



Development and application of a poly(2,2'-dithiodianiline) (PDTDA)-coated screen-printed carbon electrode in inorganic mercury determination

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ARTICLE INFO

Article history:

Received 15 August 2008

Received in revised form 7 January 2009

Accepted 10 January 2009

Available online 20 January 2009

Keywords:

Inorganic mercury determination

Anodic stripping voltammetry

Co-polymer

Polyaniline-poly(2,2'-dithiodianiline)

SPCE

ABSTRACT

In this work, monomer solutions of aniline (ANI) and 2,2'-dithiodianiline (DTDA), an aniline derivative containing –S–S– links, were prepared and used in the electrochemical copolymerisation of ANI and DTDA by cyclic voltammetry on a screen-printed electrode (SPE) in 1 M HCl. Electropolymerisation of aniline on the surface of the screen-printed working electrode was performed by sweeping the potential between –500 and +1100 mV (vs. Ag/AgCl) at a sweep rate of 100 mV/s. Electrocopolymerisation was performed with a mixture of ANI and DTDA by sweeping the potential between –200 and +1100 mV (vs. Ag/AgCl) at a sweep rate of 100 mV/s [J.L. Hobman, J.R. Wilson, N.L. Brown, in: D.R. Lovley (Ed.), *Environmental Microbe Metal Interactions*, ASM Press, Herndon, Va, 2000, p. 177]. The cyclic voltammogram (CV) for each of the electrochemically deposited polyaniline (PANI) and the mixture of ANI and DTDA for the copolymer polymerisation on SPCE were recorded for electrochemical analysis of the peak potential data for the mono and copolymer. Anodic stripping voltammetry (ASV) was used to evaluate a solution composed of (1×10^{-6} M HgCl₂, 0.1 M H₂SO₄, 0.5 M HCl), in the presence of the co-polymer sensor electrode. The Hg²⁺ ions were determined as follows: (i) pre-concentration and reduction on the modified electrode surface and (ii) subsequent stripping from the electrode surface during the positive potential sweep. The experimental conditions optimised for Hg²⁺ determination included the supporting electrolyte concentration and the accumulation time. The results of the study have shown the use of a conducting polymer modified SPCE as an alternative transducer for the voltammetric stripping and analysis of inorganic Hg²⁺ ions.

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1. Introduction

The extent of mercury poisoning in the environment has been an important concern throughout the world for many decades. Since mercury is a liquid with a high thermal conductivity and many other unique properties, it is often used in many industrial applications whereas mercuric salts have been extensively used by humans for various activities such as the use of mercuric ointment as a remedy for skin and eye complaints since the first century, while metallic mercury and mercuric chloride have been used in medicine since the Middle Ages. Recent applications of mercurial compounds include diuretics, dental amalgam fillings and antiseptics [1–3].

Other sources of mercury poisoning include organomercury (e.g. methylmercury, MeHg) compounds that are extremely toxic and can cause central nervous system disorders (e.g. nephrotoxicity, neurotoxicity), intellectual deterioration and even death. Methylmercury usually enters and can be accumulated in the human body after consuming fish that was contaminated. Hair is one of the main accumulation and identification sites of mercury [4–7].

Classical methods and techniques for determining mercury in the environment include atomic adsorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), atomic emission spectroscopy (AES), inductively coupled plasma mass spectroscopy (ICP-MS), and capillary electrophoresis (CE). These are well-established methods and are characterised by low detection limits (i.e. 0.02 ppb for AAS; 0.001 ppt for AFS; 0.01 ppt for AES and 0.08 ppt for ICP-MS). However, these classical techniques require expensive instrumentation and cannot be used for field and on-site measurements [1,6,8–12].

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Alternatives to the classical methods and techniques include electrochemical methods of mercury determination (e.g. ion-selective electrodes (ISE); anodic stripping voltammetry (ASV); potentiometric stripping analysis (PSA); current stripping chronopotentiometry (CSP); and differential pulse voltammetry (DPV). However, these methods suffer the drawback of high detection limits [1,13–17].

The principal motivation for designing of sensors for toxicity monitoring is to produce a tool that will provide a reliable alternative technique, that is simple and rapid when compared to the more classical methods currently in use, e.g. AAS, ICP-MS, GC-MS, HPLC-MS. Although the classical techniques are very powerful for monitoring toxic analytes such as pesticides and heavy metals, they are known to be expensive, time-consuming and not adapted for *in situ* and real time detection and requires highly trained personnel [1,8–10,18].

Biosensors offer a novel approach towards measuring the bio-available mercury fraction in substrates, while both chemical sensors and biosensors provide a means of measuring mercury ions in aqueous solutions. Several advances have been made with the use of chemical sensors for the detection of heavy metal ions and pollutants in the environment [1,19–22]. With the determination of Hg in the environment a priority, but not having an effective tool that will enable on-site analysis in the field, the development of chemical sensors and biosensors have become a necessity.

