

Determination of chromium in cement by catalytic adsorptive stripping voltammetry

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Chromium determination in cement by catalytic adsorptive stripping voltammetry using a hanging mercury drop electrode is described. The composition of medium for Cr(VI) determination is the following: CH_3COONa 0.15 mol l^{-1} , diethylenetriaminepentaacetic acid 5 mmol l^{-1} , NaNO_3 0.7 mol l^{-1} , pH 6. The optimal voltammetry conditions: accumulation potential -0.9 V , accumulation time 5–10 s, square wave voltammetry stripping mode. The detection limit for Cr(VI) is about $0.05 \mu\text{g l}^{-1}$, and the relative standard deviation does not exceed 3%. Chromium species are extracted from cement with water or nitric acid. The total chromium is determined after the quantitative oxidation of Cr(III) to Cr(VI) by addition of $0.1\text{--}0.3 \text{ mmol l}^{-1}$ of permanganate ions to the cement extracts. The concentration of Cr(III) is evaluated as the difference between total chromium and Cr(VI).

Key words: chromium, speciation, catalytic adsorptive stripping voltammetry, hanging mercury drop electrode, cement

INTRODUCTION

Chromium compounds are found in the environment due to weathering of chromium-containing rocks, volcanic eruptions and anthropogenic input [1–3]. Chromium can exist in several chemical forms with oxidation states from zero to six, but only Cr(III) and Cr(VI) are stable enough to occur in the natural environment. Chemically, these two chromium species are very different – mainly as regards solubility, redox and complexation activities [3, 4]. As a result, the prevailing chemical form in the natural environment is Cr(III). Well known is the great difference in the toxicity of the two chromium species. Whereas Cr(III) is considered to be a trace element essential for the proper functioning of living organisms, Cr(VI) is toxic and carcinogenic to humans when inhaled and can induce allergies and dermatitis through skin contact.

The anthropogenic contamination by Cr(VI) can occur directly when Cr(VI) compounds are used in electroplating, pigment, tanning or other industries. In such industries as metallurgy, production of refractories or cement, Cr(III) in

raw materials is oxidized to Cr(VI) by oxygen during high temperature processes. The most widespread industrial product containing soluble Cr(VI) is Portland cement. It is the most common type of cement, and its world production reached 3.3 billion tonnes in 2010 [5].

Cr(VI) is a well-known skin sensitizer, and the sensitization reactions in cement workers can be explained by its action [6]. Moreover, wet cement has $\text{pH} > 12$, and this facilitates the penetration of water-soluble Cr(VI) through the skin during manual handling of wet mortar and concrete by construction workers. Therefore, since the beginning of 2005, in all cements sold in Europe the Cr(VI) content was restricted by EU Directive 2003/53/EC which states that cement may not be marketed if it contains more than 0.0002% ($2 \mu\text{g g}^{-1}$) of soluble Cr(VI) of the total dry weight of the cement when there is a risk of contact with the skin [7]. Usually, Cr(VI) content in cement clinker exceeds the $2 \mu\text{g g}^{-1}$ limit; therefore, special Cr(VI)-reducing additives are added in the final stages of cement production.

To determine separately the toxic Cr(VI) and non-toxic Cr(III) concentrations in cement samples, the analytical methodologies capable of speciation analysis are necessary. The main analytical methods used for chromium specia-

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tion in solid matrices are summarized in a recent review [8]. Atomic spectrometric techniques, such as electrothermal atomic absorption spectrometry and inductively coupled plasma-atomic emission spectrometry, dominate in this field [9–11]. However, more and more often spectrometric techniques are coupled with ion chromatography and HPLC to minimize contamination [12, 13]. The serious drawbacks of these modern techniques are high costs of the instrumentation and the determination itself. Therefore, low-cost electroanalytical methods of chromium determination, based on catalytic adsorptive stripping voltammetry (CASV) [3, 14], can be a promising alternative for chromium speciation. Recently, the procedures for extraction and determination of Cr(VI) in complicated natural soil samples by CASV have been described [15–17].

