Simultaneous extraction and catalytic adsorptive stripping voltammetric measurement of Cr(VI) in solid samples

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Abstract

A fast, simple, sensitive and economical method for Cr(VI) extraction and determination in solid samples was developed and evaluated. The presented protocol for Cr(VI) determination in solid samples allows for simultaneous extraction and determination of Cr(VI) in one step. The procedure is based on a quantitative extraction method in which the complexing properties of diethylenetriaminepentaacetic acid (DTPA) were exploited to extract total Cr(VI) (soluble and insoluble forms) from the solid sample. A catalytic adsorptive stripping voltammetric technique is employed for direct determination of Cr(VI) in the extract. The effects of analytical parameters such as temperature, pH, composition and concentration of the supporting electrolyte (which simultaneously plays the role of extractant), extraction and accumulation time were investigated. The accuracy of the proposed procedure was tested by analyzing certified reference materials CRM 013 Paint Chips and CRM 019 Ash. The results obtained were compared with the results obtained using two other reference extraction procedures. The effects of potentially interfering ions which generally accompany Cr(VI) in natural samples on the Cr(VI) determination, with special notice to Cr(III) interference, are reported.
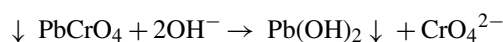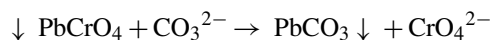© 2008 Elsevier B.V. All rights reserved.

Keywords: Extraction; Speciation; Chromium; Voltammetric measurements

1. Introduction

Hexavalent chromium is one of the technogenic pollutants of the environment and occurs mainly as a result of human activities through production of waste water in metal smelting, electroplating, tanning, metallurgy and dyestuff industries [1,2]. The toxicity of chromium to living organisms is well established and considerable interest exists in the determination of this metal in environmental samples at trace levels. Two stable chromium species are known in the environment: Cr(III) and Cr(VI), and their toxicity is a function of the oxidation state and concentration of species. Cr(III) appears to be essential for mammals, whereas Cr(VI) has toxic and carcinogenic effects [3,4]. The toxic hexavalent form of chromium is present as an air-, water-, and solid-pollutant in the environment. Determination of Cr(VI), especially in solid samples, is regarded as a one of the most challenging speciation tasks because quantitative extraction of soluble and insoluble Cr(VI) into a solution is necessary. The extraction is a time-consuming and critical step, because the change of individual forms of chromium, e.g. the oxidation of Cr(III), reduction of Cr(VI) or incomplete extraction of Cr(VI) are often reported [5,6].

Most commonly used extraction mixtures contain sodium carbonate salts and/or sodium hydroxide. In these methods the metal ions that form an insoluble chromate like Pb(II) are precipitated as carbonate or hydroxide and Cr(VI) as a soluble salt goes into the solution according to the following reactions:

$$\downarrow PbCrO_4 + CO_3{}^{2-} \rightarrow PbCO_3 \downarrow + CrO_4{}^{2-}$$

$$\downarrow PbCrO_4 + 2OH^- \rightarrow Pb(OH)_2 \downarrow + CrO_4{}^{2-}$$

The most common of such extraction procedures of Cr(VI) uses a solution of $0.28 \, mol \, L^{-1}$ $Na_2CO_3 + 0.5 \, mol \, L^{-1}$ NaOH (pH about 12) [6–8]. In this case the extraction is quantitative both for the soluble and insoluble forms of Cr(VI), but as shown in [5,8,9] a partial oxidation of Cr(III) is observed. Quantitative recovery of Cr(VI) was also reported using as the extractant a solution containing 10% $Na_2CO_3 + 2\%$ $NaHCO_3$ [10] followed by an addition of a magnesium sulphate in a phosphate buffer. The addition of Mg(II) to the alkaline

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extraction solution prevented risks of Cr(III) oxidation, which may lead to overestimation of Cr(VI), particularly in samples with high Cr(III)/Cr(VI) ratios [6]. Another procedure exploits as an extractant $0.1\,mol\,L^{-1}$ NaOH with sonication but according to [7] the recovery of Cr(VI) using the procedure is lower as compared to the extraction with $0.28\,mol\,L^{-1}$ $Na_2CO_3 + 0.5\,mol\,L^{-1}$ NaOH. The procedure which exploits an ammonium sulphate/ammonium hydroxide buffer as an extraction mixture [11–13] was also used for Cr(VI) extraction, however, in more recent paper it was reported that insoluble Cr(VI) is not extracted using this buffer [14]. To quantify and define only operationally soluble and exchangeable forms of Cr(VI), phosphate buffer extraction is often recommended [7]. So the procedures exploiting an ammonium or phosphate buffer as an extraction mixture to measure total Cr(VI) in solid samples are not suitable.

