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Speciation of Cr(VI) and Cr(III) in Water Samples by Adsorptive Stripping Voltammetry in the Presence of Pyrogallol Red Applying a Selective Accumulation Potential

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An adsorptive stripping voltammetric procedure for the speciation of Cr(VI) and Cr(III) in the presence of pyrogallol red (PGR) is presented. The method is based on the previous reduction of Cr(VI) to Cr(III) at the electrode surface, its complexation with PGR, and the later reduction of Cr^{III}–PGR to Cr^{II}–PGR at −0.85 V. The effects of various operational parameters such as *pH*, ligand concentration (C_{PGR}), and accumulation potential and time (E_{ads}, t_{ads}) were optimized. These studies were carried out using individual Cr(VI) and Cr(III) solutions and also mixtures of them. The results showed that the proper choice of the adsorptive potential produces selectivity for Cr(VI) in the presence of Cr(III). At an E_{ads} of 0.00 V only Cr(VI) produces the reduction signal of Cr^{III}–PGR at −0.85 V, while at an E_{ads} of −0.68 V both Cr(VI) and Cr(III) produce this signal. Total chromium was determined after oxidation of Cr(III) to Cr(VI) by UV radiation in the presence of H_2O_2. The concentration of Cr(III) was evaluated as the difference between total chromium and Cr(VI). Under the best experimental conditions (*pH* 4.5; C_{PGR} 0.25 μmol L^{-1}; E_{ads} −0.68 V and t_{ads} 60 s), the peak current is proportional to the total Cr concentration up to 20.0 μg L^{-1}, with a 3σ detection limit of 0.05 μg L^{-1}. The relative standard deviation for a Cr(VI) solution (9.8 μg L^{-1}) was 1.8 % for six successive assays. The method was validated using synthetic sea water (ASTM D665) spiked with Cr(VI) and Cr(III), and with a certified reference water (NCS ZC76307). In this reference material total chromium was determined as Cr(III) other aliquot of reference sample was oxidized and the total chromium determined as Cr(VI). Finally, the method was applied to the determination of Cr(VI) and Cr(III) in sea water samples

Keywords: Chromium(VI) and chromium(III); Speciation; Complexation with PGR; Adsorptive stripping voltammetry.

1. INTRODUCTION

Contamination of natural waters with chromium can be caused by anthropogenic sources such as leather tanning, pigment production, electroplating industry, and rinse waters, which mostly contain Cr(III) and/or Cr(VI). The toxicity of these two forms differs considerably: while Cr(III) is considered essential in mammals for the maintenance of glucose, lipid and protein metabolism for many living organisms, Cr(VI) species are known to be toxic and carcinogenic, causing health problems such as liver damage, pulmonary congestions, vomiting, and severe diarrhea [1]. It has been reported that Cr(VI) compounds are 10 to 100 times more toxic than Cr(III) compounds when both are administered orally [2]. Sea water contains between 0.1 and 0.5 μg L^{-1} and unpolluted river water from 0.3 to 0.6 μg L^{-1}. The World Health Organization (WHO) and the European Community Directive (ECD) for drinking water has set the limit of total chromium not exceeding 50 μg L^{-1}, while the maximum concentration criterion for Cr(VI) in freshwater is 16 μg L^{-1} [3,4]. Since the concentration of chromium, mainly Cr(VI), is very low in many natural waters, a highly sensitive and selective method is required for its speciation. To differentiate chromium species some investigators have separated Cr(VI) from Cr(III) by solvent extraction with S,S−ethylendiamine−N.N'−trisodium salt [5], sorption with iron phosphate [6], sorption with modified silica MCM−41 [7], sorption with Chelex−100 and anionic resin for retention of cationic Cr(III) and anionic Cr(VI) species, respectively [8], or solid phase extraction on Chromosorb 108 resin using dithizone as complexing agent [9]. Electroanalytical techniques, in particular adsorptive stripping voltammetry (AdSV), are suitable for the direct determination of Cr(VI) and Cr(III) without previous separation. However, satisfactory results depend on the choice of a suitable working electrode. The hanging mercury drop electrode (HMDE) is a nearly ideal electrode, especially for cathodic processes. However, Professor Zuman [10] has reported a certain and unjust “mercurophobia” or “mercury hysteria” due in part to the toxicity of organometallic compounds and Hg vapors; but metallic mercury is not poisonous. AdSV requires the presence of a complexing agent for Cr(III) and the complex must be formed quantitatively and quickly in solution and it must be adsorbed on the electrode surface. One of the most adequate and most widely used ligands for chromium determination is diethylenetriaminepentaacetic acid (DTPA), which was first studied by Zarebski and by Golimowski et al. [11,12]. In short, Cr(VI) is reduced to Cr(III)−DTPA complex at the accumulation potential, and then in the scan reduction step from Cr(III) to Cr(II) it is adsorbed at the surface of the working electrode. Because Cr(III) is very inert, it has been reported that DTPA forms a complex only with the Cr(III) just generated from the reduction of Cr(VI) at the accumulation potential and not with the Cr(III) present in the solution. This is favorable because the technique is adequate for the determination of Cr(VI) in the presence of Cr(III). This methodology is more sensitive in the presence of oxidizing agents, such as nitrate, nitrite, bromate, etc., which catalyze the back electrochemical reaction Cr(II) to Cr(III) [13]. Catalytic adsorptive stripping voltammetry (CAdSV) with DTPA and nitrate appears as the most sensitive and useful method, and it has been widely applied in analytical practice [14−29]. AdSV of Cr(VI) and Cr(III) has also been studied using pyrocatechol violet [30,31] and ethylenediamine−N,N,N',N'−tetraacetic acid (EDTA) [32].