The aim of this work was to develop a simple and fast procedure for trace determination of Cr(VI) and Cr(III) in cement by catalytic adsorptive stripping voltammetry, using a hanging mercury drop electrode.

EXPERIMENTAL

Voltammetric measurements were carried out using a PU-1 polarograph (Russia) in a square wave voltammetry mode ($f = 25$ Hz, $V = 100$ mV s⁻¹, $E_{sw} = 90$ mV). Voltammograms were recorded by an *xy*-recorder N 307 (Russia). A 303 SMDE static mercury drop stand controlled by a PAR 174A polarograph (Princeton Applied Research, USA) was used to form a hanging mercury drop electrode (HMDE). The surface area of the mercury drop was 1.16 mm². All potentials were measured against a saturated Ag/AgCl reference electrode. The auxiliary electrode was platinum wire. The stirring of the solutions during the accumulation step was carried out by a magnetic stirrer.

All reagents were of analytical grade, and solutions were made using distilled water (specific conductivity $\kappa = 5$ – 8 μ S cm⁻¹). Diethylenetriaminepentaacetic acid (DTPA) was obtained from Fluka. Stock standard solutions of Cr(VI) and Cr(III), concentration 1 g l⁻¹, were prepared by dissolving in distilled water the weighed amounts of K₂CrO₄ or KCr(SO₄)₂ · 12 H₂O. Before voltammetric measurements, the solutions had been deoxygenated by purging with nitrogen.

The CEM IIA-L42,5N Portland cement, purchased in a supermarket in 2010, was used in chromium determination experiments.

Procedures

Determination of Cr(VI) and total chromium in water extract of the cement. About 0.1 g of dry cement was weighed and added to 50 ml of distilled water for 24 hours. An aliquot of 0.1 ml was taken for Cr(VI) determination and pipetted into an electrochemical cell with 14 ml of solution containing 0.15 mol l⁻¹ CH₃COONa, 5 mmol l⁻¹ DTPA and 0.7 mol l⁻¹ NaNO₃. The pH of the mixture was adjusted to pH 6 by acetic acid. The solution was deaerated by 8 min purging with

nitrogen. A mercury drop was formed, and accumulation at -0.9 V for 5–10 s was carried out from the stirred solution. After 10 s of equilibration without stirring, the voltammogram was recorded at a scanning potential from -0.9 V to -1.4 V. Three consecutive additions, 1–2 μ g l⁻¹ Cr(VI) each, were performed for standard addition procedure.

For the total chromium determination, 0.1 mmol l⁻¹ KMnO₄ was added to 10 ml of water extract of the cement, and after 10–15 min the aliquot of 0.1 ml was pipetted into the electrochemical cell. The rest steps of the procedure were the same as for Cr(VI) determination.

Determination of Cr(VI) and total chromium in nitric acid extract of the cement. About 0.1 g of dry cement was weighed and added to 5 ml of concentrated HNO₃ for 15 min. After cement dissolution, the extract was diluted to 50 ml by distilled water and filtrated. An aliquot of 0.1 ml was taken into the electrochemical cell, and the rest steps of the procedure for Cr(VI) determination were the same as for the water extract.

For the total chromium determination, 0.3 mmol l⁻¹ KMnO₄ was added to a diluted extract of the cement, and the pH was adjusted to pH 4 by ammonia solution. The mixture was boiled for 3 min, and after cooling an aliquot of 0.1 ml was pipetted into an electrochemical cell. The rest steps of the procedure were the same as for Cr(VI) determination in a water extract.

