

# Indirect determination of hexavalent chromium ion in complex matrices by adsorptive stripping voltammetry at a mercury electrode

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## Abstract

A sensitive method for the determination of chromium ion(VI) in complex matrices such as crude oil and sludge is presented based on the decreasing effect of Cr(VI) on cathodic adsorptive stripping peak height of Cu–adenine complex. Under the optimum experimental conditions (pH 7.5 Britton–Robinson buffer,  $5 \times 10^{-5}$  M copper,  $8 \times 10^{-6}$  M adenine and accumulation potential  $-250$  mV versus Ag/AgCl), a linear decrease of the peak current of Cu–adenine was observed, when the chromium(VI) concentration was increased from  $5 \mu\text{g L}^{-1}$  to  $120 \mu\text{g L}^{-1}$ . Detection limit of  $2 \mu\text{g L}^{-1}$  was achieved for 120 s accumulation time. The relative standard deviations (R.S.D., %) were 1.8% and 4% for chromium(VI) concentrations of  $18 \mu\text{g L}^{-1}$  and  $100 \mu\text{g L}^{-1}$ , respectively. The method was applied to the determination of chromium(VI) in the presence of high levels of chromium(III), in various real samples such as crude oil, crude oil tank bottom sludge, waste water and tap water samples. Effects of foreign ions and surfactants on the voltammetric peak and the influences of instrumental and analytical parameters were investigated in detail. The accuracy of the results was checked by ICP and/or AA.

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## 1. Introduction

Trace element concentrations in ground water systems at levels above established water quality standards are problematic. The toxicity of metal ions is extremely dependent on the valence state of the metal species. These elevated levels are often associated with anthropogenic inputs. Chromium is unique among regulated toxic elements in the environment in that different species of chromium, specifically Cr(III) and Cr(VI), are regulated in different ways based on their differing toxicities.

Chromium is in a reduced state in primary minerals. Low solubility, strong adsorption of Cr(III) and a number of possible reductants combine to keep Cr in the Cr(III) state. Therefore, the presence of elevated Cr(VI) levels in moisture films in these soils is not expected. This may be from dissolution of sparingly soluble chromates, an anthropogenic source

of Cr(VI) or oxidation of Cr(III) would be involved [1]. On the other hand, previous investigation of natural waters has shown that the predominant oxidation state of chromium in oxygenated waters is Cr(VI), whereas Cr(III) is most significant under anoxic conditions [2].

Cr(III) is considered essential in mammals for maintenance of glucose, lipid, and protein metabolism [3] while Cr(VI) is known to damage mucous membranes and cause renal damage and has been classified as carcinogenic to humans [3,4]. Katz and Salem [5] reviewed the toxicology of chromium with respect to chemical speciation; these authors pointed out that the hexavalent form is up to 1000 times more toxic than the trivalent form.

The European Community Directive [6] for drinking water standards has put the limit of total chromium not exceeding  $50 \mu\text{g L}^{-1}$  ( $1 \times 10^{-6} \text{ mol L}^{-1}$ ). The criterion maximum concentration (CMC) for Cr(VI) in freshwater is  $16 \mu\text{g L}^{-1}$  [7].

Many spectroscopic methods have been employed for the determination of the chromium species [8–14]. Also,

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several methods are available for the analysis of chromium in different biological media, but these methods need expensive instrumentations and suffer from instrumental difficulties due to matrix interferences [9]. Some methods such as colorimetry often suffer from spectral interferences due to the presence of co-existing organic substances [15].

Electrochemical methods, especially, adsorptive stripping voltammetry are known as simple, sensitive and inexpensive methods [16]. Several catalytic cathodic stripping voltammetry (CCSV) [5,17–32] and adsorptive stripping voltammetry (AdSV) [4,33–43] with different ligands have been reported in the literature for the determination of Cr(VI) in different samples.

In most procedures [22,23,36–38], the determinations of Cr(VI) can be carried out in the presence of only 10–100-fold excess of Cr(III).

Extraction of chromium as Cr(VI) from complex matrices and prevention of the oxidation of Cr(III) or reduction of Cr(VI) are important steps in determination of Cr(VI). Alkaline digestions methods [44–46], have been introduced as procedures for specific extraction of Cr(VI) from different samples.

In our previous work, we introduced a method for trace determination of copper based on adsorptive stripping voltammetry of copper–adenine complex on hanging mercury drop working electrode (HMDE) [47] and it had been observed that Cr(VI) decreased the adsorptive signal of copper complex.

The purpose of this work is to describe a new electro-analytical system for measuring Cr(VI) in complex matrices. The effect of surfactants was examined and the elimination of this effect was studied. The interference effect of Cr(III) was lower than the previously reported methods. The presence of high concentrations of Cr(III) did not have any significant effect on Cr(VI) signal.

The method is based on the decrease in peak height of the adsorbed Cu(I)–adenine species in a solution containing Cu(II) and adenine at an appropriate pH value.

## 2. Experimental

### 2.1. Chemical and reagents

The stock standard solution of adenine, copper and Britton–Robinson (B–R) buffer were prepared as described previously [47].