Screen-printing technology has been adapted from the micro-electronics industry and has offered high-volume production of extremely inexpensive, and yet highly reproducible and reliable single-use sensors, a technique which holds great promise for on-site monitoring of environmental pollutants. The use of screen-printing technology in the serial production of disposable low-cost electrodes for the electrochemical determination of a wide range of substances is currently undergoing widespread growth. The application of single-use chemical sensors, based on advanced microfabrication technology, is particularly attractive for field deployment due to their extremely low cost and compatibility with hand-held potentiostats, analysers and other appropriate voltammetric instruments. Screen-printed electrodes (SPEs), in particular, can combine ease of use and portability with simple, inexpensive fabrication techniques. The thick-film, screen-printing, technology is capable of mass producing extremely inexpensive, and yet highly reproducible electrochemical sensor strips that can be used with hand-held voltammetric instruments. In the production of screen-printed electrodes the printing of different inks (chemical compounds, polymers, functional compounds, etc.) on various types of plastic or ceramic substrates is performed. Polyester screens are generally used for printing with patterns designed by the analyst in accordance with the analytical purpose in mind. The composition of the various inks used for printing on the electrodes determines the selectivity and sensitivity required for each analysis [23,24].

The main aim of the work presented here was to investigate the construction of chemical sensors that utilise specific conducting polymers for inorganic mercury (Hg^{2+}) determination. The first objective was to optimise the conducting polymer parameters for the electrode preparation. Secondly, the possibility of developing a stripping voltammetric assay for mercury ions (Hg^{2+}) in aqueous solutions using a disposable screen-printed carbon electrode, was explored. Voltammetry was used to investigate the electrochemical behaviour of Hg^{2+} in solution and to define the optimum instrumental conditions for the differential pulse anodic stripping voltammetric (DPASV) measurement of Hg^{2+} in aqueous solutions. Future work will focus on obtaining new electrochemical sensors adapted to the determination of different species of mercury and other heavy metals applied to real samples, combining both, the incorporation of different and more selective receptor molecules at the screen-

printed carbon electrode (SPCE) surface and the selection of the adequate electrochemical reaction.

2. Experimental

2.1. Materials and reagents

The reagents aniline (99%) and *N,N*-dimethylformamide (98% atom D) and were obtained from Aldrich, Germany. Potassium chloride, sulphuric acid (95%) and hydrochloric acid (32%) were purchased from Merck. Mercury (II) chloride (99.5%, ACS) and methylene blue (95%, extra pure) were purchased from Fluka (Germany) and used as received. All solutions were always prepared using Milli-Q (Millipore) water.

2.2. Instrumentation

Electrochemical protocols were performed with a BioAnalytical Systems (BAS) 100B electrochemical analyser using cyclic voltammetry (CV), linear sweep stripping voltammetry (LSSV) or differential pulse anodic stripping voltammetry amperometric modes. A conventional three-electrode system was employed consisting of a single connector screen-printed working electrode, a BAS 3 M NaCl-type Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. High purity argon gas was used to displace oxygen from the electrochemical cell before results were collected [25]. SPCEs were obtained from the Sensors and Separations Group, Department of Chemical Sciences, Dublin City University, Dublin 9, Ireland. The fabrication of the SPCE is described in the papers of [26] and Grennan et al. [27].

2.3. Preparation of polyaniline-poly(2,2'-dithiodianiline) (PANI-PDTDA) polymer film

A 10-ml solution consisting of 0.2 M aniline, 0.02 M 2,2'-dithiodianiline and aqueous 5 M H_2SO_4 was prepared and heated in a water bath to 70 °C to dissolve the 2,2'-dithiodianiline crystals. The co-polymer film of polyaniline (PANI) and poly(2,2'-dithiodianiline) was grown electrochemically on the surface of a SPCE by repetitive cyclic voltammetric scanning at 50 mV/s from –200 to +1100 mV, for 10 cycles at 25 °C. Polyaniline was also electropolymerised as a monopolymer on a SPCE surface, using a 10-ml solution of 0.2 M aniline and aqueous 1 M HCl, and cycling repetitively at 100 mV s⁻¹ from –200 to +1100 mV for 10 cycles at 25 °C. Each SPCE was then rinsed with deionised water and immersed in deionised water until use [27,28].

2.4. FTIR spectroscopic characterisation

Solutions for subsequent spectroscopic studies were obtained by collecting the different polymer layers, after electrodeposition on the SPCE surface and dissolving it from the electrode surface in DMF. The Fourier Transform Infrared (FTIR) spectra for 400–4000 cm⁻¹ of the polymer samples dissolved in DMF were recorded with a Bruker ALPHA-T, FT-IR spectrometer fitted with a Bruker Optics aligned RockSolid™ interferometer [29,30].

2.5. Voltammetric electrode evaluation

After preparation of the SPCE/PANI-PDTDA (or SPCE/PANI) sensor electrode, the electrode was washed with deionised water and immersed in a 2-ml solution of mercury chloride (HgCl_2). For all the experiments performed a supporting electrolyte of 0.1 M H_2SO_4 was used since a pH of 1 is very suitable for mercury (II) determination [31]. The effect of chloride ion concentration in Hg(II) determination was investigated and HCl concentrations of 0.0,

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