RESULTS AND DISCUSSION

Determination of Cr(VI) by catalytic adsorptive stripping voltammetry is an extremely sensitive and at the same time a very complicated electroanalytical procedure [14]. The accumulation step includes two consecutive processes: the electrochemical reduction of Cr(VI) to Cr(III) at a hanging mercury drop electrode in the presence of DTPA ligand, and the adsorption of the Cr(III)–DTPA complex at the mercury electrode surface. During the stripping step, the potential scan in the negative direction and the electrochemical reduction of the adsorbed Cr(III)–DTPA complex to Cr(II)–DTPA is performed. Simultaneously, the Cr(II) is immediately oxidized chemically back to Cr(III) by nitrate ions. As a result, a substantial enhancement of the electrochemical reduction current occurs. The interference of Cr(III) into Cr(VI) determination is negligible due to the fact that the formation of the electrochemically active Cr(III)–DTPA complex is fast only in the case when Cr(VI) is converted into Cr(III) at the electrode surface.

The complex combination of chemical and electrochemical processes in chromium determination by CASV requires optimization of the experimental conditions for each particular application. The main conditions to be optimized are pH, the concentration of DTPA ligand and nitrate ions, the potential and duration of the accumulation.

The 0.15 mol l⁻¹ sodium acetate solution has been chosen as a medium with a sufficient buffering capacity for most of

the procedures in Cr(VI) determination. The pH of the medium was adjusted by adding acetic acid. Figure 1 illustrates the effect of pH on the analytical signals of Cr(VI). It can be concluded from the shape of the curve that the optimal pH range is 6.0 ± 0.2 . The deviations from pH 6 by ± 0.5 pH unit result in a decrease of the analytical signals by 30%. Since the stock solution of DTPA is basic due to ammonia added to achieve its better solubility, it is very important to adjust the pH of the solution upon adding the ligand.

The effect of DTPA concentration on the chromium analytical signals is shown in Fig. 2. One can see that at least 0.6 mmol l^{-1} of DTPA is necessary to achieve high analytical signals when Cr(VI) concentration is $2 \text{ } \mu\text{g l}^{-1}$. Consequently, for the Cr(VI) concentrations up to $20 \text{ } \mu\text{g l}^{-1}$ the optimal DTPA concentration range is about $5\text{--}7 \text{ mmol l}^{-1}$. It has been found that Cr(VI) analytical signals increase linearly when the nitrate ion concentration is increased up to about

$1 \text{ mol l}^{-1} \text{ NaNO}_3$. Therefore, as high as $0.7 \text{ mol l}^{-1} \text{ NaNO}_3$ concentration was used in the Cr(VI) determination procedure.

The voltammetric experiments have shown that Cr(VI) reduction to Cr(III) at the HMDE in the acetate buffer starts at a potential of about -0.05 V . However, the most efficient adsorptive accumulation of the Cr(III)–DTPA complex on the mercury surface occurs at about -0.9 V , and the obvious dependence of the analytical signals on accumulation time at this potential confirms it. Therefore, the potential of -0.9 V has been chosen as the accumulation potential for Cr(VI) determination. The dependence of the analytical signals on accumulation time is close to linear up to about 5 min for the Cr(VI) concentration range $1\text{--}12 \text{ } \mu\text{g l}^{-1}$.

The background voltammogram and three voltammograms after consecutive additions of Cr(VI) under optimized conditions are shown in Fig. 3.