The purpose of the present study was to carry out the speciation of Cr(VI) and Cr(III) in water samples by AdSV in the presence of pyrogallol red (PGR) applying a selective accumulation potential.

Pyrogallol red has been used in AdSV with HMDE as a chelating agent for Ge(IV) [33], Cu(II) [34], Al(III) [35], Sb(III) [36], Co(II) [37] and Pb(II)−Cd(II) [38]. Nevertheless, its use in the determination of chromium has not yet been reported and neither the selectivity obtained by changing the accumulation potential.

2. EXPERIMENTAL PART

2.1. Apparatus

The voltammograms were obtained on a Metrohm model 797 VA Computrace in a three−electrode configuration. The hanging mercury drop electrode (HMDE) was used as working electrode with an Ag/AgCl/KCl 3 mol L^{-1} reference electrode, and a platinum wire auxiliary electrode. pH measurements were performed with an Orion–430 pH meter.

2.2. Chemicals and samples

Water used for sample preparation, and also for dilution of the reagents and rinsing purposes, was obtained with a Milli–Q system (18.2 Ohm. Millipore, USA). All the chemicals (nitric acid, hydrochloric acid, peroxide, methanol, etc.) were analytical grade from Merck (Darmstadt, Germany). A standard stock solution of 1.0 mg L^{-1} of Cr(VI) was prepared from standard Cr(VI) 1000 mg L^{-1} solution (Merck, Darmstadt, Germany). A standard stock solution of 1.0 mg L^{-1} of Cr(III) was prepared from chromium atomic absorption standard solution (1005 mg L^{-1}. Sigma, USA). The stock solutions of pyrogallol red (Aldrich) and sodium dodecyl sulfate (Sigma) were prepared by dissolving the reagents in methanol and water, respectively. Acetic acid−acetate solutions (0.4 mol L^{-1}) were used to investigate pH in the 3.2−6.5 range and were prepared by mixing the corresponding amounts of acetic acid and sodium hydroxide solution (Merck). Synthetic sea water (ASTM D665, Aldrich) spiked with Cr(VI) and/or Cr(III), and certified reference water (NCS ZC76307. Beijing, China) were used for validation measurements. Synthetic sea water contains Na^+, K^+, Sr^+, Ca^{2+}, Mg^{2+}, Sr^+, Cl^-, $SO_4^=$, HCO_3^-, Br^- and F^-, and the certified reference material water contains K^+ 2.2; Na^+ 23, Ca^{2+} and Mg^{2+} 11 mg L^{-1} in 0.5 mol L^{-1} HNO_3 with certified values of Cd 0.100; Cr 0.500; Cu 1.00; Ni 0.500; Pb 1.00 and Zn 5.00 μg g^{-1}. Sea water samples were obtained from a beach close to several industries in a highly populated and touristic area (city of Quintero, South Pacific coast, Chile). For the oxidation of Cr(III) to Cr(VI) the samples were digested under UV irradiation for 90 min at 90 ^oC (10.0 mL of sample with 100 μL of 30% H_2O_2) using a 705 UV–digester (Metrohm).

