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METROLOGICAL CHARACTERISTICS AND COMPARISON OF ANALYTICAL METHODS FOR DETERMINATION OF CHROMIUM TRACES IN WATER SAMPLES

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Abstract

The analytical performance of the inductively coupled plasma mass spectrometry, absorption spectrophotometry and catalytic adsorptive stripping voltammetry has been compared for trace chromium determination in water samples. The following metrological characteristics were calculated: trueness, precision, linear analytical range, detection and quantification limits. The limit of detection, and the limit of quantification were calculated by the ULA method, which takes into consideration the uncertainties of the slope and the intercept of the calibration plot, designed especially for this purpose, as well as by traditional way as the 3- and 10-fold multiply of the blank standard deviation.

The possibility of the speciation study of both chromium oxidation states, Cr(VI) and Cr(III), has also been considered. The ICP MS procedures were applied to the determination of total chromium in river water samples. The catalytic adsorptive stripping voltammetric method with DTPA and nitrate is sufficiently sensitive for the determination of chromium traces at the level of 0.01 to 0.1 μg/L and suitable for the chromium speciation studies.

Key words: chromium, speciation, ICP MS, catalytic adsorptive stripping voltametry, adsorption spectrophotometry

Introduction

Chromium contamination of surface and ground waters is a persisting problem in many countries. Chromium(III) is an important microelement for plant and animal nutrition and essential for the maintenance of glucose as well as for the lipid and protein metabolism. With regard to human health, chromium(III) is a required nutrient, with 50 to 200 μg per day recommended for adults.[1] On the contrary, chromium(VI) is toxic and

carcinogenic for the human body,[2,3] leading to lung cancer, skin allergy and probably also to asthma and renal diseases. A toxic effect for the biological systems is attributed to the ability of chromium(VI) to migrate across the cell membrane, thus enhancing the intracellular chromium concentration.

Total chromium content typically ranges from 0.1 to 0.5 μg/L in seawater, from 0.3 to 0.6 μ g/L in non-polluted river and surface water, 5–50 μg/L in polluted river water, whereas it can reach 200 μg/L in severely polluted water systems.[4] For the crops irrigation, the U.S. Environmental Agency recommended limit for chromium is 100 μg/L. With regard to drinking water, chromium(VI) is regulated under the 50 μg/L maximum contaminant level (MCL) for total chromium.[5,6] However, total chromium determination does not provide sufficient information about possible health hazards and chromium speciation methods are urgently needed. The U.S. Department of Health Services will be soon adopting an MCL that is specific for chromium(VI).[1]

Results of monitoring drinking water sources by public water systems in California show nearly 70 percent of sources with chromium(VI) below the 1 μg/L detection limit for purposes of reporting; most of the reported detections are at or below 5 μg/L.[1] Hence, the determination of chromium traces as well as its speciation in water samples is a very important task because of the environmental impact, toxicity and bioavailability of chromium. Due to a rather low chromium concentration in natural water and the complex character of the water matrix, sensitive and accurate instrumental methods are required for its analysis. Very frequently also proper pre-treatment procedures are needed involving separations and/or pre-concentration steps.

The various instrumental techniques for the Cr(VI) and Cr(III) trace determination may be divided into two main kinds: (1) Valence–specific techniques, which enable the direct measurement of Cr(VI) in the presence of Cr(III), such as molecular absorption spectrophotometry or voltammetry.[7,8] These methods are based on a different ability of Cr(III) and Cr(VI) to form complexes. (2) Valence-non-specific methods, which enable only the determination of total chromium. The speciation study by means of the above methods require the preliminary valence-specific separation of both chromium forms or the selective removal of one chromium species from the sample, followed by the subsequent non-specific measurement of the separated form, mostly using the Flame or Electrothermal Atomic Absorption Spectrometry (AAS, ET AAS), Inductively Coupled

Plasma Atomic Emission Spectrometry (ICP AES), Inductively Coupled Plasma Atomic Mass Spectrometry (ICP MS), or sometimes also X-ray Fluorescence Spectroscopy (XFS) and Neutron Activation Analysis (NAA). The separation step comprises mainly extraction, ion exchange chromatography or co-precipitation procedures, as well as sorption on membranes or in micro columns in the flow systems.[9-12]

