



Short communication

Determination of chromium in estuarine waters by catalytic cathodic stripping voltammetry using a vibrating silver amalgam microwire electrode

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ARTICLE INFO

Article history:

Received 18 July 2012

Received in revised form

28 September 2012

Accepted 7 October 2012

Available online 17 October 2012

Keywords:

Chromium determination

Silver microwire electrode

Cathodic stripping voltammetry

Vibrating electrode

ABSTRACT

Chromium (Cr^{VI}) in water can be determined by adsorptive catalytic cathodic stripping voltammetry in the presence of diethylenetriaminepentaacetic acid (DTPA) and nitrate on the hanging mercury drop electrode (HMDE). Predominately Cr^{VI} is detected and the water is UV-digested to convert all Cr to Cr^{VI} prior to analysis. We develop here an alternative to the HMDE by using a silver amalgam electrode based on a vibrating microwire. The microwire electrodes were 12.5 μm in diameter and electrochemically coated with mercury, and were stable for a week. Conditions were re-optimised, and we used a DTPA concentration of 5 mM, 30 mM acetate pH buffer (pH 5.5 in seawater and pH 5.8 in pure water), and 1.5 M nitrate solution. The microwire was reactivated prior to each scan by applying a negative potential (-3 V) for 2 s which removed all deposited Cr. The detection limit for chromium in pH buffer was found to be 0.2 nM Cr^{VI} and in seawater 0.3 nM Cr^{VI} at a deposition time of 30 s. The response increased linearly with the concentration of Cr^{VI} up to 60 nM Cr^{VI} in seawater. The limit of detection is less good than using the HMDE, but the linear range is good and the microwire electrode could form the basis of apparatus for flow-analysis. The method was successfully tested on water samples from the estuary of the river Mersey (Liverpool Bay) giving chromium concentrations between 1.48 nM and 2.29 nM.

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1. Introduction

Chromium is an ecotoxic trace metal which is present in natural waters in two oxidation states: the reactive and toxic Cr^{VI} and the relatively inert Cr^{III} . Cr^{VI} is an inhaled carcinogen, toxic to humans and other mammals, while Cr^{III} is an essential mineral supplement at trace level [1]. Major sources of chromium contamination are metallurgy, electroplating industry, pigment production, tannery, mining and refractory materials [2]. Several sensitive methods exist in the literature for the determination of chromium, some of these based on voltammetry, which has advantages related to sensitivity and ability to measure in seawater. Cathodic stripping voltammetry (CSV) makes use of adsorption of an electroactive complex with an added ligand. CSV has good sensitivity and can be used to determine metal speciation as well as its concentration in seawater. The CSV procedure for Cr in natural waters typically makes use of diethylenetriaminepentaacetic acid (DTPA) which forms a species with Cr^{III} that adsorbs on a hanging mercury drop electrode (HMDE) [1,3,4]. The Cr^{III} is freshly produced by reduction of Cr^{VI}

at potentials $< -0.1\text{ V}$. The freshly produced Cr^{III} is $30\times$ more reactive than existing Cr^{III} in the solution, so Cr^{VI} is the main contributor to the voltammetric response [5]. Nitrate is added to increase the sensitivity through a catalytic reaction in which Cr^{III} is the catalyst, which causes reduction of nitrate when the voltammetric scan reaches its reduction potential. The CSV method mechanism has been developed further [1,5] and modified using a different ligand (cupferron), and different electrode materials including a bismuth film electrode [6,7] and a silver-amalgam film [8,9]. Methods were recently reviewed [2]. An interesting modification has been the introduction of a more negative deposition potential in which the Cr^{VI} is plated as metallic Cr, then re-oxidised and re-adsorbed as the Cr^{III} -DTPA species [10]. This modification is included in this work.

The CSV procedure using the mercury is a “batch analysis” method, which is laborious because reagents are added to the voltammetric cell, either manually or using automated burets, for each analysis separately. This method would benefit from the introduction of flow analysis, but this is complicated with a mercury drop electrode as it is not easily adapted to flow analysis. Automation has been achieved using an HMDE [10] making use of pumped medium exchange of a batch cell. Mercury drop electrodes have been incorporated in flow-cells [11] but this has not caught on generally probably because of difficulties of stabilising a mercury drop in flow conditions and of environmental risk

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when using it in the field. Here we develop a solid electrode to determine Cr^{VI} by CSV. A solid electrode can be readily converted to flow analysis by fitting in a flow-cell, which is much easier than with the HMDE. Another advantage of the solid electrode is that the use of mercury is much reduced although this electrode is mercury-coated.

Silver-amalgam electrodes (made similarly to dental amalgam) have been proposed before for voltammetry [12] but that design is not readily made into a microelectrode. Solid electrodes have been used before for CSV. The mercury surface is particularly suitable for the adsorptive preconcentration step, but bismuth coated have also been used for several applications of cathodic stripping voltammetry [13,14]. A silver macro-electrode, physically coated with mercury prior to each scan, has been used before for the determination of Cr^{VI} [9] and cobalt and nickel [15] by CSV. Similarly a silver–bismuth alloy [16] and bismuth-coated carbon [17] have been used for CSV of nickel and cobalt, and mercury-coated gold for CSV of iron [18]. Alloys of silver and copper have been used for CSV of Ni [19].

