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# A study on the determination of chromium as chromate at a carbon paste electrode modified with surfactants

Ivan Svancara*, Petr Foret, Karel Vytras

*Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Namesti Cs. Legii 565, CZ-53210 Pardubice, Czech Republic*

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Dedicated to the memory of Professor Jaroslav Churacek.

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## Abstract

A procedure for the determination of chromium is described based on synergistic pre-concentration of the chromate anion at a carbon paste electrode modified in situ with quarternary ammonium salts such as 1-ethoxycarbonylpentadecyltrimethylammonium bromide (Septonex®), cetyltrimethylammonium bromide (CTAB) or cetylpyridinium bromide (CPB). The proper electrochemical detection utilises the reduction Cr(VI) → Cr(III) performed in the differential pulse cathodic voltammetric mode. In discussion, considerable attention has been paid to the accumulation mechanism at the carbon paste electrode in the presence of surfactants. Furthermore, after optimising the corresponding experimental conditions (0.1–0.3 M HCl + 0.1 M NaCl as the supporting electrolyte, 2.5–25 μM as the total concentration of modifier, pre-concentration at +0.7 V versus Ag/AgCl and the stripping from +0.7 to −0.4 V), the analytical performance of the method has been evaluated. The signal of interest was reproducible within ±8% and proportional to the concentration in a range of 0.5–50 μM $CrO_4^{2-}$, with a limit of detection (S/N = 3:1) of about $5 \times 10^{-8}$ M $CrO_4^{2-}$ (with accumulation for 300 s). Interference studies were focused mainly on the species capable of forming ion-pairs with the modifier; i.e., $TlCl_4^-$, $AuCl_4^-$, $PdCl_4^{2-}$, $PtCl_6^{2-}$, $VO_4^{3-}$, $MnO_4^-$ and $I^-$. Practical applicability of the method was tested on model solutions via the recovery rates (typically 90–110%) or using selected certified reference materials (tea, bush leaves, clover) and two samples of black tea when the respective results were compared to those obtained by the reference determinations with ICP-AES.

*Keywords:* Stripping voltammetry; Modified carbon paste electrode; Chromium determination

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## 1. Introduction

At present, the determination of chromium and identification of its two common oxidation states represent one of the most frequent problems of inorganic trace analysis. Whereas, the Cr(III) ions are known to act as bioessential species, chromate and polychromate anions are highly toxic and potentially carcinogenic substances [1]. Although, some chromates can occur in the nature (e.g. crocoite, $PbCrO_4$), the dominant amount of compounds with hexavalent chromium is produced by industrial activities of mankind [2].

Among instrumental techniques applicable to the determination of chromium in both forms, electroanalytical measurements offer a number of various approaches based on redox transformations Cr(III) → Cr(VI), often in combination with reactions involving suitable complexing agents. For instance, pyrocatechol violet (PCV) was reported to give rise to a reduction peak of the $Cr^{III}$-PCV complex formed after preceding cathodic reduction of the Cr(VI) species [3]. Another complexing agent of choice is being diethylpentaminopentaacetic acid (DTPA) that forms a complex readily adsorbable at the electrode surface and then reducible cathodically according to the scheme: $Cr^{III}$-DTPA → $Cr^{II}$-DTPA [4–6]. The corresponding method originally proposed as voltammetric measurement with the hanging mercury drop electrode (HMDE [4]) can be adapted for highly sensitive detection at mercury film electrodes (MFEs) operating below $1 \times 10^{-9}$ M Cr [5,6]. Efficient

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* Corresponding author. Tel.: +420 466 037 031; fax: +420 466 037 068.
*E-mail address:* Ivan.Svancara@upce.cz (I. Svancara).

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complexation of chromium has also been accomplished with the aid of ammonium pyrrolidine-dithiocarbamate [7] or, in particular, with 2,2′-bipyridine. In this case, the analyte is detected via catalytic wave of nitrates, which allows one to achieve extremely low concentrations; reportedly, down to the picomolar level of Cr [8]. Similar catalytic effect of the $NO_3^-$ ions has been exploited in a method where the Cr(VI), reduced electrolytically, is complexed with triethylenetetranitrilo-hexaacetic acid (TTHA). The complex formed exhibits again a strong affinity to be adsorbed and subsequently reduced at the electrode: $Cr^{III}$-TTHA → $Cr^{II}$-TTHA [9]. Finally, a special reagent 2-(5′-bromo-2′-pyridylazo)-5-diethyl aminophenol (5-Br-PADAP) was proposed recently [10]. The respective procedure, however, seems to be rather time-consuming as a pre-heating of the individual samples is required in order to complete kinetically driven complex formation.

Occasionally, electroanalytical methods for the determination of chromium employ also carbon paste electrodes (CPEs), into which complex-forming agents can be admixed as modifiers [11,12]. This is the case of carbon pastes modified with classical analytical reagents such as 8-hydroxyquinolinol [13] or 1,5-diphenylcarbazide [14]. Both methods demonstrating advantages of direct modification of the electrode material were capable to differentiate between Cr(VI) and Cr(III), which enabled their use for speciation analysis of selected samples. Beside this, even unmodified carbon pastes made of various liquid binders could be used for the determination of chromium as $CrO_4^{2-}$ [15] when using potentiometric titrations based on the ion-pair formation principles [16,17]. Coupling of more sensitive voltammetric detection with ion-pairing of chromate at a CPE has for the first time been reported in a study comparing the performance of bare carbon paste with that containing chitine [18]. Despite expected benefit of the modifier, the measurements did not provide sufficient selectivity since numerous other anions such as $MnO_4^-$, $VO_4^{3-}$, $[Fe(CN)_6]_4^-$ or $NO_2^-$ competed with $CrO_4^{2-}$ in the ion-exchange process.