2.3. Procedure

Water (10.0 mL), 100 μL of acetic buffer (0.4 mol L^{-1}, pH 4.5), 40 μL of PGR solution (0.3 mmol L^{-1}) and aliquots of Cr(VI) and/or Cr(III) solution (1.0 mg L^{-1}) were pipetted into the voltammetric cell. The measurements were performed in the absence and presence of SDS. The

solution was purged with nitrogen (saturated with water vapor) for 300 s in the first cycle and for 60 s in each successive cycle. Then, after eliminating some drops, a new mercury drop (size:8) was extruded to initiate the preconcentration for a given t_{ads} and E_{ads} at a stirring rate of 1400 rpm. After an equilibration time of 10 s, the adsorptive voltammograms were recorded, while the potential was scanned from –0.30 to –1.10 V, using square wave modulation with 5 mV voltage step, 10 mV pulse amplitude, and a frequency of 25 Hz (scan rate 126 mV s^{-1}). The calibration curves were obtained and linear regression and detection limits were calculated. For validation measurements of chromium in certified samples, the solution was prepared by mixing 10 mL of water, 40 µL of sample, 100 µL of acetic acid buffer (0.4 mol L^{-1}, pH 4.5), 50 µL of 0,4 mol L^{-1} NaOH solution. Aliquots of PGR solution were added until the free ligand signal was observed, and the determination was carried out using the standard addition method. The voltammograms were carried out in triplicate.

3. RESULTS AND DISCUSSION

The addition of aliquots of pyrogallol red (PGR) (0.4 mmol L^{-1}) to a solution that contained Cr(VI) (9.8 µg L^{-1}) at pH 4.5 gave a reduction peak at a potential of −0.85 V, which increased as PRG was added until the Cr(VI) to PGR ratio was 1:1 and the reduction of free ligand was not observed. These voltammograms and the corresponding plots of peak current *vs*. M:L ratio are shown in Fig.1. Chromium(VI) on the electrode surface is reduced in the presence of PGR, which forms a complex with Cr(III). The signal at −0.85 corresponds to the reduction of the Cr^{III}−PGR complex to Cr^{II}−PGR. The presence of nitrate as catalytic agent only showed a small effect on the peak reduction current of Cr^{III}−PGR. To find the best sensitivity in the determination of Cr(VI), the influence of different parameters such as *pH*, C_{PGR}, E_{ads} and t_{ads} was investigated.

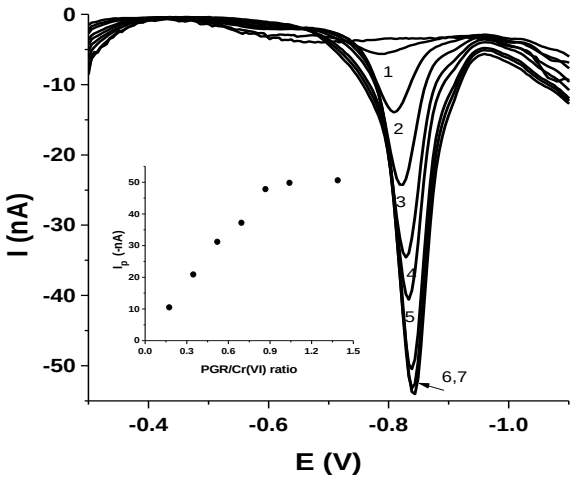

Figure 1. Adsorptive voltammograms of Cr(VI) solutions in the presence of aliquots of PGR, and plot of I_{peak} *vs*. Cr:PGR ratio. Conditions: *pH* =4.5 (4 mmol L^{-1}acetic buffer); $C_{Cr(VI)}$ = 0.19 µmol L^{-1}; C_{PGR} = 0.0 to 0.28 µmol L^{-1}; E_{ads} = –0.68 V; t_{ads} = 60 s; voltage step = 5 mV; amplitude = 10 mV; frequency = 25 Hz and scan rate 126 mV s^{-1} (mode SWV)

