# Studies on the stripping voltammetric determination and speciation of chromium at a rotating-disc bismuth film electrode

E.O. Jorge [a,1], M.M. Rocha [b], I.T.E. Fonseca [b], M.M.M. Neto [a,b,*]

[a] Unidade de Investigação de Química Ambiental, Instituto Superior de Agronomia, Tapada da Ajuda, TULisbon, 1349-017 Lisboa, Portugal
[b] Centro de Ciências Moleculares e Materiais (CCMM), Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, Ed. C8, 1749-016 Lisboa, Portugal

## ARTICLE INFO

## ABSTRACT

An adsorptive stripping voltammetric protocol coupled with a rotating-disc bismuth film electrode for the determination and speciation of chromium (III) and chromium (VI) in the presence of diethylene-triaminepentaacetic acid (DTPA) is presented. The developed methodology involves a mass-transport controlled preconcentration step, during which a Cr(III)–DTPA complex is adsorbed onto a pre-plated rotating-disc bismuth film electrode held at −0.4 V, followed by a reductive square wave stripping scan. At −1.07 V vs. Ag/AgCl, a peak is recorded due to the catalytic reduction of Cr(III)–DTPA to Cr(II)–DTPA. As a result of different chemical behaviours of Cr(III) and Cr(VI) in the presence of DTPA, the corresponding voltammetric signals presented different stabilities in time. A univariate optimization study was performed with several experimental parameters as variables. For Cr(VI) and total chromium, Cr(III) + Cr(VI), an accumulation time of 60 s at −0.4 V vs. Ag/AgCl resulted in detection limits of 0.336 and 0.414 nM and quantification limits of 1.12 and 1.40 nM, respectively. The relative standard deviation for 10 measurements of 5.0 nM chromate was 2.4%. Interference of other electroactive trace metals and surfactants was considered. A simple speciation scheme was proposed and satisfactorily applied to Cr(III) and Cr(VI) determinations in river water samples.

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## 1. Introduction

Chromium is a metallic element usually found in aquatic systems in two oxidation states, Cr(III) and Cr(VI). Cr(III) appears to be an essential trace element species since it plays an important role in some metabolic processes [1], while Cr(VI) is highly toxic and potentially responsible for carcinogenic effects in humans [2]. The contamination of ecosystems with chromium is mainly due to effluent discharges from a variety of industries, such as the production of steel, metal electroplating, spray painting, leather tanning, wood preserving and mining. The guideline value set by World Health Organization (WHO) for Cr(VI) in groundwater is 50 ppb [3]. The development of precise and accurate analytical methods for chromium speciation and determination at trace level is extremely important because of the high toxicity and potential environmental hazard of its hexavalent form.

Many analytical procedures using different techniques have been reported in the literature to quantify chromium species, atomic absorption spectroscopy (AAS) and inductive coupled plasma mass spectrometry (ICP-MS) being the most frequently employed [4–6]. In general, previous treatment of samples involving preconcentration and separation schemes is required, such as chromatography [6], coprecipitation [7], extraction [8], electrophoresis [9] or ion-exchange resins [10]. However, these methods are not profitable enough to be adapted to routine analysis, since they are somewhat complicated and time-consuming, and usually involve expensive instrumentation.

Electrochemical methods appear very attractive for analytical purposes because they are reliable, sensitive and require less expensive equipment [11]; for chromium in particular, they allow direct redox speciation with no separation step [12–35]. These are significant advantages for monitoring programmes. Voltammetric methods have been described in the literature for the detection of Cr(VI) using metallic nanoparticle-modified carbon screen-printed electrodes [12], pyridinium-based sol–gel film [13] and self-assembled monolayer [14] modified electrodes; gold electrodes have also been used [15,16]. Adsorptive cathodic stripping voltammetry (AdCSV) has been employed to preconcentrate and determine traces of chromium in aqueous solutions [17–35]. In this technique, the voltammetric determination is preceded

* Corresponding author at: Unidade de Investigação de Química Ambiental, Instituto Superior de Agronomia, Tapada da Ajuda, TULisbon, 1349-017 Lisboa, Portugal. Tel.: +351 213653437; fax: +351 213653180.
*E-mail address:* mm.neto@netcabo.pt (M.M.M. Neto).
[1] Present address: Department of Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden.

by adsorption of a Cr(III) complex on the electrode surface. Different ligands have been used, such as pyrocatechol violet [17,18], hydroxyethyl-ethylenediaminetriacetic acid (HEDTA) [18], ammonium pyrrolidine dithiocarbamate [19], ethylenediaminetetraacetic acid (EDTA) [20], triethylenetetraaminehexaacetic acid (TTHA) [21], diethylenetriaminepentaacetic acid (DTPA) [20–33], cupferron [21,34,35], among others.

While Cr(VI) has been successfully determined with detection limits below nanomolar [20], the determination of Cr(III) is not such an easy task, since a continuous decrease of the voltammetric signal has been observed [23–26]. Using DTPA as a complexing agent, Li and Xue [26] developed an entire protocol for chromium speciation at subnanomolar level, which was applied to natural samples. In other works [22–27], reaction schemes were proposed for the complexation and redox reactions of Cr(III) and Cr(VI) with DTPA in the presence of nitrate at mercury electrodes, under catalytic adsorptive stripping voltammetric conditions. Cr(VI) is present in solution as chromate, which diffuses to the electrode surface where it is rapidly reduced to Cr(III) at potentials as low as $-0.05$ V [26]. A Cr(III)–DTPA complex is then formed and adsorbed; its reduction to a Cr(II)–DTPA species takes place, originating a well-defined reduction peak. On the other hand, Cr(III) is easily complexed in bulk solution with DTPA; the complex diffuses to the electrode surface where it is weakly adsorbed and then reduced. However, this process is hindered because only a small fraction of the complex reaches the electrode; during its transport, the conversion to a non-electroactive complex species occurs. Recently, Bobrowski et al. [36] reviewed the characteristics of voltammetric determination and speciation of chromium. An interesting multivariate calibration methodology for the simultaneous determination of Cr(III) and Cr(VI) by differential pulse adsorptive stripping voltammetry at the HMDE, using PCV and HEDTA as complexing agents, is reported; it was successfully applied to the speciation of chromium in different water samples [17,18].

Due to the favourable electrochemical behaviour of mercury as an electrode material, mercury electrodes have been for many years the preferred tools for stripping voltammetry. Literature widely reports AdCSV of chromium at the hanging mercury drop electrode (HMDE) [17–29] and the mercury film electrode (MFE) [30,31,34], but in analytical practice, less toxic electrode materials should replace mercury, which is clearly responsible for unavoidable contamination of the environment. In the last decade, bismuth film electrodes have appeared as a good alternative, with an equivalent performance to mercury electrodes [37]. Moreover, additionally to its low toxicity, bismuth films offer other advantages including good mechanical stability that enables operation under hydrodynamic conditions. This is particularly useful for on-line monitoring in flow systems. Recently, the suitability of the bismuth film electrode (BFE) for AdCSV measurements of trace Cr(VI) was demonstrated, using cupferron [35] and diethylenetriaminepentaacetic acid (DTPA) [32,33] as complexing agents. The results obtained by Lin et al. demonstrated a better stripping performance for the BFE in comparison with the MFE [33].