Recently, the use of some surfactants as modifiers for selective ion-pairing at a CPE has been tested with quarternary ammonium salts of the $R'R''_3N^+Br^-$ type [19]. The whole study has demonstrated a high efficiency of pre-concentration of selected anions combining advantageously the lipophilicity of the cationic moieties of surfactants with their firm anchoring onto the hydrophobic carbon paste surface. The respective investigations had also involved preliminary assays with $CrO_4^{2-}$, suggesting a certain promise for its determination.

In this article, such an approach employing a CPE modified in situ with cationic surfactants for accumulating chromate via its ion-associates has been examined in more detail. Possibilities and limitations of its adaptation for analytical purposes are summarised in the following sections.

## 2. Experimental

### 2.1. Chemicals, reagents, stock and standard solutions

All chemicals used for the preparation of stock and standard solutions were of analytical reagent grade and purchased from Lachema (Brno, Czech Republic) or Merck unless stated otherwise. Stock solutions of the supporting electrolytes, sample or model solutions were made 1 M in concentration; the standards of metal ions were 0.01 M. Where required, the solutions were diluted to the desired concentration. All the standards with concentrations lower than 1 mM were stabilised by acidifying with 65% $HNO_3$ to yield pH ca. 2.

Ion-pairing agents were prepared as 0.001 M solutions by weighing the appropriate amount of 1-ethoxycarbonylpentadecyltrimethylammonium bromide (Septonex®, Slovakofarma a.s., Hlohovec, Slovakia), cetyltrimethylammonium bromide (CTAB) and of cetylpyridinium bromide (CPB) into 500 ml of water. Adequate volumes of these stock solutions were added directly to the samples in order to modify the working electrode in situ. In some comparative studies, a solution of non ionic surfactant polyethylene glycol P-1,1,3,3-tetramethylbutylphenyl ether (Triton X-100®; Orion) was also used.

In pH-dependence investigations, standardised buffering mixtures were used. For measurements at pH $<2$, it was a Clark–Lubs mixture containing 0.2 M KCl + 0.2 M HCl at chosen ratio; less acidic media were then adjusted by Britton–Robinson buffers.

Water which was used throughout the experimental work was obtained by passing deionised water through a laboratory-made distillation unit. All solutions to be analysed were deoxygenated by purging with argon (purity 99.99%, Linde Technoplyn, Prague).

### 2.2. Instrumentation

#### 2.2.1. Apparatus

A modular electrochemical system AUTOLAB equipped with PGSTAT-10 and ECD modules (Eco Chemie, Utrecht, Holland) was used in combination with a control by GPES software (Eco Chemie) commanded in Windows®. This assembly was connected to an external electrode stand (Laboratorni pristroje a.s., Prague, Czech Republic) incorporating the three-electrode system and cylindrical voltammetric vessel (glass workshops, University of Pardubice); all being fixed in a Teflon®-made head. Stirring was devised with a magnetic bar (length: 12 mm, diameter: 2 mm ) agitated by electromotor at 300 rpm.

#### 2.2.2. Other instrumentation, equipment and accessories

The pH was measured using a portable pH-meter (model CPH 52, Elteca, Turnov, Czech Republic) and a combined glass pH-sensor (OP-0808P, Radelkis, Budapest, Hungary). Ohmic resistance of newly made carbon paste was checked with a Voltcraft® multimeter (VC 404, Conrad Electronics, Germany).

All the solutions used for voltammetric measurements were introduced to cell using a set of automatic transfer-pipettes with adjustable volumes from 10 μl to 10 ml (Finnpipette; Labsystems, Finland).

### 2.3. Electrodes

#### 2.3.1. Carbon paste electrode

The paste was prepared by intimately homogenising a mixture of 0.50 g spectroscopic graphite powder (RW-B, Ringsdorff Werke, Germany) + 0.20 ml silicone oil (Lukoil MV 15500; Lucebni zavody Kolin, Czech Republic). The ready-made paste with ohmic resistance of about 5 Ω was then packed into a piston-driven carbon paste holder [20], representing an assembly referred below as the carbon paste electrode of the C/SO type. The electrode surface was renewed by extrusion of approximately 0.5 mm carbon paste from the holder and smoothing with a filter paper. Typically, such mechanical renewal of the carbon paste surface was made when starting a new series of measurements (e.g. prior to analysis of each sample).

#### 2.3.2. Other electrodes

In studies on accumulation mechanism, a glassy carbon electrode (GCE; Metrohm, Switzerland) was also employed as alternate working electrode. Prior to use, its surface was polished with an alumina slurry (0.5 μm) in usual way. A self-made Ag/AgCl reference electrode containing 3 M KCl as the inner electrolyte and a Pt-plate (ca. 0.5 cm$^2$) as the auxiliary electrode completed the cell throughout the experiments.

### 2.4. Preparation of model and sample solutions

Typical model solution had contained a mixture of 0.25 M HCl + 0.1 M NaCl + 2.5 × $10^{-6}$ M Septonex® (eventually CTAB or CPB, respectively) as the supporting electrolyte which was spiked with the desired amount of the $CrO_4{}^{2-}$ standard.

To verify the performance of the method, either certified reference materials (CRMs) or selected samples of black tea were analysed. For the latter, the results of electrochemical analysis were compared to those obtained by the reference determinations by ICP-AES. As CRMs, the specimens of black tea and bush leaves (GBW07603 and GBW07605; Institute of Geophysical and Geochemical Exploration, Langfang, China) or of clover (Internal Reference Material No. 9020; UKZUZ Brno, Czech Republic) were selected. Real samples then represented two different types of black tea purchased in a common shopping centre.