The second group of procedures for Cr(VI) extraction is based on complexing reactions, for example:

$$\downarrow PbCrO_4 + H_2DTPA^{3-} \rightarrow PbDTPA^{3-} + CrO_4{}^{2-} + 2H^+$$
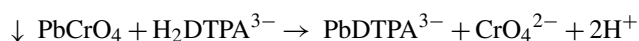
In these procedures the metal ions that form an insoluble chromate like Pb(II) are complexed with a chelating agent, e.g. ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) with the formation of a soluble complex, e.g. $PbDTPA^{3-}$. Simultaneously Cr(VI) as a soluble salt (sodium or potassium chromate) goes into the solution. This mechanism of transferring Cr(VI) from the solid samples to the solution provides the quantitative extraction of all Cr(VI) species, both soluble and insoluble forms [15,16]. The important advantage of this mechanism is the fact that Pb(II) is in the form of a soluble complex. On the contrary, when extraction is carried out using alkaline carbonate solutions, Pb(II) is precipitated in the form of $Pb(OH)_2$ and during the neutralisation of the extract Cr(VI) can form insoluble $PbCrO_4$ and the results of Cr(VI) determination are too low [17]. It must be noted that the presence of a complexing agent in the extraction mixture additionally prevents the oxidation of Cr(III) to Cr(VI) as was described in the literature [16,18]. Unfortunately, in the course of Cr(VI) extraction with the exploitation of complexing agents Cr(III) also partially goes into the solution, so to determine Cr(VI) in extract a species selective method must be exploited.

The analytical techniques available for the direct determining Cr(VI) in the presence of Cr(III) are: spectrophotometric (the most common is based on the reaction of diphenylcarbazide with Cr(VI) at pH of 1.0 ± 0.3) [19–22] and electroanalytical methods [22–27]. Stripping voltammetry is the commonest electroanalytical method used as it is a low cost technique and offers high sensitivity. The remarkable sensitivity obtainable with stripping analysis is attributed to the deposition step in which the target analyte is preconcentrated onto the working electrode [28].

Until now, many procedures have been developed to determine Cr(VI) in solid samples, but all of them consist of two or more steps. This paper presents a new simple protocol for Cr(VI) determination in solid samples which allows for simultaneous extraction and determination of Cr(VI) in a one step. For an effective extraction of Cr(VI) the addition of a chelating agent (DTPA) to the extraction solution was used. For direct determi-

nation of Cr(VI) a catalytic adsorptive stripping voltammetric technique based on the accumulation of the reduced form of Cr(VI) as a $Cr(III)–H_2DTPA$ complex and its reduction in the presence of nitrate was employed [29,30]. Choosing the optimal conditions of the extraction and voltammetric measurement allows for simultaneous carrying out of both processes in a single voltammetric cell and the extractant simultaneously plays the role of supporting electrolyte for voltammetric measurements. Thanks to that the need for the additional equipment and reagents is eliminated, which leads to significant minimization of the procedure time and cost.

2. Experimental

2.1. Reagents

CH_3COOH, KNO_3, Suprapure NaOH and morpholinoethanesulfonic acid (MES) were obtained from Merck (Darmstadt, Germany). KNO_3 was additionally purified by recrystallisation. DTPA was obtained from Sigma (St. Louis, USA). Stock standard solutions of Cr(VI) as K_2CrO_4 and Cr(III) as $CrCl_3$ with concentrations of $1\,g\,L^{-1}$ and insoluble chromate salt $PbCrO_4$ were obtained from Fluka (Buchs, Germany). SiO_2 (naturally occurring microcrystalline silica) was obtained from Sigma–Aldrich (St. Louis, USA). Certified reference materials CRM 013 Paint Chips and CRM 019 Ash were obtained from Resource Technology Corporation, USA. All solutions were made using triply distilled water.

2.1.1. Buffers and complexing agent preparation

Acetate buffer contained $0.5\,mol\,L^{-1}$ of acetic acid, and was adjusted to pH 6.2 with sodium hydroxide.

MES buffer contained $0.5\,mol\,L^{-1}$ of 2-(*N*-morpholino) ethanesulfonic acid, and was adjusted to pH 6.2 with sodium hydroxide.

DTPA solution contained $0.2\,mol\,L^{-1}$ of DTPA dissolved at pH > 7 in the presence of sodium hydroxide, and was adjusted to pH 6.2 with acetic acid.

2.1.2. Solid samples preparation

The mixtures of $PbCrO_4$ containing known concentrations of Cr(VI) were prepared by a serial dilution of $PbCrO_4$ with SiO_2, as described previously [16]. The dilutions were made by weighing appropriate amounts of a more concentrated mixture of $PbCrO_4$ and SiO_2 and then a homogenization of the mixture for 1 h in a ball mill. The mixtures of $PbCrO_4$ and Cr_2O_3, $PbCrO_4$ and $CrCl_3$ were prepared in the same way.