The stock solution of Cr(VI) was prepared by dissolving appropriate amounts of potassium dichromate in a volumetric flask to make 500 mg L<sup>-1</sup> chromium.

Buffer extraction solution (BE) was prepared by dissolving 20.0 ± 0.05 g NaOH and 30.0 ± 0.05 g Na<sub>2</sub>CO<sub>3</sub> in water and diluting to 1 L in a volumetric flask. The solution was stored in a tightly capped polyethylene bottle at 20–25 °C. This solution was stable up to 1 month. The pH of the

digestion solution must be checked before use. The pH must be 11.5 or greater [44–46].

Phosphate buffer (0.5 M K<sub>2</sub>HPO<sub>4</sub>/0.5 M KH<sub>2</sub>PO<sub>4</sub>) at pH 7 was prepared by dissolving 87.09 g K<sub>2</sub>HPO<sub>4</sub> and 68.04 g KH<sub>2</sub>PO<sub>4</sub> in water and diluting to 1 L in a volumetric flask.

Magnesium sulfate solution was prepared by dissolving 9.90 g of anhydrous MgSO<sub>4</sub> in water and diluting to 100 mL. The solution was prepared monthly.

All reagents were of the highest grade available and used without further purification. Deionized water was obtained by means of a Millipore Milli-Q water system and used throughout.

### 2.2. Instrumentation

Voltammetric measurements were made with a Metrohm 694 (Herisau, Switzerland) VA Stand coupled with a Metrohm 693 VA Processor. Adsorptive and voltammetric experiments were carried out in a three-electrode arrangement with an Ag/AgCl, 3 M KCl reference electrode, platinum wire counter electrode and multi-mode mercury drop electrode. Dissolved oxygen was removed by argon. For pH measurements, a Metrohm 691 pH meter was used. All potentials are given versus Ag/AgCl.

### 2.3. Procedure

#### 2.3.1. General voltammetric procedure

Voltammetric measurements were made using the following procedure. The solution (containing, 5 × 10<sup>-5</sup> M copper, 8 × 10<sup>-6</sup> M adenine at pH 7.5 Britton–Robinson buffer) was first de-oxygenated, the stirrer was connected and deposition began for a certain period of time (i.e. 120 s) at the appropriate deposition potential (i.e. -250 mV). When the time had elapsed, the stirrer was switched off, and the solution was left to settle for an equilibration time of 5 s. The voltammogram was then recorded by making a cathodic sweep in differential pulse mode and  $I_{\text{Cu-Ade}}$  (the current due to reduction of the Cu–Ade complex) was recorded as the blank signal.

Now, the pH of sample solution was adjusted with HNO<sub>3</sub> or NaOH to approach pH 7–8. After adding appropriate volumes of sample solution to the voltammetric cell, the solution was purged for 30 s and the cathodic adsorptive stripping procedure was repeated and the current response ( $I_{\text{Cu-Ade} + \text{Cr(VI)}}$ ) was recorded. The decrease in the cathodic peak current of Cu–Ade is given by  $\Delta i = I_{\text{Cu-Ade}} - I_{\text{Cu-Ade} + \text{Cr(VI)}}$  and recorded as the sample signal.

#### 2.3.2. Procedure for extraction of Cr(VI) from real samples [44]

Fifty milliliters of BE was added to each sample (1–2 g sludge or crude oil or 10 mL waste water) using a graduated cylinder, followed by the addition of 10 mL of magnesium sulfate solution and 1 mL of phosphate buffer. The sample was covered with glass watch. The solution was stirred continuously (unheated) for at least 5 min using an appropriate

stirring device. The solution was heated to 90–95 °C, and the temperature was maintained at 90–95 °C for at least 60 min with continuous stirring. The solution was gradually cooled, with continued agitation to room temperature. The contents was transferred quantitatively to the filtration apparatus; rinsing the digestion vessel with three successive portions of deionized water. The washed solution was transferred to the filtration apparatus. The inside of the filter flask and filter pad was rinsed with deionized water and the filtrate and the wash solution were transferred to a clean volumetric flask.

### 2.3.3. Procedure for minimizing the effect of the surfactants

To avoid surface active interference in real samples, a separation step was performed as follows. Two milliliters of sample solution was extracted with 1 mL of dichloromethane. After vigorous shaking, the solution was allowed to form the two phases. The aqueous solution was saved as the analyte.

