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Characterisation of Screen-Printed Electrodes for Detection of Heavy Metals

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Abstract. The characterisation of disposable screen-printed electrodes for stripping analysis is described. The graphite surface of the working electrode is used as substrate for plating a thin mercury film, which allows the electrochemical preconcentration of heavy metals. Optimisation procedures and experimental results are presented. Detection limits around the ppb level were obtained for different metals [Pb(II), Cd(II), Cu(II)].

Key words: screen-printed electrodes; heavy metals; anodic stripping voltammetry; potentiometric stripping analysis.

Heavy metals are important environmental pollutants: they are extremely toxic, not biodegradable and tend to be bioaccumulated in animal and vegetable tissues. Thus knowledge of their content in various matrices is mandatory. There is a growing need for on-site tests in environmental analysis. This relates both to the elimination of errors associated with sampling, storage and long transportation times to the main laboratory, and to the need for rapid monitoring of heavy metals for the characterisation of contaminated sites.

Many techniques are employed in metal determination such as stripping voltammetry, atomic absorption spectrometry, atomic emission spectrometry with inductively coupled plasma excitation, X-ray fluorescence, neutron activation analysis, etc. Among these, stripping analysis can be considered the most powerful technique for in-field analysis, due to the small size of the equipment, easy installation and the possibility of multielement detection. Problems remain, however, related to the use of conventional electrochemical cells and to the need for a deaeration step. Improvements can be achieved by the elimination of classical bulky electrodes and cells and their replacement with disposable screen-printed strips and use of electrochemical techniques less influenced by oxygen interference.

The coupling of disposable screen-printed electrodes with stripping techniques is a revolution in comparison with conventional stripping analysis: the design and operation are greatly simplified, in accordance with the requirements of a decentralised assay [1].

Screen-printed electrodes are planar devices realised by printing layers of different electroconductive and insulating inks with controlled thickness and shape on a plastic substrate. In this work the carbon surface of the screen-printed working electrode was employed as substrate for a thin mercury film (TMF). Some papers report the use of this kind of device for heavy metal detection either with electrochemical preconcentration [1–3] or with non-electrolytic accumulation [4–6].

The aim of this work was to prepare screen-printed electrodes and evaluate the influence of different electrochemical parameters for stripping analysis. Two kinds of disposable systems were used: a strip with a single carbon working electrode, and a strip with two electrodes, a carbon working electrode and a silver reference electrode. Experimental results are shown for different voltammetric procedures such as square wave anodic stripping voltammetry (SWASV) and potentiometric stripping analysis (PSA). The square wave form is reported to facilitate stripping

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measurements in the presence of dissolved oxygen [7]. Such a capability can be attributed to the electrolytic depletion of oxygen at the surface prior to the fast scan. Reduction of oxygen takes place during metal reduction at the electrode surface, if the potential of the electrode is kept sufficiently negative during the deposition. This should minimise, in the second step, the extent of chemical stripping of the reduced metal by oxygen. If the scan is completed before significant amounts of oxygen diffuse to the electrode surface the resulting voltammogram should be similar to that obtained from a deaerated solution [8]. Thus a substantial reduction in analysis time can be achieved by eliminating the need for deaeration. Even with the use of PSA the deaeration of samples is generally unnecessary since dissolved oxygen can be used as the oxidant. This technique is based on potentiostatic preconcentration and on potentiometric recording. The analysis comprises two phases: an electrolysis step and a stripping step. During the electrolysis, the metals are accumulated in a mercury film on the surface of a working electrode to which a reducing potential is applied. During the stripping step, the applied electrolysis potential is removed. The oxidising agent, in this work a constant current of 1 μA, strips the amalgamated metals off the electrode, and the metals diffuse, in ionic form, back into the solution. Measurement of the electrode potential as a function of time provides quantitative as well as qualitative information about the metals present in the solution [9].

SWASV was used only with a carbon working electrode and a saturated calomel electrode (S.C.E.) with a double junction, to eliminate interference of chlorides, which results in increased electrical noise under our experimental conditions. The presence of chlorides in PSA had less influence and thus the two-electrode strip, which was easier to handle and to use, was employed.

Experimental

Apparatus and Reagents

Square-wave anodic stripping voltammetry was performed with an Amel polarographic analyser Model 433/W (Milano, Italy), and PSA experiments with an Autolab PSTAT 10 System Ecochemie (Utrecht, Netherlands). SWASV experiments were realised by using a screen-printed working electrode, a saturated calomel electrode (S.C.E.) as reference electrode, and a platinum counter-electrode (BAS). Screen-printed strips, with working and reference electrodes, were employed for PSA experiments.

