VILNIUS UNIVERSITY

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DETERMINATION OF MANGANESE AND CHROMIUM BY ELECTROANALYTICAL STRIPPING METHODS RESEARCH

Summary of doctoral dissertation

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VILNIAUS UNIVERSITETAS

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MANGANO IR CHROMO NUSTATYMO INVERSINIAIS ELEKTROANALIZINIAIS METODAIS TYRIMAI

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1. INTRODUCTION

With regard to heavy metals and their compounds, usually meant higher their levels those are dangerous to humans, plants and animals that may have both acute and chronic effects. Heavy metal emission sources and their access routes to the biosphere differ in their variety, but it can be divided into two main groups, namely natural contamination and anthropogenic pollution. As heavy metals are natural components of the earth's crust, so they can get into the environment during natural processes such as natural rock weathering, volcanic activity, forest fires. However, the biggest sources of environmental pollution are anthropogenic: acquisition and mineral processing, industrial processes, industrial waste water and even acid rain, which washes soil from heavy metals into rivers, lakes and groundwater.

Manganese is an essential element for all living organisms and does not belong to very toxic metals. Manganese is a naturally occurring element that is found in rock, soil, and water. Manganese ions are common in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions, and these are the most important sources of drinking water. For example, in more than 40% of groundwater for centralized water supply in Lithuania manganese concentrations are above 100 $\mu g\ l^{-1}$. The EU Directive on the quality of water intended for human consumption gives the limit value 50 $\mu g\ l^{-1}$ for manganese. Later, the same value was accepted in the Lithuanian hygiene standard for drinking water. Various spectroscopic techniques are nowadays widely used for manganese determination; however, the electroanalytical techniques remain to be interesting alternatives due to their high sensitivity, straightforward procedures and low cost.

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 in solubility, redox and complexation activities. As a result the prevailing chemical form in the natural environment is Cr(III). Well known is the great difference in toxicity of 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 most widespread industrial product containing soluble Cr(VI) is Portland cement. Cr(VI) is a well-known skin sensitizer and the sensitization reactions in cement workers can be explained by its action. Moreover, wet cement has 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 year 2005 in all cements sold in Europe Cr(VI) content was restricted by EU Directive 2003/53/EC which states that cement may not be placed to the market if it contains more than 0.0002% (2 $\mu g\ g^{-1}$) of soluble Cr(VI) of the total dry weight of the cement where there is risk of contact with the skin.

To determine separately the toxic Cr(VI) and non-toxic Cr(III) concentrations in the cement samples the analytical methodologies capable for speciation analysis are necessary. Atomic spectrometric techniques as electrothermal atomic absorption spectrometry and inductively coupled plasma-atomic emission spectrometry dominate in this field. However, more and more often spectrometric techniques are coupled with ion chromatography and HPLC to minimize contamination. 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) can be a promising alternative for chromium speciation.

The aim of the work was to develop a reliable and simple technique for the determination of manganese in drinking water in the range of real concentrations, using anodic stripping voltammetry (ASV) at a mercury film electrode. Also to develop a simple and fast procedure for trace determination of Cr(VI) and Cr(III) in cement by catalytic adsorptive stripping voltammetry, using hanging mercury drop electrode.

The main tasks set to achieve the aim were as follows**:**

1. To research the methods of inverse voltammetry, electrodes and electrochemical experimental procedures,
2. To investigate determination of manganese and chromium by electroanalytical stripping methods and optimize,
3. To evaluate the characteristics of determination manganese and chromium by electroanalytical stripping methods – sensitivity and detection limits, and to investigate the influence of other metals,

4. To compare the method of manganese determination in drinking water by anodic stripping voltammetry with standardized spectrophotometric method using formaldoxime,
5. To develop a simple and fast procedure for trace determination of Cr(VI) and Cr(III) in cement.

Statements for defence:

1. The method of anodic stripping voltammetry can be used to determinate divalent manganese in drinking water in the range of real concentrations,
2. Determination of manganese by the method of anodic stripping voltammetry in drinking water is equivalent to the determination of manganese using standardized spectrophotometric methods with formaldoxime,
3. Determination of Cr(VI) by catalytic adsorptive stripping voltammetry using catalytic adsorptive Cr(III)-DTPA and NO_3^- ions system allow to obtain determinatio limit of 0,05 $\mu g\ l^{-1}$,
4. Catalytic adsorptive stripping voltammetry can be used to determinate different chromium forms Cr(VI) and Cr(III) in cement.

2. EXPERIMENTAL

2.1. Determination of manganese

A PU-1 polarograph in a square wave voltammetry mode (f = 25 Hz, V = 100 mV s^{-1}, ESW = 90 mV) was used for manganese accumulation / stripping and for the deposition of a mercury film. Voltammograms were recorded with an *xy*-recorder N 307.