For the two last years our team investigated the transformation cycle of the chromium species originating from tannery wastewater in the upper Dunajec river catchment (Carpatian Mountains, South Poland) where mainly the contents of total Cr, Mn and Fe in river samples, suspended matter, bottom sediments and water outflow from the wastewater treatment plant were measured.[13-15] Moreover, the oxidation state speciation study of the Cr(VI) and Cr(III) was undertaken in water samples from the rivers, streams and reservoirs of the catchment, in which the concentration of total chromium ranged from ca. 0.1 μg/L in unpolluted mountain streams to 100 μg/L in the most polluted part of the Dunajec main river. In order to select the optimal analytical methods that would enable quick, efficient and sensitive determination of Cr species in the investigated samples, several spectrometric and electrochemical techniques were tested. This paper presents chemometric characteristics and comparison of the analytical performance of the investigated methods for the total Cr as well as for Cr(VI) determination in water samples, used directly without any preconcentration or separation steps.

With regard to total chromium determination the ICP MS method is applicable in a broad range of chromium concentrations; moreover, it is sufficiently fast and enables a quick determination of several replicates, which is important from metrological aspects. The limit of detection and the limit of quantification are calculated here by the ULA method, recommended by IUPAC.[16,17] In this approach, the uncertainties of the slope and the intercept of the calibration plot as well as the uncertainty of the mean blank signal are taken into consideration.

Since the ICP MS method is valence-non-specific, the speciation study of both chromium oxidation states, Cr(VI) and Cr(III), is performed by catalytic adsorptive stripping voltammetry (CAdSV). For the same purpose, but at a higher concentration level, spectrophotometry with 1,5-diphenylcarbazide is also considered.

Experimental

Reagents and Samples

All used reagents were of analytical grade. Chromium(VI) and Cr(III) standard stock solutions (1 g/L) were obtained from Merck and diluted as required. All dilutions and sample preparations were made using deionised water (Millipore, 18.2 Mohm resistivity, or an ion-exchange system Cobrabid-Aqua, Warszawa, Poland, conductivity below 0.08 μS/cm). Diethylenetriammine-N,N,N',N'',N''-pentaacetic acid (DTPA) and sodium nitrate were purified by recrystallisation from ethanol and water, respectively. Certified reference material SRM 1643d Trace Elements in Water (NIST) was used for determination of trueness in order to validate the used analytical method. Nant d'Avril is a small river located in the west part of Geneva canton, from which the environmental water sample was collected and was used as the internal in-house reference material coded by the same name.

Apparatus

The ICP MS HP 4500 spectrometer was applied for the determination of the total chromium in the selected water samples using a Cr^{53} standard calibration graph method. Digital spectrophotometer Spekol 11 with 1 cm cuvette was used for spectrophotometric measurements. Electrochemical experiments were carried out with a multipurpose electrochemical analyzer EA9 (Unitra-MTM, Krakow, Poland). The electrochemical cell consisted of a Control Growth Mercury Drop Electrode with the surface area of 1.2 mm^2 as a working electrode used in a HMDE mode; a silver-silver chloride (3 mol/L KCl) and a platinum wire were used as the reference and auxiliary electrode, respectively. UV Digestor (Mineral, Warszawa) was applied to oxidize the Cr(III) to Cr(VI) in water samples. All spectrophotometric and electrochemical experiments were performed at room temperature.

Analytical procedures

Standard filtration procedure.

The water samples were collected in cleaned polypropylene bottles and filtered through a 0.45 μm cellulose acetate membrane filter in the Sartorius device. The filtrate

was divided into three subsamples: (1) One part of the filtered samples was acidified with nitric acid to the final concentration of 0.5 mol/L and used for the ICP MS analysis. (2) Another subsample with natural pH from 7.9 to 8.5 was used for Cr(VI) voltammetric analysis without any additional pre-treatment. The samples were transported and stored at 4 °C in a refrigerator and the determination was performed within 20 h after sampling. (3) In the third subsample the total chromium content was determined after 4 h UV irradiation. In case of storing for a longer time (up to 3 days) the samples were acidified with HCl to pH = 2 for the sample preservation. Before the UV-irradiation process they were neutralized with diluted NaOH to pH 7.2.

ICP measurements.

In the ICP MS measurements the ^{53}Cr isotope was used for total chromium determination using the external standard calibration procedure. All instrumental parameters such as forward power, plasma torch position, nebulizer, plasma and auxiliary gas flows were optimised for the best signal of chromium to noise ratio. The ^{103}Rh solution containing 50 μg/L Rh was used as an internal standard to correct the signal drift and long term instrumental instability.