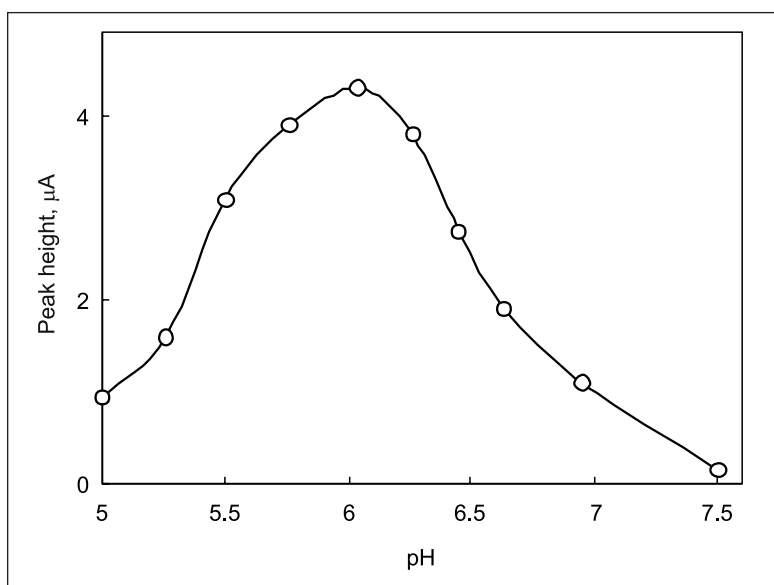


Fig. 1. The effect of pH on the analytical signals of Cr(VI). Conditions: $0.15 \text{ mol l}^{-1} \text{ CH}_3\text{COONa}$, $7 \text{ mmol l}^{-1} \text{ DTPA}$, $0.7 \text{ mol l}^{-1} \text{ NaNO}_3$, $2 \text{ } \mu\text{g l}^{-1} \text{ Cr(VI)}$; accumulation potential -0.9 V , accumulation time 60 s

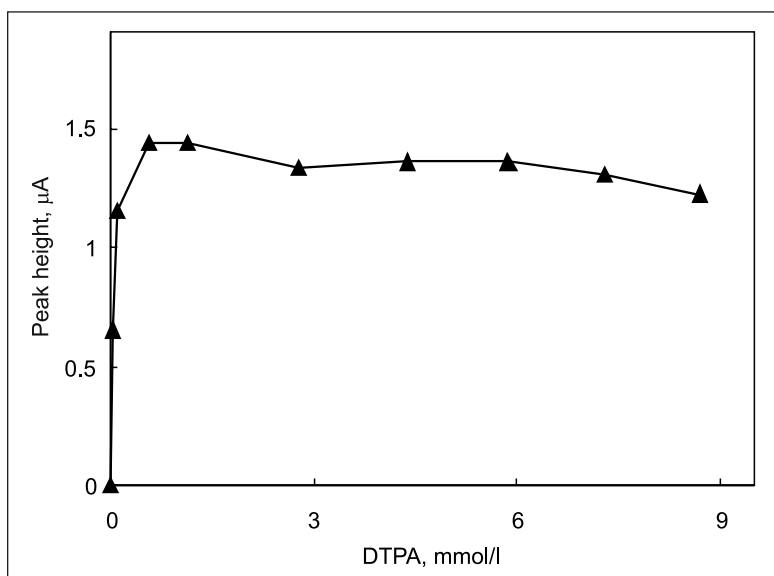


Fig. 2. The effect of DTPA concentration on the analytical signals of Cr(VI). Conditions: $0.15 \text{ mol l}^{-1} \text{ CH}_3\text{COONa}$, $0.7 \text{ mol l}^{-1} \text{ NaNO}_3$, $2 \text{ } \mu\text{g l}^{-1} \text{ Cr(VI)}$; accumulation potential -0.9 V , accumulation time 30 s