Visual observation shows that certified reference materials CRM 013 and CRM 019 are not homogeneous, so before the extraction they were homogenised. To avoid the formation of conglomerates in the course of homogenisation of the samples they were mixed with SiO_2. In the case of CRM 019 one part of SiO_2 was mixed and homogenised with one part of the sample in a ball mill for 1 h. In the case of CRM 013 containing a higher concentration of Cr(VI) the sample was prepared by serial dilution with SiO_2. Finally, CRM 013 was diluted with SiO_2 by a factor of 600.

2.2. Instruments

A PGSTAT 10 potentiostat (Ecochemie, Utrecht, Netherlands) and a hanging mercury drop electrode (HMDE) (MTM, Krakow, Poland) were used in this study. All experiments were performed employing a three-electrode water jacketed voltammetric cell of volume 15 mL consisting of an Hg working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode. The Hg drop area was $1.7\,mm^2$. The temperature of the cell did not differ more than $\pm0.5\,°C$ from the chosen one and was controlled using a thermostat (PolyScience, Niles, USA).

2.3. Preparation of the mercury film electrode

The ex situ mercury film electrode (MFE) was prepared by the deposition of mercury at $-0.8\,V$ for 30 s and then at $-1.1\,V$ for 90 s from a $0.01\,mol\,L^{-1}\,HNO_3 + 2 \times 10^{-4}\,mol\,L^{-1}\,Hg(NO_3)_2$ solution.

The in situ MFE was prepared by 30 s deposition at $-0.8\,V$ and next 90 s deposition at $-1.0\,V$ from a standard solution (described below) $+ 2 \times 10^{-4}\,mol\,L^{-1}\,Hg(NO_3)_2$. At the same time the accumulation by the adsorption of $Cr(III)$–H_2DTPA active complex also occurs.

2.4. General procedure/standard conditions

The measurements were performed in a thermostatic voltammetric cell. When the temperature of the electrochemical cell reached the required value the acetate buffer, MES buffer, KNO_3 and DTPA were added. The final volume of the solution was equal to 15 mL and the concentrations of the reagents were equal to $0.04\,mol\,L^{-1}$ acetate buffer; $0.02\,mol\,L^{-1}$ MES buffer; $0.5\,mol\,L^{-1}\,KNO_3$; $0.01\,mol\,L^{-1}$ DTPA, the final pH was 6.2 ± 0.1. Then the weighed solid sample (or 10 mg of $0.5\,mg\,kg^{-1}\,Cr(VI)$ as $PbCrO_4$ in a SiO_2 used for standardization of the procedure conditions) was added into the cell and the solution was deaerated with nitrogen for 5 min. Within this time Pb(II) from insoluble $PbCrO_4$ is complexed with DTPA, and Cr(VI) as a sodium or potassium chromate goes into the solution. The nitrogen atmosphere over the analyzed solution was maintained until the measurements on the studied solution were finished. Before each measurement a new drop was formed using HMDE and an accumulation was carried out for 30 s at $-1.0\,V$. In the course of deaeration and accumulation steps the solutions were stirred using a magnetic stirring bar. After a rest period of 5 s a differential pulse voltammogram was recorded, while the potential was scanned from -1.0 to $-1.375\,V$ at a scan rate of $25\,mV\,s^{-1}$. The amplitude was $-50\,mV$. Next a known amount of a standard solution of K_2CrO_4 was added to the sample solution and the measurement was repeated. On the basis of the obtained voltammograms the recovery of Cr(VI) from a sample was calculated.

3. Results and discussion

The proposed procedure for simultaneous extraction of Cr(VI) from solid samples and catalytic adsorptive stripping voltammetric determination of it in extracts is performed in a single voltammetric cell and consists of two main steps:

- simultaneous (i) deaeration of the supporting electrolyte, (ii) extraction of Cr(VI) through complexing reaction metal ions that form an insoluble chromate with DTPA, so Cr(VI) as a soluble salt goes into the solution and (iii) removing of interferences from extracted Cr(III) by its complexation with DTPA with the formation of a complex converting with time to a nonactive electrochemical form [29],
- accumulation of the reduction product of the extracted Cr(VI) in the form of the $Cr(III)$–H_2DTPA active complex on the mercury electrode and then reduction of the complex in the presence of nitrates to enhance the analytical peak current as a detection step.

The optimization of the proposed procedure was mainly concentrated on the selection of the optimum conditions for simultaneous quantitative extraction of Cr(VI) from solid samples and its determination in extract. The procedure of removing interferences from Cr(III) by complexation with DTPA with the formation of a complex converting with time to a nonactive electrochemical form has already been described [29,30].

