

Voltammetric Determination of Cr(III) and Cr(VI) in Tropical Estuarine Waters: Advantages and Limitations*

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The adsorptive-catalytic voltammetry of Cr(VI) and total chromium using DTPA is optimized for application to estuarine waters with high content of dissolved organic substances. The sensitivity of the method, better than $2 \text{ nA nM}^{-1} \text{ s}^{-1}$, is adequate to the intended goal of speciation. However, the instability of Cr(VI) in the presence of organic material imposes restrictions to the use of this methodology in large scale surveys and monitoring activities.

INTRODUCTION

Chromium has been introduced in the aquatic environment through a number of human activities including agriculture, mining and industry. The behavior of chromium in water is complex involving several oxidation states and the formation of oxyanions which are powerful oxidizing agents.¹ The main oxidation states are +2, +3 and +6. Cr(II) is a strong reducer while Cr(III) usually forms inert complexes that are responsible for slow re-oxidation kinetics.

In natural waters Cr(VI) should predominate²⁻⁴ as the soluble species chromate. In presence of Fe(II)⁵ and organic matter or under anoxic conditions Cr(VI) is reduced to Cr(III). In the natural pH of seawater Cr(III) can be slowly re-oxidized to Cr(VI) by manganese oxide.⁶ The inter-conversion Cr(III)-Cr(VI) is an important mechanism that controls the transport and bioavailability of chromium, especially in estuaries. This, because of the different bio-physical-chemical behavior: Cr(III) species are biologically essen-

* Dedicated to Marko Branica on the occasion of his 65th birthday.

tial while Cr(VI) is considered toxic; Cr(III) reacts strongly with surfaces responsible for the transport of chromium to the sediments,^{7,8} and Cr(VI) remains basically in solution.

The determination and speciation of chromium in seawater is not trivial. Because of the low concentration (0.5–2 nM)^{9,10} most available detection techniques^{11–16} require pre-concentration, a procedure that disturbs the original distribution of species. There are also problems of sample storage.

Electroanalytical techniques, based on the electroactivity of Cr(VI) over the entire pH range,¹⁷ seem to offer advantages in the speciation of chromium oxidation states in seawater. The problems of the chromium electroanalytical determination are related to the irreversible reduction of Cr(III) to Cr(II), to the hydrolysis and condensation of Cr(III) complex ions^{18,19} and to the instability of Cr(VI) in the presence of organic matter.^{12,17,20–22}

Voltammetric techniques,^{23–27} especially the adsorptive-catalytic stripping voltammetry (ACSV), are the most sensitive amongst the electroanalytical ones and do not require pre-concentration for detection of chromium in seawater. The application of square wave modulation reduced the time of analysis and improved the sensitivity by at least two orders of magnitude, in comparison to differential pulse. A large number of organic ligands has been used in the chromium determination by ACSV: cupferron,²⁷ dimethylglyoxime,²⁸ aminopolycarboxylic acids^{10,29–32,42} among others. Nearly all methods proposed are based on the work by Tanako and Ito³³ that studied the polarographic wave of Cr(III)–EDTA in acetate buffer using the catalytic effect of nitrate to increase sensitivity. The method allows determination of Cr(VI) and Cr(III) as the formation of Cr(III)–EDTA complex occurs only at the surface of the electrode where Cr(III) is formed by reduction of Cr(VI).²⁹ The process of complexation is not significant in the bulk of solution because of the inert character of Cr(III) complexes.

In the present work we discuss the results of our attempts to determine Cr(VI) and Cr(III) in waters of Guanabara Bay using adsorptive-catalytic stripping voltammetry.

Guanabara Bay, located in Rio de Janeiro, Brazil, is an estuary under severe environmental impact due to the discharge of heavy loads of domestic sewage and industrial wastes. The main sources of chromium to the bay are leather manufactories, electroplating and chemical industries.

EXPERIMENTAL

Water samples used in the analytical tests were collected from a single station in Guanabara Bay (Boa Viagem Island) located close to the bay mouth and far from direct influence of chromium sources. All materials used for sampling, storage and filtration were carefully cleaned by immersing in Extran 5% and HNO₃ 1:10 solutions over several days. Final washing was made with Suprapur HNO₃ or HCl and

water from the sampling location. Water from a MILLI-Q system was used in the preparation of washing and stock solutions. Samples were filtered under a clean hood in 0.45 μm cellulose acetate filters immediately after collection and the determination of chromium concentration was made within 2 h of sampling. All reagents were Suprapur grade except for the diethylenetriaminepentaacetic acid (DTPA).