Screen-printed electrodes were prepared with a DEK Model 245 screen-printer (Weymouth, England), using different inks obtained from Acheson Italiana (Milan, Italy), as previously reported [10]. A graphite-based ink (Elettrodag 423), a silver ink (Elettrodag 477 ss rfu) and an insulating ink (Elettrodag 6018 ss) were used.

Sodium acetate, potassium chloride, acetic, nitric and hydrochloric acids were Suprapur grade (from Merck, Darmstadt, Germany). The water used for preparation of solutions was from a

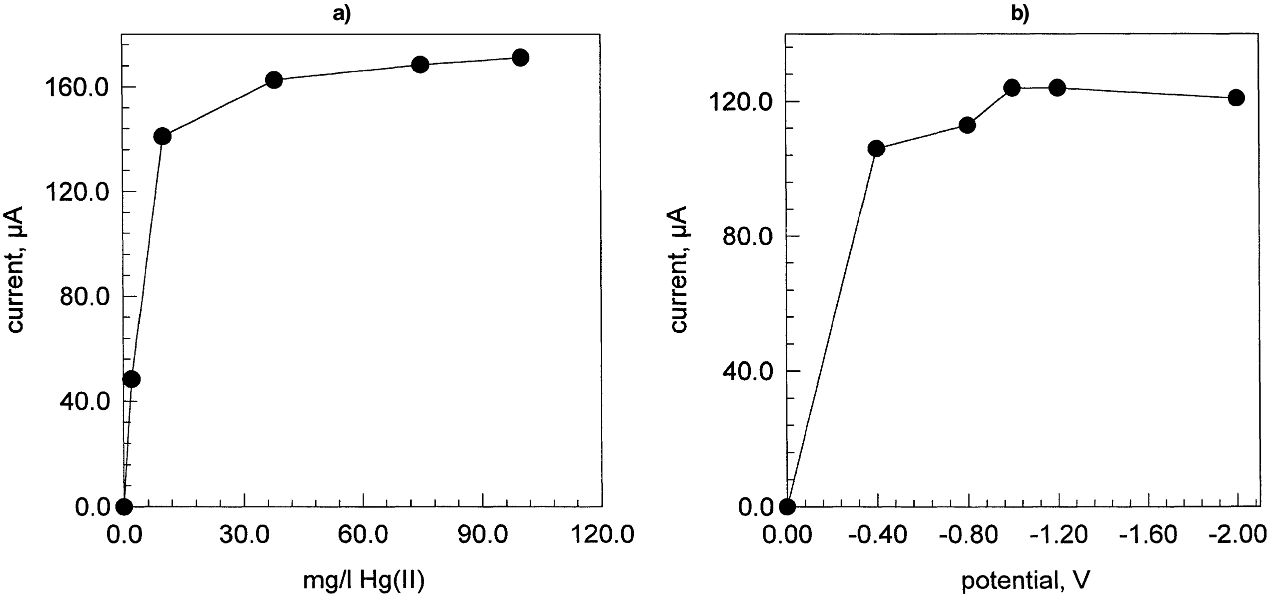

Fig. 1. Effect of mercury(II) chloride concentration (a) and mercury deposition potential (b) on lead anodic stripping current. Lead concentration 0.05 mg/l, acetate buffer 30 mM, pH 4.7. SW parameters: amplitude 25 mV, step 5 mV, frequency 10 Hz, deposition time 5 min; (a) mercury deposition potential −1 V; (b) mercury(II) chloride concentration 80 mg/l

reagent-grade ion-exchange system, Milli-Q (Millipore, Bedford, MA 01730). Heavy metal stock solutions were prepared by diluting copper(II), lead(II) and cadmium(II) standard solutions (Fluka Chimica, Milan, Italy). Mercury(II) chloride and potassium hexacyanoferrate(II) were obtained from Merck.

Procedure

The mercury film was pre-plated from a stirred mercury (II) chloride solution in hydrochloric acid, by holding the working electrode at the deposition potential for a fixed time; the potential was then switched to −0.2 V for a cleaning period of two minutes. Subsequent ASV or PSA cycles consisted of the metal deposition and the stripping steps. Experiments were performed in stirred solution and in the presence of dissolved oxygen during the deposition step. The stripping step was performed in a quiescent solution.

The surface area of the working electrode was calculated from the Cottrell equation, applied to results for the oxidation of 1 mM potassium hexacyanoferrate(II), in 1 M potassium chloride, for 1 min at +0.8 V *vs* S.C.E. [11]. The surface area values are respectively 0.43 cm^2 and 0.106 cm^2 for the single carbon SPE and for the working carbon electrode of the two-electrode device.