3.1. The extraction solution/supporting electrolyte

In order to determine chromium in the presence of DTPA and nitrates an electrolyte containing the acetate buffer to stabilize pH was usually used [29,30]. The effect of the acetate buffer pH on the recovery of Cr(VI) from a solid sample was investigated. The pH of the supporting electrolyte was adjusted to the range from 5 to 7 and then after 5 min of deaeration time NaOH or HNO_3 was added to obtain the pH 6.2, and voltammetric determination of Cr(VI) was performed. The results obtained are presented in Fig. 1A. The influence of the supporting electrolyte pH in the range from 5 to 7 on the catalytic peak current of Cr(VI) was also examined and the results obtained are presented in Fig. 1B. On the basis of the received results the pH of the supporting electrolyte equal to 6.2 ± 0.1 was chosen for further study. Because an acetate buffer at pH 6.2 possesses small buffering capacity, additionally an MES buffer pH 6.2 was added to the supporting electrolyte. Fig. 2 shows the effect of the concentration of the MES buffer on the recovery and catalytic peak current of Cr(VI). The results show that in the whole tested range of concentration from 0.005 to $0.08\,mol\,L^{-1}$ comparable and acceptable recoveries of Cr(VI) above 96% were obtained, however, the catalytic peak current of Cr(VI) distinctly decreased with the concentration of the MES higher than $0.03\,mol\,L^{-1}$, so for further measurements an MES buffer concentration of $0.02\,mol\,L^{-1}$ was chosen.

The effect of concentration of the acetate buffer and DTPA on the recovery and catalytic peak current of Cr(VI) was also investigated. The results show that the concentrations of the acetate buffer in the range from 0.01 to $0.08\,mol\,L^{-1}$, as well as the concentration of the DTPA in the range from 0.005 to $0.02\,mol\,L^{-1}$, enable achieving the satisfying recovery of Cr(VI) above 96% and constant catalytic peak current of Cr(VI). For further study
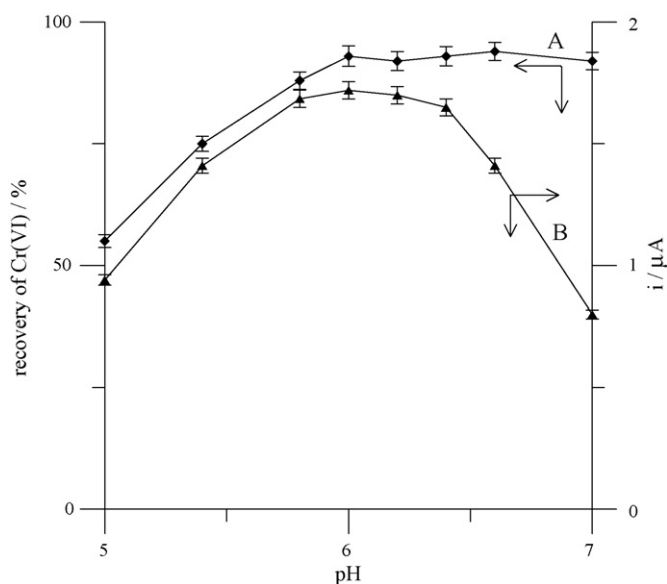
Fig. 1. Effect of the pH of supporting electrolyte/extraction solution on: (A) Cr(VI) recovery from a sample containing $0.5\,mg\,kg^{-1}$ Cr(VI) as $PbCrO_4$ in a SiO_2 matrix; (B) Cr(VI) catalytic peak current from the solution containing $1 \times 10^{-8}\,mol\,L^{-1}$ of K_2CrO_4.

a concentration of the acetate buffer and DTPA equal to 0.04 and $0.01\,mol\,L^{-1}$ were chosen, respectively.

3.2. Effect of temperature

The effect of temperature on the extraction process was investigated using standard conditions, but the temperature of measurements was being changed from 10 to 40 °C. The results obtained show that in the whole range of the studied temperatures acceptable and comparable results were obtained.
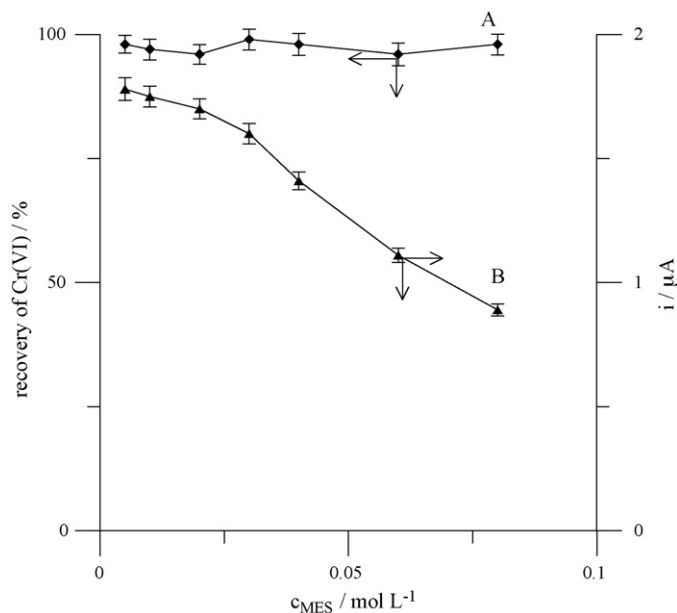