The main purpose of this work was to explore the potentialities of a rotating-disc bismuth film electrode for the speciation of chromium by adsorptive cathodic stripping voltammetry, after complexation with DTPA. A square wave voltammetric scan was used in the determination step due to its inherent benefits, including fast analysis with high sensitivity in the presence of dissolved oxygen. The rotating-disc electrode was employed to improve transport of chromium species to the electrode surface. An optimization study of the operational conditions for the here proposed chromium speciation scheme was performed. Although the voltammetric data obtained appear to corroborate the previously proposed mechanism for the electrochemical reduction of Cr(III) and Cr(VI) at mercury electrodes, some discrepancies were

found on the stability of the Cr(III) signal at the rotating BFE after addition of DTPA to solutions. The influence of potentially interfering species was considered. River water samples were successfully analysed using the established methodology with the proposed environmental-friendly bismuth film sensor.

## 2. Experimental

### 2.1. Apparatus

Voltammograms were generated with a computer controlled Autolab Basic PGSTAT 12 potentiostat from Eco Chemie (Utrecht, The Netherlands) driven by GPES software (Version 4.9). A Solaar M Series AA atomic absorption spectrophotometer (Unicam) was employed for the photometric determination of chromium.

The rotating-disc electrode assembly (Eco Chemie, Utrecht, The Netherlands) consisted of a RDE70270 glassy carbon disc electrode (area: $0.283 \, cm^2$) coupled with an Autolab Rotator. The three-electrode system was completed with an Ag|AgCl (3 M KCl) reference and a platinum foil counter electrode, both from Metrohm. A 100 mL glass made voltammetric cell was used. The pH measurements were performed by a combined pH electrode pHC 3005-8 with a Radiometer MeterLab PHM201. Ultraviolet irradiations were carried out using a CAMAG UV lamp.

All potentials are referred to Ag|AgCl (3 M KCl) reference electrode.

### 2.2. Reagents and glassware

Solutions were prepared from analytical-reagent grade chemicals using Millipore Milli-Q ultrapure water (resistivity $\geq 18.0 \, M\Omega \, cm$) and stored in Pyrex glass flasks. Suitable amounts of acetic acid and sodium acetate (Sigma–Aldrich) were mixed to make 0.1 M acetate buffer (pH 4.6). A stock solution of 0.1 M DTPA (Sigma–Aldrich) was prepared by dissolving the appropriate amount of the ligand and adding 2 M potassium hydroxide until pH 6.0. A stock solution of 0.1 M potassium nitrate (Riedel-de Haën) was also obtained. The bismuth(III) plating solution was prepared from $Bi(NO_3)_3 \cdot 5H_2O$ (AnalaR). Chromium(VI) and chromium(III) stock solutions were made from $K_2CrO_4$ (Sigma–Aldrich) and $Cr(NO_3)_3 \cdot 9H_2O$ (Merck), respectively. The interferences studies were performed using the following reagents: Triton X-100 from Sigma–Aldrich, $Pb(NO_3)_2$ and $Co(NO_3)_2 \cdot 6H_2O$ (AnalaR-grade), $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ from Merck, and $Zn(NO_3)_2 \cdot 6H_2O$ from Panreac.

All the glassware was carefully cleaned by soaking the pieces, overnight, in a 2% diluted RBS 25 detergent, washed several times with distilled water and finally with Millipore water.

### 2.3. Procedures

#### 2.3.1. Preparation of BFE

Before bismuth film formation, the glassy carbon electrode surface was polished with Alpha Micropolish alumina 0.3 μm particle size (Buehler), thoroughly washed with Milli-Q water and dried. It was then activated in 0.1 M acetate buffer (pH 4.6) by continuous potentiodynamic cycling ($n = 10$) at 50 mV s$^{-1}$, between $-1.2$ and $+0.25$ V. Bismuth was plated onto the glassy carbon electrode substrate from 2.0 μM bismuth(III) nitrate in 0.1 M acetate buffer at $-1.4$ V, for 120 s. The electrode was kept under rotation at 240 rpm.

#### 2.3.2. SWAdCSV measurements of chromium

For square wave adsorptive cathodic stripping voltammetric (SWAdCSV) measurements of chromium, the supporting electrolyte was obtained by adding the suitable volume of potassium

nitrate stock solution to the acetate medium, to a final concentration of 0.3 M $KNO_3$; pH was checked and adjusted to 6.0 with potassium hydroxide. After 5 min nitrogen bubbling [33], the solution was spiked with the required volume of DTPA stock solution to final concentrations of 5.0 and 3.0 mM, for Cr(III) and Cr(VI) determinations, respectively. Prior to the addition of chromium, a voltammogram of the blank was recorded.

The most adequate operational sequence to perform SWAdCSV experiments of Cr(VI) was found to be as follows: first, accumulation of chromium by potentiostatic adsorption of its DTPA complex at −0.4 V, for 60 s, followed by an equilibration period of 3 s at open circuit; secondly, application of a negative going square wave potential scan, starting at −0.8 V to a final potential of −1.4 V. A cathodic stripping voltammogram was simultaneously recorded. For Cr(III) measurements, the whole procedure was preceded by a reaction time of 30 min in order to get a stable electrode response. The electrode was continuously rotating at a speed of 300 rpm. The selected square wave parameters were: frequency 25 Hz, amplitude 40 mV and scan increment 7 mV. Between measurements, an electrochemical pre-cleaning step was applied to the BFE to prevent memory effects. The electrode was held at −1.2 V for 10 s, to guarantee the efficient removal (by reduction and desorption) of the DTPA complex from the surface. After a series of measurements, the electrode was held at +0.3 V for 30 s to remove the bismuth film electrochemically.

Experiments were conducted at room temperature of $(22 \pm 1)$ °C.

### 2.3.3. Determination of Cr(III) and Cr(VI) in real samples

River water samples collected from the River Tagus estuary were analysed after a minor pre-treatment, consisting of successive filtration through Whatman filter no 1 and Minisart (0.45 μm). The samples were then spiked with the appropriate volumes of acetate buffer and $KNO_3$ stock solutions to obtain the adequate supporting electrolyte concentrations and pH was adjusted to 6.0 with KOH. After deaeration with nitrogen for 5 min, DTPA was added. For Cr(VI) determination ($C_{Cr(VI)}$), standard additions of Cr(VI) were carried out. For determination of total chromium ($C_{totCr}$), the samples were previously UV irradiated (λ: 254 nm) for 4 h to decompose organic matter including surface-active compounds, release and oxidise Cr(III) to Cr(VI) [23,29]. DTPA was then added and the SWAdCSV measurements were performed after standard additions of Cr(VI). The Cr(III) concentration ($C_{Cr(III)}$) was calculated by subtraction ($C_{totCr} - C_{Cr(VI)}$).