Mercury films were deposited electrochemically on a 8 mm^2 glassy carbon electrode F 3500 (Radiometer) from stirred 50 mg l^{-1} Hg^{2+} ion solution in 0.05 mol l^{-1} HCl. The deposition potential and time were –1.1 V and 5 min, respectively. The surface of the glassy carbon electrode was thoroughly polished with 3 μm diamond paste and re-polished with alumina slurry (0.3 μm) before each experiment. After 10–15 measurements, the mercury film was wiped out from the glassy carbon electrode with wet filter paper, and after a short polishing with alumina slurry a new film was deposited. All potentials were measured against a saturated Ag/AgCl reference electrode. The auxiliary electrode was platinum wire.

The electrochemical cell was a glass beaker about 4 cm in diameter. The volume of the solution in the cell was 30 ml. The stirring of the solutions during the deposition was carried out by a magnetic stirrer.

The salts used in the experiments were of analytical grade: $MnSO_4 \cdot 5H_2O$, $Hg(NO_3)_2 \cdot H_2O$, $NaHCO_3$, $Fe(NO_3)_3 \cdot 9H_2O$, $CaCl_2$ (anhydrous), $MgSO_4 \cdot 7H_2O$. Manganese 1 g l^{-1} stock solution was prepared by dissolution of a weighed amount of manganese sulfate in 1 mol l^{-1} HCl. A formaldoxime solution was prepared from hydroxylamine hydrochloride (Fluka) and 35% formaldehyde solution (Sigma-Aldrich). Distilled water (specific conductivity κ = 5–8 μS cm^{-1}) was used throughout the study. All the experiments were carried out in nondeaerated solutions.

Drinking water samples from Antaviliai (AV) and Vingio parkas (VP) wellfields were taken from water-taps. The concentration of calcium and magnesium in drinking water samples was determined by ion chromatography. The alkalinity of drinking water samples was determined by potentiometric titration using hydrochloric acid.

2.2. Determination of chromium

Voltammetric measurements were carried out using a polarograph PU-1 in a square wave voltammetry mode (f = 25 Hz, V = 100 mV s^{-1}, E_{SW} = 90 mV). Voltammograms were recorded by *xy*-recorder N 307. A 303 SMDE static mercury drop stand controlled by polarograph PAR 174A (Princeton Applied Research) was used to form a hanging mercury drop electrode (HMDE). The surface area of the mercury drop was 1.16 mm^2. All potentials were measured against 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 κ = 5-8 $\mu S\ cm^{-1}$). Diethylenetriaminepentaacetic acid (DTPA) was obtained from Fluka. Stock standard solutions of Cr(VI) and Cr(III), concentration 1 g l^{-1} were prepared by dissolution in distilled water of the weighed amounts of K_2CrO_4 or $KCr(SO_4)_2 \cdot 12\ H_2O$, respectively. Before the voltammetric measurements the solutions were deoxygenated by purging with nitrogen.

The Portland cement CEM IIA-L42,5N made by Lithuanian company “Akmenės cementas AB” and purchased from supermarket in 2010 was used in chromium determination experiments.

Recommended procedures

Determination of Cr(VI) and total chromium in water extract of the cement. About 0.1 g of dry cement is weighted and added to 50 ml of distilled water for 24 hours. An aliquot of 0.1 ml is taken for Cr(VI) determination and pipetted into electrochemical cell with 14 ml of solution containing 0.15 mol l^{-1} CH_3COONa, 5 mmol l^{-1} DTPA and 0.7 mol l^{-1} $NaNO_3$. The pH of the mixture is adjusted to pH = 6 by acetic acid. The solution is deaerated by 8 min purging with nitrogen. A mercury drop is formed and accumulation at –0.9 V for 5-10 s is carried out from stirred solution. After equilibration time of 10 s without stirring the voltammogram is recorded scanning potential from –0.9 V to –1.4 V. Three consecutive additions of 1-2 $\mu g\ l^{-1}$ Cr(VI) each are performed for standard additions method procedure.

For the total chromium determination 0.1 mmol l^{-1} $KMnO_4$ is added to 10 ml of water extract of the cement and after 10-15 min the aliquot of 0.1 ml is pipetted to

electrochemical cell. The rest steps of the procedure are 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 is weighted and added to 5 ml of concentrated HNO_3 for 15 min. After the cement dissolution the extract is diluted to 50 ml by distilled water and filtrated. An aliquot of 0.1 ml is taken to electrochemical cell and the rest steps of the procedure for Cr(VI) determination is the same as for water extract.

For the total chromium determination 0.3 mmol l^{-1} $KMnO_4$ is added to diluted extract of the cement and pH is adjusted to pH = 4 by ammonia solution. The mixture is boiled for 3 min and after cooling an aliquot of 0.1 ml is pipetted to electrochemical cell. The rest steps of the procedure are the same as for Cr(VI) determination in water extract.