## 3. Results and discussion

### 3.1. Adsorptive characteristics of copper with adenine and chromium

In our previous work, the adsorptive properties of copper with adenine complex (Cu–Ade) on the mercury electrode were demonstrated [47]. Cr(VI) decreased the peak height of Cu–Ade (Fig. 1) and was registered as serious interference. No new peak was observed due to Cr(VI) under the experimental conditions for Cu–Ade system. Also no adsorptive peak was found for Cr(VI) and adenine system. Cr(VI) not only decreased the peak height but also affected the peak potential. The cathodic adsorptive stripping peak potential was shifted from –540 mV to –600 mV. It has been

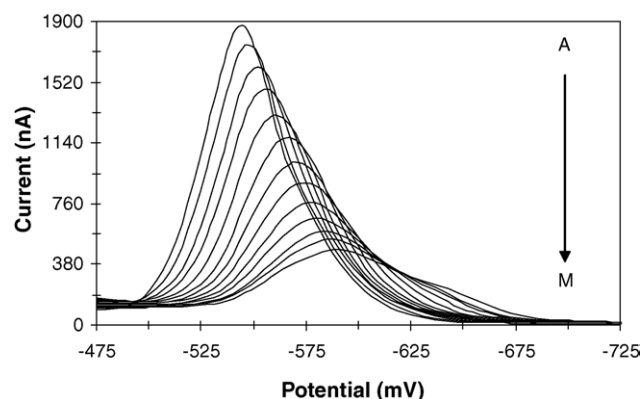


Fig. 1. Effect of chromium(VI) concentration on the peak height: [Cu] =  $5 \times 10^{-5}$  M; [Ade] =  $8 \times 10^{-6}$  M; pH 7.5;  $E_{acc} = -250$  mV; differential pulse mode;  $\nu = 120$  mV s $^{-1}$ ;  $t_{acc} = 120$  s; pulse height = 100 mV;  $\Delta I_p$  was recorded after adding: [Cr(VI)] = A, blank; B, 20  $\mu\text{g L}^{-1}$ ; C, 32.5  $\mu\text{g L}^{-1}$ ; D, 45  $\mu\text{g L}^{-1}$ ; E, 57.5  $\mu\text{g L}^{-1}$ ; F, 70  $\mu\text{g L}^{-1}$ ; G, 82.5  $\mu\text{g L}^{-1}$ ; H, 95  $\mu\text{g L}^{-1}$ ; I, 107.5  $\mu\text{g L}^{-1}$ ; J, 120  $\mu\text{g L}^{-1}$ ; K, 132.5  $\mu\text{g L}^{-1}$ ; L, 145  $\mu\text{g L}^{-1}$ ; M, 157.5  $\mu\text{g L}^{-1}$ .

postulated that Cu(I)–Ade is adsorbed on the mercury electrode and the method is based on the reduction of this complex in stripping step. Therefore, any substance that decreased the concentration of Cu(I) or adenine at the electrode surface can interfere in this method. Cr(VI) can interact with adenine. In other words, the competitive adenine complex formation reaction between Cu(I) at the electrode surface and chromium ions in solution cannot be ruled out in here. The peak was decreased with increasing the Cr(VI) concentration. Thus, it seems that there is an interaction between Cr(VI) and adenine, although no adsorption peak was obtained under our experimental conditions for the Cr(VI)–adenine adduct.

### 3.2. Effects of operational parameters

#### 3.2.1. Effect of analytical parameters

3.2.1.1. *Effect of variation of pH.* The effect of the solution pH on the Cu–Ade complex was investigated by measuring the decrease ( $\Delta I_p$ ) of peak height of Cu–Ade after addition of Cr(VI) at different pH values (Fig. 2). Maximum decrease ( $\Delta I_p$ ) of peak height of the Cu–Ade complex was obtained at pH of 7.5.

3.2.1.2. *Effect of ionic strength.* The effect of ionic strength was studied by increasing the concentration of sodium nitrate in the solution. The cathodic adsorptive stripping peak of Cu–Ade remained constant up to 1.1 M of sodium nitrate.

3.2.1.3. *Extraction steps.* The extraction procedure had two steps. The first includes stabilization and extraction of Cr(VI) from real samples and the second is removal of surface active substances (if present).

Alkaline digestions with the option for total Cr(VI), includes extraction of Cr(VI) with a boiling sodium carbonate–sodium hydroxide (pH 12) solution for 45 min. This process prevents the reduction of Cr(VI) to Cr(III) but

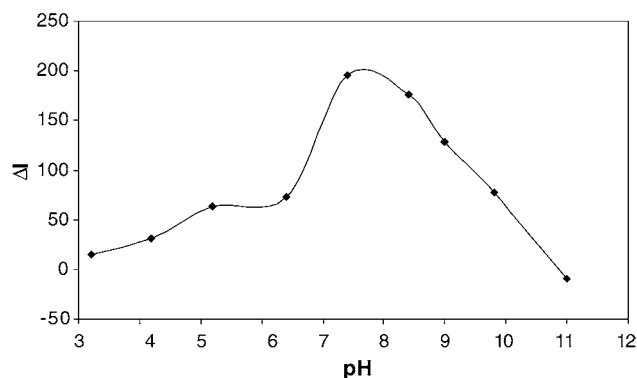


Fig. 2. Effect of pH: [Cu] =  $1 \times 10^{-4}$  M; [Ade] =  $8 \times 10^{-6}$  M;  $E_{acc} = -250$  mV;  $t_{acc} = 10$  s;  $\nu = 80$  mV s $^{-1}$ ; differential pulse mode; pulse height = 100 mV;  $\Delta I_p$  was recorded after addition of 100  $\mu\text{g L}^{-1}$  of [Cr(VI)].

