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Disposable sensors for environmental monitoring of lead, cadmium and mercury

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A B S T R A C T

Miniaturization is an increasing trend in the field of analytical chemistry as a response to the need to develop new analytical techniques for food, clinical, and environmental applications. There is therefore also an increasing trend towards the use of miniaturized disposable sensors, which are inexpensive and designed to be one-shot and do not require pre-treatment prior to use or cleaning between measurements. This review describes disposable sensors for detection of lead, cadmium and mercury in the environment, taking into account their analytical performance. Further, we also discuss the role of certain factors, such as the immobilization procedure and surface modification affecting the analytical characteristics of sensors. Finally, we comment on future applications and potential research interest in this field.

Contents

1. Introduction

The presence of potentially toxic elements (PTEs) in the environment is of particular concern due to their adverse effects on ecosystems and human health. PTEs, namely lead, cadmium and mercury, were listed as priority substances in the field of water policy by Directive 2008/105/EC of the European Union Parliament and of European Council on environmental quality standards in the field of water policy [1]. In this list, cadmium and mercury, as well as being priority substances, were also identified as priority hazardous substances [1]. The standard and traditional techniques for analysis of traces of PTEs require some costly analytical techniques, such as atomic absorption spectroscopy and atomic fluorescence spectrometry [2], inductively-coupled plasma-mass spectrometry (ICP-MS) [3], optical emission spectroscopy (OES) [4], and X-ray fluorescence spectrometry [5], and specialized personnel to carry out the operational procedures [6]. In these methodologies, besides sample collection and transport to the laboratory, a sample pre-treatment step and pre-concentration of the target compounds in the sample are required and are labor intensive. Efforts are ongoing to develop rapid and inexpensive techniques, such as enzymatic biosensors [7], for *in-situ* analysis of PTEs for the early detection of pollution in several environmental compartments. There has therefore been an increasing trend to develop miniaturized sensing strategies because of their advantages, such as disposability, simplicity, rapid response, and readiness for field application.

The introduction in the past few years of nanomaterials, such as metal nanoparticles (NPs), quantum dots, magnetic NPs or nanotubes (NTs), which enhance selectivity, sensibility, and

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Table 1
Selected examples of screen-printed disposable sensors used for detection of Pb(II), Cd(II)and Hg(II) in environmental samples

Immobilization procedure/sensor fabrication	Transducer	Analytes	LOD	Linear range	Tested sample	Ref.
Dropping $AuCl_4$ on the screen-printed electrode surface at constant current intensity Deposition of the MWCNT–COOH dispersion on the electrode surface	Electrochemical	Hg(II)	$0.2\ \mu gL^{-1}$	$0.5–50\ \mu gL^{-1}$	Tap water (spiked with Hg(II) River water	[13]
Dropping $AuCl_4$ on the electrode surface at constant current intensity Deposition of the graphene oxide dispersion on the working electrode surface	Electrochemical	Hg(II)	$1.9\ \mu gL^{-1}$	$0.5–50\ \mu gL^{-1}$	Tap water (spiked with Hg(II)) River water	[13]
Manual drop-casting of poly(3-octylthiophene–2,5 diyl) (POT) onto carbon-screen printed electrodes	Electrochemical	Pb(II)	1.20 nM	–	River water	[20]
Electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) from its monomer onto carbon-screen printed electrodes	Electrochemical	Pb(II)	10.9 nM	–	River water	[20]
Grafting by reduction of 4-CPD in H_2SO_4 by chronoamperometry onto carbon-based screen-printed electrodes	Electrochemical	Pb(II)	1.2×10^{-9} M	7.5×10^{-9}– 7.5×10^{-8} M	Water spiked with Pb(II)	[21]
Deposition of gold onto screen-printed electrode surface	Electrochemical	Pb(II) Hg(II)	$0.5\ \mu gL^{-}$ $1.5\ \mu gL^{-1}$	$4–16\ \mu gL^{-1}$ $2–16\ \mu gL^{-1}$	Tap water (spiked with Pb(II) and Hg(II))	[22]
Deposition of gold onto screen-printed electrode surface	Electrochemical	Hg(II)	$1.1\ ngmL^{-1}$	–	NIST 1641d Mercury in Water Standard Reference Material NCS ZC 76303 Mercury in Water Certified Reference Material Rainwater	[23]
Screen-printed gold-film electrode	Electrochemical	Hg(II)	$0.8\ \mu gL^{-1}$	$1.2–280\ \mu gL^{-1}$	River water Wastewater (not specified)	[24]
Bi film plated *in-situ* on screen-printed electrodes coated with multi-walled carbon nanotubes (MWCNTs) dispersed into a Nafion solution	Electrochemical	Pb(II) Cd(II)	$0.01\ \mu gL^{-1}$ –	$0.05–100\ \mu gL^{-1}$ $0.5–80\ \mu gL^{-1}$	Tap water (spiked with Pb(II) and Cd(II)) Lake water	[25]
Bi film plated *in-situ* onto screen-printed electrode coated with graphene-poly(sodium 4-styrenesulfonate) composite film	Electrochemical	Pb(II) Cd(II)	$0.089\ \mu gL^{-1}$ $0.042\ \mu gL^{-1}$	$0.5–120\ \mu g\ L^{-1}$	Lake water	[26]