3. RESULTS AND DISCUSSION

3.1. Determination of manganese by anodic stripping voltammetry

Since manganese can be deposited on the electrode only at very negative potentials (about –1.7 V), acidic media cannot be used due to a hydrogen wave on the voltammograms. Therefore sodium hydrocarbonate solution was tested as a working medium. The 0.0036 mol l^{-1}concentration of $NaHCO_3$ was chosen because such alkalinity had been determined for drinking water from the tap. The background voltammogram and the voltammogram upon adding 10 μg l^{-1} of manganese are

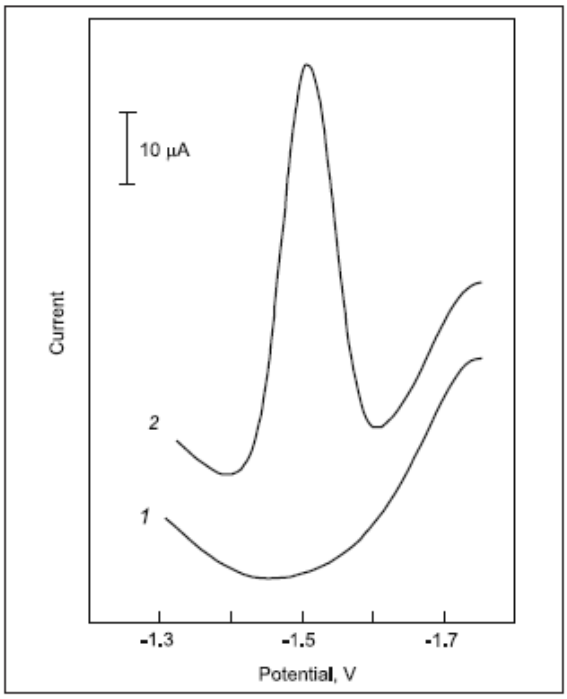

Fig. 1. Voltammograms of manganese in the 0.0036 mol l^{-1} $NaHCO_3$ solution. *1* – background voltammogram, *2* – 10 μg l^{-1} Mn^{2+}. Conditions: deposition potential -1.75 V, accumulation time 10 s.

presented in Fig. 1. One can see that the well-defined analytical signal of manganese with the peak potential about –1.5 V can be obtained after 10 s of accumulation.

The main accumulation parameters that influence the determination sensitivity are the deposition potential and accumulation time. Figure 2 illustrates the dependence of manganese analytical signals on the deposition potential. It can be concluded that the potentials for manganese accumulation should be more negative than –1.7 V. The value of –1.75 V was chosen since more negative potentials do not increase the analytical signals substantially but can influence negatively the durability of the mercury film. The effect of accumulation time on manganese analytical signals for two manganese concentrations is shown in Fig. 3. The dependence is clearly linear for the manganese concentration of 2.3 μg l^{-1}; however, it deviates from linearity substantially when the concentration is about ten times higher. The non-linear increase of the analytical signals with accumulation time at higher concentrations may be caused by the low solubility of manganese in mercury. Also, it should be noted that the intercepts on the *y*-axis after the extrapolation of both curves result from applying a 10 second rest period when the stirring is stopped in order to perform anodic stripping in the quiescent solution. Due to the low accumulation efficiency, the rest period is normally

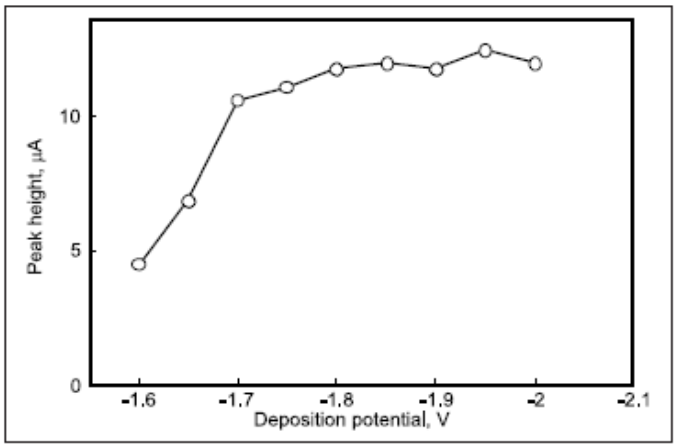

Fig. 2. Dependence of manganese analytical signals on deposition potential. Conditions: drinking water AV with addition of 20 μg l^{-1} Mn^{2}, accumulation time 5 s.

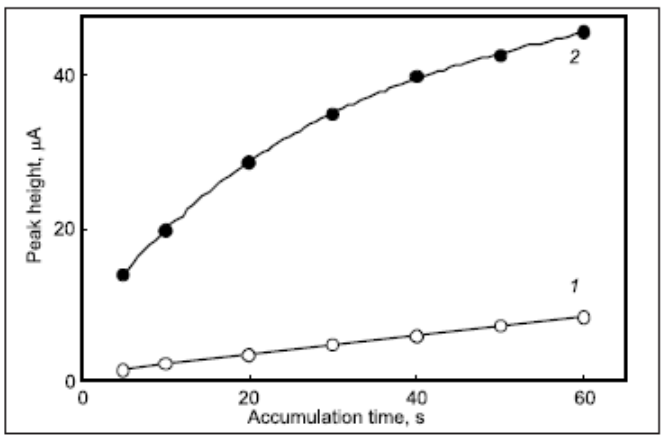

Fig. 3. Dependence of manganese analytical sinals on accumulation time in drinking water. *1* – drinking water AV containing 2.3 μg l^{-1} Mn^{2+}, *2* – the same water sample with addition of 20 μg l^{-1} Mn^{2+}. Condition: deposition potential -1.75V.

not attributed to the accumulation time, but it has some effect on the analytical signals, especially at short accumulation times.