Results and Discussion

Optimisation of Mercury Deposition

The first step was the optimisation of the thin-film mercury deposition, using a screen-printed carbon working electrode coupled with an S.C.E. reference and a platinum counter-electrode. Optimisation of the mercury deposition step was realised by varying the different parameters [deposition time and potential, mercury(II) concentration] and evaluating the square wave stripping current of a solution of 0.05 mg/l lead(II) in acetate buffer.

The optimised mercury(II) chloride concentration for the pre-plating solution was 80 mg/l in 20 mM hydrochloric acid. No significant increase in sensitivity was recorded (Fig. 1a) with higher concentrations. The deposition potential was also optimised (Fig. 1b), and the value of −1 V was used in the following experiments.

It is well known that to obtain high sensitivity and good resolution in anodic stripping analysis the mercury film should be sufficiently thin; various film thickness have been reported in the literature, ranging from 10 to 1000 nm [12].

The thickness (l) of the mercury film can be calculated by using the following equation [12]:

$$l = 2.445 \times 10^{-5}\, it/r^2$$

where i is the reduction current of mercury(II), t is the mercury reduction time, and r is the radius of the electrode surface area, experimentally calculated from the Cottrell equation. With increase in the mercury deposition time, the thickness of the mercury film increases linearly. For a two-minute deposition time the calculated film thickness was 20 nm. The time for the cleaning step and the value of the potential applied during this step were chosen according to the literature [2].

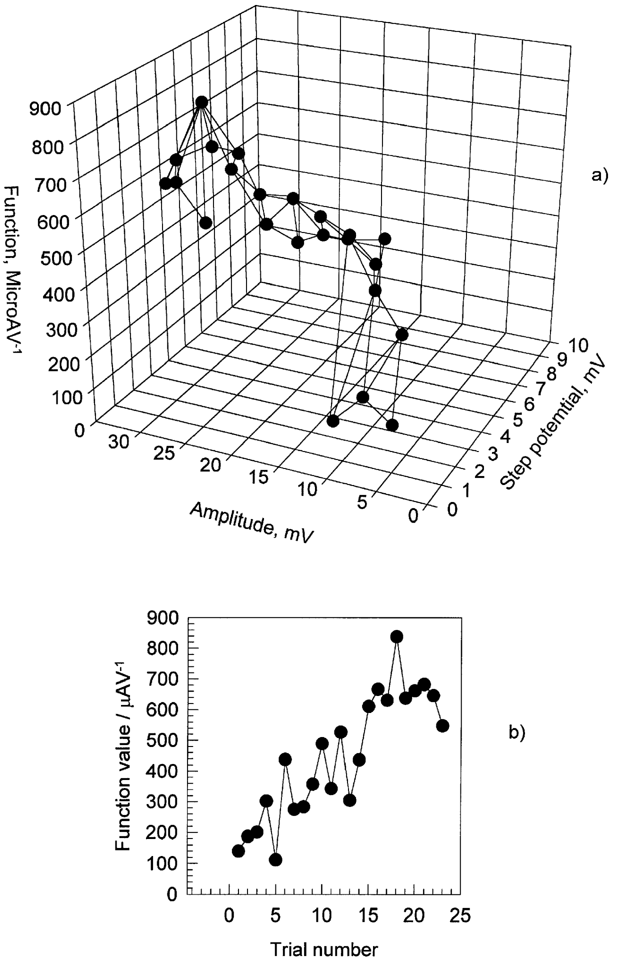

Fig. 2. Movement of the simplex during the optimization of the anodic stripping of lead (a) and progress of the objective function value during the optimization (b). Conditions: lead 0.05 mg/l, acetate buffer 30 mM, pH 4.7, frequency 10 Hz, deposition time 5 min

Optimisation of Square Wave Voltammetry Parameters

The instrumental parameters of the stripping step, such as square wave amplitude, frequency and step potential were optimised. Square wave amplitude and

