



Gold-based screen-printed sensor for detection of trace lead

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Abstract

The application of a novel gold-based screen-printed sensor to lead detection is described. The sensor consists of a screen-printed three electrode cell: a gold working electrode, a silver pseudo-reference electrode and a graphite counter electrode. It is used in combination with square wave anodic stripping voltammetry (SWASV). Sensor characterisation experiments as well as the optimisation of the analytical procedure are reported. The optimised parameters allow the detection of micrograms per litre of lead concentrations following short analysis time (detection limit $0.5 \mu\text{g l}^{-1}$ at 120 s deposition). Measurements of other metals such as copper, cadmium and mercury are reported.

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Keywords: Gold screen-printed electrodes; Square wave anodic stripping voltammetry; Lead; Cadmium; Copper; Mercury

1. Introduction

Stripping analysis is a powerful tool for measuring heavy metals in environmental, clinical and industrial samples [1–4]. For these applications mercury-based electrodes have been traditionally employed in order to obtain high reproducibility and sensitivity. However, the growing interest in decentralised analysis, coupled with environmental issues, requires new approaches involving mercury-free electrochemical sensors.

Gold electrodes of different forms (solid as well as gold-film electrodes) have been used to detect heavy metals such as lead, copper and mercury by stripping analysis [3,5–12].

Also some examples of gold-based screen-printed sensors have been already reported in literature; screen-printing technology is a particularly attractive technique for the mass production of cheap and disposable sensors [13,14]. Gold-coated carbon screen-printed electrodes were used for trace measurement of lead in connection with potentiometric stripping analysis [8]. In this work, the gold film was electrochemically preplated from a gold solution. The experiments employed a conventional Ag/AgCl reference electrode and a platinum wire auxiliary electrode. Detection limits of 0.1

and $0.6 \mu\text{g l}^{-1}$ lead were estimated following 20 and 4 min deposition, respectively. Disposable screen-printed carbon electrodes with a coating of Au were also used in potentiometric stripping analysis for the determination of trace quantities of inorganic as well as organic mercury compounds such as dimethylmercury [10]. A detection limit of $2.5 \mu\text{g l}^{-1}$ mercury for 4 min deposition was reported.

Gold-sputtered screen-printed electrodes were also recently used in lead detection by stripping voltammetry in a flow injection system [12]. The sensor allows underpotential analyte preconcentration and consists of a carbon–silver working electrode modified with a sputtered gold layer, silver–silver chloride reference electrode and a carbon–silver counter electrode. The optimised flow injection system allows detection limit of $0.8 \mu\text{g l}^{-1}$ of lead at 120 s deposition. Quantitative determination of lead was performed using square wave anodic stripping voltammetry (SWASV).

The present paper describes the application of a gold-based screen-printed sensor to lead detection. The working surface of these screen-printed electrodes is obtained by printing a thermoplastic ink which contains gold particles. Hence, to perform the analysis, no plating or sputtering steps are required. Lead is accumulated on the pretreated gold surface by applying a suitable reduction potential in an acidic medium (HCl 0.1 M). Thereafter, SWASV measurement is performed.

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Effects of various parameters (accumulation time, supporting electrolyte concentration, deposition potential) on reproducibility and sensitivity were studied. A detection limit of $0.5 \mu\text{g l}^{-1}$ at 120 s of accumulation time was obtained.

The performance of the sensor for the detection of other heavy metals such as cadmium, copper and mercury was evaluated and an application to real sample analysis was shown.

2. Experimental

2.1. Reagents

Suprapur grade hydrochloric acid was purchased from Merck (Italy). The water used for preparation of solutions was from a Milli-Q System (Millipore, Italy). Heavy metal stock solutions were prepared by diluting Cd(II), Pb(II), Cu(II) and Hg(II) standard solutions AAS grade (Fluka, Italy).