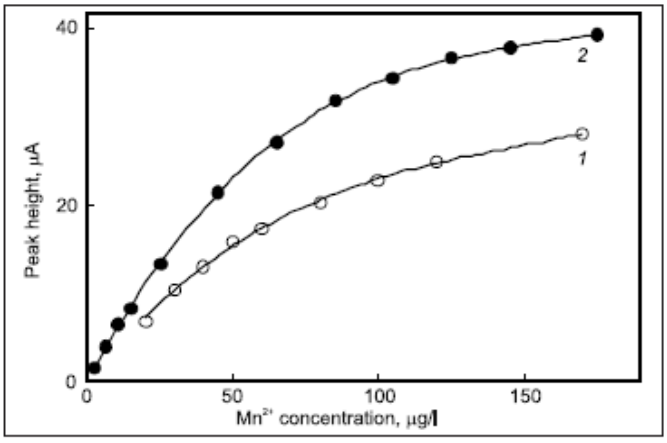

Fig. 4. Dependence of analytical signals on manganese concentration. *1* – 0.0036 mol l^{-1} $NaHCO_3$, *2* – drinking water AV containing 2.5 μg l^{-1} Mn^{2+}. Conditions: deposition potential -1.75 V, accumulation time 5 s.

The dependence of the analytical signals on manganese concentration in $NaHCO_3$ solution and drinking water AV sample is shown in Fig. 4. One can see that the shapes of the curves generally do not favour the quantification of manganese determination results. However, for the manganese concentration range up to 30–40 μg l^{-1}, the dependence may be considered as linear enough ($r \approx 0.9950$) for the method of standard additions. Since the reason for the non-linearity is the same as for the dependence on accumulation time, the linearity range, in principle, could be expanded by using a very short accumulation time.

However, the accumulation time shorter than 5 s is not convenient in practical analysis. Therefore, the possibility to dilute the samples having high manganese concentrations before the determination was examined. The sample of drinking water was spiked with 40–60 μg l^{-1} of manganese, and the concentration of manganese was determined by the method of standard additions after a fivefold dilution with 0.0036 mol l^{-1} $NaHCO_3$. The positive error in manganese determination could be expected in the case of deviation from the linearity of the dependence of manganese concentration on the analytical signal. The results of the determination presented in Table 1 show that dilution of a sample can expand the working range of determinable manganese concentrations substantially.

The repeatability of manganese analytical signals was tested by performing a series of 9–10 measurements in $NaHCO_3$ solution and drinking water samples for the manganese concentration range 1.3–50 μg l^{-1}. It has been shown that repeatability does not depend on manganese concentration, and the value of relative standard deviation does not exceed 0.05–0.06. The analytical signals obtained in the same solution using different

mercury films are more scattered; however, even in this case the relative standard deviation does not exceed 0.10. However, this higher relative standard deviation does not influence the accuracy of manganese determination because the same mercury film is used during the whole determination procedure by the method of standard additions. Normally, a mercury film is suitable for at least 10–15 manganese deposition/stripping cycles. The detection limit evaluation based on three standard deviations for the manganese concentration of 1.5 μg l^{-1} gives the value of about 0.4 μg l^{-1} for a 30 s accumulation time.

Table 1. Determination of manganese is spiked and dituted drinking water samples.

Condition: drinking water AV sample; fivefold dilution with 0.0036 mol l^{-1} $NaHCO_3$; deposition potential -1.75V; accumulation time 5s; initial concentration of manganese in water was determined by ASV method.

Mn^{2+} concentration in a sample, μg l^{-1}			RSD (n = 3)	Recovery, %
Initial	Added	Determined		
3.4	40	43.8	0.013	100.9
3.4	50	54.3	0.038	101.7
3.4	60	63.6	0.031	100.3

The determination of manganese in drinking water by the ASV method does not need any pretreatment of a sample, except that a water sample from the tap should be kept for 0.5–1 hour at room temperature so as to achieve an equilibrium with air gases. Ignoring this equilibration time can result in a worse reproducibility of the analytical signals. Manganese concentrations in such untreated drinking water samples have been found to remain stable for up to one week at room temperature.

To elucidate the possible interferences with the determination of manganese in drinking water, the influence of calcium, magnesium and iron ions was investigated. Normally, drinking water samples AV and VP contain about 60 mg l^{-1} of calcium ions, about 16 mg l^{-1} of magnesium ions and less than 95 μg l^{-1} of iron ions (the allowable maximum value for iron according to is 200 μg l^{-1}). Such concentrations of calcium, magnesium and iron ions were found to have no effect on manganese analytical signals; however, the further artificial increase of calcium and magnesium concentrations

gradually decreases the manganese analytical signals. For example, manganese analytical signals are roughly two times lower when calcium and magnesium concentrations 3–4 times exceed the natural level. It is possible that these major ions could form insoluble compounds at the surface of the mercury film when the near-electrode layer of the solution becomes more alkaline during the accumulation step. However, in spite of the lower analytical signals, the manganese concentration determined by the method of standard additions in drinking water samples with increased concentrations of calcium and magnesium ions is very close to that without addition of these major ions. One can see from Table 2 that a fourfold increase of calcium concentration and a sixfold increase of magnesium concentration practically do not influence the manganese determination results. Addition of 0.9 mg l^{-1} iron ions, i. e. increasing the iron concentration about ten times in comparison with natural concentrations, has no effect on manganese determination results, either (Table 2). Moreover, increasing iron ions to at least 1.2 mg l^{-1} did not decrease manganese analytical signals.

