Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 65 (2005) 74–80

Talanta

www.elsevier.com/locate/talanta

# Reduction of hexavalent chromium at solid electrodes in acidic media: reaction mechanism and analytical applications

Christine M. Welch, Olga Nekrassova, Richard G. Compton*

*Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK*

Received 9 January 2004; received in revised form 11 March 2004; accepted 12 May 2004
Available online 14 July 2004

## Abstract

The electrochemical detection of hexavalent chromium species was investigated. It was found that Cr(VI) can undergo chemically irreversible reduction in acidic solutions at gold, glassy carbon and boron-doped diamond electrodes. The process was found to be diffusionally controlled at all three electrodes studied. The response obtained at a gold electrode towards the reduction of chromium(VI) produced an electrochemically reversible wave in contrast to those recorded at glassy carbon and boron-doped diamond electrodes. The analytical response of the hexavalent species was studied at gold electrodes in the presence of common environmental interferences: $Ni^{2+}$, $Cu^{2+}$, $Fe^{3+}$, $Cr^{3+}$ and Triton X-100 (surfactant), with an LoD of 4.3 μM obtained in the presence of 5 mM Cr(III).

*Keywords:* Chromium; Boron-doped diamond electrode; Gold electrode; Environmental samples

## 1. Introduction

The detection of chromium species is a challenging task because of the different possible oxidation states in which the element can occur. The two environmentally relevant valence states of chromium Cr(III) and Cr(VI) have a contrasting impact on environment and health. Trivalent chromium is relatively harmless and plays an essential role in biological processes, whereas hexavalent chromium is about 100–1000 times more toxic [1] because of its high oxidation potential and is limited in groundwater by a WHO provisional guideline value of 0.05 mg $L^{-1}$ (50 ppb) [2]. The main sources of anthropogenic chromium pollution in ground water are plating industries, cooling towers, timber treatment [3], leather tanning, wood preservation and steel manufacturing [4].

Up-to-date methods for speciation and detection of chromium(VI) can be divided into indirect and direct approaches. Indirect methods require prior separation; they include chromatography [5,6], extraction [7,8] or coprecipitation [9,10]. However, all of these suffer from interference by Cr(III), which is normally present in relatively high concentrations in natural samples [11]. Direct detection of chromium is often carried out by using spectrophotometric techniques, where a complex of chromium with various complexing agents (1,5-diphenylcarbamize, methylene blue, iodonitrotetrazolium chloride, tetrazolium violet, dibenzyldithiocarbamate) is detected [12]. Recently, diphenylcarbamate reaction with chromium (VI) was developed into a portable flow-injection analyzer, giving 0.25 mg $L^{-1}$ for the LoD value [13]; however, no studies about potential interferences have been reported. In contrast, electrochemical techniques offer an opportunity for the rapid and accurate detection of hexavalent chromium species even in the presence of excessive concentrations of Cr(III) ([14], and references cited within).

The electrochemical detection of Cr(VI) has been reported at mercury electrodes [15–19], where it is claimed that hexavalent chromium is active over the entire pH range [20]. Moreover, the electrode reaction mechanisms of chromium (VI) and (III) at mercury electrodes have been explored recently [21,22]. However, in analytical practice, because of the potential toxicity of mercury and its operational limitations, mercury electrodes have subsequently been replaced by solid substrates. Notably, the reduction of Cr(VI) has been studied on gold [23–25] and platinum [24] electrodes. Also, different chemical and physical modifications of platinum

---

* Corresponding author. Tel.: +44 1865 275 413;
fax: +44 1865 275 410.
*E-mail address:* richard.compton@chem.ox.ac.uk (R.G. Compton).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.05.017

[26,27] and gold [11,28] have been employed for the analytical determination of chromium. However, at present there is little common understanding of the reaction mechanism at solid electrodes. Literature data varies and this might in part be explained by the highly corrosive conditions typically associated with Cr(VI), or passivation of the electrodes; nevertheless, gold electrodes are thought to be stable towards corrosion and passivation [23].

It was suggested that the rate of reduction of Cr(VI) in acid solution is influenced by the nature of the electrode material, whereby the process is electrocatalytic in character with active surface metal atoms playing a significant role in hexavalent chromium reduction [24]. Also, the effect of the supporting electrolyte has been investigated and it has been suggested that supporting electrolyte anions may play an important role in the reduction rate. This is sometimes rationalized by formation of films at the electrode surface, which might inhibit the reduction rate. Under other conditions it has been suggested that chromate ions discharge via a CE mechanism [23,25], whereby the chemical step involves electrolyte anions, which are inactive at the gold electrode [23]. Because of the fact that experimental conditions (working concentration and pH, in particular) differ from author to author it is hard to relatively evaluate the various reports.