The solutions of three CRMs and two tea samples were prepared using the procedure described [14]. Precisely weighed amount of the sample (1–3 g) was added to ca. 50 ml pre-heated water and boiled for approximately 25 min until the volume was reduced to a half. After filtration, the solution obtained was mixed with 1 ml 1 M NaOH and 100 μl 10% $H_2O_2$.

The mixture was subsequently heated again to ensure the quantitative conversion ($Cr^{III} \rightarrow Cr^{VI}$) and to evaporate another portion of water. The resultant concentrate having approximately 10 ml in volume was transferred to a volumetric flask, cooled down and filled up with redistilled water to the mark. Finally, the same procedure was used to prepare a “blank” sample.

The proper samples were prepared by pipetting the chosen volume of the extract to a measuring vessel together with 5 ml 1 M HCl + 2 ml 1 M NaCl. After making the final volume with water, sample solutions obtained in this way were subjected to voltammetric analysis as described below.

### 2.5. Procedures and methods

#### 2.5.1. Differential pulse cathodic stripping voltammetry

After preparing the solution to be analysed (see Section 2.4) and its bubbling with inert gas for 5 min, the measurements were carried out in the differential pulse cathodic stripping voltammetric mode (DPCSV). Typical voltammetric experiment consisted of three steps: the preconcentration at +0.7 V versus Ag/AgCl for 60 s, the rest period (15 s) and a polarisation (“stripping”) from +0.7 to −0.4 V by applying a scan rate of 50 mV s$^{-1}$ and the pulse amplitude of 50 mV.

#### 2.5.2. Analysis of model and sample solutions

Both model and sample solutions were analysed by the standard addition method with two or three aliquots. When using the DPCSV procedure, the corresponding runs had usually been repeated to control the repeatability.

The individual analytical signals were evaluated as the peak areas using manual base-line setting by the PGSTAT-10 software. The results of determinations were calculated by means of a statistical method recommended for small sets of experimental data [21].

## 3. Results and discussion

### 3.1. Ion-pairing of chromate with quarternary ammonium salts

In this study, the behaviour of chromate and the respective ion-pairing agent was observed in more detail in an effort to obtain a deeper insight into the mechanism of the whole process and its effective utilisation in electroanalytical measurements.

The optimal concentration of the $R'R''_3N^+$ cation in the sample solution was investigated first. Some results are summarised in Fig. 1 showing a set of voltammograms for the

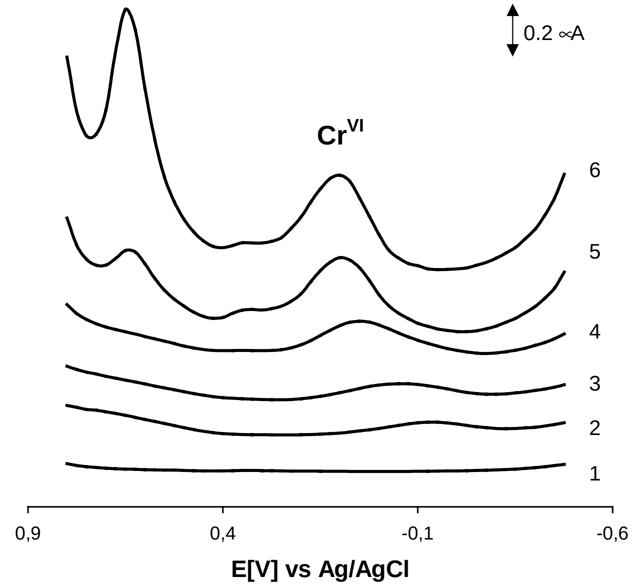

Fig. 1. Effect of different concentration of the modifier on the reduction signal of chromate and upon the base-line. (1) Blank (supporting electrolyte); (2) $+1\,\mu$M Cr(VI); (3–6) 0.25, 25, 50 and 100 $\mu$M Septonex®*. Experimental conditions: differential pulse cathodic stripping voltammetry (DPCSV); carbon paste electrode, C/SO; 0.1 M HCl + 0.1 M NaCl (pH 0.95); accumulation (= initial) potential, +0.8 V vs. Ag/AgCl; accumulation time, 60 s; final potential, −0.5 V; scan rate, 50 mV s$^{-1}$; the pulse height, 50 mV*. For specification, see Experimental (Section 2.1).

reduction of chromate in the presence of Septonex® at increasing concentrations.

Because this substance exhibited some electroactivity in more concentrated solutions (seen as additional peaks in curves 5 and 6), its content corresponding to the total concentration of approximately 25 $\mu$M (curve 4) was found to be maximum for enhancing the signal of interest without deformation of the base-line. Nevertheless, the overall effect of surfactant was still significant. Similar relations were observed with two remaining surfactants, CTAB and CPB, used also as in situ modifiers. In all cases, a mixture of HCl + NaCl was selected as the proper supporting medium [19].

A pivotal study on the behaviour of chromate and its ion-pairing as a function of pH is illustrated in Fig. 2. The entire spectrum of voltammograms can be divided into four regions differing from the total acidity of the solutions tested. At pH $\ll$0.5, the reduction response was the highest and being registered almost as the only one signal. At pH values comprised between 0.5 and 4.0, the response splitted into two peaks which shifted slightly towards the more negative potentials by decreasing acidity. Whereas, the smaller peak (with $E_{P1}$ about +0.3 V) was approximately constant, the second larger signal ($E_{P2}$ ca. 0 V) exhibited a decrease. At pH 4–7, the first signal disappeared and the second one diminished likewise with a marked shift into the negative direction. Finally, in basic and alkaline solutions (pH >7), no response was obtained within the potential range of interest.