reproducibility, has been of paramount importance for improving limits of detection (LODs) and to allow adequate miniaturization of the sensing devices [8,9]. Furthermore the combination of the nanomaterials using the techniques and the tools of surface modification can give rise to highly selective, sensitive, cost-effective, disposable sensors for PTEs.

In this review, we summarize the different environmental applications of disposable sensors in the determination of PTEs, namely lead, cadmium, and mercury. We discuss the role of various factors affecting the analytical characteristics of sensors, including the immobilization procedure used. We also consider the selectivity of sensors towards PTEs and their operational characteristics. We report trace-level LODs for lead, cadmium and mercury.

2. Disposable sensors

Disposable sensors are economical in nature and designed to be one-shot, so they do not experience so-called memory effects; they do not require further pre-treatment prior to use or cleaning between measurements and they are very versatile in different applications [10,11]. Disposable sensors and biosensors have many areas of application, such as environmental protection [12–14], food analysis [15–17], and medical diagnosis [11,18,19]. Various disposable sensors for environmental monitoring of Pb, Cd and Hg were fabricated using different technologies, such as screen-printing, toner transfer, and lithography, which we discuss in the following sub-sections.

2.1. Screen-printed

Table 1 shows selected disposable screen-printed sensors [13,20–26] used for determination of Pb(II), Cd (II) and Hg(II) in environmental samples, taking into account their analytical figures of merit, such as LOD and linear range [27].

Screen-printed sensors (Fig. 1) are miniaturized devices fabricated by depositing metal or graphite-loaded inks on a support, and, due to their disposability, they avoid cross-contamination [28–30]. These sensors have several advantages, such as low cost of production, flexibility in design, and ease of mass production with consistent chemical performance [28–30]. There are many commercial sources of screen-printed sensors in different configurations, and they

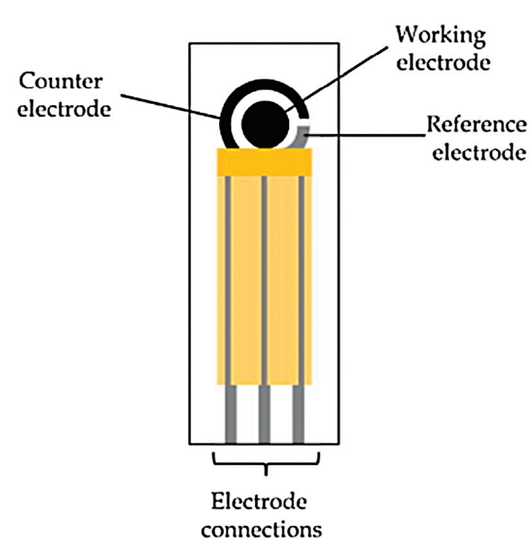

Fig. 1. Screen-printed device with three-electrode configuration.{Reprinted from [28], © 2013 with permission from Elsevier}.