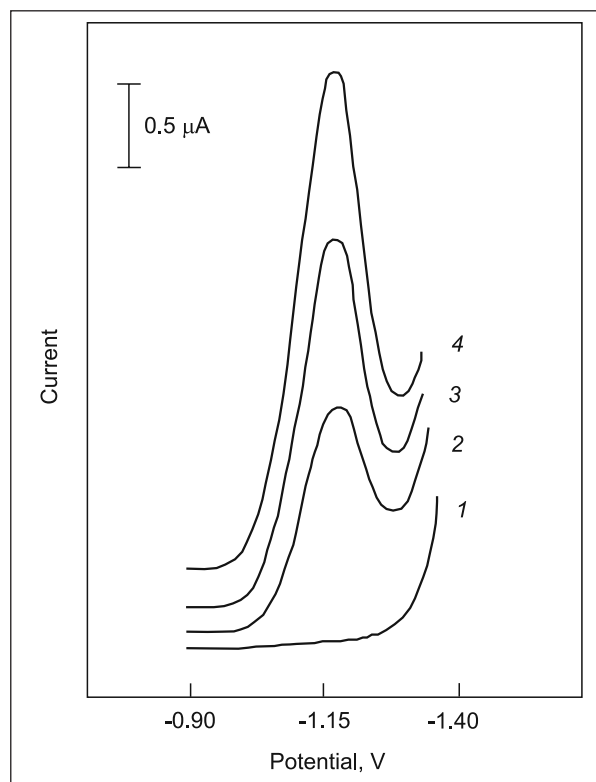


Fig. 3. Voltammograms of Cr(VI) under optimal conditions: 1 – background voltammogram, 2–4 – 1, 2 and 3 $\mu\text{g l}^{-1}$ Cr(VI), respectively. Conditions: 0.15 mol l^{-1} CH_3COONa , 5 mmol l^{-1} DTPA, 0.7 mol l^{-1} NaNO_3 , accumulation potential -0.9 V , accumulation time 30 s

The dependence of the analytical signals on concentration tends to deviate from the linearity when long accumulation times are applied for higher Cr(VI) concentrations. However, if the accumulation time does not exceed 1 min, the dependencies are strictly linear ($r \sim 0.9998$) at least up to 10 $\mu\text{g l}^{-1}$ Cr(VI) concentrations. This concentration range is sufficient for the determination of Cr(VI) in real samples of cement extracts by the method of standard additions.

The repeatability of Cr(VI) analytical signals has been tested by performing a series of ten measurements for the chromium concentration range 0.5–25 $\mu\text{g l}^{-1}$. The relative standard deviation for this concentration range is 2.5–3.0% and about 1.5% for higher chromium concentrations. The detection limit evaluation, based on three standard deviations for Cr(VI) concentration 0.5 $\mu\text{g l}^{-1}$, gives the value of about 0.05 $\mu\text{g l}^{-1}$ for a 3-min accumulation time.

It should be noted that analogous optimization experiments of direct Cr(III) determination are impossible. Immediately after Cr(III) addition its analytical signal can be observed at the same potential as of Cr(VI); however, due to the formation of the electrochemically inert Cr(III)–DTPA complex, it rapidly decreases and in 20–30 min practically disappears. The solution of the problem could be the quantitative chemical oxidation of Cr(III) to Cr(VI) in order to evaluate the total chromium concentration, with the subsequent calculation of the Cr(III) concentration as a difference between the total chromium and Cr(VI) concentration. Various chemicals can be used for Cr(III) oxidation, and permanganate ions are perhaps the optimal choice [18].

Experiments using permanganate ions have shown that the oxidant influences also Cr(VI) analytical signals. It can be seen from Fig. 4 that immediately upon adding 0.05 mmol l^{-1} of permanganate ions to Cr(VI) solution, the analytical signals increase about four times and then come back to the initial value in about 5 min. When a 1 mmol l^{-1} permanganate ion concentration is used, the Cr(VI) analytical signals increase similarly, but it takes them more than 20 min to return to the initial value. Most likely permanganate ions contribute to the catalytic effect of nitrate ions, but simultaneously their concentration declines due to the reduction processes in the acetate medium. The discoloration of the solution with the analytical signals coming back to their initial value confirms the reduction of permanganate ions. Thus, using permanganate ions for Cr(III) oxidation the excess of the oxidant should be removed