For comparison, determination of Cr(III) in samples was also carried out by the standard addition method. SWAdCSV measurements were performed after 30-min contact time between the sample, containing added DTPA, and each standard addition of Cr(III).

## 3. Results and discussion

### 3.1. SWAdCSV of Cr(III) and Cr(VI) at the rotating-disc BFE

Solutions containing Cr(III) or Cr(VI) in background electrolyte (pH 6.0) produced a voltammetric peak at the rotating-disc BFE ($E_p = -1.07$ V) owing to reduction of Cr(III)–DTPA complex, previously adsorbed on the electrode surface, to Cr(II)–DTPA. Fig. 1 shows a typical SWAdCSV response of BFE to Cr(VI).

Under the experimental conditions mentioned in caption of Fig. 1, the electrode response to Cr(VI) was stable in time for at least 1 h, whereas the Cr(III) signal was found to be dependent on time after addition of DTPA to solution. Unlike previously published studies using mercury electrodes [23,26], which show the voltammetric signal of Cr(III) decreasing with time, our experimental data
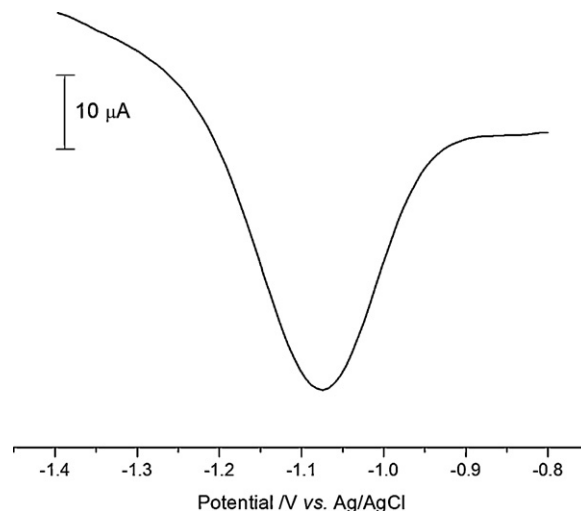


**Fig. 1.** Typical square wave adsorptive cathodic stripping voltammogram of 2.0 nM Cr(VI) at a rotating-disc bismuth film electrode. Supporting electrolyte: 0.1 M acetate buffer (pH 6.0) + 0.3 M $KNO_3$ + 3.0 mM DTPA. $E_{acc}$: −0.4 V; $t_{acc}$: 60 s; $t_{eq}$: 3 s; rotation speed: 300 rpm; square wave amplitude: 40 mV; $\Delta E_s$: 7 mV; square wave frequency: 25 Hz.

exhibited differently. An increase of peak current ($I_p$) over time was observed following addition of DTPA to solutions containing Cr(III); after *ca* 20 min of contact time the peak height became stable (Fig. 2). The transport of the Cr(III)–DTPA complex formed in bulk solution to the electrode surface is here favoured by convective-diffusion, which may cause a delay in its gradual conversion to the electro-inactive complex species [23,26]. Thus, after DTPA addition, an increasing current is firstly observed but a stable response to Cr(III) is then attained when equilibrium is reached. A similar performance of a mercury film-based flow probe for trace chromium monitoring was previously reported [31].

Adsorptive stripping voltammetric experiments involving Cr(III)/Cr(VI) mixtures were also performed in two concentration ratios, 1:2 and 2:1. The dependence of the electrode response on DTPA contact time was analysed for 1 h; the data are shown in Fig. 3. At a Cr(III):Cr(VI) concentration ratio of 1:2, a stable voltammetric signal is observed within 15–20 min, reflecting a continuous
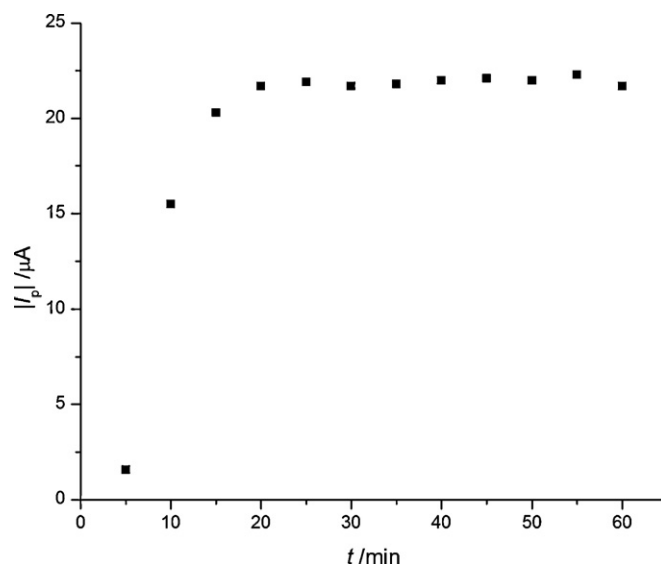


**Fig. 2.** Variation of peak current of SWAdCSV for 20 nM Cr(III) over time. $C_{DTPA}$: 5.0 mM, other conditions as in Fig. 1.
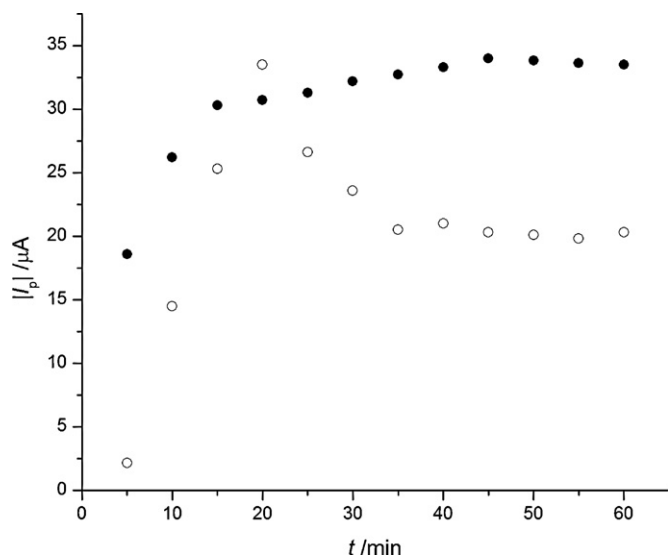
**Fig. 3.** Variation of peak current of SWAdCSV over time for solutions containing (●) 10 nM Cr(III) + 20 nM Cr(VI) and (○) 20 nM Cr(III) + 10 nM Cr(VI). Other conditions as in Fig. 2.

process of formation, adsorption and reduction of Cr(III)–DTPA complex at the electrode surface. For the solution containing Cr(III) and Cr(VI) in a concentration ratio of 2:1, peak current increases until reaching a maximum after 20 min of DTPA addition, then decreases and starts to level off at *ca* 30 min contact time (Fig. 3). Being Cr(III) the prevalent species, it plays an important role in the electrode process and, in fact, DTPA may kinetically promote formation of the electroactive Cr(III)–DTPA complex at the beginning. However, after a period of 30 min, the contribution of the dissolved Cr(III) to the reduction peak becomes constant, probably due to the establishment of an equilibrium between the Cr(III)–DTPA reaching the electrode and the amount of complex converted in bulk solution to the electrochemically inert complex.