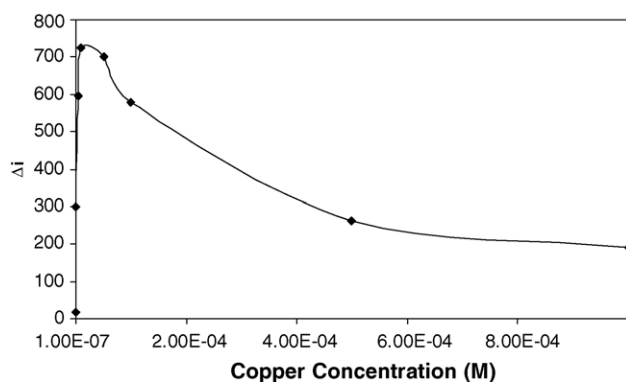


Fig. 3. Effect of concentration of copper on the peak height:  $[Ade] = 8 \times 10^{-6}$  M; pH 7.5;  $E_{acc} = -250$  mV;  $t_{acc} = 90$  s;  $v = 80$  mV s $^{-1}$ ; differential pulse mode; pulse height = 50 mV;  $\Delta I_p$  was recorded after addition of  $100 \mu\text{g L}^{-1}$  of  $[\text{Cr(VI)}]$ .

can oxidize water-soluble Cr(III) to Cr(VI) in the presence of manganese dioxide or oxygen [44]. The pH of the digest must be carefully adjusted during the digestion procedure. Failure to meet careful pH adjustment will necessitate re-digestion of the sample. The sample is digested using BE and heating at 90–95 °C for 60 min to dissolve Cr(VI) and stabilize it against reduction to Cr(III). The addition of  $\text{Mg}^{2+}$  to BE in a phosphate buffer has been shown to suppress this oxidation [44–46].

Surface active agents, if present, could interfere in voltammetric determination procedure. For obtaining higher accuracy and sensitivity and lower background, separation of other organic materials which were registered as interferences in voltammetric procedure could be performed by organic solvents such as hexane, dichloromethane, chloroform or carbon tetrachloride. Dichloromethane was the best solvent for removal of the surface active substances.

**3.2.1.4. Effect of variation of copper concentration.** The effect of copper concentration on peak height is shown in

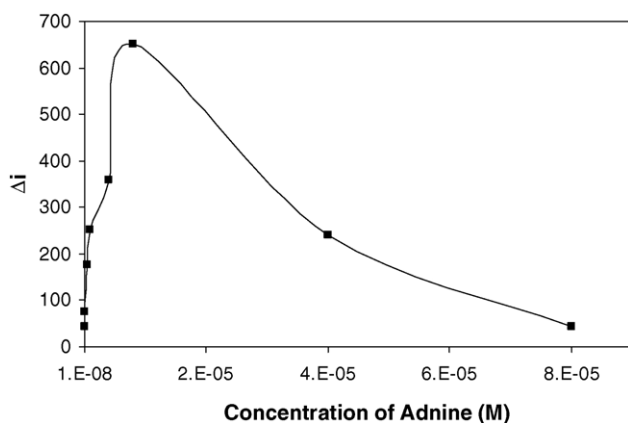


Fig. 4. Effect of concentration of adenine on the response:  $[\text{Cu}] = 5 \times 10^{-5}$  M; pH 7.5;  $E_{acc} = -250$  mV;  $t_{acc} = 90$  s;  $v = 80$  mV s $^{-1}$ ; differential pulse mode; pulse height = 50 mV;  $\Delta I_p$  was recorded after addition of  $100 \mu\text{g L}^{-1}$  of  $[\text{Cr(VI)}]$ .

Fig. 3. As it can be seen,  $\Delta I_p$  increases with increasing copper concentration and reaches a maximum at  $5 \times 10^{-5}$  M of copper and then decreases as a result of precipitation of copper as copper hydroxide. Thus,  $5 \times 10^{-5}$  M of copper was chosen for further analysis. It should be mentioned that the concentration of copper was in excess of that of adenine concentration to ensure complete complex formation between copper and adenine.

**3.2.1.5. Effect of variation of adenine concentration.** The concentration of adenine and copper had considerable effect on the linear range and the sensitivity of procedure. Fig. 4 illustrates that  $\Delta I_p$  increases first with increase in the concentration of adenine up to  $8 \times 10^{-6}$  M and then decreases. Therefore, the adenine concentration value of  $8 \times 10^{-6}$  M was chosen for the analysis.

### 3.2.2. Effect of instrumental parameters

**3.2.2.1. Effect of variation of accumulation potential ( $E_{acc}$ ).** The adsorption of Cu(I)–adenine on the mercury electrode proceeds only if an external potential (less than  $-50$  mV) is applied to the cell [47]. The adsorptive stripping peak height decreased when the accumulation potential was lowered from  $-50$  mV. This is because, the formation of the complex of adenine with copper requires the production of Cu(I) at the electrode surface during the accumulation step, and under our experimental conditions Cu(I) is produced at potentials above  $-50$  mV. An accumulation potential of  $-250$  mV was therefore, chosen for obtaining high sensitivity and minimum interference effect from some ions such as chloride.