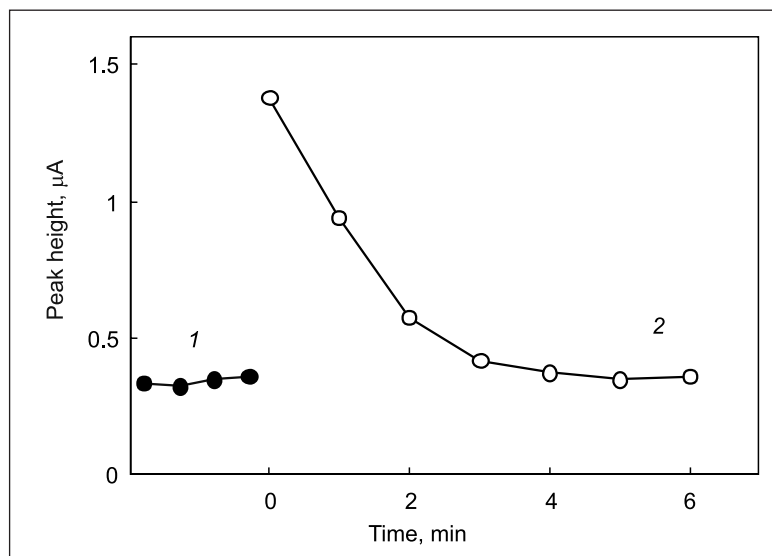


Fig. 4. The influence of permanganate ions on the analytical signals of Cr(VI). 1, 2 – analytical signals before and after addition of permanganate ions, respectively. Conditions: 0.15 mol l^{-1} CH_3COONa , 5 mmol l^{-1} DTPA, 0.7 mol l^{-1} NaNO_3 , 4 $\mu\text{g l}^{-1}$ Cr(VI), 0.05 mmol l^{-1} KMnO_4 ; accumulation potential -0.9 V , accumulation time 5 s

Table 1. Influence of permanganate ion addition on Cr(III) and Cr(VI) determination results. Conditions: $0.15 \text{ mol l}^{-1} \text{ CH}_3\text{COONa}$, $5 \text{ mmol l}^{-1} \text{ DTPA}$, $0.7 \text{ mol l}^{-1} \text{ NaNO}_3$; accumulation potential -0.9 V , accumulation time 5 s

Added		$\text{KMnO}_4, \text{ mmol l}^{-1}$	Determined
Cr(III), $\mu\text{g l}^{-1}$	Cr(VI), $\mu\text{g l}^{-1}$		Cr(VI), $\mu\text{g l}^{-1}$
–	2.0	–	1.97 ± 0.18
–	2.0	0.05	2.00 ± 0.25
2.0	–	0.05	2.00 ± 0.29
2.0	2.0	–	2.03 ± 0.14
2.0	2.0	0.05	3.97 ± 0.28

Table 2. Determination of Cr(VI) and Cr(III) in water and nitric acid extracts of cement. Conditions as described in Procedures

Chromium content	Water extract		HNO_3 extract	
	Cr(VI)	Cr(VI) + Cr(III)	Cr(VI)	Cr(VI) + Cr(III)
Extract, $\mu\text{g l}^{-1}$	26.3 ± 7.1	27.3 ± 4.2	25.4 ± 5.2	108.6 ± 13.2
Cement, $\mu\text{g g}^{-1}$	13.1 ± 3.5	13.7 ± 2.1	12.7 ± 2.6	54.4 ± 6.6

by keeping the solution for some time at room or higher temperature.

Table 1 illustrates the influence of permanganate ion addition on Cr(III) and Cr(VI) determination results. One can see that in the case of Cr(VI) the same results are obtained both with and without adding permanganate ions. If the solution contains only Cr(III) species, they are quantitatively oxidized and determined as Cr(VI). When a mixture of chromium species is analysed, the total chromium is determined upon adding permanganate ions, and only Cr(VI) is determined without using the oxidant. It should be noted that data in Table 1 demonstrate also that chromium concentrations in the range $2\text{--}4 \mu\text{g l}^{-1}$, determined by the method of standard additions, do not differ by more than $\pm 2\%$ from the values of chromium concentrations added.