There is still lack of information to explain such experimental evidence. For mixtures containing the same Cr(III):Cr(VI) concentration ratios, i.e., 1:2 and 2:1, a previous square wave adsorptive stripping voltammetric study of the system Cr(III)–DTPA + NO$_3^-$ at a wall-jet mercury film electrode produced peak current vs. time plots identical to the ones shown in Fig. 3 (unpublished data). The unexpected results reported in this section were confirmed by carrying out three independent set of experiments under the same experimental conditions.

In the present work, all SWAdCSV measurements involving the presence of Cr(III) in solutions were performed with a 30 min delay after the addition of DTPA with the electrode under rotation, in order to get a stable voltammetric signal due to reduction of Cr(III)–DTPA. The Cr(VI) measurements were carried out immediately upon the DTPA addition, since the Cr(III) signal was still negligible at that stage.

### 3.2. Optimization of experimental conditions for SWAdCSV of chromium at a BFE

To establish the most adequate experimental conditions for a SWAdCSV protocol to determine trace chromium using the rotating-disc BFE, a univariate optimization study was carried out with the parameters that may affect the voltammetric signal of the target species as variables. The influence of the following parameters was investigated: bismuth film thickness, DTPA and nitrate ions concentrations, adsorptive accumulation time ($t_{acc}$) and potential ($E_{acc}$) of the chromium–DTPA complexes, electrode

rotation speed ($\omega$), equilibration time ($t_{eq}$) and square wave amplitude ($a$), frequency ($f$) and potential increment ($\Delta E_s$).

#### 3.2.1. Effect of Bi film thickness

The accessible potential window of the BFE in acetate buffer was already established in a previous paper [38]. To start the optimization study, the effect of bismuth film thickness on the voltammetric signal of chromium at the BFE was examined. Following the procedure described in Section 2.3.1, bismuth was plated onto the glassy carbon electrode surface from Bi(III) solutions of nine different concentrations varying from 0.6 to 2.8 μM. The BFE prepared from each Bi(III) concentration was transferred to the voltammetric cell containing 20 nM Cr(VI), 0.1 M acetate buffer (pH 6.0), 0.25 M KNO$_3$ and 10 mM DTPA as the complexing agent. After 120 s accumulation time at −0.4 V, SWAdCSV of chromium was performed. All recorded voltammograms exhibited a well-defined cathodic peak ($E_p = -1.07$ V), with peak current showing to be markedly enhanced by the increased bismuth concentration of the corresponding plating solutions. However, at BFEs prepared from the more concentrated solutions ($C_{Bi(III)} > 2.0$ μM), peak height started to increase slowly, tending to stabilize. This behaviour suggests the occurrence of multilayer deposition, which may cause weak adhesion of bismuth to glassy carbon. In all subsequent works, a 2.0 μM Bi(III) solution was employed for *ex situ* preparation of the BFE, at −1.4 V for 120 s. This adopted Bi(III) concentration value is in accordance with previous work dealing with the voltammetric determination of thallium at an *in situ* plated BFE [38].

#### 3.2.2. Effect of DTPA and nitrate ions concentrations

The effect of DTPA concentration on the analytical signals of Cr(VI) and Cr(III) was examined. As the DTPA concentration was varied from 1.0 to 15 mM in a solution containing 4.0 nM Cr(VI), the peak currents increased attaining a maximum for 3.0 mM DTPA. A similar effect was observed with a 4.0 nM Cr(III) solution, when DTPA concentration was 5.0 mM. At higher DTPA concentrations, peak currents decreased. Thus, subsequent studies of Cr(VI) and Cr(III) were conducted using 3.0 and 5.0 mM of DTPA, respectively. The analytical signals obtained for Cr(VI) are higher than for Cr(III), the latter being even null when $C_{DTPA}$ is 0.1 mM. This can be explained taking into account the mechanisms proposed for the complexation and redox reactions of Cr(VI) and Cr(III) with DTPA at mercury electrodes, under voltammetric conditions [22,23]. Cr(VI) diffuses as chromate from the bulk solution to the electrode surface, where it is reduced to Cr(III) at slightly negative potentials (<−0.05 V at Hg electrodes). In the presence of DTPA, the freshly produced Cr(III) is rapidly complexed and adsorbed at the electrode surface; when a negative going potential scan is applied, the Cr(III)–DTPA complex is electrochemically converted to Cr(II)–DTPA, originating a cathodic well-defined peak ($E_p = -1.07$ V). On the other hand, when Cr(III) is the initial species in solution, a stable Cr(III) hexaquo complex should be present in the bulk [23,27]. The addition of DTPA promotes the formation of an electroactive Cr(III)–DTPA complex, which is weakly adsorbed at the electrode surface and subsequently reduced to Cr(II)–DTPA, at −1.07 V. Moreover, during its diffusion from the bulk to the electrode surface, the Cr(III)–DTPA reacts with a second DTPA ligand, originating a stable electrochemically inactive complex [23].

