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Miniaturized voltammetric stripping on screen printed gold electrodes for field determination of copper in atmospheric deposition

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ABSTRACT

The applicability of commercial screen-printed gold electrodes (SPGEs) connected to a portable potentiostat and a laptop has been explored to optimize a new square wave anodic stripping voltammetric method for on-site determination of soluble Cu(II) in atmospheric deposition samples taken around an industrial complex. Electrode conditioning procedures, chemical and instrumental variables have been optimized to develop a reliable method capable of measuring dissolved copper with a detection limit of 3.7 ng mL^{-1}, useful for pollution monitoring or screening purposes. The proposed method was tested with the SLRS-5 River Water for Trace Metals (recoveries 109.9–113.1%) and the SPS-SW2 Batch 121 Elements in Surface Waters (recoveries 93.2–97.6%). The method was applied to soluble Cu(II) measurement in liquid samples taken by a total atmospheric deposition collector modified with a quartz filter for soluble and insoluble elemental speciation. The voltammetric measurements on field samples were tested in the lab by a reference ICP-MS method, with good agreement. The proposed method proved capability for field operation during a two weeks monitoring campaign.

1. Introduction

Heavy metal monitoring in atmospheric deposition provides key information to estimate anthropogenic impact on the atmospheric environment composition, and potential effects of precipitating material to the soil–plant–water system. Elemental profiles in atmospheric deposition are usually measured in air quality networks on samples collected and transferred to centralized laboratories for applying ICP-OES or ICP-MS protocols. The European EMEP network [1], the US NADP [2], and the EN 15841 standard methodologies [3] are good examples of this approach. While these are qualified strategies for standardized heavy metal monitoring, new approaches based on low cost, portable and miniaturized equipments for decentralized, on-site or even in situ measurements are desirable to obtain a closer and more flexible view of atmospheric deposition composition, with a better spatial and temporal data resolution. This is particularly appropriate when monitoring metallic pollutants deposition around industrial areas, where pollution patterns are highly dynamic, meteorological and production variability being the most relevant variability factors.

Voltammetric techniques are particularly well suited for field applications due to the availability of simple, conveniently sized, low cost and easy to operate instrumentation [4,5]. A variety of field-oriented analytical protocols and devices have been described in the literature including water [6,7], soil extracts [8] and biomonitor samples [9]. The advent of screen-printed electrodes coupled with miniaturized potentiostats has opened new possibilities that are being intensively explored in the recent years [10].

In this work, we present a new voltammetric method based on gold screen-printed electrodes (SPGEs) for on-site copper monitoring in speciated atmospheric deposition, with application to environmental assessment around a copper smelter. The environmental impact of copper, although tempered by their low toxicity, is powered by the magnitude of mineral extraction, the diversity of industrial processes and the wide dissemination of its products. Copper in atmospheric particulates is a tracer element for traffic [11], burning oil [12], pigment production [13] and obviously copper smelters [12,14,15]. Anodic stripping voltammetry of copper on mercury electrodes is widely described in the literature [16–18] including its determination in samples of atmospheric particulate matter [19]. Gold electrodes are increasingly being

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considered for replacement of mercury in many voltammetric applications, including copper analysis, due to environmental concern. A few publications have described voltammetric analysis of copper on screen-printed carbon [20], and gold electrodes. Laschi et al. (2006) [21] briefly described the analytical behavior of Cu(II) on gold-based screen-printed electrode (SPE) in a publication devoted to the assay of Pb(II) in river water samples, whereas Meucci et al. (2009) [22] used a graphite-based SPE modified with mercury for the determination of Cu(II) in fish samples, using square wave anodic stripping voltammetry. No reference has been found about on-site heavy metal monitoring in atmospheric deposition by screen-printed voltammetric sensors, so we explore this approach here for rapid and reliable pollution assessment in the field, taking copper as a model analyte.