3.1. Effect of operational parameters

3.1.1. Effect of pH

The pH of the solution is very important because the position of the free ligand and complex peaks depends on the pH value. PRG contains one sulfonic group and three hydroxyl groups, and in acidic solutions the $–SO_3H$ group is deprotonated, while the hydroxyl groups at positions 3, 4 and 5 have dissociation constants of 6.28, 9.75 and 11.94 (μ=0.2), respectively [39]. The influence of pH on the stripping peak current was studied in the pH range 3.2−6.5 using acetic acid/acetate solutions. These measurements were carried out in the absence and presence of SDS. The experimental conditions were $C_{Cr(VI)}$ =9.8 μg L^{-1}; C_{PGR} = 0.32 μmol L^{-1}; E_{ads} = −0.40 V and t_{ads} = 60 s. The results are shown in Fig.2. It was found that in the presence of SDS the peak current of the Cr^{III}–PGR complex is higher than in the absence of this anionic surfactant, and these values attained a maximum at pH 4.5, while without SDS the peak current is almost constant from pH 4.0 to 6.0. The peak potentials of both the Cr^{III}–PGR complex and free PGR shifted towards more negative values with increasing pH, and the separation of the signals was greatest at pH 4.5. For this reason this pH value was chosen for the whole study. To check the influence of surfactants on the peak current of the Cr^{III}–PGR complex, the measurements were performed in the presence of anionic (SDS) and cationic (CPB) surfactants. According to the dissociation constant of PGR, the net charge of the complex at pH 4.5 is positive, $[Cr^{III}–PRG]^{2+}$, and in the presence of SDS it had a positive effect, increasing the peak current slightly, while in the presence of CPB the peak current remained almost constant.

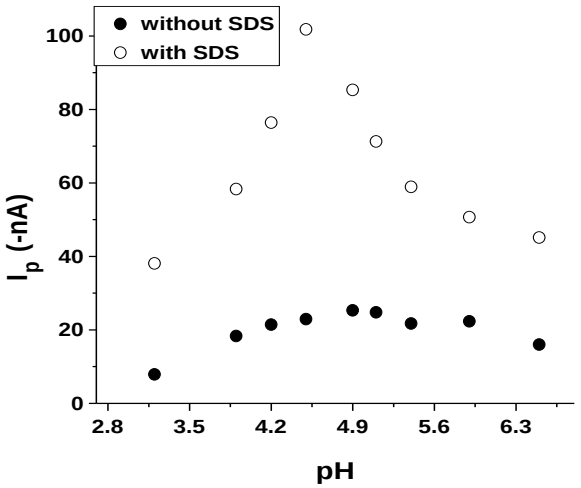

Figure 2. Effect of pH on the peak current of the Cr^{III}–PGR complex in the absence (•) and presence (o) of SDS (9.8 μmol L^{-1}). Conditions: $C_{Cr(VI)}$ = 9.8 μg L^{-1}; C_{PGR} = 0.32 μmol L^{-1}; E_{ads} = −0.40 V; t_{ads} = 60 s.

3.1.2. Influence of PGR concentration

The effect of the variation of C_{PGR} on the peak current of Cr^{III}–PGR in the absence and presence of SDS was studied in the range 0.00 to 0.60 μmol L^{-1}. The results are shown in Fig.3. The

experimental conditions were *pH* = 4.5 (4 mmol L^{-1}acetic buffer), $C_{Cr(VI)}$ = 9.8 μg L^{-1}; C_{SDS} = 2.0 μg L^{-1}; E_{ads} = –0.30 V and t_{ads} = 60 s. The peak current increased with increasing C_{PGR} up to 0.25 μmol L^{-1} (M:L ratio 1:1.3). At concentrations higher than 0.25 μmol L^{-1} the peak current decreased slightly with increasing concentration of free PGR, probably due to the competition of PGR with the complex for adsorption on the electrode. An optimum C_{PGR} of 0.25 μmol L^{-1} was used for further experiments, but in the analysis of certified or real samples higher C_{PGR} were used to bind all de metal ions present in the solution.

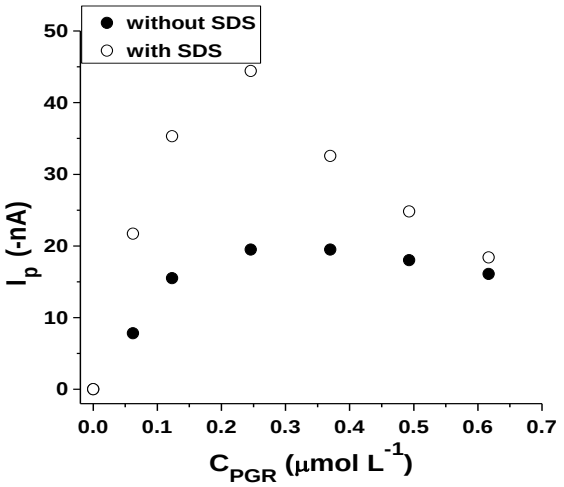

Figure 3. Effect of ligand concentration on the peak current of the Cr^{III}–PGR complex in the absence (•) and presence (o) of SDS. Conditions: *pH* 4.5 (acetic buffer); $C_{Cr(VI)}$ = 9.8 μgL^{-1}; C_{SDS} = 2.0 μg L^{-1}; t_{ads} = 60 s; E_{ads} = −0.40 V.