The role of potassium nitrate in the supporting electrolyte is to amplify the analytical signal of chromium by a catalytic effect [39]. In the presence of nitrate ions the reduction of the Cr(III)–DTPA complex appears to follow a catalytic mechanism, involving the chemical re-oxidation of the still non-desorbed Cr(II)–DTPA to Cr(III)–DTPA, which is subsequently re-reduced at the BFE. Zarebski [40] firstly suggested this catalytic effect for the process at a mercury electrode. Different amounts of nitrate were added to solutions containing 20 nM of Cr(VI) and Cr(III), respectively. The obtained
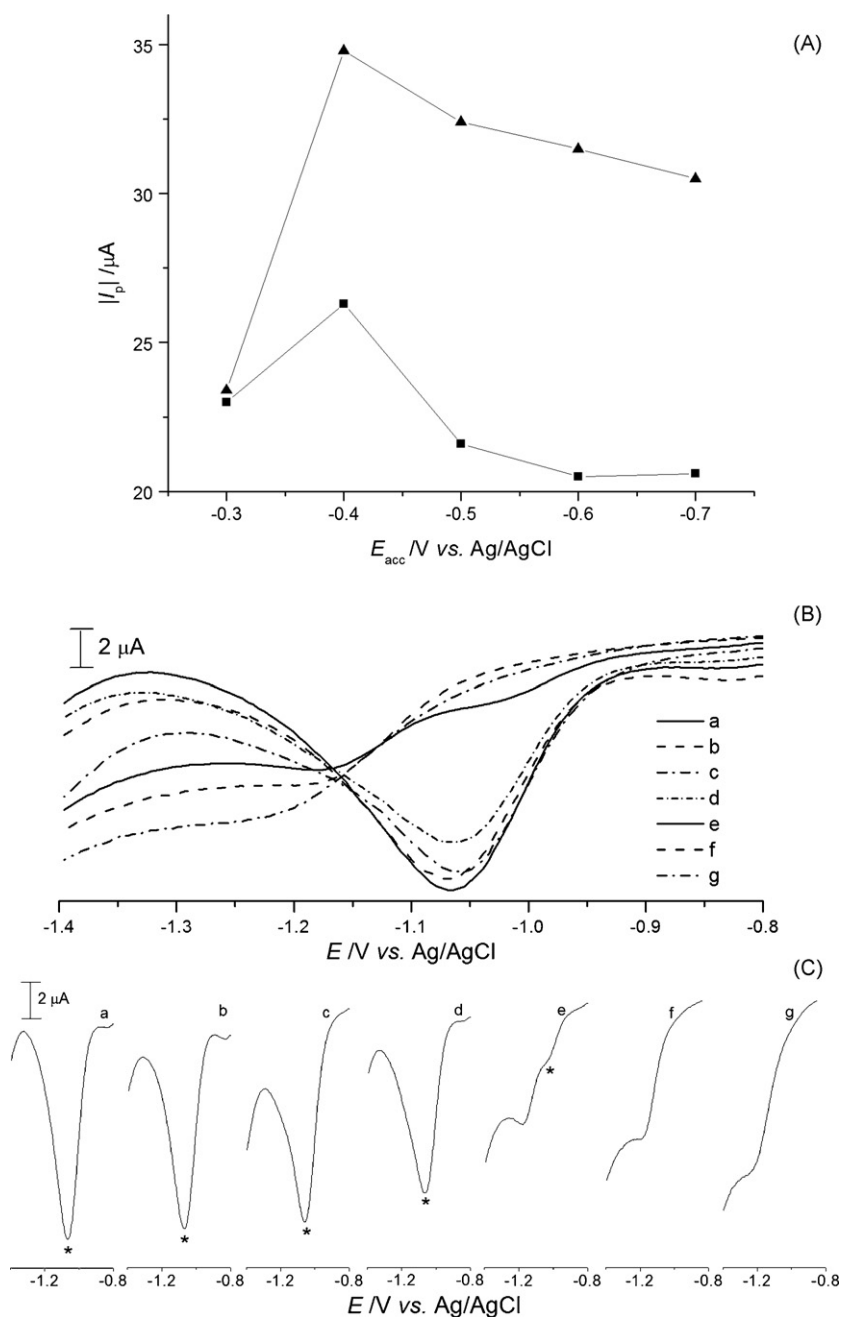
**Fig. 4.** (A) Effect of accumulation potential on stripping peak current, $I_p$, of (■) 20 nM Cr(III), $C_{DTPA}$ = 5.0 mM and (▲) 20 nM Cr(VI), $C_{DTPA}$ = 3.0 mM. Other conditions as in Fig. 1. (B) SWAdCSV for 20 nM Cr(VI) at different accumulation potentials, $E_{acc}$, (a) −0.4 V, (b) −0.5 V, (c) −0.6 V, (d) −0.7 V, (e) −0.8 V, (f) −0.9 V and (g) −1.0 V. (C) Sequence of the previous voltammograms (a–g) emphasizing the evolution of the peak at −1.07 V, marked with *.

results show increasing peak currents as nitrate concentration is raised up to 0.3 M, this tendency being more noticeable for Cr(III); for higher nitrate concentrations, the peak currents level off. Hence, nitrate was added to the working solutions to a final concentration of 0.3 M in all further experiments.

### 3.2.3. Effect of accumulation potential, accumulation time and rotation speed

SWAdCSV experiments were carried out with solutions containing 20 nM Cr(VI) and Cr(III), respectively, to study the effect of the accumulation potential ($E_{acc}$). Holding the BFE at five different potential values in a window ranging from −0.3 to −0.7 V, the following data were observed. For Cr(VI) solution, peak currents sharply increase as the accumulation potential is incremented from

−0.3 to −0.4 V, whereas for Cr(III) only a slight increase of peak current is observed; when $E_{acc} < -0.4$ V, peak currents diminished, more emphatically for the Cr(III) solution (Fig. 4A). As expected [41], in progressing to more negative accumulation potentials, i.e., $E_{acc} < -0.8$ V, chromium is predominantly reduced to Cr(II) by charge transfer rather than by mass transport; in addition, the amount of Cr(III)–DTPA complex formed is definitely much smaller (Fig. 4B). Ill-defined peaks of very small magnitude were obtained denoting both the irreversible nature of the reduction process and the hindering effect of the hydrogen evolution wave (Fig. 4C). This is clearly shown when $E_{acc}$ is equal to −1.0 V. To ensure diffusion-controlled reduction of Cr(III)–DTPA to Cr(II)–DTPA generating well-defined peaks, an accumulation potential of −0.4 V was chosen in all subsequent works.
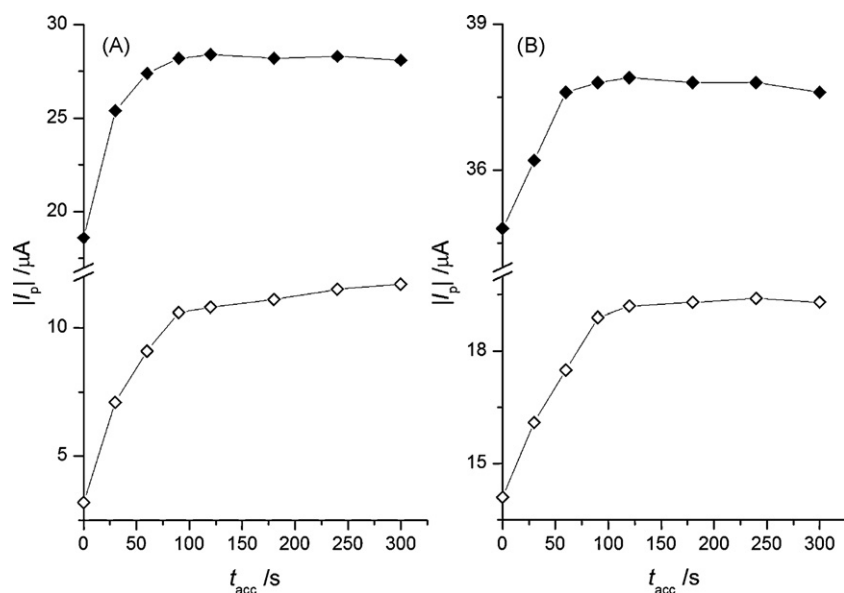
**Fig. 5.** Effect of accumulation time on stripping peak current, $I_p$, for solutions containing (◇) 2.0 nM and (◆) 20 nM (A) Cr(III) and (B) Cr(VI). Other conditions as in Fig. 4A.