Fig. 2. Effect of the MES buffer concentration (pH 6.2) on: (A) Cr(VI) recovery from a sample containing $0.5\,mg\,L^{-1}$ Cr(VI) as $PbCrO_4$ in a SiO_2 matrix; (B) Cr(VI) catalytic peak current from the solution containing $1 \times 10^{-8}\,mol\,L^{-1}$ of K_2CrO_4.
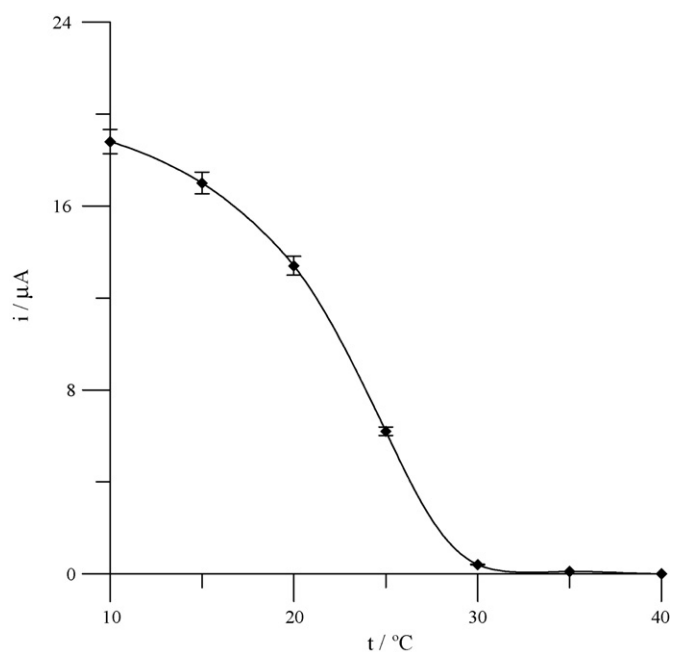

Fig. 3. Effect of the temperature of the measurements on the decrease of Cr(III) peak current. Concentration of Cr(III) added as $CrCl_3$ was $5 \times 10^{-7}\,mol\,L^{-1}$.

Because the extraction process is not selective for Cr(VI) the differentiation between chromium species must be taken into account. One of the methods which allows for selective determination of Cr(VI) in the presence of Cr(III) exploited the fact that the analytical signal corresponding to Cr(III) present in the solution decreases with time in the presence of DTPA [30]. In the paper [29] it was found that increasing the temperature significantly shortens the time of decrease of the Cr(III) signal so its influence on the Cr(III) signal in the proposed procedure was also investigated. The results obtained are presented in Fig. 3. Because at the temperature of 40 °C a substantial enhancement of selectivity of the Cr(VI) measurements was observed and at the same time a stable signal for Cr(VI) was obtained, further measurements were performed at this temperature.

3.3. Effect of extraction time

The extraction process was carried out at standard conditions while the time of extraction was being changed from 5 to 20 min. Acceptable recoveries of Cr(VI) were obtained for the time as short as 5 min and did not change with its prolongation. For further study an extraction time of 5 min was chosen and it was sufficient to obtain the quantitative recovery of Cr(VI). Times shorter than 5 min were not studied because this time is indispensable to deaerate the sample solution before the stripping voltammetric measurement.

3.4. Effect of a mass of the sample to volume of extractant ratio

Effect of a mass of the sample to volume of extractant ratio was studied at standard conditions at a constant volume of the extractant equal to 15 mL, while the mass of solid samples of
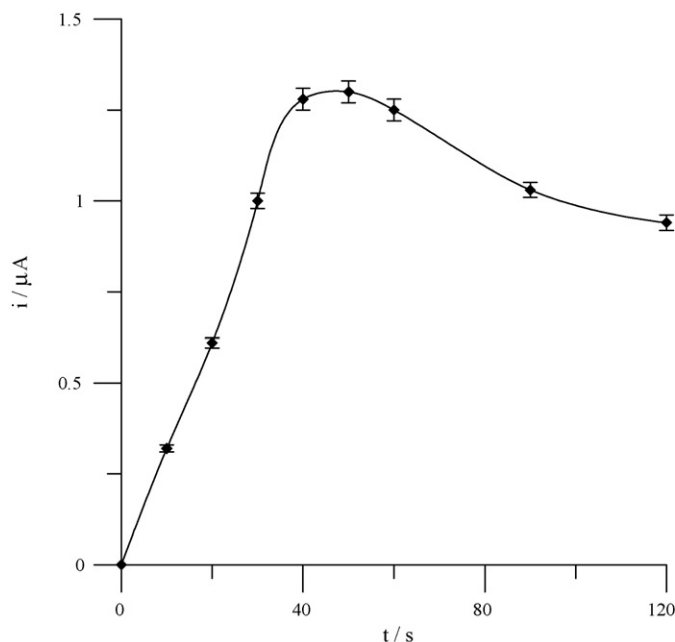
Fig. 4. Effect of accumulation time on catalytic peak current of Cr(VI) studied for 10 mg of 0.5 mg kg^{-1} Cr(VI) as PbCrO$_4$ added to the 15 mL of supporting electrolyte.