2. Experimental

2.1. Reagents

All chemicals used for the preparation of stock and standard solutions were of analytical grade. 1000 mg L^{-1} stock solutions of Cu(II) and In(III) were supplied by Scharlau (Barcelona, Spain) and Panreac (Barcelona, Spain), respectively. Working solutions were prepared by dilution with ultrapure water obtained from a Wasserlab Ultramatic (Navarra de Tratamiento del Agua S.L., Pamplona, Spain) system. Dilute standards and real samples were adjusted to pH 2 with sub-boiled HNO_3 obtained from a quartz sub-boiling system (Kürner, Rosenheim, Germany). Dilute standards for calibration were prepared directly into the voltammetric cell. Hiperpur grade HCl purchased from Panreac (Barcelona, Spain) was used for the preparation of supporting electrolyte. Glassware and polyethylene containers were thoroughly conditioned for trace analysis i.e. soaked in hot nitric acid at 10% for 48 h, rinsed with ultrapure water, dried in stove and kept in hermetic plastic bags. Methacrylate voltammetric cells were similarly immersed in nitric acid at 10% for 24 h, rinsed in ultrapure water and air dried before use.

2.2. Reference materials and real samples

Certified Reference Materials SPS-SW2 Batch 121 Elements in Surface Waters (Spectrapure Standards, Norway) and SLRS-5 River Water for Trace Metals (Institute for National Measurement Standards, Canada), were used for accuracy testing.

Weekly, liquid atmospheric deposition samples were collected from several air quality monitoring stations in the vicinity of a copper smelter located at Puchuncaví, Chile. The samples were obtained by a normalized homemade total atmospheric deposition polyethylene collectors (as described e.g. in European Norm EN 15841:2009), consisting in an upper funnel connected to a lower bottle. The collectors were modified with an internal quartz filter, placed between the funnel and the bottle for separating the liquid and solid phases of the atmospheric deposition. An untreated aliquot of the liquid phase was analyzed on-site for copper content by SWASV. The rest of the sample was acidified with HNO_3 to pH 2, transferred to the lab and stored at 4 °C until analysis by ICP-MS.

2.3. Instrumentation

Lab based square wave voltammetric measurements for method development were performed on a CH Instrument model 660 D potentiostat/galvanostat (Austin, Texas, USA) interfaced with a laptop and controlled by CHI660D PC software.

Field voltammetric measurements were taken by a computerized hand-held, battery-powered μ Stat 200 DropSens potentiostat/galvanostat (DropSens, Oviedo, Spain) interfaced with a laptop. The whole analytical procedure is controlled by the DropSens PC software, including stirring of the samples by a battery operated stirrer.

SPGEs strips were purchased from Ecobioservices (Firenze, Italy). They are designed in a three electrode configuration printed on the same platform. Working electrode (Ø 3 mm), counter electrode and pseudo-reference electrode are made of gold, graphite and silver, respectively. An insulating layer serves to delimit the working area and silver electric contacts. A macroporous structure similar to that described by Metters et al. [23] was observed in an inspection of the working gold electrode with SEM. A specific connector allows the direct connection of the electrochemical strip to the potentiostat. A methacrylate voltammetric cell (DropSens, Oviedo, Spain) was used to perform the analysis. It is especially suitable for immersing SPEs in 5–10 mL samples. The screen-printed strip is immersed in the solution, leaving the electrical connections outside. Deaireation process and standard additions are able to perform in this configuration.

The portable voltammetric equipment composed by the analytical cell and stirrer, the screen printed electrodes, the handheld DropSens potentiostat and the laptop is easily transportable in the laptop bag, and can be deployed in the field within less than 30 min after arriving to the sampling point.

A standard ICP-MS protocol for Cu(II) determination was applied on a PerkinElmer ELAN 9000 equipment (Waltham, MA, USA) for accuracy check of the electrochemical results. The instrument conditions and measurement parameters used in the analytical determination were 1000 W RF power, a carrier gas flow rate of 1 L min^{-1}, lens voltage of 7.25 V, a wash time of 35 s and three replicates for each sample. Quantification of Cu(II) was performed by an internal standard protocol with In(III).