The influence of accumulation time and rotation speed on the response of the rotating BFE was studied for two different concentrations of the target species, 2.0 and 20.0 nM Cr(VI), and Cr(III). The results depicted in Figs. 5 and 6 show similar profiles of $I_p$ vs. $t_{acc}$ and $I_p$ vs. $\omega^{1/2}$, for identical concentrations of both Cr(VI) and Cr(III). Peak currents increase nearly linearly with $t_{acc}$ up to 90 s, for 2.0 nM solutions, and up to 60 s, for 20.0 nM (Fig. 5). This behaviour reflects the increasing of the surface concentration of the adsorbed species on the electrode surface, as the accumulation time increases. Then, as illustrated in Fig. 5, for higher accumulation times peak currents increase more slowly and a plateau is reached at 120 s, reflecting the saturation of the electrode surface. It is worth highlighting that a large signal is still obtained even in the absence of accumulation step, i.e., when $t_{acc} = 0$ s, most probably due to the catalytic effect of nitrate in the determination step. An accumulation time of 60 s was adopted for SWAdCSV of chromium at BFE. It is worth stressing that, for Cr(III) solutions, the accumulation times were considered after 30 min of reaction with DTPA.

Improved sensitivity is expected to be achieved using the rotating-disc configuration, due to the increase of mass transport to the BFE. The adsorptive accumulation process should be favoured by the enhanced flux of solution generated by forced convection, since the diffusion rates of both Cr(VI), as chromate, and Cr(III), as the electrochemically active Cr(III)–DTPA complex formed in the bulk, to the electrode surface are increased. SWAdCSV of 2.0 and 20.0 nM Cr(VI) at BFE was performed for rotation speeds ranging from 60 to 2500 rpm. A study involving solutions containing identical Cr(III) concentrations, 2.0 and 20.0 nM, was also carried out. Peak currents significantly increase with electrode rotation speed and then tend to level off. Linear plots of stripping peak current vs. $\omega^{1/2}$ were obtained up to 500 and 1000 rpm, for the 2.0 and 20.0 nM concentrations, respectively, for both Cr(VI) and Cr(III) species, demonstrating that the reductive process is diffusion-controlled [42]. The corresponding data are given in Fig. 6.

For the larger selected values of rotation speed, the electrode response deviates from linearity, denoting that the saturation sur-
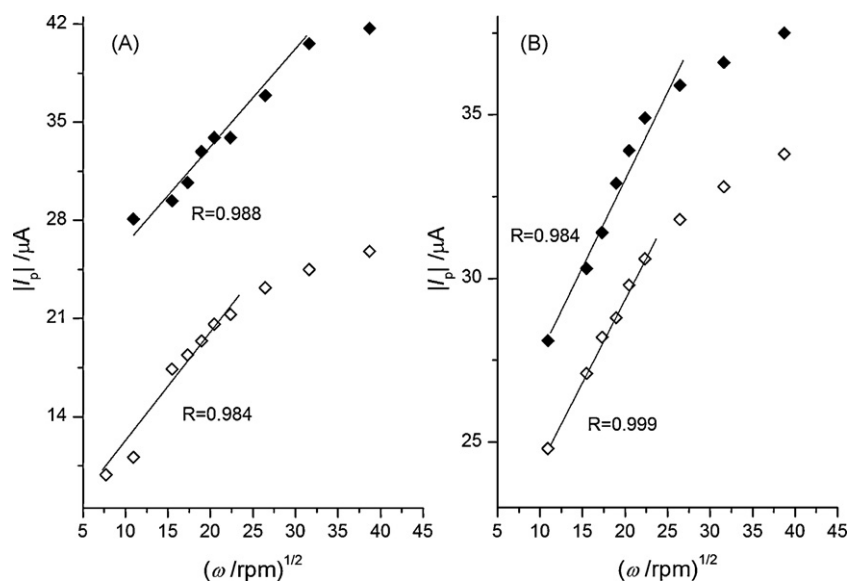


**Fig. 6.** Effect of electrode rotation speed on peak current, $I_p$, for solutions containing (◇) 2.0 nM and (◆) 20 nM (A) Cr(III) and (B) Cr(VI). Other conditions as in Fig. 4A.
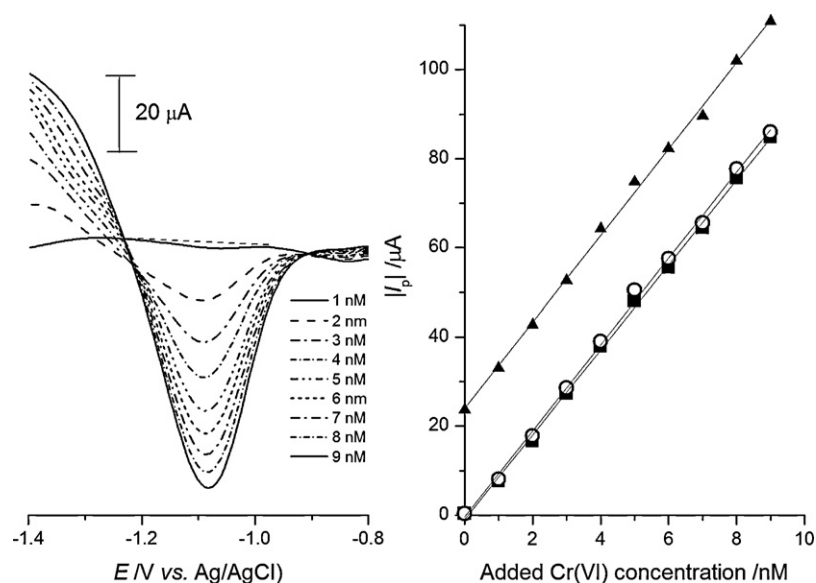
**Fig. 7.** SWAdSV at a rotating-disc BFE for increasing concentrations of Cr(VI). $E_i = -0.8$ V to $E_f = -1.4$ V. Other conditions as in Fig. 1. Also shown on the right are calibration plots for successive additions of Cr(VI) to supporting electrolyte (■) in the absence of Cr(III); in the presence of 2.5 nM Cr(III) (○) before and (▲) after UV-irradiation.

face concentration of the adsorbate, Cr(III)–DTPA complex, is being attained. Furthermore, the disruption of the mechanical stability of the bismuth film at high rates of convective mass transport will certainly contribute to poorly reproducible voltammetric signals. The speed of 300 rpm was selected in a compromise between high sensitivity, mechanical stability and reproducibility of the BFE.