**3.2.2.2. Effect of variation of accumulation time ( $t_{acc}$ ).** The accumulation time is one of the important parameters in stripping procedures that has a pronounced effect on both sensitivity and linear range. The accumulation times were examined in the range of 0–240 s. The peak height was increased with increasing the accumulation time up to 120 s. After that, it remained unchanged up to 180 s as a result of the saturation of the electrode surface. However, the peak height decreased at longer deposition times (above 180 s), a characteristic feature of adsorptive stripping with stirred solution. This is because the molecules metastably adsorbed on the electrode surface are in dynamic interaction with orientation and others being lost to the solution [47]. On this basis, an accumulation time of 120 s was employed in the present study.

**3.2.2.3. Effect of variation of scan rate and pulse height.** Several different scan rates were examined in the range of 40–240 mV/s. The scan rate of 120 mV/s offered the best sensitivity and was used for all determinations. Another parameter that had effect on sensitivity was pulse height, the effect of which was studied in the range of 10–100 mV. A pulse amplitude of 100 mV which gave the best sensitivity was chosen as an optimum value.

## 4. Analytical applications

### 4.1. Analytical figures of merit: reproducibility, linear range and detection limit of the method

Under the optimum experimental conditions, the calibration curve was linear over the range of  $5 \mu\text{g L}^{-1}$  to  $120 \mu\text{g L}^{-1}$ . The equation for calibration graph and the correlation coefficient ( $r$ ) were  $Y_{\text{NA}} = 11.2 \times [\text{Cr(VI)}]_{\mu\text{g L}^{-1}} - 25.5$  and 0.998, respectively. The detection limit ( $Y_{\text{DL}} = \bar{X}_{\text{B}} + 3S_{\text{B}}$ , where  $Y_{\text{DL}}$  is the signal for detection limit,  $\bar{X}_{\text{B}}$  is the mean of blank signal and  $S_{\text{B}}$  is the standard deviation of blank signal, [48]) was obtained as  $2 \mu\text{g L}^{-1}$  for an accumulation time of 120 s.

The relative standard deviations (R.S.D., %) for five measurements were 1.8% and 4% for chromium(VI) concentrations of  $18 \mu\text{g L}^{-1}$  and  $100 \mu\text{g L}^{-1}$ , respectively.

### 4.2. Effect of interfering substances

The EPA method (3060A) was used to extract Cr(VI). Method 3060 [44] is an alkaline digestion procedure for extracting Cr(VI) from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments,

and similar waste materials. To quantify total Cr(VI) in a solid matrix, three criteria must be satisfied: (1) the extracting solution must solubilize all forms of Cr(VI), (2) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III), and (3) the method must not cause oxidation of native Cr(III) contained in the sample to Cr(VI). Method 3060 meets these criteria for a wide spectrum of solid matrices [44]. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The addition of  $\text{Mg}^{2+}$  in a phosphate buffer to the alkaline solution has been shown to suppress oxidation, if observed.

The effect of interfering substances on the analysis of  $1.9 \times 10^{-7} \text{ M}$  ( $10 \mu\text{g L}^{-1}$ ) Cr(VI) was studied using the proposed method (Table 1). The study of the effect of interfering substances was categorized in three parts as follows.

#### 4.2.1. Effect of interfering anions

The EPA extraction method cannot remove the effect of interfering anions but as it is shown in Table 1; most of the common anions have no interference in the determination of the Cr(VI). Some anions such as chloride, bromide and tartrate decreased the sensitivity. However, if they are added to the supporting electrolyte, their interfering effect could be eliminated (the labeled anions as “a” Table 1). The

Table 1

The effects of various species on the analysis of  $1.9 \times 10^{-7} \text{ M}$  ( $10 \mu\text{g L}^{-1}$ ) hexavalent chromium:  $[\text{Cu}] = 5 \times 10^{-5} \text{ M}$ ;  $[\text{Ade}] = 8 \times 10^{-6} \text{ M}$ ; pH 7.5;  $E_{\text{acc}} = -250 \text{ mV}$ ;  $t_{\text{acc}} = 120 \text{ s}$ ;  $v = 120 \text{ mV s}^{-1}$ ; pulse height = 100 mV