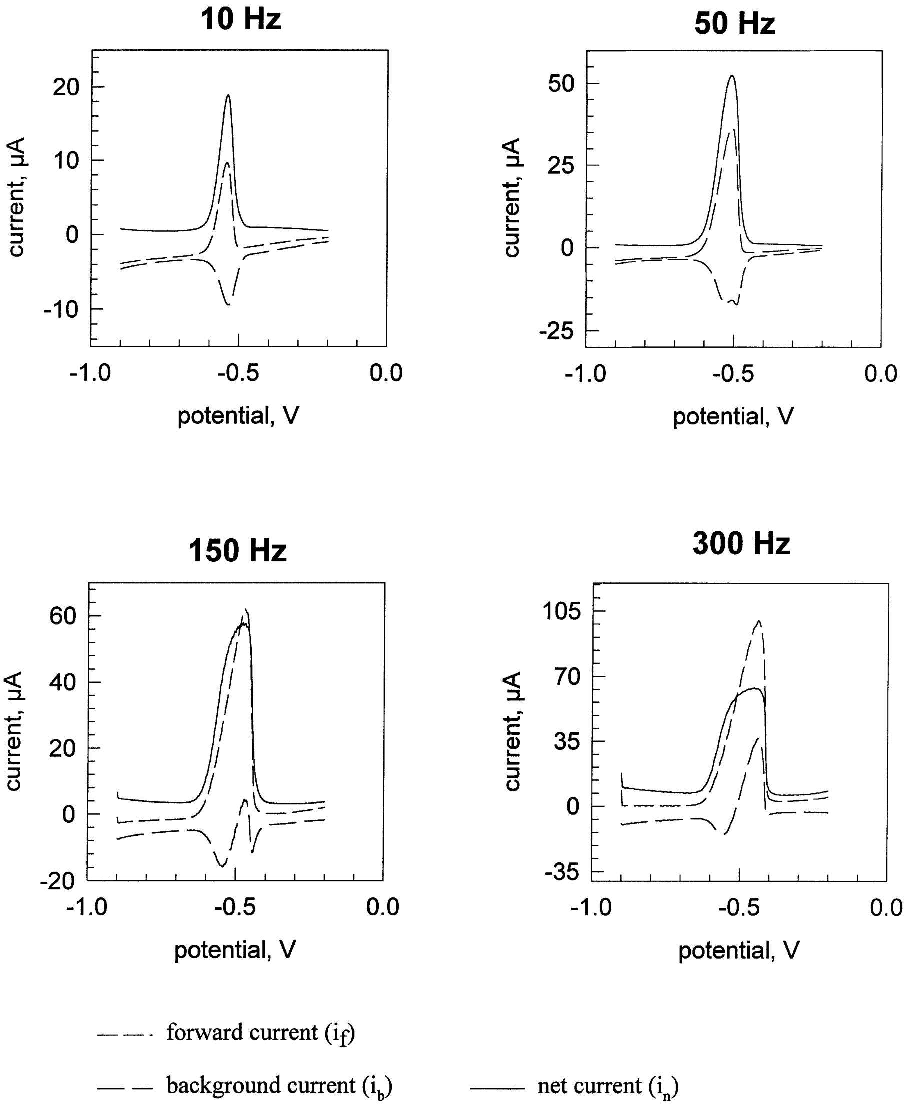

Fig. 3. Influence of the square wave frequency on the anodic peak current of lead. Lead concentration 0.05 mg/l, acetate buffer 30 mM, pH 4.7. SW parameters: amplitude 28 mV, step 3 mV, deposition time 5 min

Table 1. Experimental values of the dimensionless parameter Λ

Time, min	l, μm	log Λ
1	0.012	−2.95
2	0.020	−2.73
3	0.029	−2.60
4	0.033	−2.53
5	0.039	−2.46

D_r $1.25 \times 10^{-5}\,\mathrm{cm^2 s^{-1}}$; f 15 Hz.

step potential were optimised by the simplex method, a chemometric procedure for optimisation of two analytical parameters at the same time. The function to be optimised was the ratio between the peak current and the peak width at half peak-height of the signal of a solution containing 0.05 mg/l lead(II). From an analytical point of view this represents optimising the trade-off of sensitivity against resolution. Figure 2a shows the response profile of the system, varying the square wave amplitude and the step potential, determined by the movement of the simplex. From a theoretical point of view, the optimised parameters can be predicted as amplitude = 50/n mV and step potential = 10/n mV where n is the number of electrons [13] involved in the electron transfer process. A maximum response can be identified at an amplitude of 28 mV and a step potential of 3 mV. Therefore the optimised values are in accordance with the theoretical ones [25 mV and 5 mV for lead(II)]. Figure 2b shows the progress of the objective function value during the optimisation.

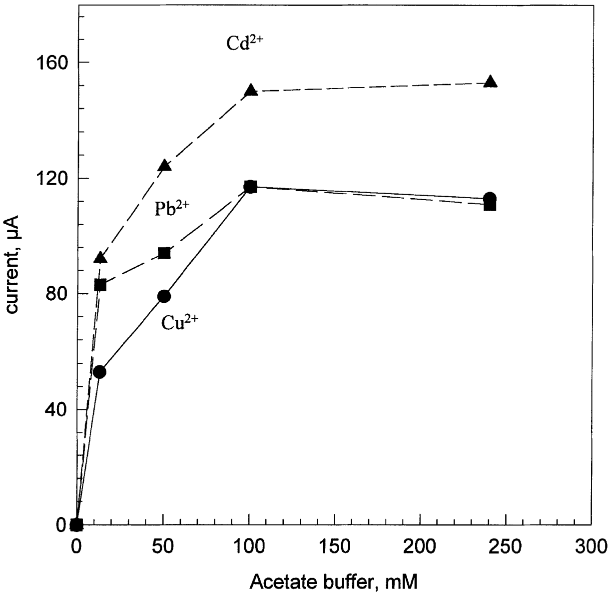

Fig. 4. Effect of the acetate buffer concentration on multielement analysis. Conditions: lead, cadmium, copper concentrations 0.05 mg/l; SW amplitude 28 mV, step 3 mV, frequency 15 Hz, deposition time 5 min