Table 2. The influence of major cations in drinking water on manganese.

Condition: drinking water VO sample; deposition potential -1.75V; accumulation time 5s.

Concentration of ions added	Mn^{2+} concentration, μg l^{-1} (RSD)		Recovery, %
	before	after	
240 mg l^{-1} Ca^{2+}	34.8 (0.04)	33.3 (0.02)	96
96 mg l^{-1} Mg^{2+}	33.7 (0.08)	32.5 (0.09)	96
0.9 mg l^{-1} Fe^{2+}	36.7 (0.06)	37.1 (0.07)	101

Although the speciation of manganese in the water environment depends on a complicated interaction between chemical and microbiological factors, the typical manganese species in groundwater are Mn^{2+} ions in weak complexes or ion pairs with major water anions. Therefore, only a few experiments have been performed to test the possible influence of other than Mn^{2+} species on the manganese determination results. It has been found that addition of ascorbic acid as a reducing agent to drinking water samples does not change the manganese determination results. This indicates that there

are no electrochemically inert manganese species in drinking water. By the way, manganese analytical signals obtained from the solution of permanganate ions are slightly higher; however, manganese determination results by the method of standard additions are the same as for the solution with Mn^{2+} species.

The results of manganese determination in drinking water samples by the ASV method were compared with those obtained by the standard photometric method employing formaldoxime. For this purpose, water-tap samples were divided to two parts, and manganese content was determined by the ASV and photometric methods. Results of a comparative determination are presented in Table 3. One can see that for drinking water VP samples in which manganese concentration ranges within 70–80 μg l^{-1} the results are really very close, whereas for drinking water AV (concentration range 2-6 μg l^{-1}) relative differences are higher. The statistical paired t-test shows that for a significance level $\alpha = 0.05$ the ASV and standard photometric methods are equivalent for both each type of drinking water samples and the total set of the results. On the other hand, it should be noted that for low manganese concentrations the photometric method can not be considered as very reliable due to its high relative standard deviations of repeated determinations. Another important advantage of the ASV method is its insensibility to iron ions, while their interference is very important for the photometric method.

Table 3. Comparison of the results of manganese determination in drinking water by anodic stripping voltammetry and photometric formaldoxime method.

Date	ASV method		Formaldoxime method	
	Mn, μg l^{-1}	RSD	Mn, μg l^{-1}	RSD
Antaviliai wellfield				
12 11 2009	5.8	0.05	6.5	0.27
16 11 2009	6.3	0.10	7.3	0.32
17 11 2009	3.8	0.08	9.7	0.10
18 11 2009	3.8	0.03	2.0	0.35
19 11 2009	2.3	0.16	2.4	0.21
Vingio parkas wellfield				
12 11 2009	81	0.07	74	0.02
16 11 2009	68	0.07	77	0.02
17 11 2009	70	0.11	70	0.02

18 11 2009	79	0.01	79	0.01
19 11 2009	78	0.05	81	0.03

3.2. Determination of chromium by catalytic adsorptive stripping voltammetry

Determination of Cr(VI) by catalytic adsorptive stripping voltammetry is extremely sensitive and together very complicated electroanalytical procedure. 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 Cr(III)-DTPA complex at the mercury electrode surface. During the stripping step the potential scan in the negative direction and electrochemical reduction of the adsorbed complex Cr(III)-DTPA to Cr(II)-DTPA is performed. Simultaneously the Cr(II) is immediately oxidized chemically back to Cr(III) by nitrate ions. As a result the substantial enhancement of the electrochemical reduction current occurs. The interference of Cr(III) to 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 to Cr(III) at the electrode surface.

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

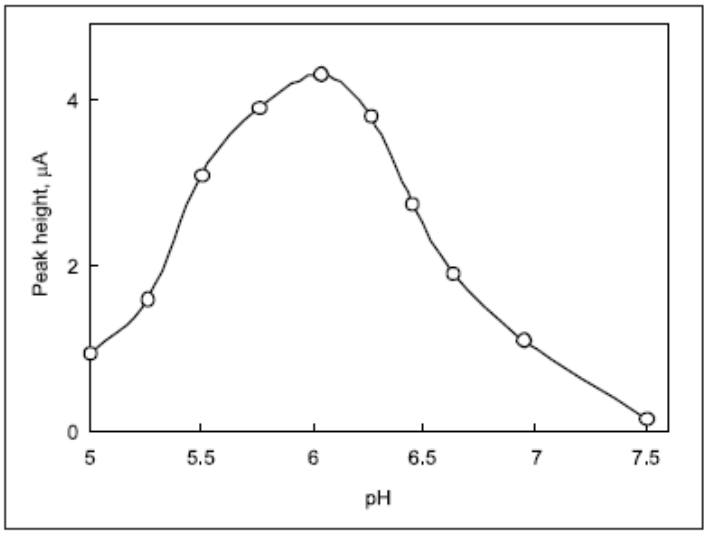

Fig. 5. The effect of pH on the analytical signals of Cr(VI). Conditions: 0.15 mol l^{-1} CH_3COONa, 7 mmol l^{-1} DTPA, 0.7 mol l^{-1} $NaNO_3$, 2 µg l^{-1} Cr(VI); accumulation potential -0.9 V, accumulation time 60 s.