2.4. Experimental procedure

The electrochemical determination of Cu(II) in atmospheric deposition samples was carried out without any pretreatment, using Square-Wave Anodic Stripping Voltammetry (SWASV) on SPGEs. 10 mL of sample was placed in the cell and HCl of a concentration of 0.1 M was added. No sample deaireation was needed. Optimal conditions for SWASV determination were: preconditioning potential between runs $+0.5$ V for 30 s, deposition potential -0.4 V for 120 s, deposition time 120 s, stirring speed 960 rpm, equilibration time 10 s, square wave amplitude 28 mV, step height 5 mV and frequency 15 Hz. Initial and final potentials of the stripping run were 0.0 and $+0.7$ V respectively. Peak potential for Cu(II) was approximately 0.2 V and quantification was performed by external calibration.

3. Results and discussion

3.1. Voltammetric method optimization

Electrochemical conditioning of the surface of SPGEs was found essential to get a good baseline and a stable voltammetric stripping response of copper. The conditioning of fresh electrodes was initially performed according to the procedure described by Laschi et al. [21] for Pb(II) determination on SPGEs, by applying 5 cycles by cyclic voltammetry (CV), using the following conditions: medium 0.1 M HCl, potential range between 0.0 and $+0.7$ V and scan rate 50 mV s^{-1}. However, this treatment revealed insufficient for obtaining a stable response when analyzing Cu(II) in standard solutions. It was found necessary to perform some voltammetric stripping test runs (about 10) to ensure a proper and stable Cu(II) signal. After this conditioning, the electrode response remained stable for about 50 analytical runs, and then a new electrode was needed.

The influence of the step potential on Cu(II) voltammetric stripping signals was studied in the range from 1 to 8 mV, by assaying a 50 ng mL^{-1} standard solution. From the experimental results, there was an increase in the value of peak current (Ip) between 1 and 5 mV and a further decrease from 5 to 8 mV, coupled with a progressive loss of signal resolution by peak broadening. These results agree with the theoretical predictions of the square wave voltammetric technique [24]. From this study, 5 mV step potential was chosen as optimal value. Modulation amplitude influence was investigated in the range from 5 to 35 mV. The experimental results showed an increase in peak current with square-wave amplitude, in agreement with theoretical predictions of the technique, but also a broadening of the peak occurs and consequently a loss of resolution that eventually produces a stabilization of the peak intensity. The maximum value of Ip was reached for values close to 28 mV amplitude, so this value was chosen as optimal. Square wave frequency was varied between 5 and 20 Hz to inspect the effect on the copper voltammetric signal. Increasing peak current were observed up to 15 Hz, higher frequencies produced lower peak currents due to electric noise and signal distortion. Finally, 15 Hz was selected as the optimum frequency for further studies.

The stirring speed during the deposition step was inspected in the range 480–1280 rpm. The experimental results (Fig. 1) showed that the increase in stirring speed produces an increase in the analytical signal up to the point that turbulences start to disturb the signals. 960 rpm was chosen as the optimum stirring speed. The effect of deposition potential was evaluated in the range from −0.7 to 0.0 V (Fig. 2). The highest voltammetric signal was obtained with a deposition potential of −0.4 V, which was chosen as optimal value.

Using the optimized parameter values, the influence of deposition time on the peak currents was finally tested in the range from 0 to 240 s, on a 50 ng mL^{-1} Cu(II) standard solution. According to the results (Fig. 3), it can be concluded that the optimum deposition time is 120 s for this concentration level.