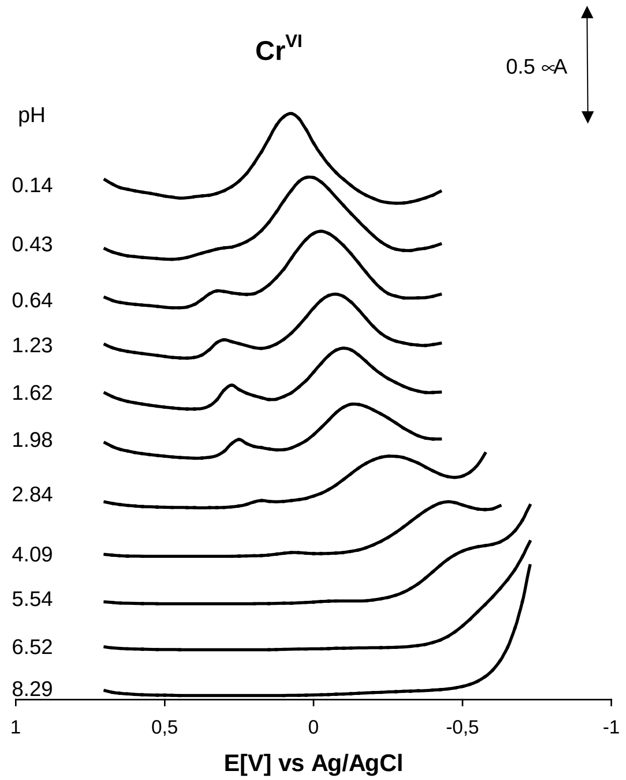

Fig. 2. Effect of pH on the response of chromate. Experimental conditions: 0.1 M NaCl + buffer (pH 0.14–8.29) + 25 $\mu$M Septonex®; $c(\mathrm{Cr^{VI}}) = 1 \times 10^{-5}$ M; accumulation time, 30 s; other conditions and parameters are given in Fig. 1.

All these observations have suggested that both main processes—i.e., (i) pre-concentration based on ion-pairing with accumulation of the ion-pairs formed onto carbon paste via adsorption or extraction [11,12,22] and (ii) the subsequent cathodic reduction—are driven by the actual chemical equilibria in the solution at the respective pH and experimental conditions. When considering the protonation of monochromate and its mutual transformation to dichromate:

$$\mathrm{CrO_4{}^{2-} + H^+ \rightleftharpoons HCrO_4{}^-} \tag{1a}$$

$$\mathrm{HCrO_4{}^- + H^+ \rightleftharpoons H_2CrO_4} \tag{1b}$$

$$\mathrm{2\,HCrO_4{}^- \rightleftharpoons Cr_2O_7{}^{2-} + H_2O} \tag{1c}$$

together with the corresponding equilibrium constants [23], one has:

$$K_a(\mathrm{HCrO_4{}^-}) = \frac{a(\mathrm{H^+}) \times a(\mathrm{CrO_4{}^{2-}})}{a(\mathrm{HCrO_4{}^-})} = 10^{-6.51} \Rightarrow 3.09 \times 10^{-7} \tag{2a}$$

$$K_a(\mathrm{H_2CrO_4}) = \frac{a(\mathrm{H^+}) \times a(\mathrm{HCrO_4{}^-})}{a(\mathrm{H_2CrO_4})} = 10^{0.20} \Rightarrow 1.58 \tag{2b}$$

$$K(\mathrm{Cr_2O_7{}^{2-}}) = \frac{a(\mathrm{Cr_2O_7{}^{2-}})}{a(\mathrm{HCrO_4{}^-})} = 10^{1.53} \Rightarrow 3.58 \times 10^1 \tag{2c}$$

Both anionic species occurring in acidic solutions according to (1a–c) may form the ion-pairs with quaternary ammonium salts [16,17]:

$$\mathrm{R'R''_3N^+ + HCrO_4^- \rightleftharpoons [R'R''_3N^+]HCrO_4^-} \quad (3a)$$

$$\mathrm{2R'R''_3N^+ + Cr_2O_7^{2-} \rightleftharpoons [R'R''_3N^+]_2Cr_2O_7^{2-}} \quad (3b)$$

The schemes (1a–c) and (3a and b) can be used to explain some relations noticeable on the voltammograms in Fig. 2. For instance, the existence of two signals in most of the media tested implies the formation of two different ion-pairs (3a and b) that are reduced at distinct potentials. Their mutual abundance in the resulting response is then dependent upon pH and the actual distribution between hydrogenchromate ("bichromate") and dichromate as seen from the comparison of the above-discussed pH intervals with the profile of the corresponding sets of voltammograms and with the values of protonation constants in 2a–c.

Such an interpretation corresponds well to the previous observations from potentiometric measurements that have revealed that the $\mathrm{HCrO_4^-}$ anion was the dominant species at pH 4–6, whereas experiments in more acidic solutions (pH <4) indicated the increasing concentration of polynuclear structures such as $\mathrm{Cr_2O_7^{2-}}$ or, eventually, $\mathrm{Cr_3O_{10}^{2-}}$ [24]. Regarding the absence of any stripping signal in basic or alkaline media, it seems that native chromate, $\mathrm{CrO_4^{2-}}$, is not capable of effective ion-pairing with the $\mathrm{R'R''_3N^+Br^-}$ counterpart. This is also in accordance with the previous results (e.g. [16]), although some reports admit possible ion-exchanging interactions at very high concentrations of chromate [24].

