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Nafion–mercury coated film electrode for the adsorptive stripping voltammetric determination of lead and cadmium in the presence of pyrogallol red

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ABSTRACT

An adsorptive stripping voltammetric (AdSV) method is presented for the simultaneous determination of Pb(II) and Cd(II) at trace levels in natural waters, based on metal complexation with pyrogallol red (PR) and subsequent adsorptive deposition on a Nafion–mercury coated glassy carbon electrode (NHgFE). Pyrogallol red forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II). Optimal analytical conditions were pH 4.0 (acetate buffer); $C_{PR}=2.8 \mu\text{mol L}^{-1}$; $E_{ads}=-0.40 \text{ V vs. Ag/AgCl}$; $t_{ads}=100 \text{ s}$. The linear calibration curves ranged from $1.0 \mu\text{g L}^{-1}$ to $16.0 \mu\text{g L}^{-1}$ for Pb(II) and from $1.0 \mu\text{g L}^{-1}$ to $13.0 \mu\text{g L}^{-1}$ for Cd(II). The detection limits ($S/N=3$) were $0.05 \mu\text{g L}^{-1}$ for Pb(II) and $0.01 \mu\text{g L}^{-1}$ for Cd(II). The relative standard deviation was 1.0% and 2.0% ($n=7$), respectively, for a solution containing $5.0 \mu\text{g L}^{-1}$ Pb(II) and Cd(II). The method was validated by determining Pb(II) and Cd(II) in certified reference waste water (SPS–WW1). Finally, the method was applied to the determination of Pb(II) and Cd(II) in commercial mineral water samples after UV digestion.

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1. Introduction

The monitoring of Pb(II) and Cd(II) in natural waters is of great importance for ecological assessments, due to the fact that these elements tend to concentrate in all aquatic environmental matrices and are taken up by marine species that form part of the human food chain. Anodic stripping voltammetry (ASV), the most popular stripping voltammetric technique, is effective for the determination of trace amounts of metal ions. Table 1 summarizes some of the published work on the application of Hg and Bi-modified electrodes for the simultaneous determination of Pb(II) and Cd(II) by ASV. For this determination modified electrodes have been used, such as Hg-coated glassy carbon [1–3], Hg-film supported on wax-impregnated carbon paste [4], Hg(II)-modified multiwalled carbon nanotubes [5], mercury film screen-printed carbon or graphite [6–8], and in the last years solid mercury amalgam [9], achieving detection limits of 0.94 ng L^{-1} , $-5.0 \mu\text{g L}^{-1}$ for Pb(II) and 1.8 ng L^{-1} , $-2.0 \mu\text{g L}^{-1}$ for Cd(II). Similarly to the mercury film electrode (HgFE), in the last 10 years the bismuth film electrode (BiFE) has been used by plating on glassy carbon [10] or modified with Nafion [11], Nafion graphene [12], 2,2'-bipyridyl

[13], poly(p-aminobenzene sulfonic acid) [14] and other substrate materials such as carbon paste [15], graphite [16], and Nafion medical stone graphite [17]. Also, electrodes made with solid vibrating Bi [18], Bi nanopowder [19] and Bi bulk [20] have been introduced, and all of them exhibited excellent performance for anodic Pb(II) and Cd(II) determination.

Over the last years the popularity of adsorptive stripping voltammetry for trace metals has been increasing. However, the large majority of the published applications on the simultaneous determination of Pb(II) and Cd(II) using modified electrodes have utilized anodic stripping voltammetry (Table 1). These electrodes were shown to be extremely useful for adsorptive stripping measurements of trace nickel, cobalt, molybdenum, vanadium and chromium. However, to our best knowledge adsorptive determination of Pb(II) and Cd(II) has been unexplored.

The aim of this study was to optimize the adsorptive stripping voltammetric technique to determine Pb(II) and Cd(II) simultaneously, using pyrogallol red (PR) (3,4,5-trihydroxy-9-(2'-sulfophenyl)-6-isoxanthone; pyrogallolsulfonphthalein) as complexing and adsorbing ligand. This compound has been used in AdSV with HMDE as a chelating agent for molybdenum [21], germanium [22], copper [23], aluminum [24], antimony [25], and cobalt [26], but its use for the simultaneous determination of Pb(II) and Cd(II), using a glassy carbon electrode modified with Hg–Nafion has not been reported yet.