Considering the influence of scan frequency on peak current, it should be noted that on increasing the frequency there was a distortion of the shape and a decrease of the height of the peak (Fig. 3). This phenomenon has been described earlier for glassy-carbon electrodes and iridium electrodes [14]. In the case of glassy-carbon electrodes it can be explained by assuming that mercury is deposited in small drops and not in a continuous film. These drops can move on the electrode surface and on the insulating layer, reducing the cohesion of the layer. The optimum frequency was found to be 15 Hz.

The shape and the position of a square wave voltammogram obtained for a system of M^{n+}/M(Hg) with a thin film mercury electrode depends on the thickness of the mercury film and on the frequency [15]. The relationship between these two parameters can be expressed by using a non-dimensional parameter:

$$\Lambda = l(f/D_r)^{1/2}$$

where D_r is the diffusion coefficient of the species in the mercury phase [16], l is the film thickness and f the SW frequency.

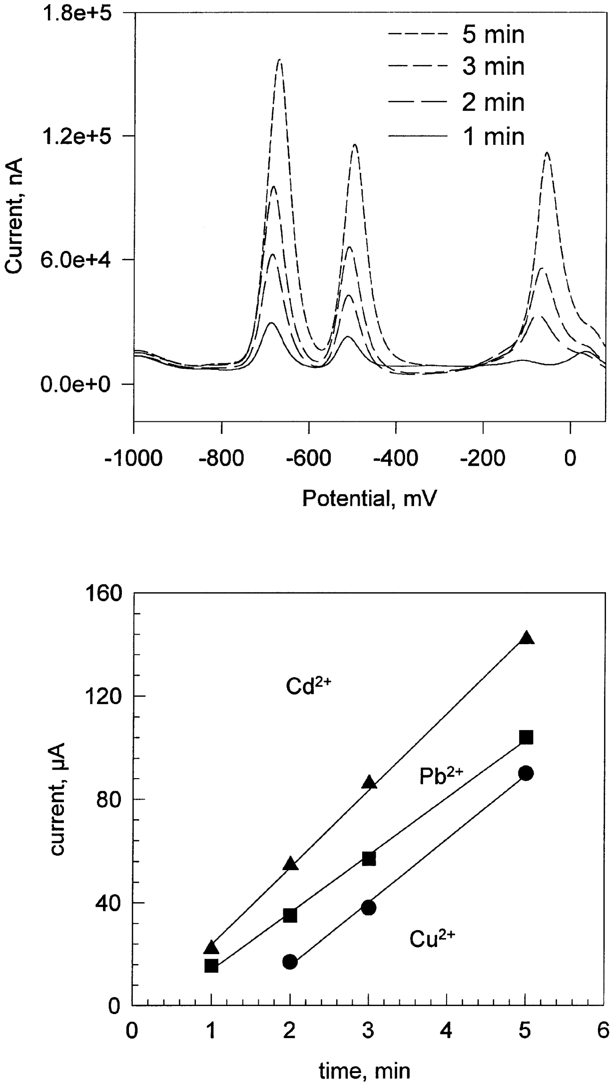

Fig. 5. Effect of deposition time on stripping current. Lead, cadmium, copper concentrations 0.05 mg/l; SW amplitude 28 mV, step 3 mV, frequency 15 Hz

It has been shown [16] that in the thin film region (where log Λ is much smaller than −1) the peak current depends on the amount of metal deposited on the mercury film; that is, for the same time and deposition potential conditions, and for the same conditions of mass transport (stirring), the peak current depends directly on the metal concentration in the solution, and is independent of the mercury film thickness. For a low frequency (15 Hz), Λ values have been calculated by varying the deposition time and then the film thickness. The experimental results show that in optimised working conditions, the log Λ value is always lower than −1, (Table 1).