We studied the application of the Cr(III)–DTPA reaction at a static mercury electrode to the speciation of chromium in Guanabara Bay. For the voltammetric determinations we used a 384B EG&G Polarographic Analyzer connected to a 303A EG&G Static Mercury Drop Electrode and the square wave modulation. Stirring was performed with the help of a magnetic bar and we used as reference electrode Ag/AgCl. The optimized instrumental conditions were: large drop size; initial potential -1.000 V; final potential -1.400 V; peak potential -1.220 V; purge time 4 min.; scan increment 2 mV; deposition 30 s; frequency 25 Hz; step height 0.025 V. The curves on figures 1 to 5 showing the results of our optimization tests were obtained by using always a new sample aliquot for each measured point.

To an aliquot of 5 mL of seawater reagents were added to make up the following optimal chemical conditions: 1.25 mM DTPA, 1.5 M NaNO_3 and pH 5.00 (10 μL acetate buffer containing 2 M acetic acid and 3.5 M sodium acetate). Fine pH adjustments were performed by adding acetic acid or ammonium hydroxide as needed. Concentrations were determined after 3 standard additions of potassium chromate or Cr(III) Titrisol solutions. All determinations were performed in triplicate.

For testing UV irradiation to determine total chromium as Cr(VI) we used a 1000 W mercury lamp. Filtered samples at natural pH were transferred to a quartz tube with cover and irradiated over four hours.

RESULTS AND DISCUSSION

Sample Storage and Preservation

West and Shendrikar³⁴ report in their study of chromium adsorption on Pyrex and polyethylene bottles that the concentration of Cr(III) in water was reduced by 17 to 25% after 15 days of storage at natural pH. They also observed an induction period of 24 h during which no changes in Cr(III) concentration could be detected. For Cr(VI) they do not report significant losses in acid medium up to pH 7. Boussebart *et al.*¹⁰ observed significant Cr(VI) and total chromium losses after storage of seawater samples at low temperature. In our experiments, on the course of 24 h storage at low temperature in polyethylene, polypropylene or quartz at natural pH the Cr(VI) reduction current was totally suppressed. We attribute this signal suppression to the reduction of Cr(VI) to Cr(III) in the presence of high concentrations of dissolved organic matter (average of 10 to 15 mgL^{-1} in Guanabara Bay). The procedure of acification to prevent Cr(III) sorption accelerated losses in Cr(VI) because the acid medium favors the reduction of this species. Consequently, the possibility of storage at pH 2 and neutralization prior to the analysis given in Galimowski *et al.*⁴² does not apply to Guanabara Bay wa-

ters. In agreement to previous observations,¹⁰ we found that speciation of chromium using voltammetric methods does not allow sample storage or acidification.

Oxidation of Cr(III) by UV Irradiation

UV irradiation in the presence of acids or/and peroxides combined to voltammetric measurements has been frequently used for determination of total metal ion concentration in natural waters.^{10,26,35,36} As Figure 1 shows the irradiation of water samples from Guanabara Bay in acid medium leads to total suppression of the Cr(VI) reduction signal. Once again, this effect results from favoring the reversal reaction, reduction of Cr(VI), in the presence of organic matter. The loss of Cr(VI) in the process of UV irradiation at pH 2 was first observed by Golimowski *et al.*⁴² We had also previously experienced similar effect when working with the system iodate/iodide³⁸ in tropical estuarine waters at natural pH.

Boussemart *et al.*¹⁰ report that the analysis of Cr(VI) in samples from estuarine origin benefitted from the addition of hydrogen peroxide. In our samples, however, irradiation after addition of hydrogen peroxide, even at

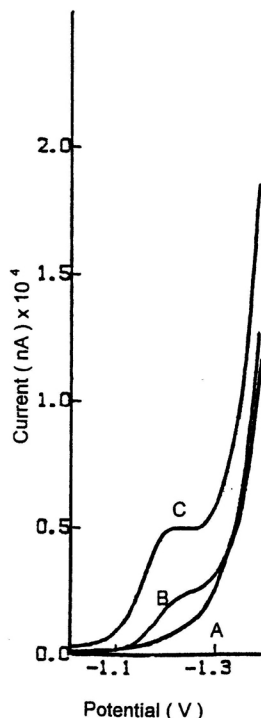


Figure 1. Effect of the medium acidity of UV irradiated samples on the voltammogram. (a) shows the voltammogram of sample, containing natural levels of Cr(VI), irradiated at pH 2.0; (b) was obtained under the same conditions as curve (a) plus 10 nM Cr(VI); c is the voltammogram of a sample irradiated at pH 8.1.

very low concentrations (<0.1% final concentration), gave rise to a broad peak at -1.0 V that masked the Cr(VI) reduction signal even in presence of 100 nM Cr(VI). This effect persisted many days after treating the sample and after aeration. We obtained good results irradiating the samples at natural pH (8.1) in absence of peroxide.