In this paper the electrochemical reduction of hexavalent chromium is studied at various electrode substrates. The reduction of hexavalent chromium was initially examined at gold, glassy carbon and boron-doped diamond electrodes. Based on voltammetric profiles obtained, further studies were focused on reduction of hexavalent chromium at gold electrode, whereby reduction was investigated in HCl solutions over the pH range 1–3 in order to understand the reaction mechanism further and to optimize the analytical response. Next, the effect of supporting electrolyte anions on the electrochemical reaction was also examined. Last, the reduction of hexavalent chromium was probed analytically in order to develop a rapid procedure for determination of the toxic form of chromium in the presence of common interferences, such as Cr(III), Cu(II), Ni(II), Fe(III) and surfactant at environmentally relevant levels. None of them was found to interfere with the signal under the conditions used.

## 2. Experimental

The electrochemical measurements were performed with an Autolab PGSTAT 30 potentiostat (Eco-Chimie, The Netherlands). Glassy carbon (GC) (0.07 cm$^2$, BAS Technocol, UK), boron-doped diamond (BDD) (0.25 cm$^2$, Element Six Ltd, UK) and gold (0.07 cm$^2$, made in-house) electrodes served as the working electrodes. A platinum wire provided the counter electrode with a saturated calomel reference electrode (SCE, Radiometer, Denmark) completing the cell assembly. A GC electrode was polished between each series of experiments with 1 μm particle size diamond pastes (Kemet, UK). The gold working electrode was polished between each series of experiments with alumina micropolish II (Buehler, UK) of decreasing particle size (2–0.3 μM). The BDD electrode had undergone no surface pre-treatment. All experiments were carried out in a cell of volume 20 cm$^3$ and at a temperature of 20 ± 2 °C.

$K_2Cr_2O_7$ and other reagents were obtained from Aldrich; these were of the highest grade available and used without further purification. All solutions and subsequent dilutions were prepared using deionised water from Vivendi (Vivendi, UK) UHQ-grade water system with a resistivity of not less than 18 MΩ cm.

## 3. Results and discussions

### 3.1. Chromium (VI) speciation in aqueous solutions

Examination of the Pourbaix diagram [29] outlined in Fig. 1 shows that in the pH range 0.75–6.45 there are two dominant species: $HCrO_4^-$ in solutions with low concentrations (less than 0.01 g L$^{-1}$) of Cr(VI) ions and $Cr_2O_7^{2-}$ in highly concentrated solutions. In the report outlined below, the working concentrations of Cr(VI) are such that the speciation is exclusively in the form of the monochromate species.

The monochromate species can undergo the following reactions in the solution: protonation to form $H_2CrO_4$, as outlined in Scheme 1A; and/or possibly the formation of com-

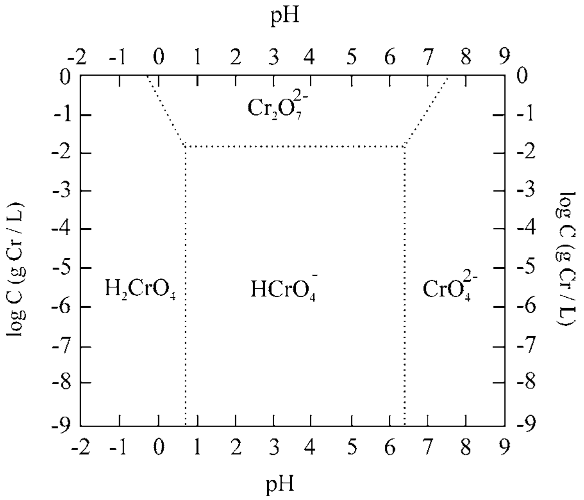


Fig. 1. Domains of relative predominance of the ions of hexavalent chromium, at 25 °C Pourbaix diagram adapted from [25].

$$\text{(A)}\quad H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \qquad K_a = 0.18\ \text{M};\ 4.1\ \text{M}$$

$$H_2O + CrO_3Cl^- \rightleftharpoons HCrO_4^- + H^+ + Cl^- \qquad K_1 = 0.09\ \text{M}^2$$

$$\text{(B)}\quad H_2O + CrSO_7^{2-} \rightleftharpoons HCrO_4^- + HSO_4^- \qquad K_2 = 2.4\ \text{M}$$

Scheme 1. Possible reactions in aqueous solutions.