2.2. Screen-printing of electrodes

The electrochemical cells were planar three electrode strips, based on a gold working electrode, a carbon counter electrode and a silver pseudo-reference electrode (Fig. 1). The electrodes were screen-printed in house using a DEK 248 screen-printing machine (DEK, Weymouth, UK). Silver-based (Electrodag PF-410) and graphite-based (Electrodag 423 SS) polymeric inks were obtained from Acheson Italiana (Milan, Italy); the gold-based ink (R-464 (DPM-78)) was obtained from Ercon Inc. (MA, USA) and the insulating ink (Vinylfast 36-100) from Argon Italiana (Lodi, Italy). A polyester flexible film (Autostat CT5), obtained from Autotype (Milan, Italy), was used as the printing substrate. The silver ink was printed to obtain the conductive tracks and the silver pseudo-reference electrode. The carbon and gold

inks were then printed to obtain the auxiliary and working electrodes, respectively. After each step, silver, carbon and gold inks were cured at 120°C for 10 min. The insulating ink was finally used to define the working electrode surface ($\varnothing = 3 \text{ mm}$). A curing period of 20 min at 70°C was applied. Typical film thickness of screen-printed sensors range from 10 to $50 \mu\text{m}$. Many parameters affect this value (screen mesh, squeegee pressure and rate, inks, drying temperature, etc.). All of these parameters were optimised obtaining an analytical reproducibility of 7%.

2.3. Electrochemical analysis

All the experiments were carried out using a PalmSens portable electrochemical analyser (Palmsens BV, Houten, The Netherlands). Square wave voltammetry conditions were:

- Cd(II), Pb(II) and Cu(II) analysis: conditioning potential (E_{cond}) $+0.5 \text{ V}$ for 30 s, deposition potential (E_{dep}) -0.5 V for 120 s, equilibration time (t_{eq}) 30 s, SW amplitude (E_{amp}) 28 mV, step potential (E_{step}) 3 mV, frequency (f) 15 Hz.
- Hg(II): conditioning potential (E_{cond}) $+0.7 \text{ V}$ for 30 s, deposition potential (E_{dep}) $+0.2 \text{ V}$ for 120 s, equilibration time (t_{eq}) 30 s, SW amplitude (E_{amp}) 28 mV, step potential (E_{step}) 3 mV, frequency (f) 15 Hz.

SW parameters E_{amp} , E_{step} , f were chosen in accordance to [12–13].

Each sensor was pretreated, before using for the first time, by applying five cycles of cyclic voltammetry (CV) using the following conditions: potential range $0/+0.7 \text{ V}$, scan rate 50 mV/s , step potential 2.44 mV . This step is necessary to obtain a stable baseline.

HCl 0.1 M was used as supporting electrolyte.

All measurements were performed without removing oxygen from the solution.

The measurements were performed immersing the sensor in 5.0 ml of solution; stirring conditions (1500 rpm) were used during the conditioning and the accumulation steps, whereas the square wave scan was performed in quiescent solution.

Spiked river water samples were analysed as follows: 0.5 ml of sample was added to 4.45 ml of deionised water. To this solution, $50 \mu\text{l}$ of HCl 10 M was added. Unspiked samples were only acidified with concentrated HCl, obtaining a final concentration of 0.1 M HCl. The same samples were also analysed using a classical mercury film electrode; experimental conditions were reported in [13].

3. Results and discussion

3.1. Characterisation of gold screen-printed electrodes

The use of gold electrodes in stripping analysis is limited mainly because of a rather low hydrogen overvoltage, the