Optimization of Analytical Conditions

Boussemart *et al.*¹⁰ report optimal conditions for the determination of chromium using the DTPA reaction. The same conditions when applied to Guanabara Bay samples produced unsatisfactory results (low sensitivity and reproducibility). We will discuss below the optimized conditions that ensured the success of the analytical determinations in our samples.

Whereas we also selected pH 5.0 as optimal, in Figure 2 we show that at pH 5.3, Boussemart¹⁰ recommended upper pH limit, the current signal is reduced by 60%. At low chromium concentrations the fine adjustment of pH seems to set the feasibility of the determination. Besides influencing analytical sensitivity due to the effect upon the DTPA active fraction, low pH values may promote reduction of Cr(VI) unrelated to the electrode process. At higher pH values, formation of Cr(III) hydroxides may interfere with the DTPA complexation reaction.

Figure 3 shows the linearity range of the current *vs.* Cr(VI) concentration relationship at several pH values. At pH 5,0 under our experimental conditions the linear range reaches 60 nM. This high limit is not of interest for estuarine waters but allows the application of the method to interstitial waters of polluted areas.

The optimal DTPA concentration for our samples was 1.25 mM. As Figure 4 shows at 0.5 mM the signal is reduced by about 150%. The current

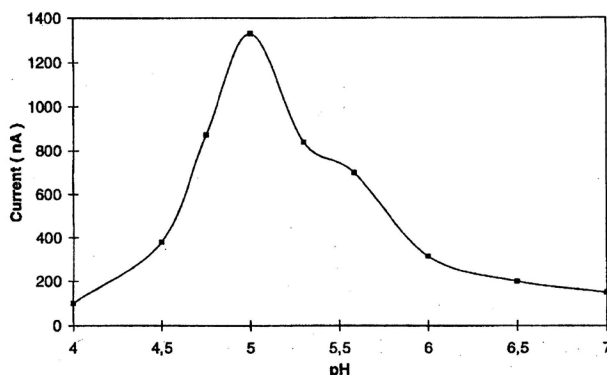


Figure 2. Variation of the Cr(VI) reduction current with pH at $[\text{Cr(VI)}] = 10$ nM

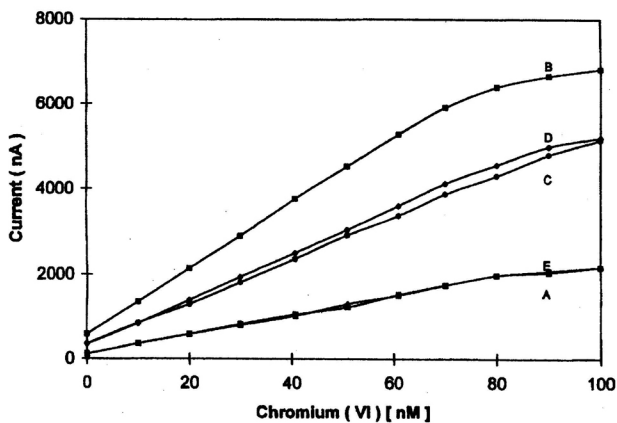


Figure 3. Dependence of the cathodic current on Cr(VI) concentration at several pH values: (a) 4.0, (b) 4.5, (c) 5.0, (d) 5.5, (f) 6.0, (g) 6.5.

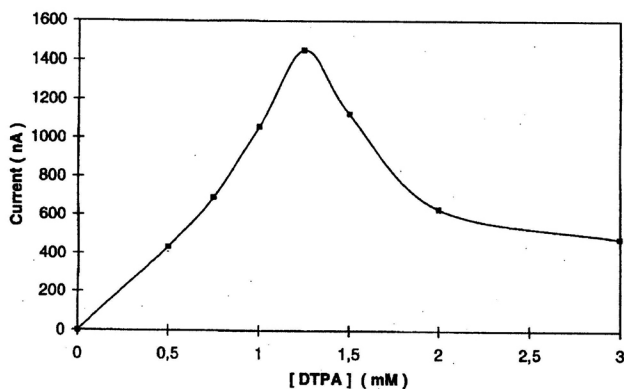


Figure 4. Dependence of the cathodic current on the DTPA concentration; [Cr(VI)] = 10 nM

signal increases linearly up to a nitrate concentration of 1.0 M. The maximum signal is registered at 2 M but the increase of 5% sensitivity between 1.5 M nitrate and 2.0 M does not compensate the use of extra amounts of reagent.