In light of some previous investigations on surfactants as specific modifiers of carbon pastes [25,26], there is another possible hypothesis of how to define the accumulation process in the presence of surfactants. It seems that the overall mechanism of pre-concentration at the CPE can be influenced by mutual interactions between a surfactant and the carbon paste itself. As already reported in pioneering studies by Adams and his research team [27], highly lipophilic chains of some surfactants are capable of repelling hydrophobic molecules of the binder from carbon particles, thus exposing their active surface in more extent. This "erosion" effect is comparable to that known for electrolytic activations [11,12] and hence, one may expect similar consequences for measurements with surfactant-modified CPEs, especially when considering the signal-to-noise characteristics and electrode kinetics [11,28].

In this work, the effect of surfactants on the carbon paste substrate was studied under "open circuit" conditions when the electrode had been left immersed for ca. 5 min in a stirred solution containing either cationic or non ionic surfactant (approximately 50 μM). Moreover, some tests were carried out in parallel with the GCE as an electrode resistant against the "erosion" effect [28]. In this case, experiments were done in open circuit in combination with measurements in the model sample solution spiked with 25 μM Septonex®.

Regarding CPEs, the subsequent scanning of eroded carbon paste surface in a surfactant-free medium revealed somewhat higher background currents in positive potential region than those registered with untreated CPE. Assays of chromate with surfactant of non ionic character such as Triton X-100 have shown that these substances may also participate in the ion-pairing process. Apart from the fact that the resulting responses were markedly lower than the signals at CPE modified with cationic surfactants, this implied that ion-associates with Triton can be formed thanks to protonation of polyoxyethylene groups in highly acidic solutions [29]:

$$\mathrm{[-(CH_2{-}O{-}CH_2)-]_{\mathit{n}} + \mathit{n}H^+ \rightleftharpoons \mathit{n}[-(CH_2{-}OH{-}CH_2)-]^+} \quad (4)$$

Thus, originally non ionic molecules can be transformed into cationic species capable of coupling with suitable counter-ions, which is the case of chromates—under experimental conditions used throughout the measurements described herein. Concerning simultaneous tests with the alternate working electrode, they have revealed that even hydrophilic surface of polished glassy carbon may pre-concentate chromate if the sample solution contained surfactants. The resulting reduction signal of $\mathrm{Cr^{VI}} \rightarrow \mathrm{Cr^{III}}$ was, however, less-developed than at the CPEs; only a small flat response was obtained, indicating apparently the direct reduction of the single $\mathrm{HCrO_4^-}$ anion at the electrode during cathodic scanning.

It can be stated that the above-summarised results of investigations on the accumulation process of chromate at surfactant-modified CPEs have allowed one to establish a

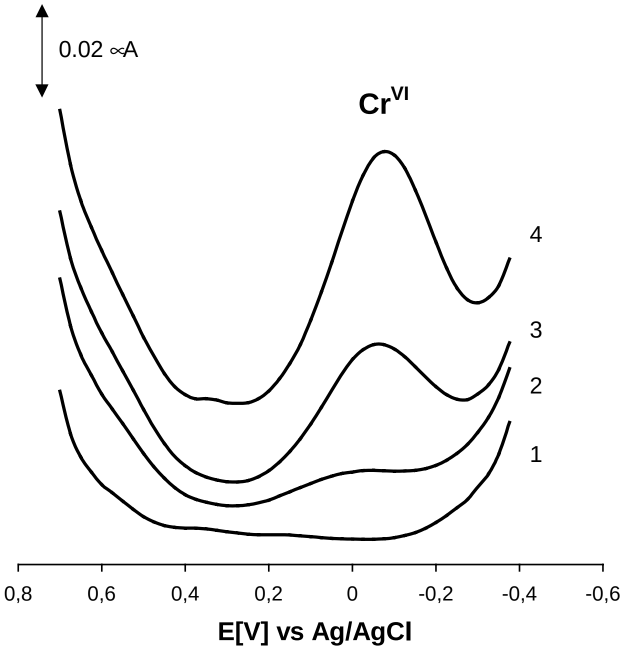

Fig. 3. Calibration stripping voltammograms of chromate at the micromolar concentration level. (1) Blank; (2–4) 1, 5, 10 μM Cr(VI). Experimental conditions: 0.3 M HCl + 0.1 M NaCl + 25 μM Septonex® (pH 0.45). For other conditions and parameters, see Fig. 1.

synergistic mechanism involving ion-pair formation as the dominant step. A high affinity of “surfactant-chromate” ion-associates to be accumulated onto the electrode surface seems to explain the results at the GCE. Finally, studies with different surfactants revealed that a phenomenon of “erosion” at the carbon paste surface has to be taken into account as well because it influences the signal-to-noise characteristics near the potential range of interest. Last but not least, some insight into the definition of a rather complex accumulation process could also be made during optimisation measurements summarised below.

### 3.2. *Optimisation of selected experimental parameters*

The composition of the supporting electrolyte and the way of modifying the electrode by applying a surfactant as modifier in situ were more or less adopted [30] based on the original procedures developed for the determination of iodide [19,31–33]. Besides, the results of studies discussed above were taken into account as well. Thus, in most experiments, a mixture of 0.3 M HCl + 0.1 M NaCl with $2.5 \times 10^{-5}$ M Septonex® (or CTAB, CPB) was used as the supporting medium of choice, providing the most satisfactory signal-to-noise characteristics. Among experimental conditions that were examined newly in the determination of Cr(VI), of particular interest were the pre-concentration potential and time as well as the scan rate.

Regarding the first parameter, comparative measurements within an interval from +0.3 to +1.0 V versus Ag/AgCl revealed a nearly proportional enhancement of the reduction response by raising the potential towards more positive values. However, because anodic deposition at potentials beyond +0.7 V gave rise to undesirably high background, this value was selected as optimum.

A study on the effect of pre-concentration time resulted in a parabolic plot exhibiting maximum at approximately 300 s, longer deposition periods had already led to a decrease of the signal of interest; probably, due to some saturation effects at the carbon paste electrode surface [12,19,34].