known amounts of Cr(VI) in the concentration range from 0.01 to 1 mg kg^{-1} as PbCrO$_4$ in a SiO$_2$ matrix was changed from 500 to 5 mg, respectively. The results show that irrespective of the mass of the sample and the contents of Cr(VI) comparable and acceptable recoveries above 95% were obtained. For standarization of the proposed procedure generally the mass of 10 mg of 0.5 mg kg^{-1} Cr(VI) as PbCrO$_4$ in a SiO$_2$ was used.

3.5. Effect of accumulation potential and time

The accumulation potential was chosen on the basis of literature data [29,31,32] and was equal to -1.0 V. The effect of accumulation time was studied for 10 mg of 0.5 mg kg^{-1} Cr(VI) as PbCrO$_4$ added to 15 mL of the supporting electrolyte. The time of accumulation was changed from 10 to 120 s and the obtained results are presented in Fig. 4. It was found that the chromium peak increased linearly up to 40 s and slightly decreased for accumulation time longer than 60 s. For further study the accumulation time of 30 s was chosen.

3.6. Analytical parameters

In order to investigate the analytical parameters of the proposed procedure a 10 mg of mixtures of PbCrO$_4$ containing a known amounts of Cr(VI) in the concentration range from 0.05 to 5 mg kg^{-1} of Cr(VI) were added to the voltammetric cell and the measurements were performed. The obtained results indicated that the calibration graph for Cr(VI) for an accumulation time of 30 s was linear in the range from 4×10^{-10} to 4×10^{-8} mol L^{-1} and obeyed the equation $y = 131x + 23$, where y and x were the peak current (nA) and Cr(VI) concentration (nmol L^{-1}), respectively. The linear correlation coefficient was

$r = 0.998$. The relative standard deviation from five determinations of chromium at a concentration of 5×10^{-9} mol L^{-1} was 4.1%. The detection limit estimated from three times the standard deviation for low chromium concentration and accumulation time of 30 s was about 1.2×10^{-10} mol L^{-1}.

3.7. Examination of the procedure on MFE

Two basic electrode systems, HMDE and the MFE, have gained wide acceptance in the development of stripping voltammetry. So the proposed procedure was also examined using MFE as a working electrode instead of HMDE (which was used for the optimization of the proposed procedure). Stripping voltammetric measurements were performed with in situ and ex situ deposited MFEs on glassy carbon. If the MFE was prepared in situ the obtained Cr(VI) signal was unstable and decreased with time. It is consistent with the literature data, where it was stated that the mercury film formed in this way was irreproducible and had poor adsorption behaviour. It was attributed to the interference of the plating process by DTPA [33]. If the MFE was prepared ex situ, a Cr(VI) signal decreased also from measurement to measurement, so it was necessary to polish the electrode prior to every measurement, which made the whole procedure long and complicated. The voltammograms obtained for the ex situ prepared MFE are shown in Fig. 5. It is obvious that the obtained signals at MFE are worse in shape as compared to those obtained at HMDE (Fig. 6). The sensitivity of the measurements of Cr(VI) concentration at MFE is also lower. Taking those facts into account the use of an MFE electrode is not recommended in the presented procedure.

3.8. Effect of interfering ions

The influence of possible matrix ions in the environmental solid samples on the extraction and determination of Cr(VI) with the proposed procedure was examined. The effect of potentially interfering ions was investigated by adding known concentrations of each ion into 15 mL of a solution containing 10 mg of
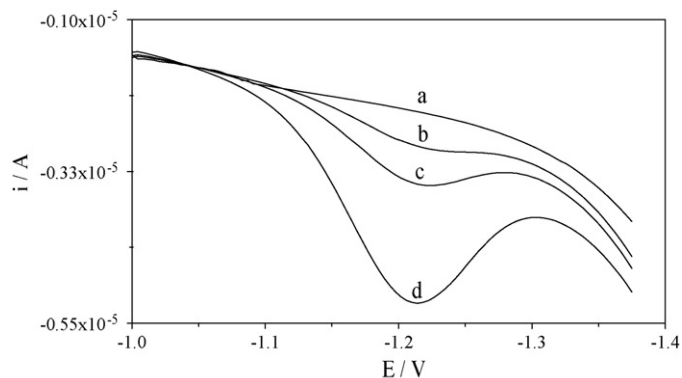