We verified the square wave frequency effect, in the range of 10 to 120 Hz (see Figure 5), on the sensitivity of the current signal. For concentrations up to 30 nM the optimal frequency was 25 Hz and the use of higher frequencies resulted in signal decrease. We assume that the kinetics of the electrochemical reaction limits the maximum signal gain that can be ob-

tained by increasing the frequency. Similar effect was described for arsenic (III).³⁷ Best sensitivity and peak resolution were obtained when setting frequency at 25 Hz and pulse height at 25 mV.

Figure 6 shows the influence of deposition time on the current signal at several Cr(VI) concentrations. Maximum current values were sampled at 30 s deposition time. The current decreases sharply and reaches at 60 s deposition time 1/3 of the value measured at 30 s. Voltammetric studies of lead and zinc in Guanabara Bay^{39,40} demonstrated the effect of surfactants present in the water samples on the sensitivity of the applied methods. The above decrease in current with increasing deposition time is probably due to the adsorption of surfactants at the drop surface. Boussemart *et al.*¹⁰ discuss the inhibition effect of surfactants and humic acids on the chromium peak.

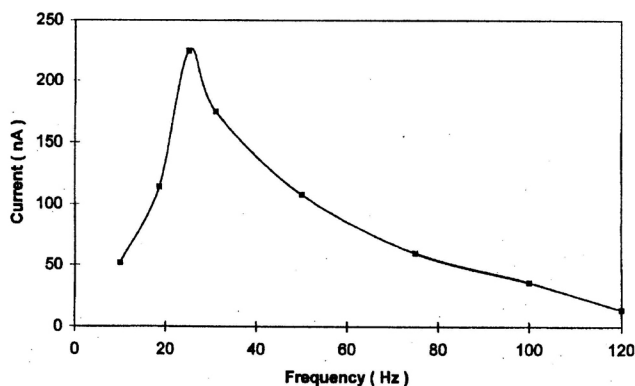


Figure 5. Variation of cathodic current with deposition time, [Cr(VI)] = 10 nM

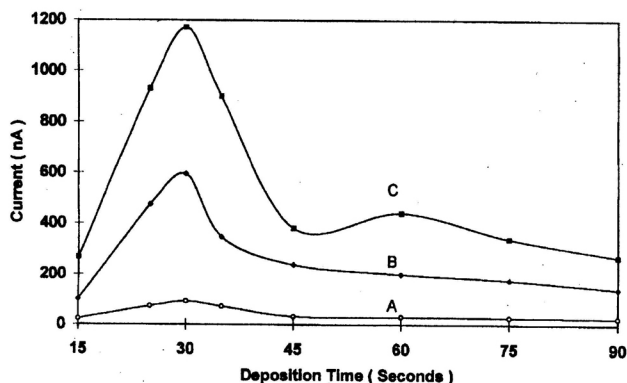


Figure 6. Stability of the current signal over the time, concentrations: A) 1 nM, B) 5 nM, C) 10 nM

We tested the interference of the Cr(III)–DTPA reaction in solution on the Cr(VI) determination by adding a known amount of Cr(III) to a sample free of chromium (see below) and measuring the resulting current signal in the presence of DTPA. Under our experimental conditions the Cr(III) addition gave a current signal 20 times smaller than that for an equivalent amount of Cr(VI). The peak potential was 24 mV more negative in the Cr(III) test and the peak shape was not well defined.

The current signal of the Cr(III)–DTPA complex formed at the drop surface (*via in situ* reduction of Cr(VI)) has a limited stability as reported by Boussemart *et al.*¹⁰ We can consider that the current signal remains unchanged up to 25–30 min. after the first voltammetric cycle and then decreases 0.3% min⁻¹. Nevertheless, the stability of 30 min. is sufficient to allow determination using three standard additions.