| Ion                         | Amount of ion (M)     | Recovery         | Ion          | Amount of ion (M)    | Recovery         |
|-----------------------------|-----------------------|------------------|--------------|----------------------|------------------|
| $\text{Br}^-$               | $1 \times 10^{-3}$    | 120              | CTAB         | $1 \times 10^{-5}$   | 98 <sup>c</sup>  |
| $\text{Br}^-$               | $1 \times 10^{-3}$    | 103 <sup>a</sup> | CTAB         | $5 \times 10^{-4}$   | 0 <sup>c</sup>   |
| $\text{Cl}^-$               | 0.3                   | 150              | Triton X-305 | $5 \times 10^{-9}$   | 97               |
| $\text{Cl}^-$               | 0.3                   | 98 <sup>a</sup>  | Triton X-305 | $2 \times 10^{-7}$   | 180              |
| Citrate                     | $1 \times 10^{-3}$    | 96               | Triton X-305 | $2 \times 10^{-7}$   | 105 <sup>c</sup> |
| Acetate                     | Bulk                  | 100              | Mn(II)       | $2 \times 10^{-4}$   | 102              |
| Borate                      | Bulk                  | 100              | Mn(II)       | 0.01                 | 100 <sup>d</sup> |
| $\text{SO}_4^{2-}$          | Bulk                  | 100              | Ni(II)       | $8.5 \times 10^{-5}$ | 102              |
| $\text{PO}_4^{3-}$          | Bulk                  | 100              | Ni(II)       | 0.01                 | 106 <sup>d</sup> |
| $\text{NO}_3^-$             | Bulk                  | 100              | Cr(III)      | $3 \times 10^{-5}$   | 103              |
| $\text{NO}_2^-$             | $3 \times 10^{-2}$    | 100              | Cr(III)      | 0.05                 | 104 <sup>d</sup> |
| $\text{HCO}_3^-$            | $4 \times 10^{-2}$    | 97               | Co(II)       | $3 \times 10^{-4}$   | 100              |
| $\text{CO}_3^{2-}$          | $4 \times 10^{-2}$    | 96               | Co(II)       | 0.01                 | 100 <sup>d</sup> |
| $\text{SCN}^-$              | $5.5 \times 10^{-5}$  | 102              | Cd(II)       | $5 \times 10^{-6}$   | 100              |
| $\text{SO}_3^{2-}$          | $5 \times 10^{-4}$    | 98               | Cd(II)       | 0.01                 | 105 <sup>d</sup> |
| $\text{S}_2\text{O}_3^{2-}$ | $4 \times 10^{-6}$    | 103              | Fe(III)      | $1 \times 10^{-4}$   | 105              |
| $\text{S}^{2-}$             | $1 \times 10^{-6}$    | 101              | Fe(III)      | 0.01                 | 101 <sup>d</sup> |
| $\text{S}^{2-}$             | $1 \times 10^{-5}$    | 125              | Al(III)      | $3 \times 10^{-5}$   | 101              |
| $\text{CN}^-$               | $5 \times 10^{-8}$    | 115              | Al(III)      | 0.01                 | 108 <sup>d</sup> |
| $\text{CN}^-$               | $5 \times 10^{-4}$    | 107 <sup>b</sup> | Zn(II)       | $1 \times 10^{-4}$   | 101              |
| Tartrate                    | $5 \times 10^{-4}$    | 80               | Zn(II)       | 0.01                 | 103 <sup>d</sup> |
| Tartrate                    | $5 \times 10^{-4}$    | 98 <sup>a</sup>  | Pb(II)       | $3 \times 10^{-6}$   | 100              |
| EDTA                        | $1 \times 10^{-5}$    | 93               | Pb(II)       | $5 \times 10^{-3}$   | 101 <sup>d</sup> |
| $\text{MnO}_4^-$            | $2.5 \times 10^{-4}$  | 100              | Mg(II)       | Bulk                 | 100              |
| Ce(VI)                      | $5 \times 10^{-4}$    | 100              | Ca(II)       | Bulk                 | 100              |
| $\text{H}_2\text{O}_2$      | $1.45 \times 10^{-3}$ | 100              | K(I)         | Bulk                 | 100              |
| CTAB                        | $5 \times 10^{-7}$    | 99               | Na(I)        | Bulk                 | 100              |
| CTAB                        | $2.5 \times 10^{-6}$  | 150              |              |                      |                  |

<sup>a</sup> The anions were added to the supporting electrolyte.

<sup>b</sup> The solution was purged before and after adding the copper and adenine.

<sup>c</sup> The extraction method (Section 2.3.3) was applied.

<sup>d</sup> The EPA method (Section 2.3.2) was applied.

Table 2  
Results of analysis of Cr(VI) in real samples

| Sample                 | Added <sup>a</sup> | Found <sup>a</sup> | Recovery (%) | Concentration in real samples <sup>b</sup> | R.S.D. (%) <sup>c</sup> | Relative error (%) |
|------------------------|--------------------|--------------------|--------------|--|-------------------------|--------------------|
| Crude oil sludge (new) |                    | 15.5               |              | 0.2  | 10                      | <8                 |
|                        | 40                 | 49                 | 88           |  |                         |                    |
| Crude oil sludge (old) |                    | 70                 |              | 1.7  | 13                      | <7                 |
|                        | 30                 | 118                | 118          |  |                         |                    |
| Crude oil              |                    | 20                 |              | 0.13                                       | 10                      | <9                 |
|                        | 70                 | 77                 | 86           |  |                         |                    |
| Waste water A          |                    | 100                |              | 160  | 16                      | <5                 |
|                        | 20                 | 145                | 120          |  |                         |                    |
| Waste water B          |                    | 80                 |              | 20   | 7                       | <5                 |
|                        | 50                 | 105                | 81           |  |                         |                    |
| Tap water              |                    | 4.9                |              | ND   | 2                       | <2                 |
|                        | 10                 | 9.5                | 95           |  |                         |                    |

<sup>a</sup> In  $\mu\text{g L}^{-1}$ .