3.2. Calibration data

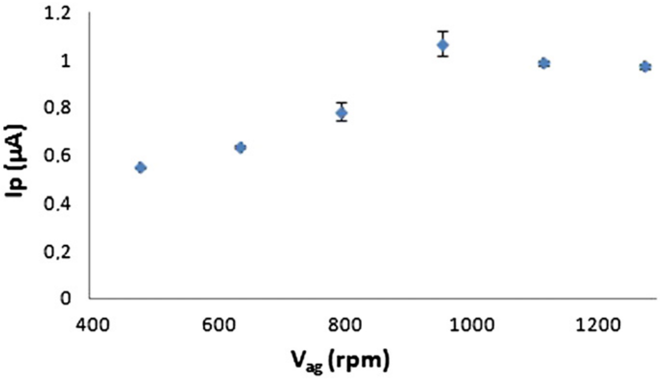

Fig. 1. Influence of stirring speed in the SWASV method. Response to Cu(II) 50 ng mL^{-1} in 0.1 M HCl at the screen printed gold electrode. Square wave voltammetric stripping measurements performed with a frequency of 15 Hz, step potential 5 mV, amplitude 28 mV, deposition potential −0.5 V and deposition time 30 s.

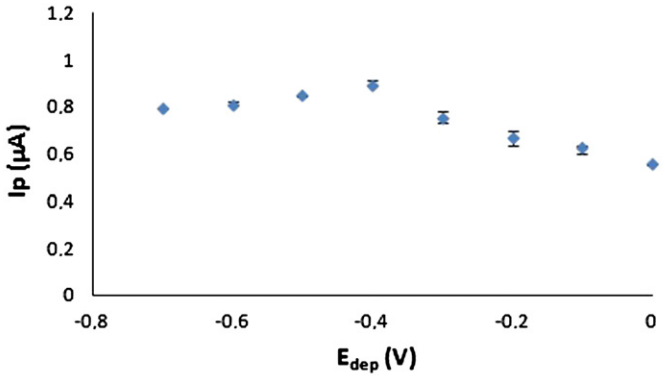

Fig. 2. Influence of deposition potential in the SWASV method. Response to Cu(II) 50 ng mL^{-1} in 0.1 M HCl at the screen printed gold electrode. Square wave voltammetric stripping measurements performed with a frequency of 15 Hz, step potential 5 mV, amplitude 28 mV, stirring speed 960 rpm and deposition time 30 s.

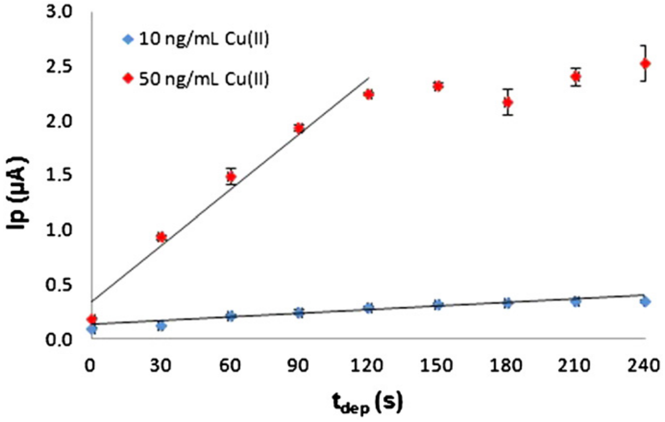

Fig. 3. Influence of deposition time in the SWASV method. Response to Cu(II) 50 ng mL^{-1} in 0.1 M HCl at the screen printed gold electrode. Square wave voltammetric stripping measurements performed with a frequency of 15 Hz, step potential 5 mV, amplitude 28 mV, stirring speed 960 rpm and deposition potential −0.4 V.

