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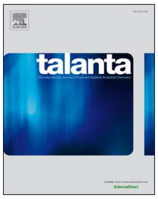

Ultrasensitive hexavalent chromium determination at bismuth film electrode prepared with mediator

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ABSTRACT

A bismuth film electrode prepared in situ with a reversibly deposited mediator (Zn) applied for ultrasensitive determination of Cr(VI) using differential pulse catalytic adsorptive stripping voltammetry is presented. The optimization of experimental conditions such as composition of the supporting electrolyte, potential and time of bismuth film formation as well as analyte accumulation, and DP mode parameters is reported. For 180 s accumulation time, very low limits of detection and quantification of Cr(VI) were obtained, with 5.8×10^{-14} and 1.9×10^{-13} mol L^{-1}, respectively. The relative standard deviation for 5.0×10^{-13} mol L^{-1} of Cr(VI) was 3.9% (n = 5). Finally, the proposed procedure was applied to determine Cr(VI) in the certified reference materials – NASS-6 (seawater), SLEW-3 (estuarine water) and TMRAIN-04 (rainwater) – as well as in river water samples. Furthermore, the obtained results show that the proposed voltammetric procedure employing the bismuth film electrode prepared with mediator appears to form a very promising tool for the speciation of chromium at ultratrace level.

1. Introduction

Chromium is one of the most widespread elements in the Earth's crust [1]. The main forms of Cr found in the environment are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). The major waste containing chromium comes from electroplating, textiles, tanneries and metallurgical industry [2]. Apart from the above, human activities such as combustion of oil and coal, welding or cement works contribute to spread of compounds containing Cr(VI). In contrast to Cr(III), which is the most stable form, which is essential for the proper functioning of the organism, Cr(VI) is highly toxic [1].

Hexavalent chromium can get to the human organisms via: direct ingestion, inhalation or dermal contact. It is able to penetrate through biological membranes and may react with nucleic acids and proteins [3,4]. DNA damages can be induced by chromium compounds in different ways which lead to creation of DNA adducts, the exchanges of sister chromatid and chromosomal aberrations [4,5]. Soluble chromium (VI) causes severe skin reactions. Direct skin contact leads to irritation, formation skin ulcers that are hard to manage, and contributes to the development of skin inflammations, allergic and eczematous dermatitis [6]. It also irritates the respiratory system, damages the tissue of the nasal cavity, causes ulceration or perforation of nasal septum, forms ulcers and contributes to epistaxis [6,7]. It can also redound to the formation of papilloma of the upper respiratory tract [8]. Prolonged exposure to chromium(VI) causes kidney and the liver damage [9]. Several studies confirm that prolonged exposure to Cr(VI) significantly increases the risk of lung cancer [10–12]. Consequently, the selective determination of Cr(VI) is a subject of considerable interest.

The analytical method proposed by the Environmental Protection Agency (EPA) of the United States for this purpose is based on the use of ionic chromatography (IC) [13]. Using this method Cr(VI) can be determined in drinking water, groundwater, and industrial wastewater effluents at 0.3–0.4 μg L^{-1} range, still the IC is a relatively expensive analytical tool. Another analytical alternatives are the combination of time-consuming and costly preconcentration/extraction strategies with, for example atomic spectrometry [14,15] and total-reflection X-ray fluorescence spectrometry [16].

When compared to other methods for Cr(VI) determination, the electrochemical method, especially stripping voltammetry stands out because of simple operation, low cost of equipment, high sensitivity and selectivity. Literature reports [17,18] prove that voltammetry is an appropriate technique enabling trace determination of chromium. Due to the toxicity, handling, volatility and disposal issues connected with mercury used in the mercury based electrodes, novel alternative electrode materials with similar performance are highly desirable, to meet the increasing demands for the determination of trace Cr(VI). Among the different types of electrodes the environmentally-friendly bismuth film electrodes stand out, offering well-defined and highly reproducible

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stripping responses, excellent resolution of neighboring peaks, high hydrogen evaluation and wide linear range [17,19,20]. However, taking the accumulation time into account the obtained detection limits of Cr(VI) for bismuth based electrodes are still higher than those for common mercury electrodes [21]. Therefore, the main aim of this study was to develop ultrasensitive voltammetric procedure for environmental monitoring of Cr(VI) using eco-friendly base electrode. To achieve this goal we used bismuth film electrode (BiFE) prepared with a reversibly deposited mediator [22–24] and differential pulse catalytic adsorptive stripping voltammetric technique (DP CAdSV) combining adsorptive preconcentration of the reduction product of Cr(VI) in the form of the Cr(III)-H_2DTPA complex with the catalytic reaction using NO_3^- as an oxidizing agent [25,26]. In this paper we demonstrate how very low concentrations of chromium can simply be determined. According to the best our knowledge this is the first application of an in situ plated bismuth film electrode prepared with mediator for the determination of chromium in environmental samples.

2. Experimental

2.1. Reagents

DTPA (diethylenetriaminepentaacetic acid) and KNO_3 were obtained from Sigma and Merck. KNO_3 was additionally purified by recrystallization. An acetate solution (pH = 6.0 ± 0.1) was prepared from acetic acid and sodium hydroxide (Suprapur, Merck). A standard solution of Cr(VI) at concertation of 1 g L^{-1} was obtained from Fluka. Working solutions of Cr(VI) were prepared by dilution of standard solutions with 0.01 mol L^{-1} HNO_3 (Merck). The standard solutions of Zn (II), Bi(III), Ni(II), Co(II), Cd(II), Pb(II), Fe(III), Cu(II), Se(VI), Mn(II), Mg(II), Ca(II) were obtained from Merck and Cr(III) together with Triton X-100 from Fluka. All solutions were prepared using ultra-purified water (> 18 MΩ cm) supplied by a Milli-Q system (Millipore, UK).