3.1.3. Influence of accumulation potential and time (Eads, tads)

The effect of accumulation potential on the stripping peak current of the Cr^{III}–PGR complex over the 0.00 to –0.90 V range was studied. The experimental conditions were *pH* = 4.5; $C_{Cr(VI)}$ = 9.8 μgL^{-1}; C_{PGR} = 0.25 μmol L^{-1} and t_{ads} = 60 s. As shown in Fig.4A, the peak current of Cr^{III}–PR complex is maximum at 0.00 V, decreases with changing potential from –0.10 to –0.50 V, and increases again to a maximum at −0.66 to −0.70 V. An adsorption potential of −0.68 V was used during this study. On the other hand, Fig. 4B shows the effect of accumulation time on the stripping peak current of the Cr^{III}–PGR complex over the 0–300 s range. The experimental conditions were $C_{Cr(VI)}$ = 9.8 μgL^{-1}; C_{PGR} = 0.25 μmol L^{-1} and E_{ads} = –0.68 V. Peak current increases with increasing accumulation prior to the potential scan, indicating that the chromium complex is readily adsorbed on the HMDE. Peak current increased with time up to 300 s. However, considering the speed of the measurement, a t_{ads} of 60 s was used for further studies, but in the analysis of real samples higher times can be used to achieve good sensitivity.

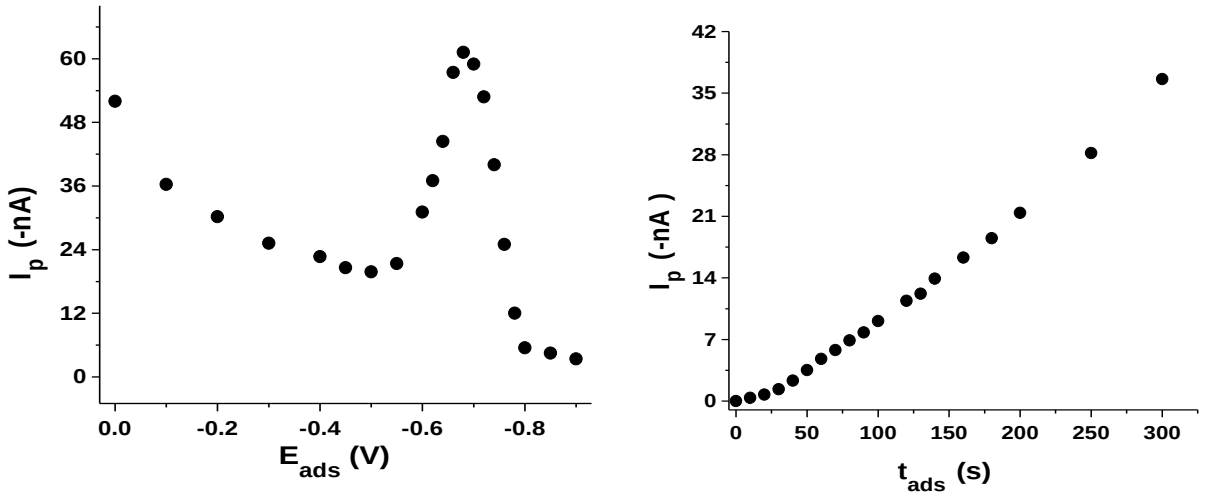

Figure 4. Effect of adsorptive potential (E_{ads}) (A) and time (t_{ads}) (B) on the peak current of the Cr^{III}–PGR complex. Conditions: *pH* = 4.5 (acetic buffer); $C_{Cr(VI)}$ = 9.8 μgL^{-1}; C_{PGR} = 0.25 μmol L^{-1}; (A) t_{ads}= 60 s; (B) E_{ads}= −0.68 V.

3.2. Linear range, detection limit, and reproducibility of the method

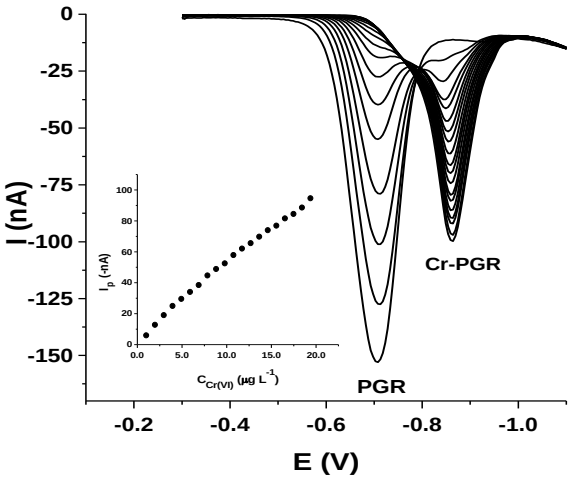

Figure 5. Adsorptive voltammograms and calibration curves for the Cr^{III}–PGR complex. Conditions: *pH* = 4.5 (acetic buffer); C_{PGR} = 2.7 μmol L^{-1}; E_{ads} = –0.68 V; t_{ads} = 60 s. Other conditions as in Fig. 1.