Similar dependence was obtained when applying various scan rates. Successive scanning at 2, 5, 10, 20, 50, 100 and 200 mV s$^{-1}$ resulted in a proportional increase of the peak up to 50 mV s$^{-1}$, higher values caused again a decrease.

### 3.3. *Analytical performance*

#### 3.3.1. *Calibration measurements*

The proportionality of the reduction signal with concentration was studied in a range from $5 \times 10^{-7}$ to $5 \times 10^{-5}$ M Cr(VI) when testing all three surfactants as the ion-pairing agents. The resulting calibration plots were linear [30] with correlation coefficients, $R^2$, varying from 0.9914 (for Septonex®) to 0.9974 and 0.9989 (for CTAB and CPB, respectively). A typical set of voltammograms is shown in Fig. 3.

#### 3.3.2. *Limit of detection (LOD)*

The detection capabilities of the method were examined for a pre-concentration period of 300 s investigating all the surfactants. By using the S/N = 3:1 criterion, the LODs for Cr(VI) were estimated as follows: $8 \times 10^{-8}$ M for Septonex®, $4 \times 10^{-8}$ M for CTAB and $1 \times 10^{-8}$ M for CPB.

#### 3.3.3. *Repeatability*

As ascertained by experiments with 10 replicates in model solutions containing the respective surfactant and additions of 5 μM Cr(VI), the signal of interest at the same electrode surface could be repeated with a relative standard deviation

Table 1
Interferences from various species on the DPCSV response of chromate [$I_P(Cr^{VI}) = 100\%$, $E_P(Cr^{VI}) = -0.15$ V vs. Ag/AgCl; concentration ratio, M(N):Cr(VI) = 2:1]

| Ion (species) | Present in form (added as) | Modifier[a] (surfactant) applied in situ | | | | | | Note(s) |
|---|---|---|---|---|---|---|---|---|
| | | Change of original response for $Cr^{VI}$ (%) | | | Peak potential of interfering signal (V) | | | |
| | | Septonex® | | CTAB | | CPB | | |
| | | $\Delta I_P$(Cr) | $E_P$(M) | $\Delta I_P$(Cr) | $E_P$(M) | $\Delta I_P$(Cr) | $E_P$(M) | |
| Fe(III) | ($Fe^{3+}$) | 0 | – | +3 | – | −5 | – | 1 |
| Au(III) | $AuCl_4^-$ | +45 | −0.08 | +50 | −0.15 | +45 | −0.13 | 2 |
| Tl(III) | $TlCl_4^-$ | +140 | −0.30 | +180 | −0.40 | +30 | −0.35 | 3 |
| Pd(II) | $PdCl_4^{2-}$ | −55 | +0.35 | −30 | +0.25 | −70 | +0.28 | 4 |
| Pt(IV) | $PtCl_6^{2-}$ | +45 | +0.02 | +10 | −0.05 | +50 | −0.01 | 5 |
| V(V) | ($VO_4^{3-}$) | +15 | −0.12 | +10 | −0.23 | +20 | −0.16 | 6 |
| Mn(VII) | $MnO_4^-$ | +5 | – | +70 | −0.02 | 0 | – | 1,7 |
| I(−I) | $I^-$ | +380 | +0.05 | +550 | −0.02 | +1200 | +0.01 | 8 |

(1) No or negligible interference observed; (2) small sharp peak of Au superimposed upon the response for Cr; (3) large and plateau-like peak of Tl, response for Cr superimposed upon and deformed; (4) sharp peak of Pd fused with another small signal at ca. +0.2 V, response for Cr deformed and partially suppressed; (5) both signals for Pt and Cr overlapped; (6) large and broad peak revealing a fusion of two very proximate signals, another smaller response at ca. −0.2 V; (7) when using CTAB, flat signal for Mn at ca. 0 V; (8) very large and broad signal, another small peak at ca. +0.3 V, response for Cr completely overlapped. Experimental conditions: model solution, 0.1 M HCl + 0.1 M NaCl + 25 μM Septonex® (or CTAB, CPB), pH 0.95; $c(Cr^{VI}) = 5 \times 10^{-6}$ mol l$^{-1}$; $c(M^N) = 1 \times 10^{-5}$ mol l$^{-1}$. Other conditions and parameters are given in Fig. 1.

[a] For specifications, see Section 2.1.

Table 2
Analysis of model solutions, certified reference materials and real samples

| Model solution, c(Cr$^{VI}$) | Modifier[a] (surfactant) applied in situ | | | | | |
|---|---|---|---|---|---|---|
| | Septonex® | | CTAB | | CPB | |
| | Found (μM) | Recovery rate (%) | Found (μM) | Recovery rate (%) | Found (μM) | Recovery rate (%) |
| 0.5 μM | 0.55 | 110 | 0.38 | 75 | 0.41 | 82 |
| 20 μM | 20.6 | 103 | 19.4 | 97 | 19.6 | 98 |
| Sample | Analysis by DPCSV[b] at the C/SO modified in situ with CTAB, found[c] [μg g$^{-1}$ Cr$^{VI}$] | Declared content, [μg g$^{-1}$ Cr$^{VI}$] | Reference determination[d] by ICP-AES, [μg g$^{-1}$ Cr$^{VI}$] | Note | | |
| Tea | 1.2 ± 0.2 | 0.80 | – | 1 | | |
| Bush leaves | 1.3 ± 0.1 | 2.60 | – | 1 | | |
| Clover | 1.3 ± 0.2 | 0.84 | – | 2 | | |
| Black tea, no. 1 | 1.0 ± 0.3 | – | 0.87 | 3 | | |
| Black tea, no. 2 | 2.4 ± 0.1 | – | 2.12 | 4 | | |

Survey of results.