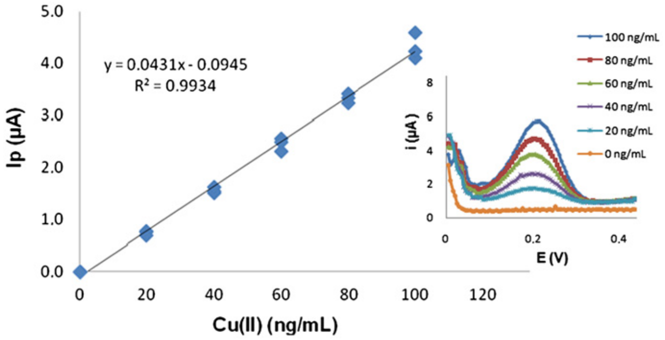

Fig. 4. Calibration curve for increasing concentrations of Cu(II) from 0 to 100 ng mL^{-1} in HCl 0.1 M by using the SWASV optimized method at the screen printed gold electrode. Step potential 5 mV, amplitude 28 mV, frequency 15 Hz, deposition potential −0.4 V and deposition time 120 s.

Voltammetric stripping calibration data for Cu(II) on the SPGEs were estimated by analyzing in triplicate standard solutions of increasing concentrations from 0 to 100 ng mL^{-1} (Fig. 4). A good correlation coefficient (R^2) of 0.993 was obtained for the regression curve, and the linearity was 98.0%. The detection limit, calculated according to the IUPAC definition, was 3.7 ng mL^{-1} for a deposition time of 120 s. This is in the range of the value found by Laschi et al. [21], 2.0 ng mL^{-1}, on a homemade SPGE. These detection limits in the low ng mL^{-1} are higher than those previously reported for Cu(II) determination on rotating disk gold electrodes by Bonfil et al. [25] (0.01 ng mL^{-1}) or rotating gold microwire electrodes by Alves et al., [26] (0.4 ng mL^{-1}). Typically lower sensitivity of the screen-printed supports is compensated by better flexibility of operation and easy and cheap electrode replacement. The LOD obtained for the proposed method is in any case suitable for determination of Cu(II) in the atmospheric deposition samples analyzed in this study. The repeatability of the measurements was examined with 15 repetitive measurements of a 50 ng mL^{-1} Cu(II) standard solution on a single SPGE, and a relative standard deviation of 6% was obtained, similar to previously reported values for screen printed electrodes [27]. The reproducibility was also evaluated by using a set of 5 different electrodes. Relative standard deviation was found to be 5% for 50 ng mL^{-1} Cu(II), an acceptable value considering the disposable nature of these low cost electrodes. This value is similar to that described in the literature for the analysis of heavy metals on SPGEs [28].

3.3. Certified reference materials

SLRS-5 River Water for Trace Metals and SPS-SW2 Batch 121 Elements in Surface Waters samples were assayed to test the applicability of SPGE and the proposed voltammetric method for Cu(II). Five subsamples were assayed using the previously optimized variables, all of them on the same SPGE. In the case of SLRS-5, a concentration of 19.5 ± 0.3 ng mL^{-1} Cu(II) was measured (certified value 17.4 ± 1.3 ng mL^{-1}). On the other hand, when analyzing SPS-SW2 a concentration of 94.9 ± 2.4 ng mL^{-1} Cu(II) was measured (certified value 100 ± 1 ng mL^{-1}). These results demonstrate the potential of the method for the measurement of copper in ambient water matrices containing relatively high concentrations of potentially interfering ions.

4. On-site voltammetric analysis of atmospheric deposition samples

Once optimized and validated, the proposed voltammetric method was applied to the analysis of Cu(II) in liquid atmospheric deposition samples from air quality sampling locations in the vicinity of the Codelco copper smelter placed at the Puchuncaví-Ventanas industrial area (V Region, Chile). The voltammetric equipment was deployed on-site using available flat surfaces. The samples were transferred from the collectors to the voltammetric cell and immediately assayed without any pretreatment. In some cases, it was necessary to dilute of samples to fit the applicability range of the calibration curve. All samples were analyzed in triplicate. Samples aliquots were acidified with HNO_3 to pH 2, transferred to the lab and assayed by ICP-MS. Fig. 5 shows the results of voltammetric and ICP-MS measurements for Cu(II) in a set of real samples. A good correlation was found with a slope close to one and a low intercept.