Optimal analytical conditions were found to be a PGR concentration of 0.25 μmol L^{-1}, pH 4.5 (acetic buffer 4 mmol L^{-1}), and an adsorption potential of –0.68 V with an adsorption time of 60 s (stirring speed 1400 rpm; step amplitude 5 mV; pulse amplitude 10 mV; and frequency 25 Hz). Under

these conditions the peak current was proportional to the concentration of chromium over the 0.0–20.0 μg L^{-1} range, with a 3σ detection limit of 0.05 μg L^{-1} with an accumulation time of 60 s. Reproducibility for a 9.8 μg L^{-1} Cr(VI) solution was 1.8 % (n = 7). Figure 5 shows calibration adsorptive voltammograms of PGR solution in the presence of Cr(VI).

3.3. Interference studies

Serious complications in metal determination can occur due competitive adsorption of the ligand, the concentration of which must be in excess. Difficulties arise mainly if the peak potential of the ligand is very close to the peak potential of the metal chelate. Interferences caused by other metals may occur due to poor specificity of the complexing agent [40,41]. In this method, Cr(VI) from bulk solution is reduced at the electrode surface to Cr(III) at a E_{ads} of 0.0 to −0.80 V in the presence of a ligand [30]. For this motive, the main interference is caused by the presence of Cr(III) in the solution. Since Cr(VI) is always present in real samples in relatively small amounts compared with Cr(III), and the toxicity of Cr(VI) is higher than that of Cr(III), it is necessary to determine Cr(VI) in the presence of Cr(III) [42]. With this purpose, Boussemart et al. [43] exploited the fact that the analytical signal corresponding to Cr(III) present in the solution decreases with time after addition of DTPA, because electrochemically active Cr(III)−DTPA complex is converted to nonactive compound after 30 min, and Grabarczyk et al. [44] found that at the temperature of 40 °C the time of decrease of the Cr(III) signal is shortened from 30 to 5 min. On the other hand, high selectivity of the measurements was obtained by application of masking agents as nitrilotriacetic acid [45], ethylenediaminedisuccinic acid [24,46] or ethylenediaminetetraacetic acid [47] for Cr(III). Our results showed that the proper choice of the E_{ads} produces selectivity for Cr(VI) in the presence of Cr(III). To achieve maximum selectivity with the AdSV method, a study of E_{ads} was carried out with a solution containing only Cr(III) and compared with a solution containing only Cr(VI) in the presence of PGR ligand (pH 4.5). Figure 6 shows the effect of E_{ads} on the peak current of the Cr^{III}−PGR complex for these solutions.

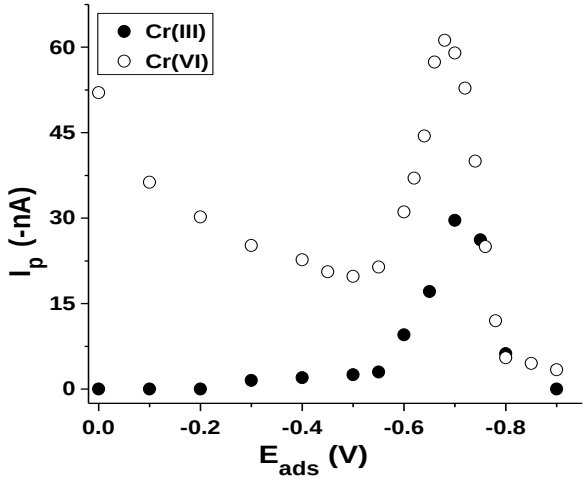

Figure 6. Effect of adsorptive potential (E_{ads}) on the peak current of the Cr^{III}−PGR complex. (•) $C_{Cr(III)}$ = 9.8 μg L^{-1}. (o) $C_{Cr(VI)}$ = 9.8 μg L^{-1}. Conditions: *pH*=4.5; C_{PGR}= 0.25 μmol L^{-1}; t_{ads}= 60 s.