[a] For other specification, see Section 2.4.

[b] Each voltammetric analysis was performed in three replicates ($n = 3$) when using three aliquots of the same sample.

[c] The results given as intervals "$x \pm \mu_0 R$" (for $\alpha = 0.05$) where, "$x$" is the arithmetic mean, "$\mu_0$" is Dean-Dixon coefficient and "$R$" is the spread between the minimal and maximal values, "$\mu_0 R$" quotient representing the standard deviation [21].

[d] Reference determination performed as single analyses, $n = 1$; (1) CRMs "GWB07603" and "GWB07605"; (2) CRM "19020"; (3) tea of Ceylon type (4) of African type.

from ±8 to ±14%. Such diversity may appear to be relatively significant; nevertheless, these values are being typical for complicated mechanisms involving accumulation of the analyte via ion-pairing and its subsequent re-release during the electrochemical detection [11,12,34].

### 3.3.4. *Interferences*

Table 1 surveys the results and observations obtained by studying selected ions as species capable of forming ion-pairs with quarternary ammonium salts [16,17]. As expected, especially iodide caused disastrous changes in the reduction response of Cr and, in the presence of this anion, the determination of chromate was impossible. In this case, unfavourable effect of iodide can be explained by the following redox reaction:

$$2\,\mathrm{HCrO_4}^- + 6\,\mathrm{I}^- + 14\,\mathrm{H}^+ \rightleftharpoons 2\,\mathrm{Cr}^{3+} + 3\,\mathrm{I_2} + 8\,\mathrm{H_2O} \quad (5a)$$

or

$$\mathrm{Cr_2O_7}^{2-} + 6\,\mathrm{I}^- + 14\,\mathrm{H}^+ \rightleftharpoons 2\,\mathrm{Cr}^{3+} + 3\,\mathrm{I_2} + 7\,\mathrm{H_2O} \quad (5b)$$

Elemental iodine released in reactions (4a and b) is readily extractable onto the carbon paste bulk and its subsequent electrode reduction gives rise to a large cathodic signal [31–33].

According to the data in Table 1, both Au(III) and Tl(III) have to be classified as serious interfering species. On the contrary, frequently occurring Fe(III) ions exhibited no effect on the signal of interest. Regarding the remaining ions, interference studies have revealed interesting behaviour of some platinum metals and of vanadium that could be exploited for their determination [30].

### 3.3.5. *Determination of chromate in model solutions and real samples*

The results of DPCSV analyses are presented in Table 2. At first, accuracy of the method was checked via recovery rate determinations in two types of model solutions containing the respective surfactant and different concentrations of the analyte. The individual results are summarised in the upper boxes of the table. When balancing synergistic accumulation mechanism of the method together with typical repeatability for such measurements (of about ±10%; see above and in [11,12]), the recovery rates achieved could be considered as satisfactory for both micromolar and sub-micromolar concentrations of chromate.

Real samples were either certified reference materials or black tea samples prepared for analysis as the aqueous concentrates when using a procedure proposed for electroanalytical measurements [14]. Fig. 4 illustrates the responses for sample solutions of CRM (specimen of tea) before and after adding the $\mathrm{CrO_4}^{2-}$ standard together with the base-line of "blank" sample. Typically, broad signals indicate again a reduction of species entrapped strongly at the electrode [12,19,31]. All the results of analyses are also given in Table 2, together with the total contents of chromium found by reference ICP-AES determinations or being declared for CRMs.

Comparison of the individual data show that the concentrations of Cr(VI) found by DPCSV with CTAB-modified C/SO are somewhat higher (except for analysis of CRM "bush leaves"); apparently, because of interference from some matrix constituent. In the case of CRMs, it could due to the presence of manganese whose content in all three speci-

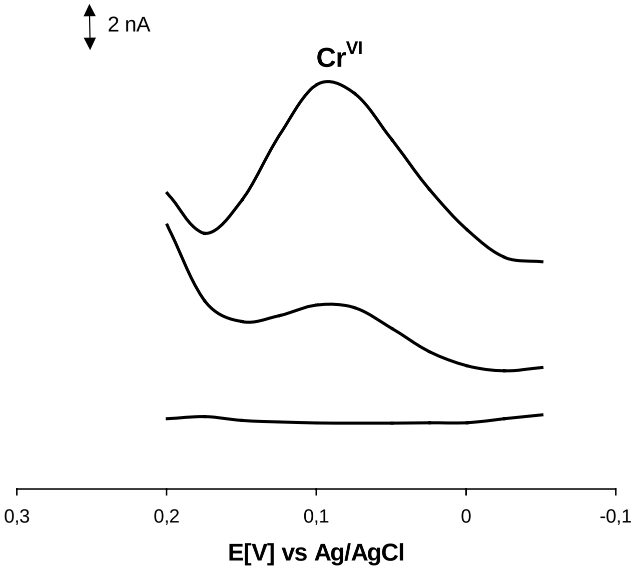

Fig. 4. Analysis of blank sample and of certified reference material (selected voltammograms). (1) Blank sample solution; (2) sample solution of CRM (tea specimen); (3) standard addition of 2 μM Cr(VI). Experimental conditions: (1) 0.3 M HCl + 0.1 M NaCl + 2.5 μM CTAB (pH 0.37); (2–3) 0.23 M HCl + 0.1 M NaCl + 2.5 μM CTAB (pH 0.41). For other conditions and parameters, see Fig. 1.

mens was declared to be minimally 20× higher than that of chromium itself. Had the sample preparation incorporated the oxidation with $H_2O_2$ (see Section 2), the resultant solutions were to contain permanganate, $MnO_4{}^-$, representing a concurrent anion to $CrO_4{}^{2-}$ in ion-pairing with CTAB [16]. By the way, interaction of these ions can also be noticed in Table 1.

