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Bismuth–silver bimetallic nanosensor application for the voltammetric analysis of dust and soil samples

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ABSTRACT

A sensitive adsorptive stripping voltammetric procedure for palladium, platinum and rhodium determination was developed in the presence of dimethylglyoxime (DMG) as the chelating agent at a glassy carbon electrode coated with bismuth–silver bimetallic nanoparticles. The nanosensor further allowed the adsorptive stripping voltammetric detection of platinum group metals without oxygen removal in solution. In this study the factors that influence the stripping performance such as composition of supporting electrolyte, DMG concentration, deposition potential and time studies, and pH have been investigated and optimised. The bismuth–silver bimetallic nanosensor was used as the working electrode with 0.2 M acetate buffer ($pH = 4.7$) solution as the supporting electrolyte. The differential pulse adsorptive stripping peak current signal was linear from 0.2 to 1.0 ng L^{-1} ($n = 3$) range (60 s deposition), with limit of detections for Pd (0.19 ng L^{-1}), Pt (0.20 ng L^{-1}), Rh (0.22 ng L^{-1}), respectively. Good reproducibility with relative standard deviation (RSD) of 4.61% for Pd(II), 5.16% for Pt(II) and 5.27% for Rh(III) ($n = 10$), for the applied sensor was also obtained.

1. Introduction

The most important problem for the analytical chemist is the quantification of the increasing number of substances in the environment. Heavy metals are always a matter of concern for the analytical chemist as new substances are reported as toxic. In the environment heavy metals accumulate and are distributed between air, water, soil and the biota [1]. Platinum group metals (PGMs) form an important group of elements of increasing usage in the technologically developing world. This group of metals consists of six metals [2], palladium, rhodium, platinum, osmium, ruthenium and iridium. These PGMs can be divided into light triad (rhodium, ruthenium and palladium) and the heavy triad (platinum, osmium and iridium) [3]. Platinum group metals have a permanent lustre and have aesthetic qualities. Like gold, PGMs is used in the manufacture of jewellery and has also an investment role. The applications of PGMs are very important and are used as a catalyst, in the enabling of petroleum, other fuels and chemicals from crude oil. It is difficult to substitute PGMs with other metals in this important application and platinum compounds are also used in cancer treatment drugs [2]. At this point of time PGMs concentrations still remains at relatively low levels and that's why the methods used for its determinations should be highly sensitive. In the analysis of PGMs spectroscopic methods are frequently used but due to their high cost, scientists have been developing new analytical alternatives [4]. Adsorptive striping voltammetry (AdSV) seems to be an alternative and is a very sensitive technique for the analysis of several metals including PGMs. In adsorptive stripping analysis its best to destroy the organic matrix to limit the carbon content of the solutions. To obtain very good results it's better to avoid nitric acid in the analysis. In the literature for the determination of PGMs using voltammetric techniques, a large number of papers involve the use of hanging mercury drop electrode as the working electrode [5–7]. Only in a few cases other electrodes such as modified carbon paste electrodes [8,9] and bismuth film electrodes [10,11] were used. According to the literature palladium, cobalt and nickel react with dimethylglyoxime (DMG) to form 1:2 complexes, e.g. $M(HDMG)_2$ and can be adsorb on bismuth [12–14], and mercury [15–18].

In the development of the latest electrochemical sensors, nanotechnology is playing an increasingly important role. The design of new and improved sensing devices makes nanoparticles (NPs) very suitable for chemical and biosensors due to their unique chemical, physical and electrical properties [19]. One of the main benefits of these microscopic NPs is their relatively large surface area causing a high reactivity to weight ratio [20–25]. It has been

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found that NPs are not merely small crystals but an intermediate state of matter somewhere between bulk and molecular materials [26]. In different analytical methods a wide variety of nanomaterials, especially nanoparticles with different properties have found broad application [27]. From the work done by Rico et al. [28], modification of carbon screen-printed electrodes, with chemically synthesised bismuth nanoparticles for voltammetric analysis of heavy metals has been used as an environmentally friendly alternative to the toxic mercury electrodes. The work done by Van der Horst et al. [29] describes the low temperature synthesis of bismuth–silver bimetallic nanoparticles. The electrochemistry results for this study illustrate that bismuth–silver bimetallic nanoparticles can used for sensor application.

This study was aimed at evaluating the potential analytical applications of bismuth–silver bimetallic nanoparticles modified with glassy carbon electrodes for the determination of PGMs within the nanograms concentration range using DPAdSV technique. Further, to optimise the chelating agent concentration, accumulation potential and time, and stability of the working electrode because this parameters are very important in DPAdSV analysis. In order to assess the practical utility of the method for real matrices analysis, preliminary data concerning the effect of other metals as possible interferent, are also reported. Bismuth–silver bimetallic nanosensors show good applicability in adsorptive differential pulse stripping voltammetry and can be used as a replacement for the toxic mercury electrodes.