Changing E_{ads} had a larger effect on the peak current of the Cr^{III}–PGR complex. At E_{ads} of −0.68 V, Cr(VI) and Cr(III) together can be determined and the sensitivity is higher, while at E_{ads} of 0.00 V only Cr(VI) is determined. A spectrophotometric method has been reported for the determination of Cr(VI), based on the ability of Cr(VI) to oxidize PGR [48]. Under our specific conditions this did not occur because the reduction potentials of free PGR and that of the complex are the same when Cr(VI) or Cr(III) are added to the solution containing PGR.

Figure 7A and 7B show adsorptive voltammograms of PGR solutions in the presence of Cr(III) applying an E_{ads} of 0.00 V and an E_{ads} of −0.68 V, respectively. As aliquots of Cr(III) solution were added, the free PGR reduction peak at −0.73 V decreased while no new reduction peak was observed (Fig. 7A). The decreased peak current of free PGR is an evidence of the formation of the Cr^{III}–PGR complex in the solution, but this complex is not adsorbed on the electrode surface at E_{ads} between 0.00 to −0.20 V. The zero charge potential of the mercury electrode is about −0.58 V; at more negative potentials the electrode surface has a negative charge, while at more positive potentials there is a positive surface charge. At E_{ads} of 0.00 V, the $[Cr^{III}–PR]^{2+}$ complex formed in the solution is not adsorbed, whereas at E_{ads} of −0.68 V, the $[Cr^{III}–PR]^{2+}$ complex formed in the solution is adsorbed, the free PGR reduction peak at −0.73 V decreases while the reduction peak at −0.86 increases (Fig. 7B). On the other hand at E_{ads} of 0.00 V, Cr(VI) reacts on the electrode surface and accumulates. For this reason at E_{ads} of 0.00 V, Cr(VI) can be determined in the presence of Cr(III) and at E_{ads} of −0.68 V, Cr(VI) and Cr(III) are determined together.

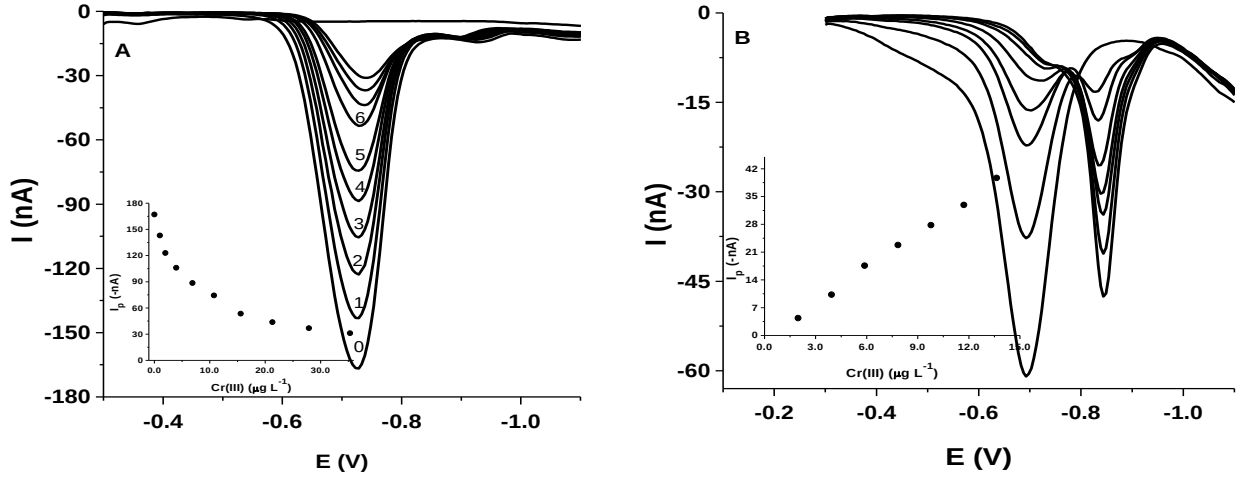

Figure 7. Adsorptive voltammograms of PGR solutions in the presence of aliquots of Cr(III), and plot of $I_{peak\ free\ ligand}$ *vs.* $C_{Cr(III)}$ obtained to E_{ads} = –0.00 V (A). AdV of PGR solutions in the presence of aliquots of Cr(III), and plot of I_{peak} *vs.* $C_{Cr(III)}$ obtained to E_{ads} = –0.68 V (B). Conditions: *pH* = 4.5 (acetic buffer); t_{ads} = 60 s. C_{PGR} = 1.0 µmol L^{-1} (A) and 0.4 µmol L^{-1} (B). Other conditions as in Fig. 1.