<sup>b</sup> In  $\text{mg L}^{-1}$ .

<sup>c</sup> Number of trials was four measurements.

serious interferences aroused from  $\text{CN}^-$  and  $\text{S}_2\text{O}_3^{2-}$ . Twenty-fold excess of  $\text{S}_2\text{O}_3^{2-}$  did not interfere with determination of Cr(VI). The cyanide ion even at 0.25-fold decreased the recovery by 15%. But the effect of the cyanide could be removed by purging the solution with argon under a fume cupboard (the labeled anions as “b” Table 1). This purging must be performed prior to the addition of copper ion [47].

#### 4.2.2. Effect of interfering cations

The alkaline characteristic of the EPA method has caused the interference removal of cations by means of precipitating them as hydroxide or carbonate. Therefore, the effect of interfering cations was studied with extraction using EPA method (see Section 2.3.2) or without extraction. The labeled cations as “d” (in Table 1) were determined after extraction with EPA method. According to the results, most of the cations could be removed by this procedure. Cr(III) did not interfere even at bulk concentration (0.1 M Cr(III)).

#### 4.2.3. Effect of interfering oxidizing agents and surfactants

The effects of some oxidizing agents like  $\text{Ce(VI)}$ ,  $\text{MnO}_4^-$  and  $\text{H}_2\text{O}_2$  were studied under the optimum experimental conditions and good recoveries were obtained.

The serious interference in electrochemistry, especially in adsorptive stripping voltammetry, is the presence of surface active substances, i.e. surfactants. They can be adsorbed onto the electrode and decreases the available electrode surface for adsorption of the copper complex. Because of the probable presence of surfactants in the environmental samples, it was attempted to remove their interference in the determination of Cr(VI). As it is shown in Table 1, even the low concentrations of these materials had a serious effect on the signal. For example, 0.025-fold Triton X-305 had no effect on the signal but concentrations more than that decreased the signal. The removal or destruction of surface active substances

is usually accomplished using ultraviolet (UV) irradiation or ozone oxidation procedures or by the standard addition method in low concentration cases [16]. In here, we used the solvent extraction method (Section 2.3.3) to remove the effect of surfactants. As it is shown (the labeled substances as “c” Table 1), the solvent extraction step minimizes the interfering effect of surfactants to a great extent. It should be mentioned that if the concentration of surfactant was high, the extraction step must be repeated.

#### 4.3. Practical application, recovery and accuracy of the method

The proposed method was applied to the speciation of Cr(VI) in the presence of Cr(III) in tap water, crude oil, crude oil tank button sludge and waste water samples. Cr(VI) was determined in unspiked and spiked samples. For this purpose, Cr(VI) and Cr(III) were added to all samples at different concentration ratios and the proposed method was followed for determination of Cr(VI). The obtained results are given in Table 2. As can be seen from Table 2, the method could be applied successfully to the determination of trace amounts of Cr(VI) in real samples.

For testing the accuracy of the method, Cr(VI) has also been determined by ICP and/or AA after extraction with the EPA method. The general extraction with EPA method was applied on six spiked and unspiked solutions and Cr(VI) was determined by ICP and/or AA (Table 2). The accuracy of the results was satisfactory. Relative error was lower than 9% for very complex matrices and lower than 5% for matrices such as waste water.

## 5. Conclusion

In this work, a voltammetric method for Cr(VI) determination has been used. The method has been successfully

applied to the speciation of chromium in some real samples. The surfactants interference effect could be removed by an extraction method. It can be concluded that the precision and accuracy of the method were satisfactory.

The interference effects from most common cations were eliminated (e.g.  $\text{Co}^{2+}$  has been registered as interference [41] by EPA method). The more negative accumulation potential in the method decreased the interference effect from anions such as chloride that interfered in a previously reported method [32]. The method was applied to the determinations of Cr(VI) in the presence of Cr(III) (400-folds without extraction with EPA standard alkaline digestions method) compared to the previously reported methods which could only tolerate Cr(III) at concentrations 10–100-fold excess of Cr(VI).