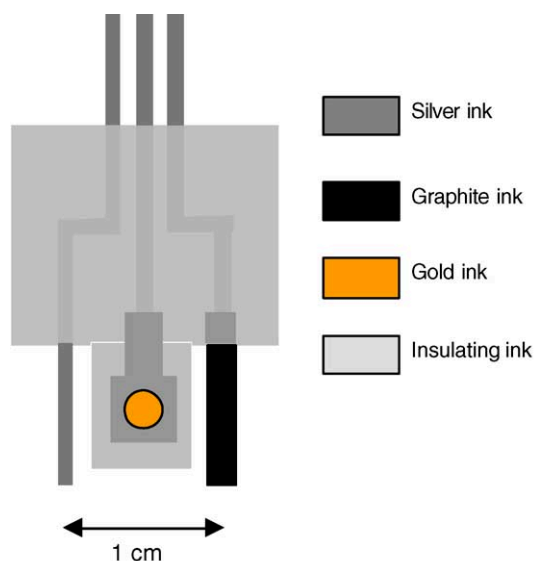


Fig. 1. Scheme of a screen-printed gold sensor.

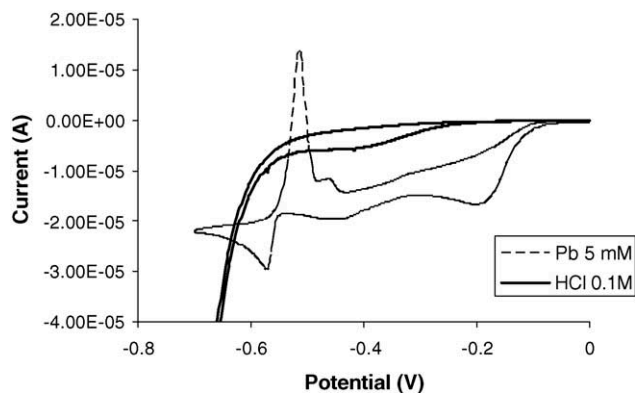


Fig. 2. Cyclic voltammograms of gold screen-printed sensors in HCl 0.1 M with (---) and without (—) 5 mM of Pb(II). Parameters used are: Potential range: 0/–0.7 V, scan rate 10 mV s⁻¹.

formation of oxide layers or the dissolution of gold at potentials more positive than +0.9/+1 V versus Ag/AgCl [3]. To characterise the gold screen-printed sensor for Pb(II) deposition, some preliminary experiments using CV in HCl 0.1 M were performed. Evolution of hydrogen starts at about –0.7 V versus Ag pseudo-reference electrode. Dissolution of gold starts at +0.9 V. In Fig. 2 the cyclic voltammograms of the gold screen-printed sensor, with and without 5 mM Pb(II), are reported. CV of 5 mM Pb(II) yields a pair of peaks corresponding to bulk deposition and bulk stripping at –570 and –512 mV, respectively, and a well shaped cathodic peak at –200 mV corresponding to the underpotential deposition (UPD) process [12]. UPD is the electrochemical deposition of foreign metals onto substrates at potentials positive relative to the reversible Nernst potential for bulk deposition [12,17]. The formation of an overlayer before the bulk deposition potential is possible because the adatom-substrate bond is thermodynamically more favourable to the adatom–adatom bond. For this reason, UPD is usually limited to a monolayer in extent, and the resulting structure of the UPD adlayer is strongly influenced by the substrate. A typical monolayer property is the saturation at higher concentration level [12,15–18].

To analyse Pb(II) in the $\mu\text{g l}^{-1}$ concentration range, square wave anodic stripping voltammetry was used. A working potential window of –0.5 V to +0.2 V was chosen. In Fig. 3, SWAS voltammograms of Pb(II) at different concentrations (0–30 $\mu\text{g l}^{-1}$) are reported. Good peak shapes were obtained, with the maximum of the stripping peak located at –240 mV.

3.2. Optimisation

3.2.1. Medium concentration

Hydrochloric acid was used as supporting electrolyte not only because is widely used for the electrochemical detection of heavy metals, also because a constant concentration of chloride ions in the supporting electrolyte medium is needed in order to stabilise the screen-printed Ag pseudo-reference electrode.