3.4. Validation of the method

25 mL of synthetic sea water (ASTM D665) was contaminated with Cr(VI) and Cr(III) solution (30.0 μg L^{-1}). A 1.0 mL aliquot was then transferred to the electrochemical cell containing 8.0 mL of water, 1.0 mL of acetic buffer (0.4 mol L^{-1}, pH 4.5) and 30 μL of PGR 0.3 mmol L^{-1}, and the determination of Cr(VI) was carried out applying E_{ads} of 0.00 V and obtaining 31.0 ± 0.3 μg L^{-1} (RE −3.3 %) (n=3). The usefulness of the present method was also evaluated by determining Cr(III) in certified reference water (NCS ZC76307. Cr 0.500 μg g^{-1}) without digesting and by determining Cr(VI) in previously digested water. The Cr(III) concentration was measured with 10.0 mL of deionized water, 40 μL of reference water, 50 μL of 0.4 mol L^{-1} of NaOH solution, 100 μL of 0.4 mol L^{-1} acetic buffer and 50 μL of PGR 0.38 mmol L^{-1} solution (E_{ads} = −0.68 V, t_{ads} = 60 s). Figure 8 shows the adsorptive voltammograms and calibration curve. In these voltammograms is possible to observe the signal due to reduction of the Cr^{III}–PGR complex to −0.85 V, this signal was not observed when E_{ads} of 0.00 V was applied. The value obtained was 0.511 ± 0.013 μg mL^{-1} (–2.2 % RE). An aliquot of reference water was digested in order to oxidize Cr(III) to Cr (VI); the concentration obtained was 0.517 ± 0.016 μg mL^{-1} (–3.4 % RE).

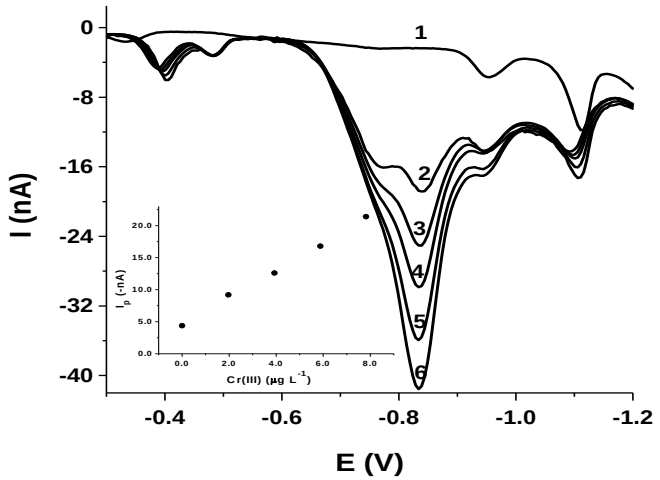

Figure 8. Adsorptive voltammograms and calibration curve for determination of Cr(III) in reference water (NCS ZC76307). Conditions: *pH* = 4.5; C_{PGR} = 1.9 μmol L^{-1}; E_{ads} = –0.68 V; t_{ads} = 60 s. pulse amplitude = 50 mV; pulse time = 40 ms, voltage step = 5 mV; voltage step time 0.1 s and scan rate = 50 mV s^{-1} (mode DPV). (1) Reference water; (2) Reference water + PGR; (6−9) Reference water + PGR + 20 μL of 1.0 mg L^{-1} Cr(III) solution.

3.5. Analysis of chromium in sea water

The proposed method was applied to the determination of Cr(VI) and Cr(III) in sea water samples with and without digestion under UV radiation in the presence of H_2O_2 solution. However Cr(VI) was not detected in any of the samples (n=6) without digestion, and it was determined as 7.2 ± 1.6 μg L^{-1} in digested samples.

4. CONCLUSIONS

The determination of Cr(VI) and Cr(III) in the presence of PGR was carried out by forming a Cr^{III}–PGR complex which is adsorbed on the HMDE. Applying an E_{ads} of −0.68 V the method is adequate for analyzing samples containing only Cr(III) or only Cr(VI) (pH 4.5), while applying an E_{ads} of 0.0 V the method is adequate for analyzing Cr(VI) alone and in the presence of Cr(III). In the presence of SDS, the peak current of the Cr^{III}−PGR complex increases mainly in the analysis of the certified and real water samples. Similar results have not yet been reported.

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