



Comparison of backing materials of screen printed electrochemical sensors for direct determination of the sub-nanomolar concentration of lead in seawater

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ARTICLE INFO

Keywords:

Electrochemistry
Screen printed electrodes
Au nanoparticles
Lead
Trace metals
Textile sensors

ABSTRACT

An anodic stripping voltammetric method is reported in this study for the determination of sub-nanomolar Pb concentration using disposable sensors, each consisting of three (counter, working and reference) screen-printed electrodes. Sensor performance was optimized for the determination of Pb through several surface modifications, by using single-walled carbon nanotubes, electro-reduced graphene oxide and gold nanoparticles. A scanning electron microscopy study of the deposition of electrogenerated gold nanoparticles of various sizes on the working electrode surface showed that spherical nanoparticles of around 100 nm provided the best results. The modification of working electrodes with graphene and gold nanoparticles permitted the determination of Pb²⁺ in seawater (Detection Limit: 3.21·10⁻¹⁰ M) without modifying the pH of the sample. The electrode systems were printed on both rigid and textile backing materials, to observe the influence of those materials on the final performance of the sensor.

1. Introduction

The presence of pollutants in the environment has increased in recent times, as a consequence of industrial development, caused mainly by factory waste discharged as effluent into seawater, degrading the environmental quality of coastal waters [1,2]. It is a serious issue for flora and fauna in contaminated ecosystems. Some of the heavy metal pollutants, among which Pb, present high toxicity, low biodegradability and accumulate in the bodies of living beings.

In addition to causing anemia and deformities in marine animals [3] the presence of Pb can also jeopardize mussel-farm production and result in economic losses. Although mussels have a detoxification mechanism, the consumption of these bivalves can produce Pb intoxication in humans, because Pb can accumulate in bones, kidneys, muscles, and the brain, as well as causing damage to the immune, reproductive, and central nervous systems [4–6].

European Directive (2013/39/EU) states that the average annual value of lead concentration in seawater is 1.3 µg L⁻¹.

Several analytical techniques have been employed for the determination of sub-nanomolar Pb concentrations in natural samples, and the presence of other heavy metals in freshwater rivers and lakes and in seawater [7]. Spectrometry techniques are widely used in the detection

of heavy metals. These techniques include flame atomic absorption spectrometry (FAAS) [8], electrothermal atomic absorption spectrometry (ETAAS) [9], graphite furnace atomic absorption spectrometry (GFAAS) [10–12], inductively coupled plasma atomic emission spectrometry (ICP-AES) [13], inductively coupled plasma mass spectrometry (ICP-MS) [14,15] and atomic fluorescence spectrometry (AFS) [16]. There is increasing interest in the use of electrochemical techniques for determining trace concentrations of pollutants, particularly the use of stripping voltammetry techniques, due to their high sensitivity, that are commonly used for quantitative analysis of electroactive species, such as heavy metal ions [17]. High metal traces have usually been studied with mercury-based electrodes, such as hanging mercury drop electrodes [18] and mercury film electrodes [19]. That choice is due to their high sensitivity, reproducibility and high hydrogen overpotential of the mercury electrodes, as well as the possibility of amalgam formation with heavy metals [20]. However, these electrode types are now replaced by mercury-free electrodes, because of the high toxicity of that element. Studies have focused on the use of gold electrodes [21], glassy carbon electrodes [22], silver electrodes [23], and modifications of the electrode surface by bismuth-coated [24], metal nanoparticles [25], and carbon nanostructures [26], such as graphene [27] and carbon nanotubes [28].

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Table 1
Analytical characteristics of Pb sub-nanomolar concentrations in seawater samples.

Sample	Electrochemical technique	Preconcentration time	LOD	Electrode material	Reference
Seawater	SWASV	120 s	8.7 nM	Graphite screen, printed electrode modified with mercury film	[34]
Seawater	SWV	60 s	12 nM	Glassy carbon modified with thiol self-assembled mono-layers on mesoporous supports and Nafion	[35]
Seawater	SWV	300 s	2.4 nM	Glassy carbon electrode modified with nanofibrillated cellulose	[36]
Acidified seawater up to 1 M HCl	SWV	–	0.5 nM	Graphite reinforced carbon electrode modified with electroreduced graphene oxide	[37]
Acidified UV-SW	SWASV	600 s	12 pM	Vibrating silver amalgam with Hg microwire electrode	[38]
Seawater	DPAdASV	60 s	4.5 nM	HMDE	[39]
Seawater	DPASV	300 s	0.321 nM	AuNP/ERGO/SPCE	This work

SWASV square wave anodic stripping voltammetry; SWV square wave voltammetry; UV-SW ultraviolet digested seawater; DPAdASV differential pulse adsorptive anodic stripping voltammetry; HMDE hanging mercury drop electrode; DPASV differential pulse anodic stripping voltammetry.