The 0.15 mol l^{-1} sodium acetate solution has been chosen as a medium with sufficient buffering capacity for most of procedures in Cr(VI) determination. The pH of the medium was adjusted by the additions of acetic acid. Figure 5 illustrates the effect of pH on

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 the 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 after the addition of the ligand.

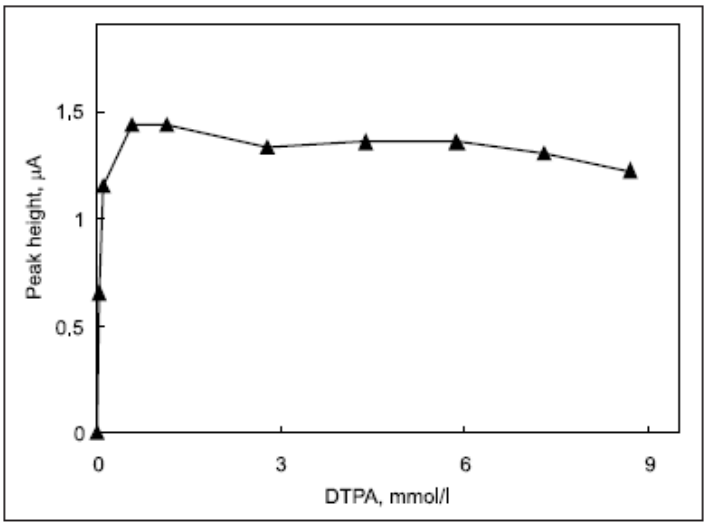

Fig. 6. The effect of DTPA concentration on the analytical signals of Cr(VI). Conditions: 0.15 mol l^{-1} CH_3COONa, 0.7 mol l^{-1} $NaNO_3$, 2 µg l^{-1} Cr(VI); accumulation potential -0.9 V, accumulation time 30 s.

The effect of the DTPA concentration on the chromium analytical signals is shown in Fig. 6. It is seen that at least 0.6 mmol l^{-1} DTPA is necessary to achieve high analytical signals when Cr(VI) concentration is 2 µg l^{-1}. Consequently, for the Cr(VI) concentrations up to 20 µg l^{-1} the optimal DTPA concentration range is about 5-7 mmol l^{-1}. It has been found that Cr(VI) analytical signals increase linearly when nitrate ion concentration is increased up to 1 mol l^{-1} $NaNO_3$. Therefore, 0.7 mol l^{-1} $NaNO_3$ concentration was used in 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 about –0.05 V potential. However, the most efficient adsorptive accumulation of Cr(III)-DTPA complex on the mercury surface occurs at about –0.9 V. This potential has been chosen as the accumulation potential for Cr(VI) determination. The analytical signals increase linearly with accumulation time up to about 5 min for the Cr(VI) concentration range 1-12 µg l^{-1}.

The background voltammogram and three voltammograms after consecutive additions of Cr(VI) under optimized conditions are shown in Fig. 7.

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 times do not exceed 1 min the dependencies are strictly

linear (r ~ 0.9998) at least up to 10 µg l^{-1} Cr(VI) concentrations. The repeatability of Cr(VI) analytical signals has been tested by performing the series of 10 measurements for chromium concentration range 0.5-25 µg l^{-1}. The relative standard deviation for 0.5-2.5 µg l^{-1} 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 µg l^{-1} gives the value about 0.05 µg l^{-1} for 3 min accumulation time.