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### References

- [1] J. Chung, R.G. Burau, R.J. Zasoski, *Water Air Soil Pollut.* 128 (2001) 407.
- [2] R.E. Cranston, J.W. Murray, *Anal. Chim. Acta* 99 (1978) 275.
- [3] J.L. Burguera, M. Burguera, C. Rondon, L. Rodriguez, P. Carrero, Y. Petit de Peña, E. Burguera, *J. Anal. At. Spectrom.* 14 (1999) 821.
- [4] A.M. Dobney, G.M. Greenway, *Analyst* 119 (1994) 293.
- [5] S.A. Katz, H.J. Salem, *Appl. Toxicol.* 13 (3) (1993) 217.
- [6] European Community Directive 80/778/EEC, L229/20, D48.
- [7] M.C.R. Alavanja, C. Brown, R. Spirtas, M. Gomez, *Appl. Occup. Environ. Hyg.* 5 (8) (1990) 510.
- [8] W. Som-Aum, S. Liawruangrath, E.H. Hansen, *Anal. Chim. Acta* 463 (2002) 99.
- [9] C.G. Brunh, J.Y. Neira, M.Y. Guzmán, M.M. Darder, J.A. Nóbrega, *Fresenius J. Anal. Chem.* 364 (1999) 273.
- [10] Y. Li, N.K. Pradhan, R. Foley, G.K.C. Low, *Talanta* 57 (2002) 1143.
- [11] R.E. Shaffer, J.O. Cross, S.L. Rose-Pehrsson, W.T. Elam, *Anal. Chim. Acta* 442 (2001) 295.
- [12] A.A. Mohamed, M.F. El-Shahat, *Anal. Sci.* 16 (2000) 151.
- [13] Method 7196: Chromium, Hexavalent (Colorimetric), Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, third ed., US EPA, Washington, DC, 1995.
- [14] E.K. Paleologos, C.D. Stalikas, S.M. Tzouwara-Karayanni, M.I. Karayannis, *Anal. Chim. Acta* 436 (2001) 49.
- [15] D. Huo, Y. Lu, H.K. Kingston, *Environ. Sci. Technol.* 32 (1998) 3418.
- [16] J. Wang, *Stripping Analysis*, VCH Publishers, Inc., 1985.
- [17] J. Golimowski, P. Valenta, H.W. Nürnberg, *Fresenius Z. Anal. Chem.* 322 (1985) 315.
- [18] K. Torrance, C. Gatford, *Talanta* 34 (1987) 939.
- [19] F. Scholz, M. Draheim, G. Henrion, *Fresenius Z. Anal. Chem.* 336 (1990) 136.
- [20] F. Scholz, B. Lange, M. Draheim, J. Pelzer, *Fresenius Z. Anal. Chem.* 338 (1990) 627.
- [21] C. Elleouet, F. Quentel, Ch. Madec, *Anal. Chim. Acta* 257 (1992) 301.
- [22] M. Boussemart, C.M.G. van den Berg, M. Ghaddaf, *Anal. Chim. Acta* 262 (1992) 103.
- [23] E.M. Souza, A.L. Wagener, P. Farias, *Croat. Chem. Acta* 70 (1997) 259.
- [24] E.P. Achterberg, C.M. van den Berg, *Deep-Sea Res.* 44 (1997) 693.
- [25] M.C. Pereira, M.L. Pereira, J.P. Sousa, *Electroanalysis* 9 (1997) 941.
- [26] O. Dominguez, S. Sanllorente, M.J. Arcos, *Electroanalysis* 11 (1999) 1273.
- [27] M. Boussemart, C.M.G. van den Berg, *Analyst* 119 (1994) 1349.
- [28] E.P. Achterberg, C.M.G. van den Berg, M. Boussemart, W. Davison, *Geochim. Cosmochim. Acta* 61 (1997) 5233.
- [29] M. Korolczuk, M. Grabarczyk, *Fresenius J. Anal. Chem.* 363 (1999) 421.
- [30] M. Korolczuk, M. Grabarczyk, *Anal. Chim. Acta* 387 (1999) 97.
- [31] M. Korolczuk, *Fresenius J. Anal. Chem.* 367 (2000) 761.
- [32] M. Korolczuk, M. Grabarczyk, *Microchem. J.* 72 (2002) 103.
- [33] J. Wang, J. Lu, K. Olsen, *Analyst* 117 (1992) 1913.
- [34] M. Paneli, A.V. Voulgaropoulos, K. Kalcher, *Mikrochim. Acta* 110 (1993) 205.
- [35] Z. Gao, K.S. Siow, *Electroanalysis* 8 (1996) 602.
- [36] M.A. Ghandour, S.A. El-Shatoury, A.M.M. Aly, S.M. Ahmed, *Anal. Lett.* 29 (1996) 1431.
- [37] D.V. Vukomanovic, G.V. van Loon, K. Nakatsu, D.E. Zoutman, *Microchem. J.* 57 (1997) 86.
- [38] I. Turyan, D. Mandler, *Anal. Chem.* 69 (1997) 894.
- [39] M. Korolczuk, M. Grabarczyk, *Talanta* 49 (1999) 703.
- [40] M. Korolczuk, M. Grabarczyk, *Microchem. J.* 62 (1999) 311.
- [41] M. Korolczuk, *Anal. Chim. Acta* 414 (2000) 165.
- [42] Y. Li, H. Xue, *Anal. Chim. Acta* 448 (2001) 121.
- [43] O. Domyngues, M.J. Arcos, *Anal. Chim. Acta* 470 (2002) 241.
- [44] USEPA, U.S. Environmental Protection Agency (<http://www.epa.gov/>).
- [45] NIOSH, The National Institute for Occupational Safety and Health (<http://www.niosh.com/>).
- [46] Occupational Safety & Health Administration <http://www.osha.gov>.
- [47] A. Safavi, N. Maleki, E. Shams, H.R. Shahbaazi, *Electroanalysis* 14 (13) (2002) 929.
- [48] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, second ed., Ellis Horwood Ltd., Chichester, England, 1992.