2.2. Apparatus

All voltammetric measurements were performed using a μAutolab analyser manufactured by Eco Chemie, the Netherlands. A classic three-electrode quartz cell with 10 mL volume was used, consisting of a modified glassy carbon working electrode (GCE) with a diameter of 1 mm, an Ag/AgCl reference electrode and a platinum wire as an auxiliary electrode. The GC electrode was polished daily on silicon carbide paper (SiC-paper, #2500, Buehler, Denmark) and alumina particles suspension (1.0, 0.3 and 0.05 μm) on a Buehler polishing pad with subsequent washing and sonication for 30 s. The certified reference materials were mineralized using a UV-digester made by Mineral (based in Poland).

2.3. Procedures

Under the optimized conditions the in situ plating of bismuth film with the use of reversibly deposited mediator metal and the determination of hexavalent chromium was carried out in a solution containing 0.1 mol L^{-1} acetate solution (pH = 6.0 ± 0.1), 0.25 mol L^{-1} KNO_3, 7.5 mmol L^{-1} DTPA, 0.3 mg L^{-1} Zn(II), 0.3 mg L^{-1} Bi(III) and Cr(VI). Oxygen was removed by passing nitrogen for 5 min. The potential of the electrode was changed in the following sequence: 0.5 V for 30 s, − 1.1 V for 60 s (E and $t_{\text{dep. of Bi and Zn}}$, respectively) and − 1.0 V for 180 s (E and $t_{\text{oxi. Zn, dep. Bi and acc. Cr(III)-H2DTPA}}$, respectively). In the first step, the electrode was electrochemically clean (oxidation of the residues from the previous measurement at 0.5 V for 30 s). Then, Bi (metal of interest) and Zn (reversible mediator) were deposited simultaneously onto the surface of glassy carbon electrode (reduction of Bi(III) and Zn (II) to the metallic state at − 1.1 V for 60 s). During the third step, Zn was stripped from surface (oxidation of metallic zinc) as Bi continued to deposit (reduction of Bi(III) to metallic state) and the accumulation of reduction product of Cr(VI) in the form of the Cr(III)-H_2DTPA complex onto the working electrode surface (adsorption of the protonated complex of Cr(III) with DTPA preceded by reduction of Cr(VI) to Cr(III)) was performed. During these steps the solution was stirred with use of a magnetic stirring bar. Then, the stirring was stopped and after 5 s equilibration time, the differential pulse voltammograms were recorded between − 0.8 and − 1.45 V with pulse amplitude (ΔE) of 150 mV and scan rate (υ) of 100 mV s^{-1}. During scanning of potential in the negative direction the reduction of Cr(III)-H_2DTPA to Cr(II)-H_2DTPA on the electrode surface was performed. The reduction current was enhanced in the presence of nitrates by chemical re-oxidation of Cr(II)-H_2DTPA to Cr(III)-H_2DTPA which was subsequently re-reduced at the electrode surface [25,27]. The background current was subtracted from each Cr (VI) measurement. The optimized procedure parameters were summarized in Table 1.

Table 1
Optimal parameters for the determination of Cr(VI) at BiFE prepared with mediator.

Parameter	Value
Acetate solution	0.1 mol L^{-1}
pH	6.0 ± 0.1
KNO_3	0.25 mol L^{-1}
DTPA	7.5 mmol L^{-1}
Zn(II)	0.3 mg L^{-1}
Bi(III)	0.3 mg L^{-1}
$E_{\text{dep. of Bi and Zn}}$	− 1.1 V
$t_{\text{dep. of Bi and Zn}}$	60 s
$E_{\text{oxi. Zn, dep. Bi and acc. Cr(III)-H2DTPA}}$	− 1.0 V
$t_{\text{oxi. Zn, dep. Bi and acc. Cr(III)-H2DTPA}}$	180 s
ΔE	150 mV
υ	100 mV s^{-1}

2.4. Water samples

The certified reference materials (CRMs), NASS-6 (seawater) and SLEW-3 (estuarine water), were obtained from the National Research Council Canada, Ottawa, Canada. The CRM TMRAIN-04 (rain sample) was obtained from the Environment Canada, Burlington, Canada. The certified reference materials were mineralized for 3 h with use of an UV-digester and then the appropriate volumes of CRMs samples were introduced into the vessel and total chromium as Cr(VI) was determined. The natural water samples were collected from Bystrzyca River (Lublin, Poland). The river water samples were filtered using a 0.45 μm Millipore filter and then introduced into the supporting electrolyte and after 60 min delay Cr(VI) was determined.

3. Results and discussion

The catalytic adsorptive stripping voltammetric procedure proposed in this paper for a ultra-trace determination of Cr(VI) is based on published procedures for mercury electrodes [27–32]. In the present study the toxic mercury electrodes used commonly for the determination of Cr(VI) were replaced, for the first time, by an eco-friendly in situ plated bismuth film electrode prepared with a reversibly deposited mediator. Before application of bismuth film electrode prepared with mediator, instead of mercury electrodes, for Cr(VI) determination, numerous experiments were performed for optimization of bismuth film formation, analyte accumulation conditions and instrument working parameters of curve registration, using differential pulse voltammetric techniques. The optimization was necessary because the adsorption of Cr(III)-H_2DTPA complex takes place on the thin bismuth film plated with mediator but not on the mercury surface.