Fig. 5. Differential pulse voltammograms obtained on ex situ MFE in the course of determination of Cr(VI): (a) blank; (b) 20 mg of 1 mg kg^{-1} Cr(VI) as PbCrO$_4$; (c) as (b) + 2.5×10^{-8} mol L^{-1} of Cr(VI) as K$_2$CrO$_4$; and (d) as (b) + 1×10^{-7} mol L^{-1} of Cr(VI) as K$_2$CrO$_4$. Accumulation time 30 s. Electrode was polished before each measurement.
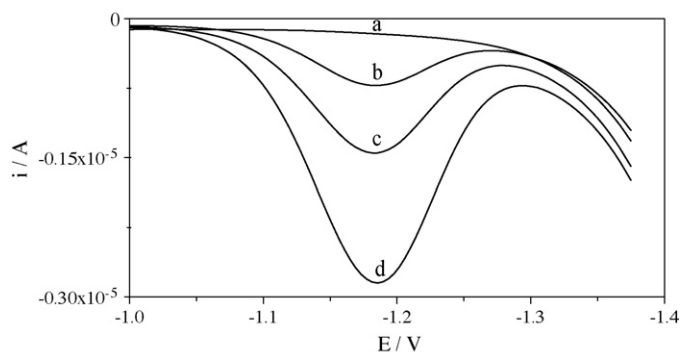
Fig. 6. Differential pulse voltammograms obtained on HMDE in the course of determination of Cr(VI) in CRM 019 Ash: (a) blank; (b) 10 mg CRM 019 Ash diluted with SiO_2 1:1 per 15 mL of supporting electrolyte; (c) as (b) + 5×10^{-9} mol L^{-1} of Cr(VI) as K_2CrO_4; and (d) as (b) + 1.5×10^{-8} mol L^{-1} of Cr(VI) as K_2CrO_4. Accumulation time 30 s.

Table 1
Results of Cr(VI) determination in the synthetic mixtures containing $PbCrO_4$ and/or Cr_2O_3 and $CrCl_3$ as insoluble and soluble forms of Cr(III), respectively

Synthetic mixtures contained known concentration of Cr(VI) and/or Cr(III) (mg kg^{-1})			Cr(VI) determined (mg kg^{-1})
$PbCrO_4$	Cr_2O_3	$CrCl_3$	
–	100	–	0.015 (8.8)
–	200	–	0.026 (7.1)
–	–	100	0.047 (8.4)
–	–	200	0.102 (6.8)
1.00	–	–	0.970 (5.2)
1.00	100	–	0.982 (6.1)
1.00	200	–	0.988 (5.7)
1.00	–	100	1.023 (4.8)
1.00	–	200	1.084 (5.6)

The measurements were performed at the temperature 40 °C for 10 mg of samples added to 15 mL of the supporting electrolyte. The time of accumulation was 30 s. In brackets the relative standard deviations in % are given ($n = 5$).

0.5 mg kg^{-1} Cr(VI) as $PbCrO_4$ in a SiO_2 matrix. The obtained results showed that at least 50 µg L^{-1} of Zn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, VO_3^-, Cu^{2+}, Fe^{3+}, MoO_4^{2-} in the solution caused a change of less than 5% in the recovery efficiency of Cr(VI). Crucially important is the influence of Fe(II) because it willingly reacts with Cr(VI). The performed experiments confirm that the presence of 50 µg L^{-1} of Fe(II) causes a decrease of the Cr(VI) peak in the time, e.g. the peak is diminished by half

in 10 min. It was observed that the permissible concentration of Fe(II) in the solution was 20 µg L^{-1}, and it caused a change of less than 5% in the recovery efficiency of Cr(VI).

In order to estimate precisely the accuracy of the speciation procedure and to test for potential valence species interconversion, different solid samples of Cr(III) compounds, Cr_2O_3 as an insoluble form and $CrCl_3$ as a soluble form, were mixed with $PbCrO_4$. The extraction and determination of Cr(VI) in those mixtures were then performed and the received results are presented in Table 1. The obtained results indicated that the studied method allows for Cr(VI) determination in the presence of about 200-fold excess of Cr(III) if it is in insoluble form without serious interference. In the case of soluble forms of Cr(III) its 200-fold excess causes overestimation of Cr(VI) results by 10%.