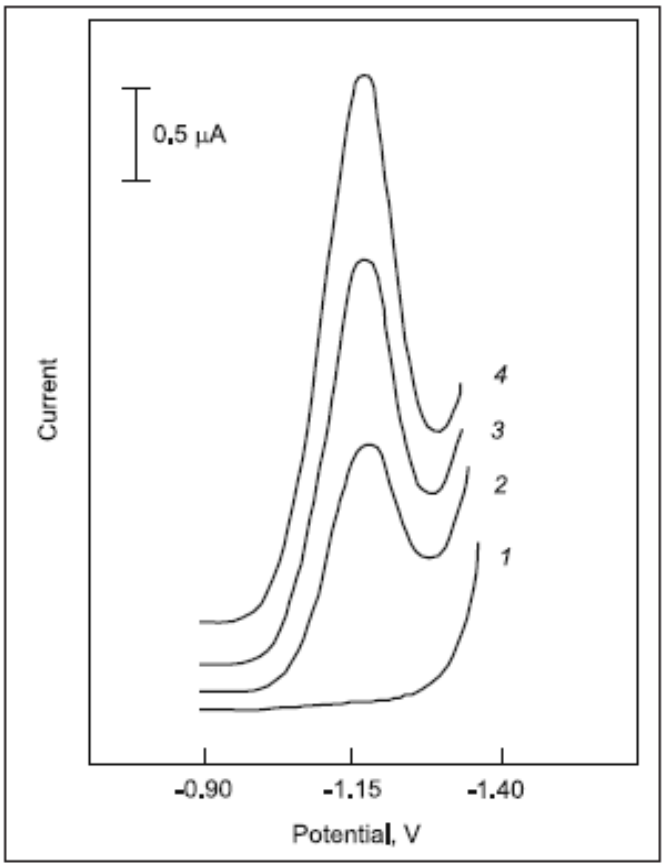

Fig. 7. Voltammograms of Cr(VI) under optimal conditions: *1* – background voltammogram, *2-4* – 1, 2 and 3 µg l^{-1} Cr(VI), respectively. Conditions: 0.15 mol l^{-1} CH_3COONa, 5 mmol l^{-1} DTPA, 0.7 mol l^{-1} $NaNO_3$, 2 µg l^{-1} Cr(VI); accumulation potential -0.9 V, accumulation time 30 s.

It has to 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 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 and then calculation 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.

The experiments using permanganate ions have shown that the oxidant influences also Cr(VI) analytical signals. It can be seen from Fig. 8 that immediately after addition of 0.05 mmol l^{-1} permanganate ions to Cr(VI) solution the analytical signals increase about four times and then come back to initial value in about 5 min. When 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 come back to 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 acetate medium. The discoloration of the solution when analytical signals come back to initial value confirms the reduction of permanganate ions. Thus it can be concluded that using permanganate ions for Cr(III) oxidation the excess of oxidant should be removed by keeping the solution for some time in room or higher temperature.

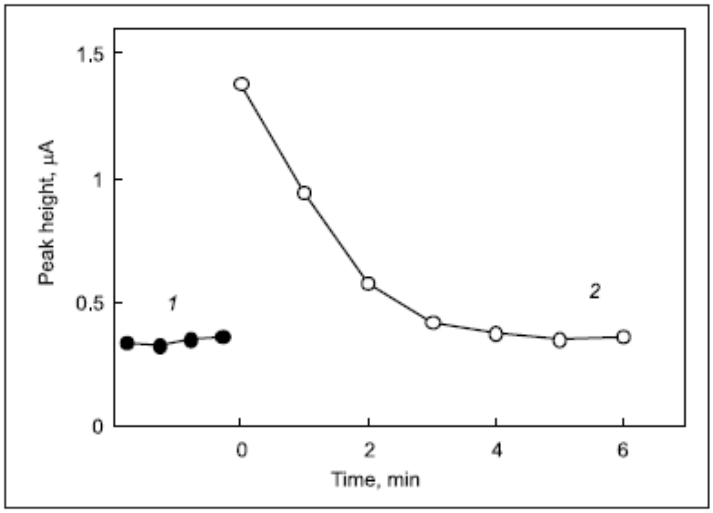

Fig. 8. The influence of permanganate ions on the analytical signals of Cr(VI). *1, 2* – analytical signals before and after addition of permanganate ions, respectively. Conditions: 0.15 mol l^{-1} CH_3COONa, 5 mmol l^{-1} DTPA, 0.7 mol l^{-1} $NaNO_3$, 4 μg l^{-1} Cr(VI), 0.05 mmol l^{-1} $KMnO_4$; accumulation potential -0.9 V, accumulation time 5 s.

Table 4 illustrates the influence of permanganate ion addition to Cr(III) and Cr(VI) determination results. It can be seen that in the case of Cr(VI) the same results are obtained both with and without permanganate ions addition. If the solution contains only Cr(III) species they are quantitatively oxidized and determined as Cr(VI). When the mixture of chromium species is analyzed the total chromium is determined after permanganate ions addition and only Cr(VI) are determined without use of oxidant. It should be noted that data in the Table 4 demonstrate also that chromium concentrations in the range 2-4 μg l^{-1} determined using method of standard additions do not differ more than ±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. In this work the water soluble Cr(VI) was leached from the cement sample by adding 0.1 g dry cement to 50 ml distilled water. After 24 hours an aliquot of 0.1 ml was taken for chromium determination by optimized CASV technique using a method of standard additions for quantification. It can be seen from the

Table 5 that the difference between Cr(VI) and total chromium values determined in the extract is not statistically significant taking into account the 95% confidential intervals of the results. Thus the water extractable Cr(VI) in dry cement can be estimated as about 13 μg g^{-1} and this value exceeds the 2 μg g^{-1} limit set by 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, possibly, the reducing additives were not used in the production of this type of the cement.

Table 4. Influence of permanganate ion addition on Cr(III) and Cr(VI) determinations results

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 5 s.

Added			Determined
Cr(VI), μg l^{-1}	Cr(VI), μg l^{-1}	Cr(VI), μg l^{-1}	Cr(VI), μg 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 5. Determination of Cr(VI) and Cr(III) in water and nitric acid extracts of cement

Conditions as decribed in Procedures.