In order to determine the amount of chromium species in cement, various extraction techniques can be used, e. g., extraction with water; boiling in sodium carbonate solution, dissolving in HCl or HNO_3 [8]. In this work, the water-soluble Cr(VI) was leached from a cement sample by adding 0.1 g of dry cement to 50 ml of distilled water. After 24 hours, an aliquot of 0.1 ml was taken for chromium determination by the optimized CASV technique using a method of standard additions for quantification. One can see in Table 2 that the difference between Cr(VI) and total chromium values in the extract is not statistically significant, taking into account the 95% confidence intervals of the results. Thus, the water-extractable Cr(VI) in dry cement can be estimated as about $13 \mu\text{g g}^{-1}$, and this value exceeds the $2 \mu\text{g g}^{-1}$ limit set by the EU Directive 2003/53/EC for water-soluble Cr(VI) in cement. Since there was no information about Cr(VI) content on the cement package, the reducing additives were possibly not used in the production of this type of cement.

Another extraction technique employed in our study was dissolving a cement sample in nitric acid. In this case, 0.1 g of cement dissolves in 5 ml of concentrated nitric acid practically completely in 15 min. After dilution and removing the negligible amount of insoluble silicates by filtration,

an aliquot was taken for chromium determination as in the case of water extract. One can see from Table 2 that Cr(VI) concentration determined in the nitric acid extract does not differ significantly from the value obtained for water extract. However, the total chromium concentration increased to about $109 \mu\text{g l}^{-1}$, i. e. about fourfold in comparison with the water extract. Consequently, Cr(III) content in the nitric acid extract is about $83 \mu\text{g l}^{-1}$, and it makes about 77% of total chromium. The content of non-toxic Cr(III) in cement is not regulated; however, it can be considered as an indicator of chromium coming from raw materials and production processes.

CONCLUSIONS

The catalytic adsorptive stripping voltammetry using a hanging mercury drop electrode can be successfully used for the determination of chromium species in cement samples; this technique is simple, fast, sensitive and low-cost. The concentrations of chromium in the electrochemical cell, even after dilution of the cement extracts, range within some micrograms per litre, and this by far exceeds the detection limit for Cr(VI), which is $0.05 \mu\text{g l}^{-1}$. Therefore, a high reproducibility and a short total duration of the analysis can be achieved. The total chromium and Cr(III) concentrations can be determined after a quantitative chemical oxidation of Cr(III) to Cr(VI) by permanganate ions.

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CHROMO NUSTATYMAS CEMENTE KATALITINĖS ADSORBCINĖS VOLTAMPEROMETRIJOS METODU

Santrauka

Straipsnyje aprašytas chromo nustatymas cemente katalitinės adsorbcinės voltamperometrijos metodu naudojant kabančio gyvsidabrio lašo elektrodą. Terpės sudėtis Cr(VI) nustatyta: 0,15 mol l⁻¹ CH₃COONa, 5 mmol l⁻¹ dietilentriaminpentaacto rūgšties, 0,7 mol l⁻¹ NaNO₃, pH = 6. Optimalios voltamperometrijos sąlygos: kaupimo potencialas -0,9 V, kaupimo trukmė 5–10 s, kvadratinės bangos voltamperometrijos režimas. Cr(VI) aptikimo riba yra apie 0,05 μg l⁻¹, santykinis standartinis nuokrypis ne didesnis kaip 3 %. Iš cemento mėginių chromas išekstrahuojamas vandeniu arba azoto rūgštimi. Bendras chromo kiekis nustatomas kiekybiškai oksiduoiant Cr(III) iki Cr(VI) į cemento ekstraktą pridėjais 0,1–0,3 mmol l⁻¹ permanganato jonais. Cr(III) koncentracija apskaičiuojama kaip bendro chromo ir Cr(VI) koncentracijų skirtumas.