3.9. Application to the real samples

According to [34] the quality control procedure should be based on the analysis of the reference material with the use of a tested analytical method and comparison of results obtained with the certified values. However, there are no certified reference materials for Cr(VI) containing insoluble Cr(VI) [14,35]. In connection with this certified reference materials certified only for total chromium were used to validate the proposed procedure. According to the literature data certified reference materials CRM 013 Paint Chips [11,13] and CRM 019 Ash [36] contain insoluble Cr(VI). These materials were analyzed using the method of standard addition. The obtained results of Cr(VI) determination in certified reference materials were compared to the results received with the use of two other extraction procedures [8,10] and different methods of detection [15,29], and they are given in Table 2. In the case of Cr(VI) determination by the method described in [29] the 0.02 mol L^{-1} MES buffer was additionally added to the solution in order to stabilise the pH value. Typical voltammograms obtained in the course of determination of Cr(VI) in CRM 019 Ash are presented in Fig. 6. The results obtained for Cr(VI) determination in CRM 013 Paint Chips sample with different methods of extraction show a good degree of agreement. It should be noted that CRM 013 Paint Chips sample contains reference value 618 mg kg^{-1} for total chromium, so the Cr(III)/Cr(VI) ratio is small (<1). In the case of CRM 019 Ash the results of Cr(VI) determination using extraction with 0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH were higher than the results obtained by two other procedures. Such results are in

Table 2
Results of Cr(VI) determination (in mg kg^{-1}) in certified reference materials: CRM 019 Ash and CRM 013 Paint Chips using different methods of extraction and determination

Sample	Method of extraction			Certified reference value for total Cr ± S.D.
	Proposed procedure	0.28 mol L^{-1} Na_2CO_3 + 0.5 mol L^{-1} NaOH [8]	10% Na_2CO_3 + 2% $NaHCO_3$ + $MgSO_4$ [10]	
CRM 019 Ash	0.62 (7.8)	0.74 (6.1)[a]	0.59 (5.5)[a]	55. 2 ± 21.4
CRM 013 Paint Chips	347 (5.2)	352 (3.4)[b]	359 (4.0)[b]	618 ± 53.6

In brackets the relative standard deviations in % are given ($n = 5$). S.D., standard deviation.
[a] Cr(VI) was determined by the method described in [28].
[b] The results are given in paper [15].

agreement with the literature data [5], where it was reported that this extraction mixture leads to oxidation of Cr(III) to Cr(VI), particularly in samples with high Cr(III)/Cr(VI) ratios. This is true in the case of CRM 019 Ash, where reference value for total chromium is 55.2 mg kg^{-1}. Analyses of paint chips and ash samples spiked with Cr(VI) as PbCrO$_4$ were also performed. The recoveries of Cr(VI) using the proposed procedure were equal to 97.4% with R.S.D. 4.8 and 98.5% with R.S.D. 6.7%, respectively.

4. Conclusion

The results of analysis of real samples for Cr(VI) indicate no significant difference between the performance of the proposed method of extraction and other methods mostly described in the literature, but the advantage of the proposed procedure is the fact that it is simpler, faster and less expensive tool for direct Cr(VI) determination in solid samples. The whole procedure is applied to a single cell, which allows for monitoring the voltammetric scan. Such a simultaneous extraction and determination of Cr(VI) is possible thanks to the fact that DTPA both quantitatively extracts Cr(VI) and then forms a Cr(III)–H$_2$DTPA complex (from Cr(III) obtained from the reduction of Cr(VI)), which is adsorbed on the mercury electrode. Additionally the Cr(III)–H$_2$DTPA complex formed from the Cr(III) present in the sample quickly passes at the temperature of 40 °C into an electrochemically inactive form, which enables the achievement of satisfying selectivity of Cr(VI) determination in the presence of Cr(III). On the basis of measurements of the Cr(VI) concentration in the synthetic mixtures of Cr(III) and Cr(VI) compounds it was observed that the 100-fold excess of Cr(III) (both in insoluble and soluble form) did not cause any apparent errors in the Cr(VI) determination but the 200-fold excess of Cr(III) in soluble form made the results of Cr(VI) determination overestimated by about 10%. The method offers a wide range of linearity of the calibration graph and a low detection limit. It can also be applied in the presence of numerous foreign ions occurring in the concentrations of at least 50 µg L^{-1} with the exception of Fe(II) ions, for which the acceptable concentration is no more than 20 µg L^{-1}.

The major advantage of the proposed procedure is simultaneous and quantitative extraction and analysis of Cr(VI) in solid samples without separation of species, so the need for the additional equipments and reagents is eliminated. It should be also noted that the whole procedure is carried out at the pH value equal to 6 in contrast to the commonly used in various procedures acidic environment which promotes the reduction of Cr(VI) by the organics present in the sample.

It must be noted that the best parameters for the proposed procedure were obtained using HMDE as a working electrode. In case of MFE the results were not satisfying.

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