2. Materials and methods

2.1. Reagents

Sodium acetate (NaOAc), ammonia (NH_3) (25%), ammonium chloride (NH_4Cl), hydrochloric acid and nitric acid were supplied by Merck (South Africa). All precious and heavy metal standards (1000 mg/L AAS), dimethylglyoxime (DMG) were purchased from Sigma–Aldrich (South Africa). Glacial acetic acid (95%), ethanol (95%) were supplied by Kimix (South Africa). A 0.2 M sodium acetate buffer (pH = 4.7) was prepared by mixing sodium acetate with acetic acid and deionised water and served as the supporting electrolyte. The 0.01 M DMG solution was prepared in 95% ethanol and served as the chelating agent. All solutions were prepared by Milli-Q (Millipore 18 M Ω cm) water.

2.2. Instrumentation

In this study electrochemical measurements were conducted with an Epsilon electrochemical analyzer (BASi Instruments, 2701 Kent Ave., West Lafayette, IN 47906, USA) using cyclic voltammetry (CV), or differential pulse adsorptive stripping voltammetry amperometric (DPAdSV) modes. A conventional three electrode system was employed, consisting of bismuth–silver nanosensor prepared by drop coating the nanoparticles on a BASi 1.6 mm diameter glassy carbon disc working electrode. A BASi 3 M NaCl-type Ag/AgCl reference electrode was used, and a platinum wire as auxiliary electrode. An Agilent 7500 series inductive coupled plasma mass spectroscopy (ICP-MS) was used for the trace PGMs determination in roadside dust and soil samples. All experiments were performed in a 20 mL electrochemical cell at conditioned room temperature [10,30–33].

2.3. Preparation of the bismuth–silver bimetallic electrode

Bismuth–silver bimetallic nanoparticles were prepared according to the procedure reported elsewhere in the literature [29]. A disk glassy carbon electrode (GCE) was used as the working electrode and was thoroughly cleaned and polished on a polish pad with 1.0, 0.3 and 0.05 μm alumina (Al_2O_3) powders. The clean GCE was first rinse with deionised water and then sonicated in ethanol and doubly distilled H_2O in turn. The GCE was transferred to the electrochemical cell for further cleaning by using cyclic voltammetry (CV) between −1.0 and +1.0 V at a scan rate of 50 mV s^{-1} in freshly prepared deoxygenated 0.5 mol L^{-1} aqueous H_2SO_4 until a stable CV profile was obtained. A 2.5 mg of bismuth–silver (Bi–Ag) bimetallic nanoparticles were dispersed through ultrasonic vibration in 50 mL solution of deionised water to form a suspension. A defined quantity of the suspension was applied to a clean surface of GCE and dried at room temperature to get a thin film on GCE surface [29,34–37]. After each voltammetric cycle the cleaning of the Bi–Ag bimetallic nanosensor was carried out by holding the potential of the electrode at +1.0 V. Traces of the remaining DMG complexes on the electrode surface were reduced and quickly desorbed at this potential. A short cleaning period of 30 s was required to refresh the electrode surface completely [38].

2.4. Procedure for the determination of PGMs

A 10 mL 0.2 M acetate buffer solution (pH = 4.7) containing 1×10^{-5} M DMG was used as electrolyte in the cyclic and stripping voltammetric procedures. The nanofilm electrode was immersed into the solution and an accumulation potential of −0.7 V (vs. Ag/AgCl) for Pd(II) and −0.6 V for Pt(II), and −0.7 V (vs. Ag/AgCl) for Rh(III) were applied while the solution was stirred. A 30 s quiet time was used and the voltammogram was scanned from +0.8 to −1.4 V (vs. Ag/AgCl) at a scan rate of 60 mV s^{-1} for cyclic voltammetry measurements, while scanning was performed from −0.8 to −0.1 V (vs. Ag/AgCl) for adsorptive differential pulse stripping voltammetry (AdSV) measurements. The PGMs were introduced into the solution after the background voltammogram was recorded. All the experiments were performed in the presence of oxygen and at room temperature [10]. According to Zhang et al. [39], the analysis of heavy metal ions using AdSV method consists of three steps such as accumulation, electrochemical reduction and stripping out. In this method both the sensitivity and the selectivity of the analysis can be enhance by the combination of accumulation and reduction prior to the stripping detection process. The efficiency of accumulation and electrochemical reduction steps plays a great role in the entire analysis.

3. Results and discussion

3.1. Electrochemical characterisation of Bi–Ag bimetallic sensor using CV

In electrochemistry cyclic voltammetry has become an important electroanalytical technique and is widely used for the study of redox processes. Cyclic voltammetry is based on varying the applied potential at the working electrode in both forward and reverse directions at different scan rates while monitoring the current. Fig. 1A showed cyclic voltammograms of a GCE/Bi-AgF nanosensor (a) and bare GCE (b) in 0.2 M NaOAc buffer solution (pH = 4.7). Two redox couples were observed at −0.1 and −0.6 V (vs. Ag/AgCl) (redox couple C/C'), and corresponding cathodic peaks at −0.3 and −0.6 V (vs. Ag/AgCl) (redox couple D/D') that represent the conversion of Bi^{3+}/Bi^{2+} (C/C') and Ag^{+}/Ag (D/D'), respectively [29]. It is known that the peak to peak separation, ΔE_p, for a reversible redox couple is 59 mV. The ratio of the cathodic peak to the anodic peak currents (I_{pc}/I_{pa}) has to be close to 1 [40]. In the cyclic voltammogram of GCE/Bi-AgF nanosensor the redox peak separation was 0.61 V with no redox activity at bare