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

Another extraction technique used was dissolving of the 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 of the negligible amount of insoluble silicates by filtration an aliquot was taken for chromium determination as in the case of

water extract. It is seen from the Table 5 that Cr(VI) concentration determined in the nitric acid extract does not differ significantly from value obtained for water extract. However, the total chromium concentration increased to about 109 $\mu g\, l^{-1}$, i.e. about fourfold in comparison with water extract. Consequently, Cr(III) amount in the nitric acid extract is about 83 $\mu g\, l^{-1}$ 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

1. Anodic stripping voltammetry using a mercury film electrode can be successfully used for manganese determination in drinking water samples. The working range of determinable manganese concentrations can be expanded up to a few hundred μg l^{-1} by dilution of samples. The detection limit for a 30 s accumulation time is about 0.4 μg l^{-1}, and the relative standard deviations in the working range of manganese concentrations do not exceed 0.10. Calcium and magnesium ions at real concentrations do not interfere directly with manganese determination.
2. A comparison of the ASV method with the standard photometric method for drinking water analysis has shown the equivalence of both methods; however, the ASV method can be used for the determination of low manganese concentrations and is insensitive to iron ions in water samples.
3. The catalytic adsorptive stripping voltammetry using hanging mercury drop electrode can be successfully used for determination of chromium species in cement samples and this technique is simple, fast, sensitive and low-cost. The concentrations of chromium in the electrochemical cell even after dilution of the cement extracts are of micrograms per liter range and this far exceeds the detection limit for Cr(VI) of 0.05 μg l^{-1}. Due to this situation the high reproducibility and short total duration of analysis can be achieved.
4. The total chromium and Cr(III) concentrations can be determined after the quantitative chemical oxidation of Cr(III) to Cr(VI) by permanganate ions.

THE LIST OF ORIGINAL PUBLICATIONS BY THE AUTHOR

Articles in journals

1. E. Panaščikaitė, S. Armalis, Determination of manganese in drinking water by anodic stripping voltammetry at a mercury film electrode. *Chemija*, vol. 22, no. 1, p. 41-45 (2011).

2. E. Panaščikaitė, I. Latvėnaitė, S. Armalis, Determination of chromium in cement by catalytic adsorptive stripping voltammetry. *Chemija*, vol. 22, no. 4, p. 210-215 (2011).

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1. **E. Panaščikaitė**, I. Latvėnaitė, S. Armalis, Determination of manganese by the method of anodic stripping voltammetry in waters, Thesis of Chemistry and Technology of Inorganic Compounds Conference, Kaunas (2008).
2. **E. Panaščikaitė**, S. Armalis, Determination of manganese by stripping voltammetry in drinking water, Thesis of Chemistry Conference, Vilnius (2009).
3. **E. Panaščikaitė**, S. Armalis, Determination of chromium by catalytic adsorptive voltammetry in cement, Thesis of Chemistry and Technology of Inorganic Compounds Conference, Kaunas (2011).

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2000-2004 studies at the Faculty of Chemistry in Vilnius University – Bachelor of Science in chemistry.

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SANTRAUKA

Pasiūlytas mangano nustatymo metodas geriamajame vandenyje inversinės voltamperometrijos metodu naudojant gyvsidabrio plėvelinį elektrodą. Manganui nustatyti vandens mėginio nereikia chemiškai apdoroti. Optimalios nustatymo sąlygos: kaupimo potencialas –1,75 V, kaupimo trukmė 5–30 s, anodinis tirpinimas atliekamas naudojant kvadratinės bangos voltamperometriją. Mangano aptikimo riba kaupiant jį 30 s yra apie 0,4 μg l^{-1}, o santykiniai standartiniai nuokrypiai darbiniame koncentracijų intervale ne didesni kaip 0,10. Realios kalcio, magnio ir geležies jonų koncentracijos geriamojo vandens mėginiuose netrukdo nustatyti manganą. Metodo palyginimas su standartiniu fotometriniu metodu parodė, kad jie yra ekvivalentiški, tačiau elektrocheminis metodas gali būti taikomas labai mažoms mangano koncentracijoms nustatyti, be to, jam netrukdo geriamajame vandenyje esantys geležies jonai.

Chromo nustatymui cemente gali būti naudojamas katalitinės adsorbcinės voltamperometrijos metodas naudojant kabančio gyvsidabrio lašo elektrodą. Terpės sudėtis Cr(VI) nustatyti: 0,15 mol l^{-1} CH_3COONa, 5 mmol l^{-1} dietilentriaminpentaacto rūgšties, 0,7 mol l^{-1} $NaNO_3$, pH = 6. Optimalios votamperometrijos 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 neviršija 3%. Iš cemento mėginių chromas išekstrahuojamas vandeniu arba azoto rūgštimi. Bendras chromo kiekis nustatomas kiekybiškai oksiduojant Cr(III) iki Cr(VI) į cemento ekstraktą pridėtais 0,1-0,3 mmol l^{-1} permanganato jonais. Cr(III) koncentracija apskaičiuojama kaip skirtumas tarp bendro chromo ir Cr(VI) koncentracijos.