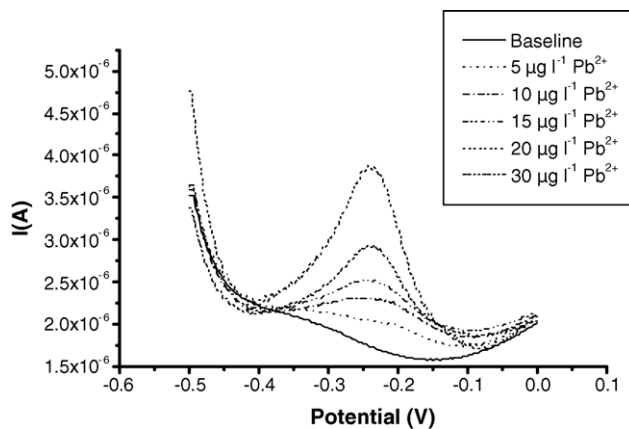


Fig. 3. SWASV scans at different concentrations of Pb(II), in HCl 0.1 M and using the following optimised conditions: E_{cond} : +0.5 V for 30 s, E_{dep} : –0.5 V for 120 s, t_{eq} : 15 s; E_{amp} : 28 mV, E_{step} : 3 mV, f : 15 Hz.

The influence of HCl concentration on the sensitivity of the measurements was evaluated; at this purpose, measurements of 50 $\mu\text{g l}^{-1}$ of Pb(II) at different HCl concentrations were performed, using the following parameters: E_{cond} : +0.2 V for 30 s, E_{dep} : –0.5 V for 120 s, t_{eq} : 15 s; for SWASV: E_{amp} : 28 mV, E_{step} : 3 mV, f : 15 Hz. The results are shown in Fig. 4. As it can be seen, high concentration levels of HCl gave rise to a decrease of the sensitivity. This phenomenon was already reported in literature [6,12,17,19], and explained assuming that chloride ions reduce the bond strength between metal adatom and the substrate [6,12,17]. Thus, a concentration of HCl 0.1 M was chosen for further experiments.

3.2.2. Deposition time and potential

The influence of the deposition time on the Pb(II) SW stripping peak current intensities is shown in Fig. 5. The accumulation time onto the gold electrode surface was varied from 0 to 420 s; investigation was made with 10 $\mu\text{g l}^{-1}$ of Pb(II). As expected, the peak current increases with increasing accumulation time; however a plateau was reached after 300 s, coupled with a large error bar (R.S.D.% = 25, n = 5). A R.S.D. higher than 10% was obtained also for time values in the range 160–300 s. Thus, 120 s as accumulation time was

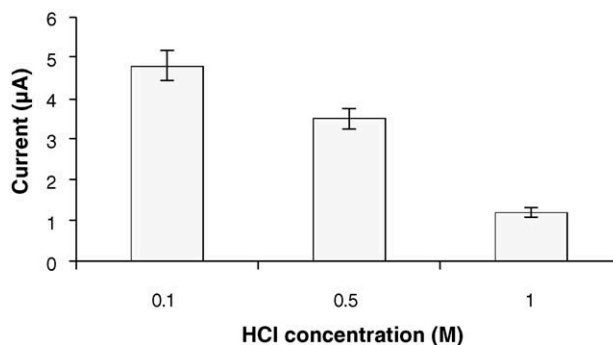


Fig. 4. HCl concentration influence on the sensitivity of measurements of 50 $\mu\text{g l}^{-1}$ of Pb(II). Experimental conditions as in Fig. 3.

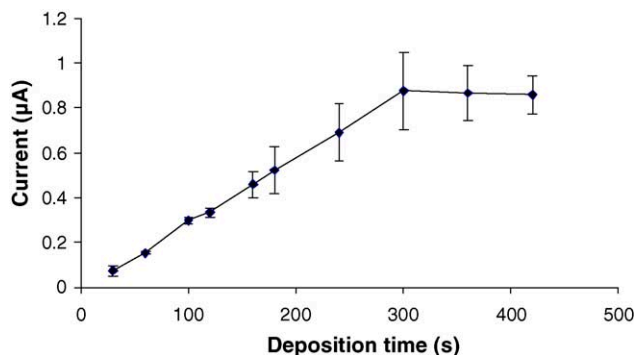


Fig. 5. Accumulation time optimisation. Response to Pb (II) $10 \mu\text{g l}^{-1}$. Parameters used: E_{cond} : +0.5 V for 30 s, E_{dep} : -0.5 V at variable times, t_{eq} : 15 s; E_{amp} : 28 mV, E_{step} : 3 mV, f: 15 Hz.

chosen as a good compromise between length of analysis, sensitivity and reproducibility.