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Table 1
Selected published data for the application of Hg and Bi modified electrodes in the anodic stripping voltammetry of Pb(II) and Cd(II).

Electrode type	Mode	Linear range ($\mu\text{g L}^{-1}$)	Detection limit ($\mu\text{g L}^{-1}$)	Dep. time (s)	Ref.
Hg-glassy carbon	Sono-SWASV		Pb(II)=0.5 [*] Cd(II)=1.0 [*]	60	[1]
Hg-Nafion-glassy carbon	SWASV	Pb(II)=0–0.2 Cd(II)=0–1.1	Pb(II)=0.02 Cd(II)=0.11	60	[2]
Hg-wax carbon paste	ASV, CV,	Pb(II)=1.0–2072 Cd(II)=0.5–1124	Pb(II)=1.12 ng L ⁻¹	120	[3]
Hg(II)-carbon nanotube	DPASV	Pb(II)=0.2–5.0 Cd(II)=0.2–5.0	Pb(II)=0.94 ng L ⁻¹ Cd(II)=1.8 ng L ⁻¹	180	[4]
Hg-Nafion-screen printed carbon	SWASV	Pb(II)=10–200 Cd(II)=10–200	Pb(II)=1 Cd(II)=2	120	[5]
Hg-screen printed graphite	SWASV	Pb(II)=10–2000 Cd(II)=10–2000	Pb(II)=1.8 Cd(II)=2.9	120	[6]
Hg-methocel-screen printed graphite	SWASV	Pb(II)=1–1000 Cd(II)=1–1000	Pb(II)=0.3 Cd(II)=1	120	[7]
Ag-Hg-Nafion-glassy carbon	SWASV	Pb(II)=1–48 Cd(II)=1–28	Pb(II)=0.342 Cd(II)=0.551	120	[8]
Bi-glassy carbon	SWASV	Pb(II)=10–100 Cd(II)=10–100	Pb(II)=6.9 Cd(II)=1.4	90	[9]
Bi-Nafion-glassy carbon	SWASV SIA	Pb(II)=6–80 Cd(II)=2–60	Pb(II)=2 Cd(II)=2		[10]
Bi-Nafion-graphene-glassy carbon	DPASV	Pb(II)=0.5–50 Cd(II)=1.3–30	Pb(II)=0.02 Cd(II)=0.02	120	[11]
Bi-Nafion-2,2'-bipyridyl-glassy carbon	SWASV	Pb(II)=0.2–414 Cd(II)=0.1–225	Pb(II)=0.077 Cd(II)=0.12	120	[12]
Bi-poly(p-aminobenzene sulfonic acid)-glassy carbon	DPASV	Pb(II)=1.0–130.0 Cd(II)=1.0–110.0	Pb(II)=0.80 Cd(II)=0.63	240	[13]
Bi-carbon paste	SWASVDPASV		Pb(II)=0.8 Cd(II)=1.0	120	[14]
Bi-graphite	SWASV	Pb(II)=2–25 Cd(II)=1.2–13.5	Pb(II)=0.497 Cd(II)=0.326	120	[15]
Bi-Nafion-medical stone-Graphite	SWASV	Pb(II)=2.0–12.0 Cd(II)=2.0–12.0	Pb(II)=0.07 Cd(II)=0.47	300	[16]
Vibrating-Bi	SWASV	Pb(II) until 310.8	Pb(II)=0.03 Cd(II)=0.017	120	[17]
Bi nanopowder-screen printed carbon paste	SWASV		Pb(II)=0.07 Cd(II)=0.15	600	[18]
Bi bulk	SWASV	Pb(II)=10–100 Cd(II)=10–100	Pb(II)=0.093 Cd(II)=0.054	180	[19]

* Human saliva.