Detection Limit and Sensitivity

The especial behavior of chromium in our samples produced seawater completely deprived of the metal ion after storage in the dark at 4 °C over 7 days. Voltammograms of stored filtered samples gave a smooth base line free of peaks. The smallest Cr(VI) concentration that when added to those samples produced a recognizable peak was 0.5 nM. The limit of detection determined using the average and standard deviation of 10 replicates for a non irradiated sample was 0.51 ± 0.01 nM Cr(VI) or 22.35 ± 0.41 nA.

We calculated the sensitivity (*S*) using the equation proposed by Acebal and Rebello.³⁹

$$S = i_p / ([Me] \times t_d)$$

where i_p is the peak current in nA, [Me] is the metal concentration in nM and t_d the deposition time in seconds. The sensitivity for Cr(VI) and total chromium determinations were rather different:

$$S_{Cr(VI)} = 1.97 \pm 0.55 \text{ nA nM}^{-1} \text{ s}^{-1}$$

$$S_{Cr_{total}} = 3.19 \pm 0.14 \text{ nA nM}^{-1} \text{ s}^{-1}$$

Those sensitivities are at least comparable to the reported by Boussemart *et al.*¹⁰ The two averages are statistically different at the 95% confidence level. The 60% increase in sensitivity after UV irradiation provides a quantitative estimate of the organic substances influence on the voltammetric determination of chromium.

Chromium in Guanabara Bay Samples

We performed 4 samplings, from February (summer) to August (winter) 1995, in the vicinity of Boa Viagem Island. The results obtained are in the range of 1.34–1.51 nM for Cr(VI) and 1.85–2.28 nM for total chromium. The standard deviations for the analysis of three aliquots of each sample were 0.04–0.17 nM for Cr(VI) and 0.01–0.09 nM for total chromium. The fraction of Cr(III) calculated by the difference between total chromium and Cr(VI) varied from 21% (winter sampling) to 33% (summer samplings). Considering that surface waters in Guanabara Bay are permanently over-saturated in oxygen those values for Cr(III) give a measure of how intensive are the processes that lead to non-equilibrium conditions in the bay. The reduced number of samplings do not allow a profound discussion on the environmental aspects of our results. However, we can expect that the relation Cr(III)/Cr(VI) will increase in the inner areas of the bay enriched both in dissolved and particulate organic substances.

Researching and Monitoring Chromium in Guanabara Bay

Our experience over years of studying environmental contamination in tropical estuarine waters shows that we must be cautious when applying analytical methodologies developed and tested in samples from temperate areas. Tropical estuaries are enriched in particulate matter, a large fraction derived from lateritic soil and, in addition, they present intensive photochemical and biological activities. Such processes will influence the water composition by promoting a milieu with high content of organic substances and transient compounds, suitable to the development of non-equilibrium conditions. Well-developed methodologies may frequently need profound adjustments to respond adequately when applied to tropical water samples. This question appears to us as fundamentally important in the establishment of standard and reference methodologies that should be used to monitor contamination in several different areas of the globe.

The voltammetric method discussed here is sensitive and fast and can be successfully applied in restricted research activities. Nevertheless, monitoring Cr(VI) in waters from Guanabara Bay, and other similar ecosystems, by directly using voltammetric techniques seem to be an impossible task. This because bottled samples are changing too fast their chromium speciation to permit storage, even over 24 hours at low temperatures. In the case of Cr(III) and total chromium, acidification to prevent Cr(III) adsorption is prohibitive because it fastens the reduction of Cr(VI). As Cr(VI) is the active species in the adsorptive voltammetry the losses by reduction will lead to incorrect results. This problem could be reduced by addition of a strong oxidant after acidification increasing, however, there are contamination risks. In order to guarantee accuracy in this case it is recommendable to apply pre-con-

centration procedures, for example, using ferric hydroxide⁴¹ to separate Cr(III) immediately at the sampling sites.

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SAŽETAK

Voltametrijsko određivanje Cr(III) i Cr(VI) u vodama tropskih ušća: prednosti i ograničenja

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Adsorptivna katalitička voltametrija Cr(VI) i ukupnog kroma upotrebom DTPA prilagođena je za primjenu u ispitivanju voda ušća s visokim sadržajem otopljenih organskih tvari. Osjetljivost metode bolja je od $2 \text{ nA mN}^{-1} \text{ s}^{-1}$, što omogućuje primjenu metode za specijaciju metala. Nestabilnost Cr(VI) u prisutnosti organskog materijala uvjetuje ograničenja u široj primjeni ove metodologije kod istražnih radova i nadziranja (»monitoringa«).