### 3.2.4. Influence of equilibration time and square wave parameters

A better performance of the BFE was found to be achieved when the solution was left to equilibrate for a short period after the adsorption step. For equilibration times varying from 0 to 7 s, a maximum peak current was obtained for a $t_{eq}$ of 3 s.

In order to perform fast analysis of chromium with high sensitivity in the presence of dissolved oxygen, the stripping step of AdCSV was carried out by scanning the potential in the negative direction using the square wave modulation. Hence, the square wave frequency, scan increment and amplitude were optimized, using solutions containing 20.0 nM of Cr(III) and Cr(VI), respectively. As frequency varies from 13.5 to 25.0 Hz, at an amplitude of 40 and 7 mV of staircase increment, peak currents increase sharply, then more slowly tending to level off, due to the hindering contribution of the capacitive background current on the total measured current. Ill-defined peaks slightly displaced to the negative direction were obtained for higher frequencies, indicating that charge transfer is predominantly controlling the reduction process. A less profound effect was observed for the staircase increment, $\Delta E_s$. At an amplitude of 25 mV, $\Delta E_s$ was varied from 1 to 12 mV; the analytical signal of chromium increased but no improvement was achieved for $\Delta E_s > 7$ mV. A staircase increment of 7 mV in combination with a square wave frequency of 25 Hz were selected to produced high scan rate and well-defined peaks, as required. The influence of square wave amplitude was also examined, in

the 10–80 mV range, for Cr(III), and from 10 to 100 mV, for Cr(VI). Greater peak currents slightly shifting towards positive direction were obtained by increasing amplitude. The dependence was found to be linear, but deviations from linearity with peak broadening were observed for larger values, above 45 mV for Cr(III), and 80 mV for Cr(VI). High sensitivity and good peak definition were achieved for both chromium species at square wave amplitude of 40 mV.

### 3.3. Analytical applicability of the BFE for chromium speciation

Under the optimized operational conditions, the analytical applicability of the rotating-disc BFE for chromium speciation was then tested.

In SWAdCSV of Cr(III) at the rotating-disc BFE, at least 20 min of contact between Cr(III) and DTPA are required before performing each measurement, in order to get a stable electrode response. Such a time-consuming operational restriction is obviously not convenient for analytical purposes and consequently it should not be included in the chromium speciation scheme.

Taking into account that the voltammetric signal for Cr(III) is negligible immediately after the addition of DTPA (see Fig. 2), calibration plots of the reduction stripping peak current measured at −1.07 V against Cr(VI) concentration were constructed by performing standard additions of Cr(VI), in the absence and the presence of Cr(III). Close fit to linearity was observed in both cases. Fig. 7 gives a series of voltammograms for Cr(VI) in the absence of Cr(III). The calibration plots shown demonstrate that measurements were not affected by the presence of 2.5 nM Cr(III). Least-squares treatment yielded slopes of $9.53 \pm 0.117$ and $9.69 \pm 0.146$ μA nM$^{-1}$, intercepts of $-1.08 \pm 0.626$ and $-0.51 \pm 0.779$ μA and correlation coefficients of 0.999 and 0.998 ($N=10$) for Cr(VI) calibration plots, in the absence and in the presence of 2.5 nM Cr(III), respectively. The cal-

**Table 1**
Results for determination of chromium in river water samples.

| Sample[a] | Speciation method | | Standard additions of Cr(III) | AAS |
|---|---|---|---|---|
| | $C_{Cr(VI)}$ (nM) | $C_{Cr(III)} = C_{totCr} - C_{Cr(VI)}$ (nM) | $C_{Cr(III)}$ (nM) | $C_{totCr}$ (nM) |
| 1 | $0.86 \pm 0.12$ | $1.60 \pm 0.25$ | $1.41 \pm 0.19$ | <20 |
| 2 | $6.10 \pm 1.30$ | $14.4 \pm 2.09$ | $13.1 \pm 4.22$ | $22.4 \pm 0.15$ |

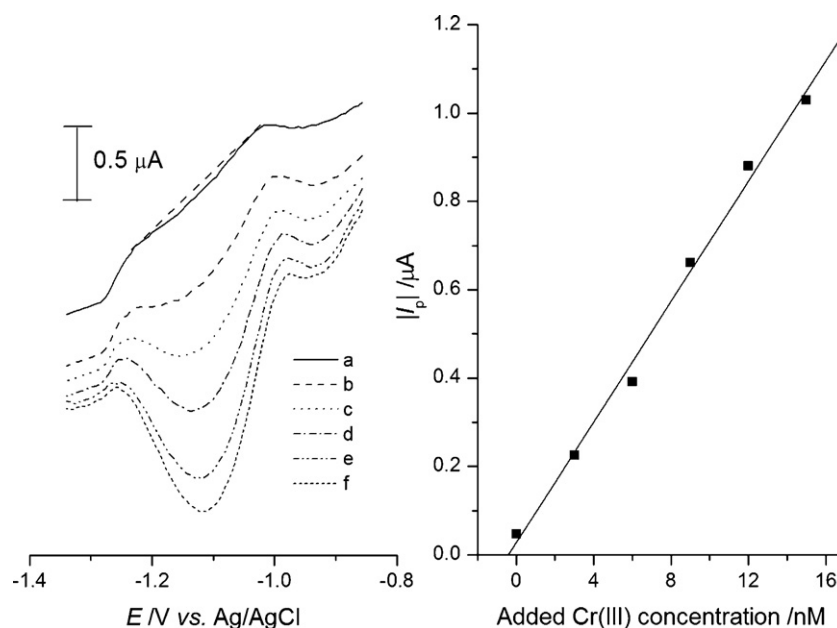[a] Samples collected from (1) Algés-Dafundo Beach and (2) Algés Beach.

**Fig. 8.** Standard additions of Cr(III) to a river water sample collected from Algés beach (sample 1) in 0.1 M acetate buffer (pH 6.0) + 5.0 mM DTPA + 0.3 M KNO$_3$ at BFE. Curves: a, sample; b, c, d, e and f, sample +3, 6, 9, 12 and 15 nM, respectively, of Cr(VI). Other conditions as in Fig. 2.

culated limits of detection and quantification [43] are (LOD) 0.336 and 0.411 nM and (LOQ) 1.12 and 1.37 nM, respectively.