All the above-discussed findings have already initiated new investigations on how to improve selectivity of the method. One possible way could be a revision of the individual operations for sample preparation, including an incorporation of an additional step to isolate interfering compounds. Or, particular attention can be focused on seeking other ion-pairing agents [19]. However, probably the most effective approach would be the transformation of the entire voltammetric method into a procedure utilising the stripping potentiometric detection [35–37]. As demonstrated recently on the determinations of $TlCl_4{}^-$ [38], $AuCl_4{}^-$ [39] or $I^-$ [40], such a conversion can often be successful and the innovated procedures adapted for measurements by constant current stripping analysis (CCSA) are superior to those originally developed in cathodic stripping voltammetric mode.

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## References

[1] http://www.seilnacht.tuttlingen.com/Lexicon/24Chrom.htm (20.10.2003).
[2] Z. Kafka, J. Puncocharova, Chem. Listy 96 (2002) 616.
[3] O. Dominguez, M.J. Arcos, Electroanalysis 12 (2000) 449.
[4] K. Torrance, C. Gatford, Talanta 34 (1987) 939.
[5] C. Hua, K.M. Sagar, K. McLaughlin, M. Jorge, M.P. Meaney, M.R. Smyth, Analyst 116 (1991) 117.
[6] S. Morais, S.G. Carvalho, J.P. Sousa, J. Trace Elem. Med. Biol. 12 (1998) 101.
[7] O. Dominguez, M.A. Alonso, M.J. Arcos, Electroanalysis 14 (2002) 1083.
[8] Z. Gao, K.S. Siow, Electroanalysis 8 (1996) 602.
[9] M. Paneli, A.V. Voulgaropoulos, K. Kalcher, Mikrochim. Acta 110 (1993) 205.
[10] W.-R. Jin, X.-L. Jia, J.-M. Lu, Electroanalysis 7 (1995) 962.
[11] K. Kalcher, J.-M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, Electroanalysis 7 (1995) 5.
[12] I. Svancara, K. Vytras, J. Zima, J. Barek, Crit. Rev. Anal. Chem. 31 (2001) 311.
[13] N.A. Ulakhovich, L.G. Shaidarova, E.P. Medyantseva, M.A. El Gakhri, Ind. Labor. 62 (1996) 542.
[14] A.R. Paniagua, M.D. Vazquez, M.L. Tascon, P. Sánchez Batanero, Electroanalysis 5 (1993) 155.
[15] X. Hu, Z. Leng, Anal. Proc. 32 (1995) 521.
[16] W. Selig, Microchim. Acta II (1979) 373.
[17] K. Vytras, Ion-Selective Electrode Rev. 7 (1985) 77.
[18] Z.-P. Bai, T. Nakamura, K. Izutsu, Anal. Sci. 6 (1990) 443.
[19] I. Svancara, I. Cermakova, K. Vytras, W. Goessler, K. Kalcher, Sci. Pap. Pardubice Univ., Ser. A 5 (1999) 95.
[20] I. Svancara, K. Vytras, R. Metelka, Czech Pat. Appl. (2002) PV 3939.
[21] R.B. Dean, W.J. Dixon, Anal. Chem. 23 (1951) 636.
[22] I. Svancara, K. Vytras, Anal. Chim. Acta 273 (1993) 195.
[23] S. Kotrly, L. Sucha, Handbook of Chemical Equilibria in Analytical Chemistry, Ellis Horwood, Chichester, UK, 1985, p. 91.
[24] T. Iimori, M. Sugawara, T. Kambara, Denki Kagaku 47 (1979) 549.
[25] K. Digua, J.-M. Kauffmann, J.-L. Delplancke, Electroanalysis 6 (1994) 451.
[26] C. Petit, A.G. Cortes, J.-M. Kauffmann, Bioelectrochem. Bioenerg. 41 (1996) 101.
[27] L.S. Marcoux, K.G. Prater, B.G. Prater, R.N. Adams, Anal. Chem. 37 (1965) 1446.
[28] M.E. Rice, Z. Galus, R.N. Adams, J. Electroanal. Chem. 143 (1983) 89.
[29] D.O. Hummel, Handbook of Surfactant Analysis: Chemical, Physico-Chemical and Physical Methods, Wiley, Chichester, UK, 1999, pp. 6–7.
[30] P. Foret, MSc. Thesis, University of Pardubice, Pardubice, 2003.
[31] J. Konvalina, I. Svancara, K. Vytras, K. Kalcher, Sci. Pap. Univ. Pardubice, Ser. A 3 (1997) 153.
[32] I. Svancara, J. Konvalina, K. Schachl, K. Kalcher, K. Vytras, Electroanalysis 10 (1998) 435.

[33] I. Svancara, K. Vytras, Sci. Pap. Univ. Pardubice, Ser. A 7 (2001) 5.
[34] I. Svancara, K. Schachl, Chem. Listy 93 (1999) 490.
[35] D. Jagner, Analyst 107 (1982) 593.
[36] P. Ostapczuk, Anal. Chim. Acta 273 (1993) 35.
[37] J.M. Estela, C. Tomas, A. Cladera, V. Cerda, Crit. Rev. Anal. Chem. 25 (1995) 91.
[38] J. Konvalina, K. Vytras, in: K. Vytras, J. Kellner, J. Fischer (Eds.), Monitoring of Pollutants in Environment, vol. II, University of Pardubice, 2001, pp. 99–104 (in Czech).
[39] J. Konvalina, K. Vytras, Chem. Listy 95 (2001) 505.
[40] I. Svancara, B. Ogorevc, S.B. Hocevar, K. Vytras, Anal. Sci. 18 (2002) 301.