Here we use a vibrating silver microwire electrode, electrochemically amalgamated with mercury, for CSV of Cr^{VI} . The surface is stable and suitable for CSV without requiring re-coating for a week, and its very thin diffusion layer thickness leads to rapid analysis with sensitivity sufficient for environmental monitoring.

2. Experimental

2.1. Apparatus

Electrochemical measurements were carried out using a μ Autolab III voltammeter (Ecochemie, The Netherlands) connected to an IME663 interface and a VA663 electrode stand (Metrohm, Switzerland). The working electrode was a 12.5 μm diameter silver microwire (Goodfellow Company, UK), the reference electrode was a double-junction Ag/AgCl, 3 M KCl, and the counter electrode was an iridium wire of 0.15 mm diameter and 2 cm length. The instrument was controlled by the software GPES 4.9 using subtraction mode for analysis. Seawater and nitrate solution used for the experiments were UV-digested using a 125 W high-pressure mercury vapour lamp during 45 min to remove dissolved organic matter prior to use.

2.2. Chemicals

All reagents were of analytical reagent grade and all solutions were prepared using Milli-Q deionised water (Elix/Gradient Milli-Q water purification system, resistivity 18 M Ωcm^{-1}). Standard solutions of Cr^{VI} were prepared either weekly or at the beginning of a set of experiments by dilution of metal atomic absorption stock solutions (1000 mg Cr L^{-1}) with water. An aqueous solution of DTPA (Acros Organics) was prepared containing 0.25 M DTPA. The pH was adjusted using a pH buffer containing 3 M ammonium acetate (AnalaR grade, England). Addition of 0.03 M of the ammonium acetate solution to seawater gave a pH of 5.5. An aqueous solution of 5 M sodium nitrate (Fisher Scientific) was employed for the catalytic effect. Contaminating Cr in the nitrate was removed by co-precipitation with 0.1 mM iron(II) chloride followed by filtration [4]. The mercury plating solution contained 2 mM monohydrated mercury nitrate (AnalaR grade, England) acidified with 10 mM HNO_3 . Seawater samples (salinity 27–32) were collected using a polypropylene hand-pump in the Mersey Estuary in Liverpool Bay during a cruise with the Liverpool University research vessel Marisa in summer 2011. The samples were immediately gravity filtered through a 0.2 μm

cellulose acetate filter cartridge (Sartobran 300, Sartorius) and stored under refrigeration.

2.3. Microwire electrode preparation

The fabrication of the silver microwire electrode was similar to that of gold wire electrodes [20]. A copper wire was passed through a 100 μL plastic pipette tip and dipped in a conductive silver solution. The end of the copper wire was then attached to a short length silver wire (12.5 or 25 μm) by gently touching it and subsequently withdrawing it into the tip, with ~ 1 mm protruding. The tip was melted by holding it for 8 s in the mouth of a tubular oven set to 450 $^\circ\text{C}$. Good sealing between plastic and the silver wire ensures long-term stability, which is obvious from a lack of water build-up in the electrode tip and from scans without noise. To obtain a vibrating electrode, a vibrating device was placed in the back of the tip [21] using an adapted method [22].

2.4. Mercury plating

A scan in 10 mM HNO_3 was performed using cyclic voltammetry (CV) from 0 to +0.4 V to check for normal electrode behaviour, which showed silver oxidation beginning at +0.4 V. Subsequently mercury was added to the same solution to a final concentration of 2 mM Hg and purged with nitrogen for 5 min. Then, mercury was electrochemically plated on the silver microwire at -0.4 V (10 min) [23] resulting in a silver-amalgam electrode. The silver-amalgam electrode was used for about 1 week of experiments and was then replaced by a new one.

2.5. Electrochemical reaction mechanism

During the deposition step at -1 V dissolved Cr^{VI} is reduced to Cr^{III} . The Cr^{III} forms a complex with the DTPA which is adsorbed on the electrode surface. This mechanism is the same as on an HMDE [4]. Subsequently, a potential scan was carried out to measure the amount of deposited Cr^{III} from its reduction current to Cr^{II} producing a peak at -1.2 V. The current was enhanced by a catalytic effect in the presence of nitrate ions, owing to the chemical reoxidation of Cr^{II} to Cr^{III} which is immediately re-reduced during the scan [4].

2.6. General procedure to determine chromium

The sample solution (10 mL) containing 5 mM DTPA, 0.03 M ammonium acetate buffer (pH 5.8 in Milli-Q water and 5.5 in seawater) and 3 mL 5 M nitrate (final concentration ~ 1.5 M nitrate) was pipetted into the voltammetric cell. The solution was deoxygenated by N_2 -purging (5 min). The silver amalgam microwire electrode was activated at -3 V (2 s) (vibration on) and Cr^{III} -DTPA complexes were adsorbed at the deposition potential (E_{dep}) (30 s) (vibration on). E_{dep} was -1.0 V in seawater and -1.1 V in Milli-Q water due to a small difference in pH and peak potential. After a 2 s equilibration time (vibrator off) the voltammogram was recorded by applying a differential pulse scan (DP) from -1.0 to -1.35 V. The electrochemical parameters were as follows: interval time 0.1 s, step-potential 2 mV, modulation amplitude 50 mV and modulation time 0.002 s. The background scan used an adsorption time of just 1 s and was otherwise the same as the analytical scan. The background scan was subtracted from the analytical scan to obtain a background-corrected scan. This was automated using the Project function of the GPES software.

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