Table 1
Estimated concentration of species calculated for different values of dissociation constant and concentration of HCl and $H_2SO_4$ based on $Cr_{tot}$ concentration

| | $K_{diss} = 0.18$ | | | $K_{diss} = 4.1$ | | |
|---|---|---|---|---|---|---|
| $[H^+]$ | $HCrO_4^-$ | $H_2CrO_4$ | $[CrO_3Cl^-]$ | $HCrO_4^-$ | $H_2CrO_4$ | $[CrO_3Cl^-]$ |
| 0.1 | 57.3% | 35.7% | 7.0% | 87.6% | 2.4% | 10% |
| 1 | 0% | 85% | 15% | 0% | 20% | 80% |
| | $HCrO_4^-$ | $H_2CrO_4$ | $[CrSO_7^{2-}]$ | $HCrO_4^-$ | $H_2CrO_4$ | $[CrSO_7^{2-}]$ |
| 0.1 | 37.6% | 35.7% | 26.7% | 57% | 2.4% | 40.6% |
| 1 | 0% | 85% | 15% | 0% | 20% | 80% |

plexes with anions present in the solution, as outlined in Scheme 1B.

The relevant constants for dissociation and complexation are defined in Eqs. (1)–(3).

$$K_a = \frac{[HCrO_4^-][H^+]}{[H_2CrO_4]} \tag{1}$$

$$K_1 = \frac{[HCrO_4^-][Cl^-][H^+]}{[CrO_3Cl^-]} \tag{2}$$

$$K_2 = \frac{[HSO_4^-][HCrO_4^-]}{[CrSO_7^{2-}]} \tag{3}$$

The following values appear in the literature: $K_a = 0.18\,M$ [29] or 4.1 [30]; $K_1 = 0.09\,M^2$ [30] and $K_2 = 0.24\,M$ [31]. These enable the speciation of Cr(VI) to be calculated for different concentrations of the monochromate anion in aqueous solutions of either HCl or $H_2SO_4$ of different concentrations. Typical obtained results are summarized in Table 1. Despite the difference of the literature values for $K_a$, the estimation of the concentration of the species present in the solution shows that the $HCrO_4^-$ species is dominant in 0.1 M acid. It can be seen that in 0.1 M acid the concentration of $HCrO_4^-$ is more than 57%, with only insignificant concentrations (less than 10%) of chromium chloride complexes formed. Analogous calculations were done for the formation of the chromium–sulfate complex showing that the $HCrO_4^-$ species is again dominant over chromium–sulfate complex. The estimation of the concentrations of the possible species in 1 M acid shows that $HCrO_4^-$ species are either protonated or form complexes.

### 3.2. Electroactivity of the chromate species

Cyclic voltammetric responses of the Au electrode to the solution of 1000 µM Cr(VI) in either 1 M HCl or 1 M $H_2SO_4$, where the dominant species are $H_2CrO_4$ or complex species as outlined in Table 1, revealed no significant voltammetric peak in the potential range studied (0.5 to −0.5 V versus SCE). This suggests that neither $H_2CrO_4$, $[CrO_3Cl^-]$ or $CrSO_7^{2-}$ are electrochemically active. Therefore, the following $HCrO_4^-$ are considered the dominant species and to be the electrochemically active species.

### 3.3. Electrochemical reduction of chromium(VI)

An initial study of the reduction of Cr(VI) was carried out using cyclic voltammetry at gold (Au), boron-doped diamond (BDD) and glassy carbon (GC) electrode materials in pH 1 (0.1 M HCl), pH 4.2 (0.1 M sodium acetate) and pH 13 (0.1 M KOH). Significant voltammetric responses towards the reduction of Cr(VI) were obtained only in 0.1 M HCl at all three electrodes studied. Fig. 2 details the corresponding cyclic voltammogram (A) plotted as current density versus potential obtained for the reduction of 1000 µM Cr(VI) in 0.1 M HCl at an Au electrode at a scan rate of 50 mV $s^{-1}$. This reveals a well-defined reduction peak, with a peak potential at +0.27 V (versus SCE). The shape of the voltammogram might be preliminarily attributed to an electrochemically reversible process, whilst the absence of corresponding oxidation peak in the potential range studied indicates a chemically irreversible reaction. Also depicted in Fig. 2 are the corresponding voltammetric responses obtained in the same solution and at the same scan rate at GC (B) and BDD (C). As can be seen, the response obtained at GC consists of a pre-shoulder at +0.25 V and a main reduction peak registered at −0.02 V. The pre-shoulder was found to appear only in solutions with high concentrations (greater than 100 µM) of hexavalent chromium. In contrast, the BDD response produced a single wave at −0.3 V. Both electrodes produced voltammograms with broad peaks.