A similar behaviour was also reported in [12], where a plateau was observed after 120 s deposition; the authors referred that beyond 120 s the peak shape became distorted and broadened, as a result of a change in gold characteristic; they explained the slight decrease in peak current after 120 s deposition considering the formation of a more compact Pb^0 film on gold surface and the possibility of an additional affect on the film which is a result of active sites of different energies.

The effect of deposition potential on stripping current was evaluated in the range -0.7 to 0.4 V. The higher current value was obtained at -0.5 V, and this potential value was chosen for further experiments.

3.3. Pb(II) analysis

The calibration plot for Pb(II) was found to be linear over the range 0–50 $\mu\text{g l}^{-1}$. Analytical parameters characterising the sensor performances are reported in Table 1. As indicated in [8], to increase the linearity range a shorter deposition time can be used. The detection limit (estimated as the concentration corresponding to the three times the S.D. of the blank divided by the slope of the calibration curve) for Pb(II) was 0.5 $\mu\text{g l}^{-1}$ at 120 s deposition.

The reproducibility of a single sensor was verified with 15 repetitive measurements of 20 $\mu\text{g l}^{-1}$ Pb(II). The relative standard deviation was 3%; after 50 repetitive measurements a 10% decrease in sensitivity was observed. The reproducibility among different sensors was also verified: calibration

curves with five different sensors were performed for Pb(II), and a R.S.D.% = 7 of calibration slopes (sensitivity) was obtained.

3.4. Analysis of other heavy metals

In Fig. 6a and b, voltammograms of the determination of Cd(II) and Cu(II) in the concentration range 0–50 $\mu\text{g l}^{-1}$ are reported. Good peak shapes were obtained for Cu(II) (Fig. 6b), whereas the sensitivity against Cd(II) detection is much more lower (Fig. 6a). Voltammograms show also that peak potential for Cd(II) (-0.18 V) and Pb(II) (-0.24 V) are quite close, indicating some overlap between the Pb(II) response and the Cd(II) peak. However, as indicated also in [8,12], the intensity of Cd(II) peaks versus those of Pb(II), is significantly smaller. Some authors [8,12] reported that cadmium level in clinical [8] as well as in some environmental samples such as drinking and tap water [12], is significantly lower than that of lead, thus no major interference in the determination of lead in these samples is expected.

Peak potential of Cu(II) is at +0.25 V versus Ag pseudo-reference electrode. Peak location and current of Pb(II) are unaffected by the presence of Cu(II) in the concentration range considered.

Other analytical parameters characterising the sensor performances for Cd(II) and Cu(II) in standard solution (HCl 0.1 M) are reported in Table 1. The data reported in the table are referred to separate analysis of each metal. In Fig. 7 are reported measurements performed in solution containing Cd(II), Pb(II) and Cu(II) under various concentration ranges.

Gold-based screen-printed electrodes were also applied to detection of Hg(II). In this case, a deposition potential of +0.2 V was applied, whereas other SW parameters used were the same as reported above. Voltammograms related to the Hg(II) calibration curve are shown in Fig. 6c. In this case a linearity for the range 0–100 $\mu\text{g l}^{-1}$ was observed ($y = 0.011x$, $r^2 = 0.9994$) with a R.S.D.% of 4 ($n = 3$ different electrodes), and a detection limit of 0.9 $\mu\text{g l}^{-1}$ at 120 s deposition time was calculated.