According to literature [23,26], Cr(III) is efficiently converted to Cr(VI) by UV-irradiation, which allows the determination of total chromium in solutions. Thus, after UV-irradiating for 4 h a solution containing 2.5 nM Cr(III) in supporting electrolyte, a calibration plot was also obtained performing standard additions of Cr(VI) (Fig. 7). Least-squares treatment gave the following characteristics: slope, $9.70 \pm 0.338 \, \mu A \, nM^{-1}$, intercept, $23.9 \pm 1.81 \, \mu A$ and correlation coefficient of 0.998 ($N = 10$). The calculated limits of detection (LOD) and quantification (LOQ) for total chromium are 0.414 and 1.40 nM, respectively.

Reproducibility of the BFE was tested for 10 consecutive measurements of 5.0 nM chromate in solution. The calculated relative standard deviation was 2.4%. Between runs, the electrode was held at −1.2 V for 10 s, to complete removal of the accumulated chromium complex from the bismuth film.

The obtained results strongly suggest the adequacy of a simple scheme for chromium speciation in real samples, as follows. Firstly, determination of Cr(VI), $C_{Cr(VI)}$, by SWAdCSV measurements following standard additions of Cr(VI), and secondly, after UV-irradiation of the sample for 4 h, determination of total chromium, $C_{totCr}$, by using the same procedure consisting of standard addition of Cr(VI). The concentration of Cr(III) in the sample can then be calculated by subtraction, $C_{Cr(III)} = C_{totCr} - C_{Cr(VI)}$. The application of the proposed speciation scheme to real samples is further presented in Section 3.5.

### 3.4. Tolerance to interfering species

The analytical methodology proposed in this paper is developed for evaluating traces of chromium in matrices of environmental interest, where potentially interfering species can be present.

Surfactants may seriously affect AdCSV measurements of trace metals at mercury [44] and bismuth film [35,45] electrodes. Triton X-100 was chosen to simulate the effect of a typical non-ionic surfactant on the SWAdCSV determination of chromium at BFE. The electrode response decreased with increasing surfactant concentration for both chromium species, but the signal of Cr(VI) was more seriously affected. At an accumulation time of 60 s, 0.3 μM

Triton X-100 decreased the voltammetric signals of 5.0 nM Cr(III) and 5.0 nM Cr(VI) by 6 and 40%, respectively. In concentrations of 30 and 1 μM, Triton X-100 led to the complete inhibition of the Cr(III) and Cr(VI) peaks, respectively. One useful approach to minimize this effect is to coat the electrode with an ion-exchange polymer [45,46]. Exposure to UV-radiation of natural samples can also be helpful to minimize or even eliminate the interference by natural surface-active compounds [23]. However, when Cr(VI) is the target species, this method cannot be applied since, if present, Cr(III) will be oxidized to Cr(VI). Recently, Niewiara et al. reported a method by means of fumed silica to eliminate the influence of high concentrations of surface-active substances on the voltammetric determination of Cr(VI) [47].

Other potential interferences in the AdCSV detection of chromium are electroactive trace metals, which may be competitively complexed by DTPA and produce reduction peaks prone to overlap or even hide the chromium peak. Pb(II), Cd(II), Ni(II), Co(II), Zn(II) and Fe(III) were tolerated, when present at $10^4$-fold more than the Cr(VI) concentration. Cu(II) does not interfere at $10^2$-fold, but at $10^3$-fold mass the analytical signal of Cr(VI) decreases; at $10^4$-fold, a new voltammetric signal is observed, which may be attributed to the reduction of Cr(II) to Cr(0). The catalytic effect of nitrate to reoxidize Cr(II)–DTPA to Cr(III)–DTPA is probably compromised by its role in Cu(II) complexation.

### 3.5. Analytical application—chromium speciation in real water samples

The proposed method for redox speciation of chromium was tested with river Tagus estuarine samples collected from two different sites of the riverbank on the outskirts of Lisbon, Algés and Algés-Dafundo beaches. The applied procedure is described in Section 2.3.3. The peak due to the presence of Cr(VI) and total Cr in the river water samples could be easily quantified by SWAdCSV measurements, following five standard additions of aliquots taken from a 10 μM potassium chromate solution, corresponding to contributions of 3.0, 6.0, 9.0, 12.0 and 15.0 nM Cr(VI). Table 1 shows the obtained results.

The higher content of chromium found in sample 2 was already expected, confirming our suspicion of high-level pollution in Algés

beach due to its configuration of a small bay. The concentrations of total chromium found in the analysed samples are comparable to those obtained by flame atomic absorption spectroscopy (AAS). Each analytical measurement was replicated five times using both SWAdCSV and AAS methods.

Standard additions of Cr(III) were then performed to the samples. After 30 min of contact time between the sample and each added aliquot of Cr(III), SWAdCSV measurements were performed. The voltammograms and the plot $I_p$ vs. added $C_{Cr(III)}$ obtained for sample 1 are shown in Fig. 8.

The calculated values of $C_{Cr(III)}$ are comparable to the ones calculated by subtraction, $C_{totCr} - C_{Cr(VI)}$, i.e., by the adopted speciation method (Table 1). Although such a time-consuming procedure is not suitable for analytical purposes, it is interesting to attest the reasonable agreement between the obtained $C_{Cr(III)}$ values. In fact, the determination of Cr(III) by standard additions of Cr(III) aliquots would make the speciation procedure very tedious and lengthy in time, specially when analysing a large number of samples. The UV-irradiation task takes 4 h, but many samples can be treated at the same time. Hence, the speciation scheme described in Section 3.3 was preferred.

In addition, it is worth mentioning that in the present analytical application no matrix effects were observed.

## 4. Conclusions

The suitability of the rotating-disc BFE to determine trace amounts of chromium in environmental aquatic samples in the presence of DTPA by SWAdCSV was demonstrated. First and foremost, the benefits of using a mercury-free voltammetric sensor should be emphasized. The hydrodynamic configuration of the sensor and the square wave potential modulation in the stripping step led to high sensitivity with no oxygen interference. The application of a simple speciation scheme allowed the determination of Cr(III) and Cr(VI) in aqueous solutions. After the optimization of experimental conditions, detection limits of 0.336 and 0.414 nM were obtained for Cr(VI) and total chromium, respectively. Good selectivity against several metal ions was observed.

A satisfactory agreement was observed when comparing the results for Cr(III) concentration in samples yielded by the speciation method and by direct SWAdCSV determination performing standard additions of Cr(III) aliquots.

The proposed methodology appears to be very promising as the basis of a sensitive and clean voltammetric procedure for speciation of chromium, at trace level, through prior adsorption as DTPA complexes on bismuth film electrodes in a hydrodynamic configuration.

Studies are planned for the near future involving Cr(III)/Cr(VI) mixtures to elucidate the time dependence of the voltammetric signals.

Another interesting research topic to be explored is the application of the environmental-friendly sensor BFE to a method that allows the simultaneous adsorptive stripping voltammetric determination of Cr(III) and Cr(VI) at trace levels, such as multivariate calibration methodology [18].

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