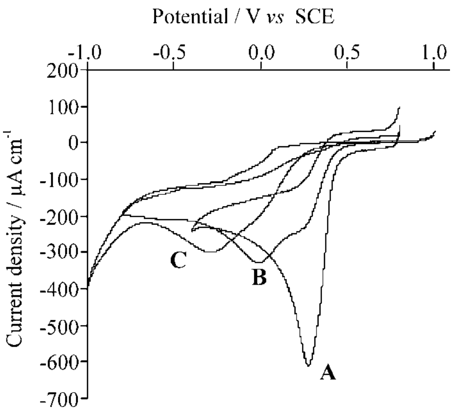


Fig. 2. Voltammetric response (scan rate = 50 mV $s^{-1}$) of Au (A), GC (B) and BDD (C) electrodes to a 0.1 M HCl solution containing 1000 µM Cr(IV) plotted as current density vs. potential.

Next, the reaction was examined further at each electrode material individually, as reported below.

### *3.3.1. Reduction of hexavalent chromium at glassy carbon*

The voltammetric responses (not shown) of 50 μM Cr(VI) in 0.1 M HCl to various scan rates (10–400 mV $s^{-1}$) obtained at GC ($A = 0.07\,cm^2$) revealed only one reduction peak, which was found to shift to more negative values with further increase of scan rate. This indicates on the electrochemically irreversible reaction, which is confirmed by the Tafel slope of ca. 300 mV per decade. The reaction process might be rationalized as the one-step reduction of Cr(VI) to Cr(III).

It should be noted that the responses of GC to solutions of 0.1 M HCl containing more than 200 μM of Cr(VI) revealed the presence of a pre-shoulder at +0.25 V (versus SCE) and a reduction wave at −0.02 V (versus SCE) analogous to that shown in Fig. 2. Further Tafel analysis of GC waves recorded at 50 mV $s^{-1}$ in solution with 1000 μM Cr(VI) suggested that first wave at +0.25 V is more reversible (Tafel slope ca. 150 mV per decade) than the second wave (Tafel slope ca. 1000 mV per decade) and might tentatively be attributed to the reduction of Cr(VI) to Cr(V), with further reduction to Cr(III) in the second wave.

The analysis of the Randles–Sevčik plot for the reduction process of 50 μM Cr(VI) at GC, which was found to be linear in the scan rate range studied, suggests that reaction is diffusion rather than surface controlled. However, in general, the reproducibility of the results was found to be poor, which can be explained by the influence of the corrosive environment on GC. Thus, GC cannot be recommended as a working electrode for analytical purposes.

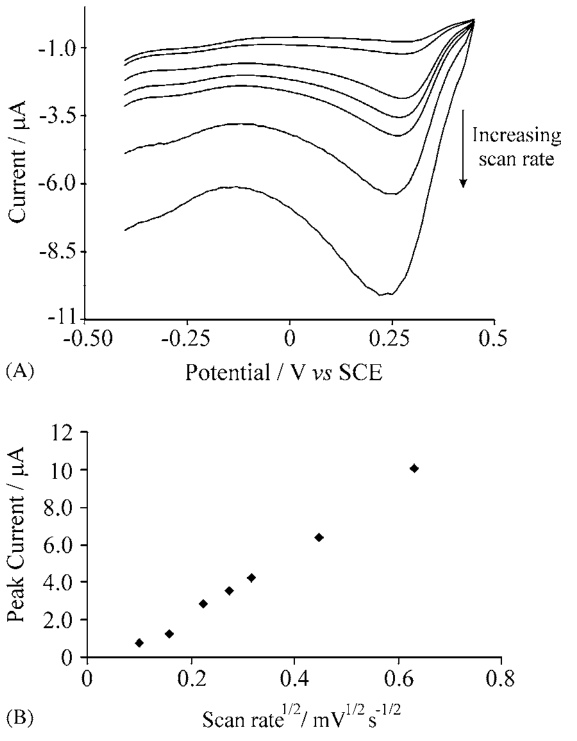


Fig. 3. (A) Linear sweep voltammograms detailing the response to differing scan rates (10–400 V $s^{-1}$) for solution containing 50 μM Cr(VI) in 0.1 M HCl at a Au electrode; (B) Corresponding plot of reduction peak current against square root of scan rate.

### *3.3.2. Reduction of hexavalent chromium at boron-doped diamond*

The response of 50 μM Cr(VI) in 0.1 M HCl to various scan rates (10–400 mV $s^{-1}$) at BDD was studied next. Obtained voltammograms (not shown) revealed voltammetric profiles analogous to that shown in Fig. 2. Recorded reduction peak was found to shift to more negative values with further increase of scan rate. This indicates a highly electrochemically irreversible reaction, which is confirmed by the Tafel slope of ca. 350 mV per decade obtained from a plot of potential versus log (current). The fact that the Randles–Sevčik plot was found to be linear ($R^2 = 0.993$) in the potential range studied indicates an irreversible diffusion-controlled process. Further, BDD was examined towards increasing additions (0–200 μM) of Cr(VI) in 0.1 M HCl. The recorded cyclic voltammograms (not shown) revealed a wave at −0.26 V (versus SCE) analogous to that shown in Fig. 2. The corresponding plot of peak current against increasing concentration of hexavalent chromium was found to be linear in the concentration range studied (20–200 μM; slope $= 8.22 \times 10^{-2}$ A $M^{-1}$; $R^2 = 1$).