The presence of Hg(II) decreases the lead response, by modification of the electrode gold surface.

3.5. Analytical application

In order to evaluate the performance of the gold sensor, three replicate determinations of Pb(II) and Cu(II) in a spiked and unspiked river water sample were carried out using the

Table 1

Gold-based screen-printed sensor: analytical results for the determination of Cd(II), Pb(II), Cu(II) and Hg(II)

	Cd(II)	Pb(II)	Cu(II)	Hg(II)
Linear range ($\mu\text{g l}^{-1}$)	0–50	0–50	0–50	0–100
Sensitivity ($\mu\text{A}/\mu\text{g l}^{-1}$)	9.8×10^{-3}	0.08	3.4×10^{-2}	1.1×10^{-2}
Detection limit ($\mu\text{g l}^{-1}$)	1.4	0.5	2.0	0.9
R.S.D. (%) ($n = 5$)	14	7	12	4

Measurements were performed in HCl 0.1 M as supporting electrolyte. %R.S.D. was calculated performing calibration curves with five different sensors.

Table 2
River water samples spiked and unspiked with Pb(II) and Cu(II)

Metals	Original concentration ($\mu\text{g l}^{-1}$)	Added ($\mu\text{g l}^{-1}$)	Mercury film electrode ($\mu\text{g l}^{-1}$)	Gold-based screen-printed sensor ($\mu\text{g l}^{-1}$)
Pb(II)	ND	100	99 ± 2	93 ± 3
Cu(II)	ND	110	110 ± 2	97 ± 3

Samples were diluted 1:10 before the analysis and acidified to get HCl 0.1 M as final concentration. N.D. = not detected.

standard addition method. Deposition time and potential, as well as SWASV parameters were the same as used previously. Table 2 shows the results obtained on river water samples as well as the comparison with classical mercury film electrode. These data demonstrate that the proposed sensor has promise for determination of Pb(II) and Cu(II) in real samples such as water samples.