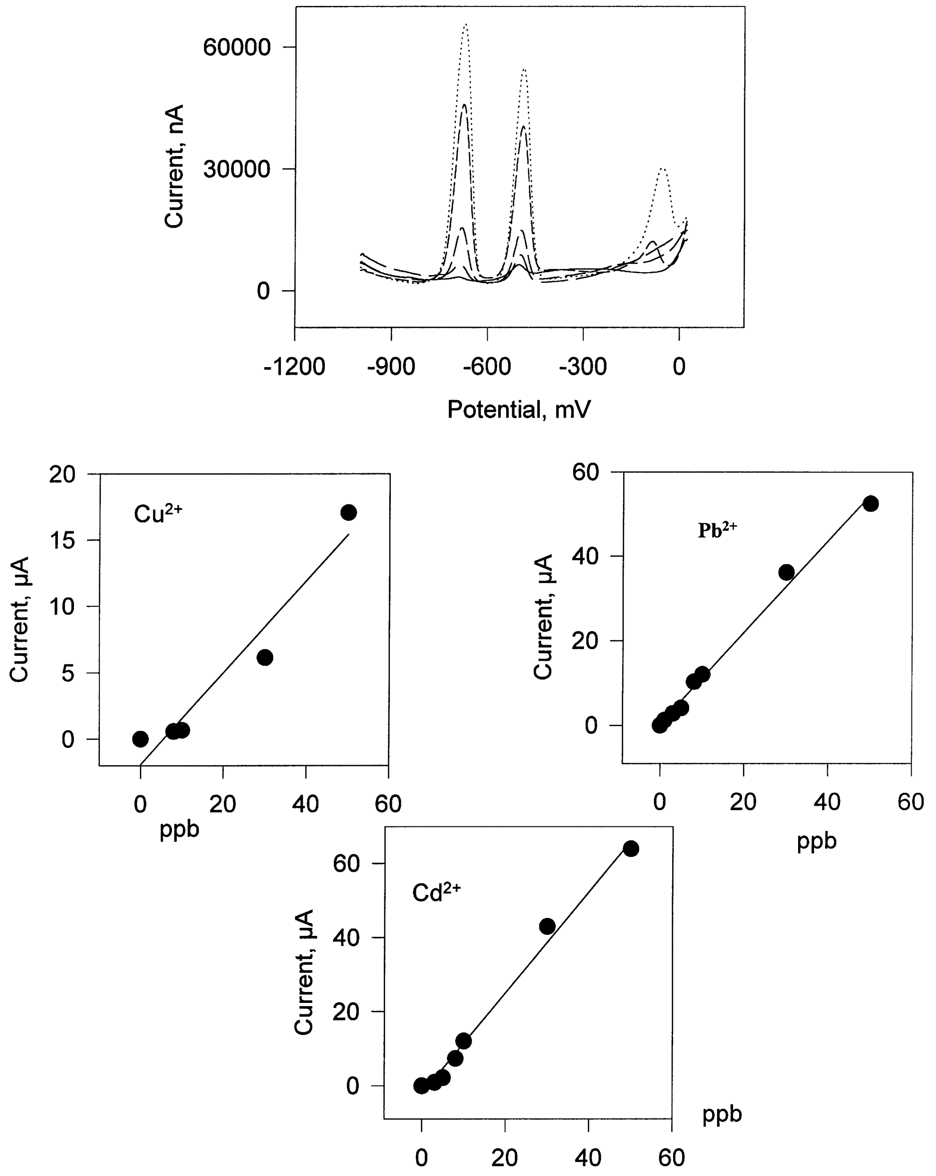

Fig. 6. Calibration curves in multielement analysis, after 3 min of deposition time. Other conditions as for Fig. 5

Heavy Metal Detection by Using SWASV

Acetate buffer was chosen as supporting electrolyte, as reported in the literature [2]. Increasing the ionic strength of the acetate buffer resulted in an increase in stripping current when analysing simultaneously for three different metals (copper, lead and cadmium). A current plateau was obtained for acetate concentrations higher than 100 mM (Fig. 4), but in control experiments the use of this buffer concentration led to a signal due to reagent impurities. The highest concentration of acetate buffer for which a signal due to impurities was not observed was 30 mM and this was chosen as the optimised value. The acetate buffer pH for the multielemental analysis was 4.7.

As expected for a stripping operation, the response was strongly dependent upon the concentration time. The longer the preconcentration period, the larger was the response (Fig. 5). Varying the preconcentration time for the metals resulted in a linear increase of the response [$r^2 = 0.991$ for Cu(II), $r^2 = 0.998$ for Cd(II) and Pb(II)], and a preconcentration time of 3 min can be considered a good compromise between sensitivity and analysis time.

