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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.

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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 Ultramatric (Navarra de Tratamiento del Agua S.L., Pamplona, Spain) system. Dilute standards and real samples were adjusted to pH 2 with sub-boiled HNO₃ 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 HNO₃ 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 Instruments 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 (\varnothing 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. Deaeration 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 deaeration was needed. Optimal conditions for SWASV determination were: pre-conditioning 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

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