffer containing 13 mM Cl using İSASV

It was shown that the magnitude of the anodic stripping peak for Pb was independent of scan rate, indicative of steady state behaviour.

A simple and rapid method was developed for the determination of Pb by LSASV at a Highree microband SPCE. This is the first report on the use of such sensors for the determination of Pb in glaze

ceramic leachates.

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