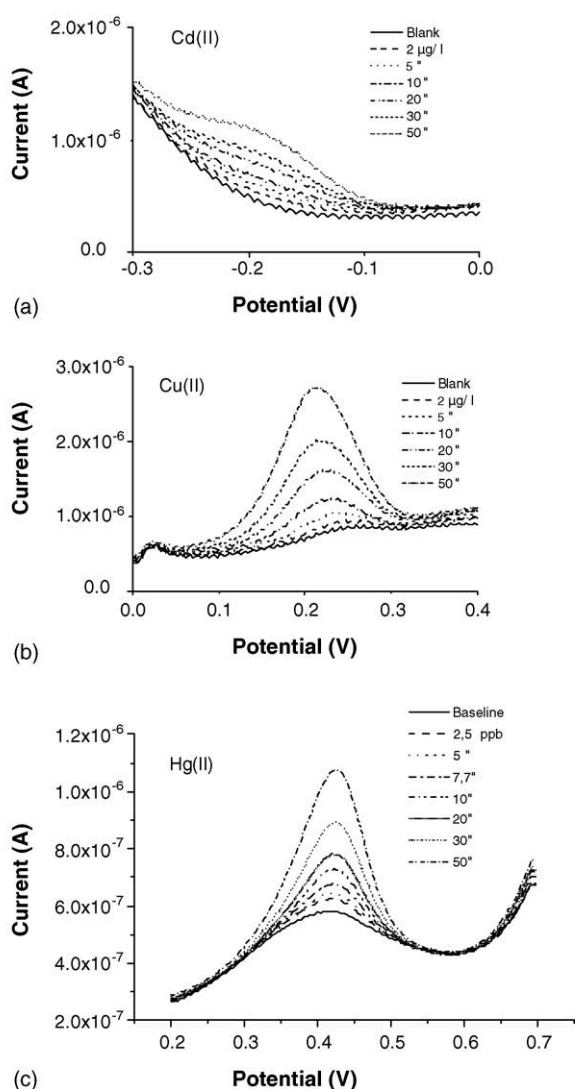


Fig. 6. SWASV scans related to calibration curves performed for (a) Cd(II) and (b) Cu(II), in HCl 0.1 M using the following optimised conditions: E_{cond} : +0.5 V for 30 s, E_{dep} : -0.5 V for 120 s, t_{eq} : 15 s; E_{amp} : 28 mV, E_{step} : 3 mV, f : 15 Hz. (c) SWASV scans related to calibration curve performed for Hg(II), in HCl 0.1 M and using the following optimised conditions: E_{cond} : +0.7 V for 30 s, E_{dep} : +0.2 V for 120 s, t_{eq} : 15 s; E_{amp} : 28 mV, E_{step} : 3 mV, f : 15 Hz.

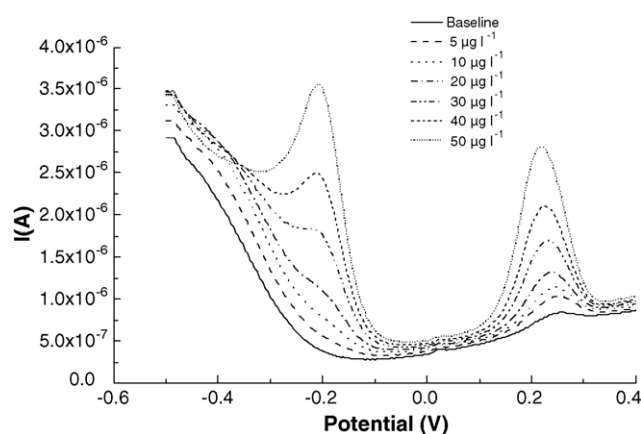


Fig. 7. SWASV scans performed in solution containing Cd(II), Pb(II) and Cu(II) at different concentration. The parameters are reported in Fig. 6.

4. Conclusion

The proposed gold-based screen-printed electrodes are suitable electrochemical devices for heavy metal detection. Analytical results show that the proposed sensor was able to detect $\mu\text{g l}^{-1}$ of Pb(II) with good sensitivity and reproducibility, even if the linearity range is not wide, in comparison with what found with mercury-based screen-printed sensors [13]. However, the reported data indicate that the proposed gold-based sensor, choosing the adequate experimental conditions, holds great promise for decentralised testing for lead using a “mercury-free” sensing surface.

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Biographies

Serena Laschi graduated in Chemistry at the University of Florence in 1998. She received the PhD in Environmental Sciences from the same university in 2002. At present she is has a PostDoc position at the Department of Chemistry of The University of Florence. Her current interests involve the development of screen-printed sensors and biosensors applied to environmental, clinical and food analysis.

Ilaria Palchetti graduated in Chemistry and Pharmaceutical Technology at the University of Florence in 1994. She received the PhD in Environmental Chemistry from the same University in 1999. At present she is an Assistant Professor at the Department of Chemistry, Faculty of Science, of the University of Florence. Her current interest involve the development of electrochemical sensors and biosensors mainly for environmental application.

Prof. Marco Mascini is a full Professor of Analytical Chemistry at the Faculty of Sciences in the University of Florence. His expertise includes preparation and evaluation of biosensors based on the coupling of electrochemical, optical and piezoelectric sensors with DNA, enzymes, antibodies, bacteria, whole tissues of animals and vegetables. He has been involved in the application of biosensors for solving analytical problems in clinical chemistry, experimental medicine, food chemistry and environmental analysis. He also is an expert in analytical procedures suitable for use with biosensor devices, i.e. flow injection analysis, flow systems, membrane technology, microdialysis, miniaturisation of electrodes and probes and immobilization of enzymes and proteins on several supports. Professor Mascini is author of more than 300 papers on sensors and biosensors development and application in the last 20 years and sits on the editorial board of several international journals such as *Analytical Letters*, *Biosensors & Bioelectronics*, *Talanta*, etc.