There is a growing need in the industrial sector to find a simple system for on-site determination of analytes [21]. Such a system would circumvent sample transportation and thereby avoid the risk of possible contamination. One of the most suitable ways to achieve that effect is through the use of screen printed electrodes (SPEs), due to their highly simplified reproducibility in serial production and inherent characteristics, such as miniaturization, and their low cost, making them a preferred choice [29]. Their small size and the integrated system of three electrodes in a single piece make SPEs ideal devices for on-site electrochemical determination when coupled to a portable potentiostat. In addition, flexible materials and textile fabrics been introduced as backing materials have over recent years in the development of screen printing systems, for the production of electrochemical sensors as usable wearable devices [30,31] and energy storage devices [32,33].

Determination of Pb in seawater has also been intensely studied using anodic stripping voltammetry (ASV) and several methods have been developed using different electrodes. However, to the best of our knowledge, to date there are only a few studies on ASV detection of Pb without a conditioning process or pH adjustment of the samples in a matrix as complex as seawater (Table 1). Considering the recent interest in the development of wearable sensors, the main objectives of this paper are, firstly, to study the influence of backing materials in sensor performances and, second, to determine the best modification of an electrode surface from among all those performed in this study for improving *in situ* Pb determination in seawater.

2. Experimental

2.1. Reagents and solutions

All the chemicals were of analytical grade and were used as received without further purification. High-quality water (Milli Q A10 system, Millipore, Bedford, USA) was employed for preparing all solutions.

Pb(NO₃)₂, HCl and H₂SO₄ were supplied by Merck (Darmstadt, Germany). AuCl₃·3H₂O, single-walled carbon nanotubes (SWCNT) and graphene oxide dispersion in water (4 g L⁻¹) and 1,2-dichloroethane (DCE) were purchased from Sigma-Aldrich (Steinheim, Germany).

C10903P14 (carbon/graphite ink) and D2071120D1 (dielectric ink) were purchased from Gwent Electronic Materials (Torfaen, U.K). Electrodag 6037 SS (Ag/AgCl ink), and Electrodag 418 (Ag ink) were supplied by Acheson Colloids (Scheemda, Netherlands).

Gore-Tex® Pro-Shell Nylon Liner and 2-Layer Gore-Tex® Paclite® Shell Ripstop Nylon fabrics were supplied by Rockywoods Fabrics, LLC (Loveland USA).

500 μm thickness polyester film (PMX981) was supplied by HiFi Industrial film (Dardilly, France).

2.2. Instrumentation

Electrochemical measurements were taken with a PalmSens®

portable electrochemical potentiostat (PalmSens® Instruments BV, Houten, The Netherlands) controlled by PS Trace software to register the data. All measurements were performed at room temperature and refer to data collected with screen printed Ag/AgCl pseudoreference electrodes.

Inductively coupled plasma mass spectrometry analyses were carried out with ICP-MS Agilent Serie 7500 (Agilent Technologies, California, U.S.A).

Solution pH was measured with an HI 221 pH meter (Hanna Instruments, USA).

Screen printed carbon electrodes (SPCEs) were fabricated on a DEK 248 screen printer (DEK, Weymouth, UK).

3. Methods

3.1. Sensor manufacturing

The SPCEs used in this study were produced in the laboratory by sequential deposition of different commercial inks, following the procedures described in a previous work [40]. The screen-printing process followed the steps shown in (Scheme 1). First, a silver ink (Electrodag 418) - was printed on the support materials and the conductive tracks were defined. Then, Ag/AgCl ink (Electrodag 6037 SS) was printed and cured to define pseudoreference electrode. Subsequently, carbon/graphite ink (C10903P14) was used to print the counter and the working electrode. Finally, printing with a dielectric ink insulated the conductive circuit and defined the geometrical area of the electrodes (geometrical working area, 12.56 mm²). The electrodes were printed on the backing materials: polyester film and two textile fabrics. Fabrics based on Gore-Tex® were selected for this purpose, because it is suitable as an electrodic support to develop screen-printed sensors, due to its inherent properties as a waterproof, inert, and resistant material.

3.2. Single-walled carbon nanotubes modified SPCE (SWCNT/SPCE) preparation

The working electrode surface was modified with a thin film of SWCNT. A volume of 5 μL of stock solution was drop-casted on the working electrode surface and the solvent was left to evaporate at room temperature. The stock solution was prepared by dispersing 0.5 mg of SWCNT in 100 mL of DCE and then ultrasonically blending the solution for thirty minutes, to obtain a homogenized dispersion before coating onto the electrode surface.

3.3. Electroreduced graphene oxide modified SPCE (ERGO/SPCE) preparation

The graphene film was generated by electroreduction of graphene oxide. A commercial solution of graphene oxide was diluted down to 0.2 g L⁻¹. The diluted mixture was subjected to ultrasonication for one

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