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Anodic stripping voltammetry of antimony using gold nanoparticle-modified carbon screen-printed electrodes

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Abstract

Carbon screen-printed electrodes (CSPE) modified with gold nanoparticles present an interesting alternative in the determination of antimony using differential pulse anodic stripping voltammetry. Metallic gold nanoparticles deposits have been obtained by direct electrochemical deposition. Scanning electron microscopy measurements show that the electrochemically synthesized gold nanoparticles are deposited in aggregated form. Any undue effects caused by the presence of foreign ions in the solution were also analyzed to ensure that common interferents in the determination of antimony by ASV. The detection limit for Sb(III) obtained was 9.44×10^{-10} M. In terms of reproducibility, the precision of the above mentioned method in %R.S.D. values was calculated at 2.69% ($n = 10$). The method was applied to determine levels of antimony in seawater samples and pharmaceutical preparations.

Keywords: Gold nanoparticles; Screen-printed electrodes; Antimony; Anodic stripping voltammetry

1. Introduction

Antimony and its compounds are listed as pollutants of priority interest by the Environmental Protection Agency of the United States and the Council of the European Communities [1]. Antimony is an element that occurs naturally because of rock weathering, soil runoff and atmospheric deposition in the environment. However, its presence in the environment is also caused by various anthropogenic activities. Compounds containing antimony are used to manufacture glass and ceramics. Road traffic is also a significant source of antimony, as a number of its compounds that are used in brake linings, flame retardants and tyre vulcanization processes that require Sb-containing additives [2]. Furthermore, ultra-trace level concentrations of antimony are commonly found in environmental materials such as seawater and marine organisms [3–5].

Antimony has also been used in medical treatment. Leishmaniasis is an inflammatory disease, occurring in tropical regions, which affects 12 million people worldwide, and 1.5–2 million new cases of leishmaniasis are estimated to occur annually [6]. Treatment with antimonial drugs is the preferred method of fighting off this disease. The first generation of antimonial drugs contained trivalent antimony. However, despite its clinical benefits, because of its toxic side effects, a second generation of antimonial drugs was developed based on pentavalent antimony.

Environmental measurements of antimony levels are normally carried out by conventional analytical techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). These techniques are impractical for on-site screening or for quantification as part of a decision tool owing to their size and high labour and analytical costs. Hence, there is a need for portable analytical systems that can be met by using electrochemical methods [7]. Voltammetric methods are among the electrochemical techniques described for the analysis of antimony. These are relatively widespread and, due to their accuracy and sensitivity, have contributed greatly to its determination at trace level [8]. Adsorptive stripping voltammetry has also been used in the determination of antimony following adsorptive accumulation

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of antimony complexes using different complexing agents with a HMDE electrode [9–11].

Screen-printed electrodes are planar devices with plastic substrates that are coated with layers of electroconductive and insulating inks at a controlled thickness. The advent of screen-printed (thick-film) technology has made it possible to mass-produce inexpensive disposable electrodes for use with electrochemical instruments [12–16].

The great versatility of screen-printed electrodes resides in their wide range of possible modifications. In fact, the composition of the inks used in the printing process can be modified by the addition of substances of a very different nature, such as metals, enzymes, polymers, complexing agents, etc. Moreover, the possibility also exists of modifying the electrodes once they have been fabricated through the deposition of films containing those substances. Screen-printed electrodes, modified with Hg-based films [17,18] have been shown to be highly effective in the analysis of different metals. However, the toxicity of this element has led different authors to use other elements such as bismuth in order to modify carbon screen-printed electrodes [19,20].

The design of new nanoscale materials has acquired ever-greater importance in recent years due to their wide-ranging applications in various fields. Among these materials, metallic nanoparticles are of great interest due to their important properties and their numerous possible applications [21,22]. There are only a few works in the bibliography describing the synthesis of gold nanoparticles on the surface of carbon screen-printed electrodes. Their including chemical synthesis by means of reduction with $NaBH_4$ [23–25], or citrate [26] and electrochemical deposition [27]. The latter provides an easy and rapid alternative for the preparation of metallic nanoparticle electrodes in a short space of time. In spite of their possibilities these nanoparticle-modified carbon screen-printed electrodes have not been very used in the analysis of toxic elements. Only two works are described about the determination of As(III) using gold nanoparticle-modified CSPE [24,25].

The aim of this work is to determine Sb(III) by differential pulse anodic stripping voltammetry (DPASV) using carbon screen-printed electrodes modified with gold nanoparticles and, to the best of the author's knowledge, presents the first ever electrochemical detection of Sb(III) with this type of nano-modified electrodes.

2. Experimental

2.1. Reagents

All solutions were prepared with deionized water obtained with a Barnstead NANO Pure II system. Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4$) was purchased from Sigma–Aldrich (analytical-reagent grade, Sigma–Aldrich, Steinheim, Germany). Stock standard solutions of Sb(III) were obtained by dissolving potassium antimony tartrate(III) (analytical-reagent grade, Sigma, Steinheim, Germany) in water. Electrodag PF-407 A (carbon ink), Electrodag 418 SS (silver ink), Electrodag 6037 SS (silver/silverchloride ink) and Electrodag 452 SS (dielectric ink) were supplied by Achenson Colloiden (Scheemda, The Netherlands). Britton–Robinson solutions were used as buffers. A 0.04 M Britton–Robinson buffer solution for the *o*-boric, *o*-phosphoric and acetic acids was prepared using Merck analytical grade reagents. Solutions of different pH values were prepared from this by the addition of 0.2 M sodium hydroxide (analytical-reagent grade, Merck, Darmstadt, Germany). Sulphuric acid was purchased from Merck (analytical-reagent grade, Merck, Darmstadt, Germany). Commercial injections of Glucantime® were obtained from Aventis. L-Cysteine stock solution was prepared by dissolving 5 g of L-cysteine (Fluka, Buchs, Switzerland) in 100 mL of 0.05 M HCl. For prereduction of antimony(V), in real samples, 2 mL of L-cysteine stock solution were added to 10 mL of sea water and drug solutions.

2.2. Apparatus

Screen-printed electrodes were produced on a DEK 248 printing machine (DEK, Weymouth, UK) using polyester screens with appropriate stencil designs mounted at 45° to the printer.

Voltammetric measurements were taken using an AUTOLAB PGSTAT 12 electrochemical system with GPES software (Eco Chemie, Utrecht, The Netherlands).

Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6460LV with an INCA elemental X-ray analysis system.

2.3. Screen-printed electrodes preparation

Hand-made screen-printed electrodes were used in the determination of Sb(III). For the construction of the screen-printed electrodes successive layers of different inks were printed onto a PVC strip substrate (30 mm × 10 mm, 0.5 mm thick) using four different screens with appropriate stencils to transfer the required design (Fig. 1). The printing procedure was as follows:

1) Firstly, three parallel conducting base-patterns were screen-printed on the PVC strip substrate with commercial silver ink, giving them an effective conductive surface, and they were then cured for 15 min at 90 °C. The base-pattern at the left was used as the counter electrode.
2) A silver/silver chloride reference electrode was screen-printed using silver/silver chloride ink on the silver base-pattern at the right, as can be seen in Fig. 1, and then cured for 15 min at 90 °C.
3) The working electrode was formed by screen printing a graphite layer over the silver base-pattern at the centre using commercial graphite ink and was then cured for 15 min at 90 °C.
4) An insulator layer was finally printed over all of the sensor strip except for the three electrode surfaces and the electrical connection at the reverse end of the sensor strip, which was subsequently cured under UV radiation.