### *3.3.3. Reduction of hexavalent chromium at gold*

The voltammetric response of hexavalent chromium to various scan rates was examined via linear sweep voltammetry at a gold electrode ($A = 0.07\,cm^2$). The voltammograms recorded at different scan rates (10–400 mV $s^{-1}$) in 0.1 M HCl solution containing 50 μM Cr(VI) are shown in Fig. 3A. These reveal process with a peak potential at +0.27 V (10 mV $s^{-1}$), which was found to shift up to +0.25 V (400 mV $s^{-1}$) with a scan rate increase. The fact that peak potential is not significantly dependent on scan rate suggests that reaction is electrochemically reversible at the Au electrode. The corresponding plot of reduction peak currents against square root of scan rate was found to be linear as demonstrated in Fig. 3B, confirming the diffusional nature of the process. Tafel analysis plotted as potential versus log (current) produced a value in the range of 60–80 mV, indicating the possible electrochemical reversibility of the process; however, the exact reaction mechanism will be clarified below after examination of the pH dependence of the process.

In order to investigate the reaction mechanism further at gold electrode, the reduction of hexavalent chromium was examined in various solutions containing different concentrations of hydrochloric acid (0.1–0.001 M), which correspond to pH 1–3, respectively. Fig. 4 illustrates the cyclic voltammetric response obtained in the solution containing 200 μM Cr(VI) in 0.1 M HCl (scan rate = 10 mV $s^{-1}$). It can be seen that the response of the gold electrode to hexavalent chromium in 0.1 M HCl produced a single wave

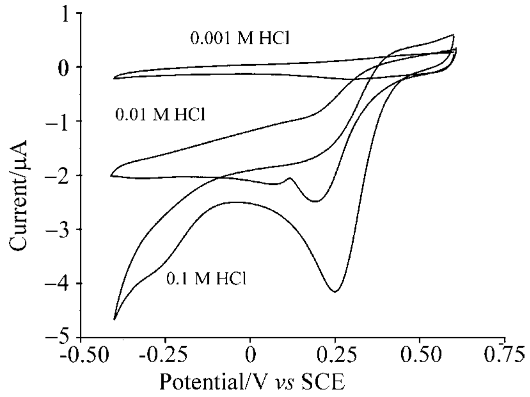
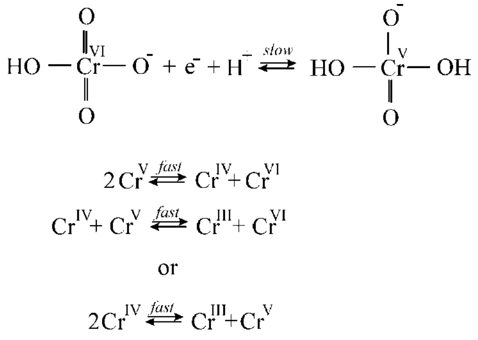


Fig. 4. Cyclic voltammograms (scan rate = 50 mV s$^{-1}$) detailing response of a Au electrode to 200 μM Cr(VI) in 0.1 M HCl, 0.01 M HCl and 0.001 M HCl.

profile, with a reduction peak at +0.27 V, analogous to that shown in Figs. 2 and 3. Fig. 4 also illustrates voltammograms obtained in 0.01 M and 0.001 M HCl. It can be seen that the electrode response in solution containing the same concentration of hexavalent chromium in 0.01 M HCl produced a wave with two peaks and lower magnitude of reduction current, indicating a proton-dependent process. The first peak potential was found to shift to more negative value by 55 mV, which, in combination with the Tafel analysis reported above, suggests that reduction of hexavalent chromium proceeds via a one-electron and one-proton reaction, followed by disproportonation as outlined in Scheme 2, where monochromate species are reduced via one-electron and one-proton reaction to pentavalent chromium, which disproportionates to Cr(IV) and Cr(VI) species. Tetravalent chromium species can undergo disproportionation either with pentavalent chromium to Cr(III) and Cr(VI) species or with other tetravalent chromium to Cr(III) and Cr(V) species [30]. At high concentrations of H$^+$ disproportionation following the reduction of Cr(VI) to Cr(V) can rapidly form Cr(III), whilst in diluted solutions of H$^+$ the further direct electrochemical reduction is probably observed. The response of the electrode recorded in 0.001 M HCl containing 200 μM Cr(VI) produced no significant analytical signal, possibly because of the low concentration of protons.