These results demonstrate the reliability of the voltammetric method developed for on-site analysis of Cu(II) in the soluble atmospheric deposition samples, even in presence of a wide set of highly concentrated potentially interfering ions, as revealed by ICP-MS results. These include e.g. As(III) (0.3–15.9 ng mL^{-1}), Sb(III) (0.1–2.6 ng mL^{-1}), Pb(II) (1.1–10.6 ng mL^{-1}), Cd(II) (0.002–0.689 ng mL^{-1}) and Zn(II) (8.6–256.0 ng mL^{-1}). A two weeks experimental campaign for on-site Cu(II) voltammetric stripping determination was conducted from July 1st to July 15th, 2011. Average Cu(II) concentration values at the atmospheric deposition sampling points were 155.9 ng mL^{-1} in La Greda, 101.5 ng mL^{-1} in Los Maitenes, 40.0 ng mL^{-1} in Puchuncaví, 31.3 ng mL^{-1} in Valle Alegre and 6.7 ng mL^{-1} in Maitencillo. Higher levels of Cu(II) in the atmospheric deposition were measured at La Greda and Los Maitenes sampling points, heavily affected by atmospheric deposition from the copper smelter due to short distance and relative position under the emission plume (SW winds are dominating in the area). Puchuncaví sampling point is also under dominant winds but farther from the emission point. Low Cu(II) levels in Valle Alegre are probably due to less impact of the industrial emission due to distance and relative position out of the dominant emission plume trajectory. Maitencillo sampling point is a reference location, far away from the influence of the copper smelter emission, so Cu(II) levels are correspondingly lower.

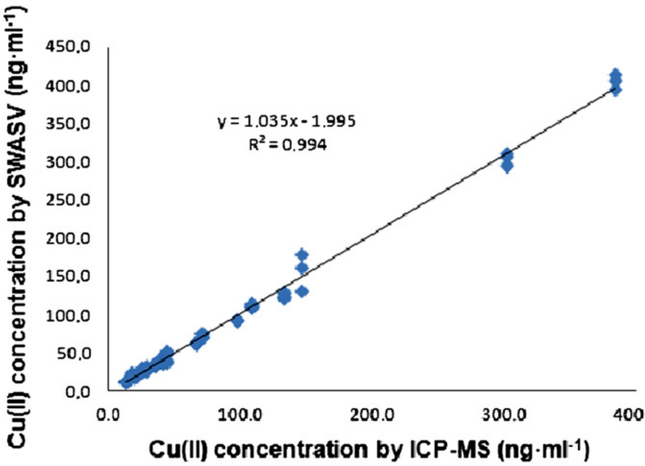

Fig. 5. Correlation between ICP-MS and the proposed voltammetric stripping method for the determination of Cu(II) in atmospheric deposition samples. Voltammetric experimental conditions as in Fig. 4.

5. Conclusions

A new voltammetric stripping procedure based on SPGEs connected to portable instrumentation was developed, optimized, validated and successfully demonstrated for on-site Cu(II) monitoring in atmospheric deposition samples, providing results in agreement with those from a standard ICP-MS method. The proposed voltammetric approach was capable of monitoring Cu(II) during a two weeks experimental campaign conducted in five atmospheric deposition sampling stations around a copper smelter, clearly showing differences among the sampling locations, derived from different impact of the emission focus.

The characteristics of the electroanalytical equipments used (screen-printed electrodes, portable potentiostat, laptop or PDA control), aside to the flexibility, ease of operation and low price of the developed method, open the possibility for routine use of the voltammetric measurements for field determination of Cu(II) in atmospheric depositions. Coupling of the electroanalytical sensor with the atmospheric deposition collector for automatic Cu(II) determination is currently being explored by our research group.

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