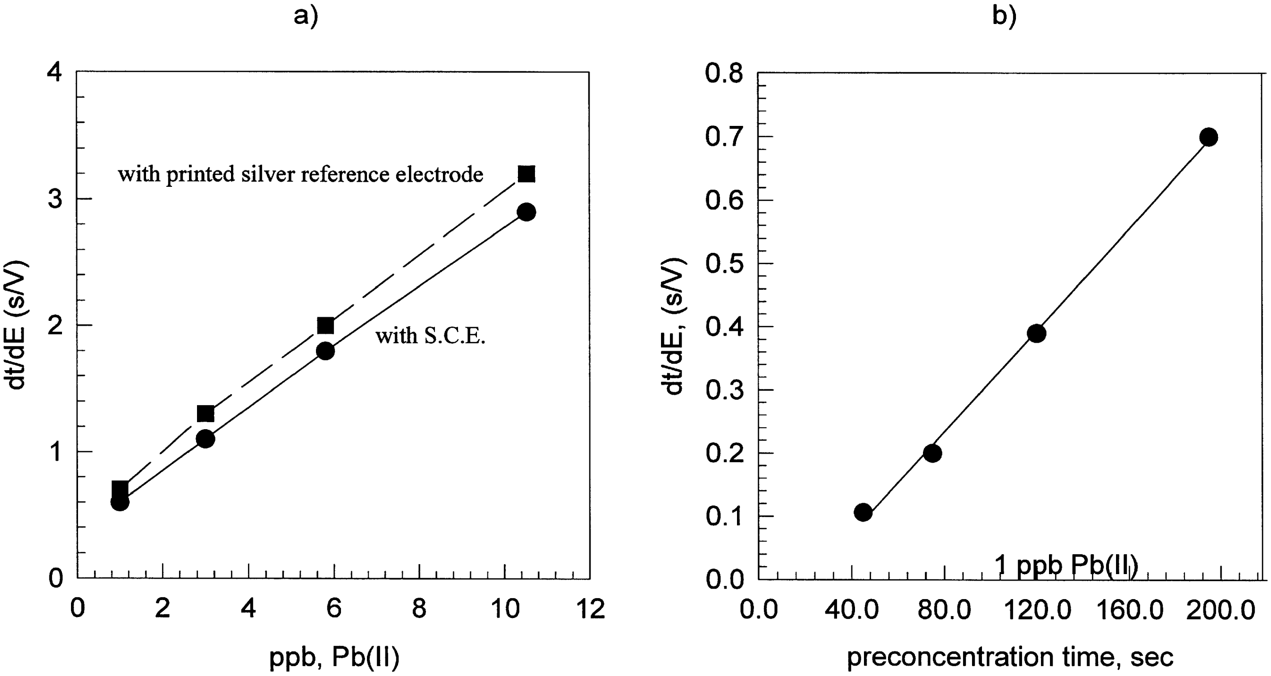

Fig. 7. Calibration curves for lead in PSA with the two-electrode screen-printed strip (■) and the single working electrode with a saturated calomel electrode (●) (a) and effect of deposition time on PSA response for 1 μg/l lead (b). Acetate buffer 30 mM, pH 4.7, KCl 10 mM

With the optimised parameters and 3 min of preconcentration, a multielemental calibration curve was obtained (Fig. 6). The detection limit, calculated as three times the signal to noise ratio at 10 ppb of the three metals, was 0.4 ppb for lead(II), 1 ppb for cadmium(II) and 8 ppb for copper(II). The relative standard deviation at 10 ppb of lead was 15%, with 3 different electrodes.

Application of Screen-Printed Strips and Potentiometric Stripping Analysis to the Detection of Heavy Metals

The strip was then employed in a different electrochemical procedure, potentiometric stripping analysis (PSA), reported to be suitable for measurements in non-deaerated solution [17]. In order to have a more practical device that excludes the use of a conventional reference electrode, the first experiments with PSA compared the performance of single working electrode strips and two-electrode strips.

The experimentally calculated carbon surface of the working electrode in the disposable two-electrode strip was 0.106 cm^2 and the mercury film thickness was 0.029 μm (the mercury deposition conditions were the same as previously optimised for SWASV). The solution for measurement was 10 mM potassium chloride in 30 mM acetate buffer, pH 4.7. The presence of potassium chloride was important to ensure stability of the printed silver reference electrode.

The two kinds of strip performed in a comparable manner (Fig. 7a) when employed to obtain lead calibration curves after 180 s preconcentration time. For this reason the two-electrode strip was used for subsequent experiments. Varying the metal [Pb(II)] preconcentration time gave a linear increase ($r^2 = 0.998$) of the response (Fig. 7b); a preconcentration time of 75 s could be used to achieve good sensitivity with short analysis time.

Figure 8 shows a multielemental [lead(II) and cadmium(II)] calibration curve obtained after 75 s preconcentration time, and application of −1.2 V deposition potential. The relative standard deviation of 9 repetitions using the same strip was 7%, with 5 ppb of lead(II), and was 14% for use of different strips. The detection limit, calculated as three times the signal to noise ratio at 5 ppb of the three metals, was 0.6 ppb for lead(II), 0.4 ppb for cadmium(II) and 0.8 ppb for copper(II).