2. Experimental

2.1. Chemicals and reagents

Standard solutions of Pb(II) and Cd(II) were prepared by diluting commercial standards containing 1000 mg L⁻¹, Merck (Darmstadt, Germany). Water purified in a Milli-Q water purification system (Millipore) was used for all solution and sample preparations ($\Omega > 18 \text{ M}\Omega \text{ cm}^{-1}$, Milford, USA). Nafion (5% w/v solution in a mixture of water and lower alcohols) and pyrogallol red were purchased from Aldrich (Milwaukee, WI). The stock solution of pyrogallol red in methanol ($1 \times 10^{-3} \text{ mol L}^{-1}$) was freshly prepared every three or four days. The method was validated by determining Pb(II) and Cd(II) in certified reference waste water (SPS-WW1). Finally, the method was applied to the determination of Pb(II) and Cd(II) in sea water and tap water samples after UV digestion.

2.2. Instrumentation

The voltammograms were obtained on a BASi CV50W with 3 mm and 2 mm \emptyset glassy carbon electrodes. The 3 mm \emptyset and the 2 mm \emptyset glassy carbons were obtained from BASi and Metrohm, respectively, but all measurements were made with a BASi instrument. The reference electrode was Ag/AgCl/KCl 3 mol L⁻¹ and the auxiliary electrode was a platinum wire. The solutions were deaerated using high-purity nitrogen. pH was measured with an Orion model 430 pH meter. UV-irradiation of water samples was carried out in quartz tubes using a 705 UV-digester (Metrohm).

2.3. Procedure for the preparation of NHgFE

Before measurement, the glassy carbon electrodes were thoroughly polished using a polishing pad with a 0.3 μm Al₂O₃ slurry, rinsed with ethanol and water in an ultrasonic bath and dried with N₂. A drop of the Nafion solution (10 μL) was placed on the electrode surface and the solvents were left to evaporate at room temperature for 10 min. The electrode was then transferred into the plating solution containing 200 mg L⁻¹ Hg(II) and the Hg film was formed by holding the working electrode potential at -1.30 V for 150 s. The same electrode was used for a series of measurements.

2.4. Mineral water samples

Commercial mineral waters (Jahuel and Puyehue) were purchased in a supermarket. Before the analysis all the samples were digested with UV irradiation for 90 min at 90 °C (10.0 mL of sample with 100 μL of 30% H₂O₂).

2.5. Procedure for obtaining adsorptive voltammograms

Water (10.0 mL), 1.0 mL of acetate buffer (0.4 mol L⁻¹), 20–40 μL of pyrogallol red solution ($1 \times 10^{-3} \text{ mol L}^{-1}$), and aliquots of Pb(II) or Cd(II) solution (0.5 or 1.0 mg L⁻¹) were pipetted into the voltammetric cell. The solution was purged with nitrogen (saturated with water vapor) for 5 min for a given t_{ads} and E_{ads} at a stirring speed of 1800 rpm. After a 10 s quiescent period, the potential was scanned between -0.20 and -1.20 V using square wave modulation with 10 mV step amplitude, 45 mV pulse amplitude, and a frequency of 15 Hz. The calibration curves were obtained and linear range and detection limits were calculated. The proposed method was applied to the determination of Pb(II) and Cd(II) in mineral water. In order to eliminate matrix effects the standard addition method was used.

3. Results and discussion

Pyrogallol red (PR) contains four donor oxygen atoms forming two functional analytical groups: 3,4-dihydroxy and 5-hydroxy-6-oxy. These groups are separated but can form complexes of two types depending on the nature of the metal and the state of the reagents. Complexation at 3,4-dihydroxy groups occurs only at pH < 6 unless the 3-hydroxy group is dissociated [26]. PR forms complexes with a metal:ligand stoichiometry of 1:1 with Pb(II) and of 1:2 with Cd(II).

Fig. 1A shows adsorptive voltammograms for 4.1 $\mu\text{mol L}^{-1}$ of PR (curve a) and in the presence of 11.5 $\mu\text{g L}^{-1}$ of Pb(II) and Cd(II) (curve b) in acetate buffer solution at pH 4.5 using a mercury film electrode (HgFE). The stripping peak of PR was observed at -0.73 V; in the presence of Pb(II) and Cd(II) the peak current of this signal decreased and a small peak was observed at -0.52 V, which corresponds to the reduction of the Pb-PR complex, while the reduction of the Cd-PR complex is overlapped with the signal

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