$$\mathrm{HO{-}\overset{O}{\underset{O}{Cr^{VI}}}{-}O^-} + e^- + H^- \xrightleftharpoons{slow} \mathrm{HO{-}\overset{O^-}{\underset{O}{Cr^{V}}}{-}OH}$$

$$2\,\mathrm{Cr^{V}} \xrightleftharpoons{fast} \mathrm{Cr^{IV}} + \mathrm{Cr^{VI}}$$

$$\mathrm{Cr^{IV}} + \mathrm{Cr^{V}} \xrightleftharpoons{fast} \mathrm{Cr^{III}} + \mathrm{Cr^{VI}}$$

or

$$2\mathrm{Cr^{IV}} \xrightleftharpoons{fast} \mathrm{Cr^{III}} + \mathrm{Cr^{V}}$$

Scheme 2. Suggested reduction pathway.

In order to further validate the diffusional nature and, in particular, to test the analytical applicability of the reduction process, the response of Au electrode to increasing additions of Cr(VI) (100–1500 μM) in 0.1 M HCl was examined. The recorded voltammogram for the reduction of 100 μM Cr(VI) (not shown) revealed a reduction process at +0.27 V analogous to that shown in Figs. 2 and 3. Voltammograms obtained with further additions of hexavalent chromium to 0.1 M HCl were analogous to that obtained for 100 μM Cr(VI). A plot of the change of reduction peak current as a function of hexavalent chromium added to the solution was found to be linear in the concentration range studied (100–1500 μM; slope = $5.07 \times 10^{-2}$ A M; $R^2 = 0.999$) consistent with a diffusion-controlled reaction.

All experimental data confirmed that the reaction mechanism is diffusion, rather than surface, controlled. At the same time, Tafel analysis plotted as potential versus log (current) suggested the reversibility of the first one-electron transfer (60 mV per decade), which encourages the use of the following equation for a reversible diffusion-controlled process for the first step of the reduction process.

$$I_{\text{peak}} = 2.69 \times 10^5 n^{3/2} D^{1/2} C_0 A V^{1/2} \quad (4)$$

where $n$ is the number of electrons transferred, $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $C_0$ is the bulk concentration of the analyte (mol cm$^{-3}$), $A$ is the area of the electrode (cm$^2$) and $V$ is the potential sweep scan rate (V s$^{-1}$). However, based on the suggested mechanism (Scheme 2), whereby the rate-limiting step is the electrochemically reversible transfer of the first electron [32], which is followed by two single homogeneous electron reduction processes, Eq. (4) can be modified to give the following expressions for the diffusion coefficient

$$D^{1/2} = \frac{I_{\text{peak}}}{3 \times 2.69 \times 10^5 n^{3/2} C_0 A V^{1/2}} \quad (5)$$

where $n = 1$, and the total number of electrons transferred is expressed by a factor of three in the denominator. The obtained value of $(1.6 \pm 0.2) \times 10^{-5}$ cm$^2$ s$^{-1}$ for the diffusion coefficient is not inconsistent with the previously reported value of $1.20 \times 10^{-5}$ cm$^2$ s$^{-1}$ obtained in 0.23 M HCl [25].

*3.3.3.1. Effect of supporting electrolyte.* The effect of supporting electrolyte was examined next in order to find optimum conditions for the analytical detection of hexavalent chromium. Davilov and Protsenko [23] found that the sensitivity of the signal in various electrolytes decreased in the following order $H_2SO_4$ > HCl > $HNO_3$. Thus, we compared responses of gold electrode to increasing additions (100–1000 μM) of Cr(VI) obtained in 0.1 M HCl, 0.1 M $H_2SO_4$ and 0.1 M $HNO_3$ at gold electrode. Voltammetric profiles recorded in all three acids studied were analogous to those shown in Fig. 2. It was also noticed that gradients of the reduction peak current against concentration of hexavalent chromium were similar for all three acids: $3.01 \times 10^{-2} \pm 2.86 \times 10^{-4}$ A M$^{-1}$ ($HNO_3$), $3.02 \times 10^{-2} \pm 2.35 \times$