Figure 9 shows a comparison between the performance of the thin-film mercury strip and a classical

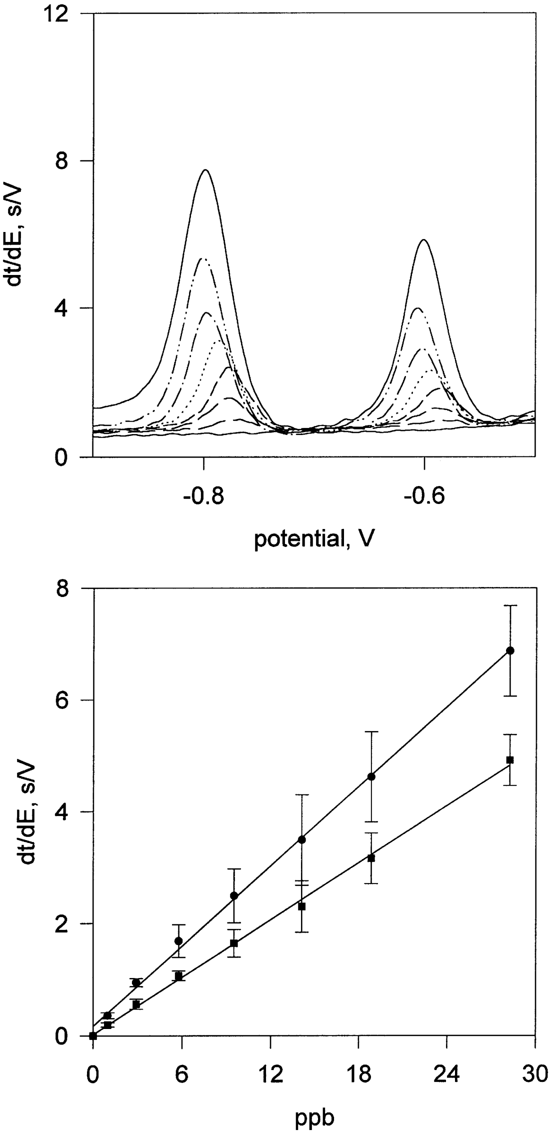

Fig. 8. Lead and cadmium calibration curves. Acetate buffer 30 mM, pH 4,7, KCl 10 mM. Deposition time 60 s, rest period 15 s

bulky hanging mercury-drop electrode (HMDE), from the analytical laboratory of the Department. The strip was employed in the potentiometric stripping analysis (75 s of preconcentration time) and the HMDE in the differential pulse voltammetry (DPV) mode (135 s preconcentration time and 10 min deaeration, scan rate 10 mV/s, amplitude 50 mV). Tap water samples were spiked with known amounts of lead and then analysed.

The correlation coefficient was $r = 0.97$, so there was significant correlation between the two methods.

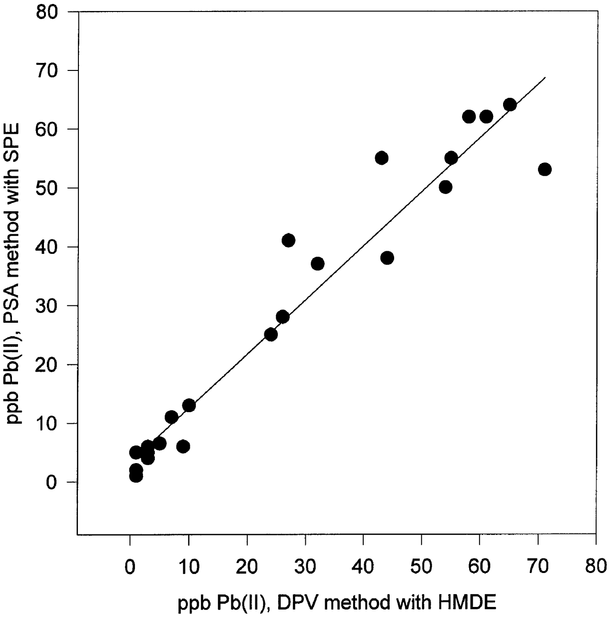

Fig. 9. Tap water samples: comparison between screen-printed strips and classical bulky HMDE

Conclusion

This work has shown that screen-printed electrodes are interesting devices for determination of heavy metals. They perform in a manner comparable with conventional electrodes for stripping analysis. Under our conditions the PSA technique is more sensitive and more rapid then SWASV. The screen-printed strips could be used with this electrochemical procedure, thus eliminating the need for deaeration. More work is required on aspects such as stirring and the mercury deposition step to improve the method for in-field analysis.

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