Table 2
Relevant analytical and statistical parameters for detection of Cr(VI) obtained in the presence of interferences for linear range 20–200 μM Cr(VI), $n = 10$ (confidence level is 90%)

| Interference | Gradient (A $M^{-1}$) | Confidence intervals | Significance level | $R^2$ |
|---|---|---|---|---|
| None | $3.52 \times 10^{-2}$ | $\pm 2.3 \times 10^{-4}$ | $1.10 \times 10^{-16}$ | 0.999 |
| 5 mM $Cr(NO_3)_3$ | $3.34 \times 10^{-2}$ | $\pm 4.11 \times 10^{-4}$ | $3.27 \times 10^{-14}$ | 0.998 |
| 250 μM $Ni(SO_4)_2$ | $3.93 \times 10^{-2}$ | $\pm 5.24 \times 10^{-4}$ | $6.84 \times 10^{-14}$ | 0.998 |
| 250 μM $Cu(SO_4)_2$ | $3.54 \times 10^{-2}$ | $\pm 6.04 \times 10^{-4}$ | $6.11 \times 10^{-13}$ | 0.997 |
| 250 μM $Fe_2(SO_4)_3$ | $3.85 \times 10^{-2}$ | $\pm 3.38 \times 10^{-4}$ | $1.57 \times 10^{-15}$ | 0.999 |
| 5.5 mM SAS[a] | $3.61 \times 10^{-2}$ | $\pm 1.35 \times 10^{-4}$ | $7.04 \times 10^{-10}$ | 0.988 |

[a] SAS: iso-octylphenoxypolyethoxyethanol (Triton X-100, Sigma).

$10^{-4}$ A $M^{-1}$ ($H_2SO_4$) and $2.97 \times 10^{-2} \pm 3.01 \times 10^{-4}$ A $M^{-1}$ (HCl). The similarity of the responses obtained in hydrochloric and nitric acids can be explained by the equimolar concentrations of protons. The analogous response recorded in sulfuric acid can be attributed to the fact that sulfuric acid dissociates completely to $HSO_4^-$, thus producing the similar concentrations of $H^+$ [33]. Thus, all three acids produce the same concentration of protons, which consequently generate the same concentration of electrochemically active $HCrO_4^-$ species. Examination of Table 1 reveals that concentration of $HCrO_4^-$ present in the 0.1 M HCl and 0.1 M $H_2SO_4$ differs by 20% ($K_{diss} = 0.18$) or 30% ($K_{diss} = 4.1$), which is because of the possible formation of the chromate complexes, $CrO_3Cl^-$ or $CrSO_7^{2-}$, having different complexation constants. However, the analogous response obtained in three acids indicates either the exclusive formation of the $HCrO_4^-$ species or the formation of complexes, which are electrochemically active and have a reduction potential similar to that of $HCrO_4^-$ or more likely that are sufficiently labile to dissociate on the voltammetric timescale allowing quantitate reaction via a CE process.

*3.3.3.2. Analytical applicability of the reaction at Au electrode.* After the reaction route was identified, the analytical utility of the reaction was studied next. The reduction of hexavalent chromium in the presence of excess trivalent chromium was investigated using linear sweep voltammetry. The choice of the chromium(III) concentration was based on the fact that the natural occurrence of trivalent Cr(III) is normally in 100-fold excess of the concentration of Cr(VI) [14]. The analysis of obtained plots of hexavalent chromium reduction peak current against concentration of Cr(VI) added in the absence and presence of 5 mM trivalent chromium are summarized in Table 2. As it can be seen no significant change in gradients of plots was observed. Also outlined in Table 2 are the corresponding plots of obtained reduction peak current against of hexavalent chromium added to the solution containing 250 μM Cu(II), 250 μM Ni(II), 250 μM Fe(III) and 5.5 mM iso-octylphenoxypolyethoxyethanol. The interference concentration choice was based on literature values found for water samples [34–37]. It can be seen from Table 2 that the slope of the corresponding plot of peak current against concentration of hexavalent chromium is independent of environmental interferences; accordingly, this procedure can be used for the electroanalytical detection of the hexavalent species in environmental samples. The limit of detection for Cr(VI) in the presence of Cr(III), calculated with 90% confidence level, is 4.3 μM (0.22 mg $L^{-1}$). This compares with 0.25 mg $L^{-1}$ reported in [13].

## 4. Conclusions

The mechanism of hexavalent chromium reduction was examined at various electrode substrates. It was found that Au, GC and BDD provided a voltammetric response towards addition of hexavalent chromium in acidic conditions. It was shown that at a gold electrode the reduction process occurs at more positive potential in comparison to that at GC and BDD. The reduction to Cr(III) at gold electrode was found to proceed via rate determining reversible electron transfer followed by rapid disproportionation of Cr(V). A diffusion coefficient of $1.60 \pm 0.02 \times 10^{-5}$ $cm^2\,s^{-1}$ for the $HCrO_4^-$ anions was deduced.

The analytical applicability was investigated, with a limit of detection found to be 4.3 μM. The response of the electrode to addition of hexavalent chromium was found to be independent of common environmental interferences, such as Ni, Cu and Cr(III).

## Acknowledgements

ON gratefully acknowledges the Analytical Division of the RSC for her PhD studentship.

## References

[1] R.M. Cespon-Romero, M.C. Yebra-Biurrun, M.P. Bermejo-Barrera, Anal. Chim. Acta 327 (1996) 37.
[2] Guidance for Drinking Water Quality, second edition, vol. 1. Recommendations, Geneva, WHO, 1993, pp. 45–46.
[3] D. Golub, Y. Oren, J. Appl. Electrochem. 19 (1989) 311.
[4] R.J. Kieber, J.D. Willey, S.D. Zvalaren, Environ. Sci. Technol. 36 (2002) 5321.
[5] J.H. Larochelle, D.C. Johnson, Anal. Chem. 50 (1978) 240.
[6] A.M. Bond, G.G. Wallace, Anal. Chem. 54 (1982) 1706.
[7] J. de Joung, U.A.Th. Brinkman, Anal. Chim. Acta 98 (1978) 243.
[8] W. Slavin, Atom. Spectr. 2 (1983) 163.

[9] A.J. Pik, J.M. Eckert, K.L. Williams, Anal. Chim. Acta 124 (1981) 351.
[10] R.E. Cranston, J.W. Murray, Anal. Chim. Acta 99 (1978) 275.
[11] I. Turyan, D. Mandler, Anal. Chem. 69 (1997) 894.
[12] J. Kalembkiewicz, E. Soso, Wiadomosci Chamiczne 56 (2002) 855.
[13] Q. Li, K.J. Morris, P.K. Dasgupta, I.M. Raimundo Jr, H. Temkin, Anal. Chim. Acta 479 (2003) 151.
[14] M. Korolczuk, M. Grabarczyk, Talanta 49 (1999) 703.
[15] S.T. Crosmun, T.R. Mueller, Anal. Chim. Acta 75 (1975) 199.
[16] C. Harzdorf, G. Janser, Anal. Chim. Acta 165 (1984) 201.
[17] J.A. Cox, J.L. West, P.J. Kulesza, Analyst 109 (1984) 927.
[18] M. Boussemart, C.M.G. van den Berg, M. Ghaddaf, Anal. Chim. Acta 262 (1992) 103.
[19] M.A. Ghandour, S.A. El-Shatoury, A.M.M. Aly, S.M. Ahmed, Anal. Lett. 29 (1996) 1431.
[20] A.C. Harzdorf, Int. J. Environ. Anal. Chem. 29 (1987) 249.
[21] S. Sander, T. Navrátil, L. Novotny, Electroanalysis 15 (2003) 1513.
[22] S. Sander, T. Navrátil, P. Bašová, L. Novotný, Electroanalysis 14 (2003) 1133.
[23] F.I. Danilov, V.S. Protsenko, Russ. J. Electrochem. 34 (1998) 276.
[24] L.D. Burke, P.F. Nugent, Electrochim. Acta 42 (1997) 399.
[25] S.B. Faldini, S.M.L. Agostinho, H.C. Chagas, J. Electroanal. Chem. 284 (1990) 173.
[26] J.A. Cox, P.J. Kulesza, Anal. Chim. Acta 154 (1983) 154.
[27] J.A. Cox, P.J. Kulesza, M.A. Mbugwa, Anal. Chim. 54 (1982) 787.
[28] H. Ge, J. Zhang, G.G. Wallace, Anal. Lett. 25 (1992) 429.
[29] E. Deltombe, N. de Zoubov, M. Pourbaix, in: M. Pourbaix (Ed.), Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, New York, 1966, pp. 256–271.
[30] J.Y. Tong, R.L. Johnson, Inorg. Chem. 5 (1966) 1902.
[31] G.P. Haight, D.C. Richardson, N.H. Colburn, Inorg. Chem. 3 (1964) 1777.
[32] V.P. Roldán, V.A. Daier, B. Goodman, M.I. Santro, J.C. Gonzáles, N. Calisto, S.R. Signorella, L.F. Sala, Helvetica Chimica Acta 83 (2000) 3211.
[33] F.A. Cotton, G. Wilkinson, P.L. Gaus, Basic Inorganic Chemistry, second edition, John Wiley & Sons, NY, 1987.
[34] I. Narin, M. Soylak, Anal. Chim. Acta 493 (2003) 205.
[35] J. Davis, M.F. Cardosi, I. Brown, M.J. Hetheridge, R.G. Compton, Anal. Lett. 34 (2001) 2375.
[36] Y.-C. Sun, J. Mierzwa, M.-H. Yang, Talanta 44 (1997) 1379.
[37] H. Chen, I.D. Brindle, X.-C. Le, Anal. Chem. 64 (1992) 667.