Spectrophotometric determination of Cr(VI) and total Cr.

For total chromium determination 1.0 mL of sulphuric acid (1+9) was added to the solution and Cr(III) was oxidized to Cr(VI) by adding 0.5 g of ammonium persulfate and 1 mL 0.1 mol/L silver nitrate. The solution was boiled for 20 min to complete the oxidation of Cr(III) to Cr(VI) and to decompose the excess of persulfate and then allowed to cool down. After adding 1.0 mL of sulphuric acid (1 + 9) and 1 mL 0.25% of 1,5-diphenylcarbazide (DPC) and subsequent dilution with deionized water to 50 mL, the concentration of Cr(VI) was determined in two sample aliquots: (1) the original one containing Cr(VI) in the presence of Cr(III), (2) the other after the oxidation step - containing only Cr(VI). The calibration curve A = f(c) for Cr(VI) was prepared using a blank solution and nine standard solutions of Cr(VI) in a concentration range 50-950 μg/L.

CAdSV procedure.

The determined water sample was mixed in an electrochemical cell with necessary reagents to obtain 10 mL of solution containing 0.1 mol/L acetic buffer of pH = 5.8 and

0.25 mol/L potassium nitrate. The solution was deaereated with argon for 5 min, then DTPA was added to final concentration 0.01 mol/L and a pre-treatment procedure was applied (new drop generation, 20 s adsorptive pre-concentration, 5 s equilibration). Quantitative measurements were then performed using the differential pulse mode (DPV) and standard addition procedure. Accumulation was performed at –0.95 V for 20 s with stirring, then after a 5 s resting period the voltammograms were recorded in the cathodic direction from –0.95 to –1.39 V. Further experimental parameters were as follows: step potential E_s = 2 mV, pulse potential ΔE = 50 mV, scan rate v = 0.025 V/s. After each standard addition the solution was deaereated at least one minute.

UV-digestion procedure.

After setting the sample pH to 7.2, the decomposition of the inert Cr(III) complexes and organic material present in natural water samples together with the oxidation of Cr(III) to Cr(VI) were performed by a 4 h irradiation step. Then the total chromium determination was made by CAdSV according to the protocol proposed earlier.[18]

Results and Discussion

Internal QC applied to the ICP MS chromium analysis

Internal Quality Control for the ICP MS chromium analysis of water samples was based on the Harmonised Guidelines for Internal Quality Control in Analytical Chemistry.[19] The choice of the ICP MS method for such a purpose was influenced by the fact that its range of application and metrological properties are the most appropriate for the chromium determination in various water samples - as it follows from further text. The following metrological characteristics were calculated: trueness, apparent recovery, precision (repeatability and reproducibility), linear response range, detection and quantification limits.

Accuracy expresses the closeness of a result to the true value. Two its components were studied separately: trueness and precision. For this study the standard reference material 1643d and the environmental sample *Nant d'Avril* were applied, which was used as is or fortified by the Cr(III) standard addition after acidification with 1% *suprapur* nitric acid.

Analytical calibration

Calibration curves for chromium determination by ICP MS were made by means of the Cr(VI) standard solutions prepared in 1% suprapur HNO_3 in deionized water in the following ranges: (a) 0.05–4.1 µg/L with 8 standard solutions, with the coefficient of determination r^2= 0.9999 received in linear regression analysis, (b) 0.05–1.0 µg/L, 11 standard solutions, with r^2= 0.9999, (c) 0.05–0.70 µg/L, 8 standard solutions, with r^2= 0.9990, (d) 0.70–15.0 µg/L, 18 standard solutions, with r^2= 0.9999, (e) 0.05–20.0 µg/L, 44 standard solutions, with r^2= 0.9971. The intercept on the signal axis (counts per second) was negligible and proved statistically insignificant in all evaluated regressions. When ^{52}Cr was used instead of ^{53}Cr, then in all cases the intercept was clearly larger and r^2 was lower, therefore ^{53}Cr is much more convenient for the ICP MS determination of chromium in water samples.

A well fitted linear calibration dependence was observed also in case when 10 standard additions comprising of 1–10 µg/L added Cr(III) were made to the Nant d'Avril environmental sample, with r^2= 0.9923.

Trueness

Trueness,[20] which expresses the closeness of agreement between the average value of the considered laboratory test and an accepted reference value, was evaluated in two ways. First it was evaluated in terms of bias through the analysis of the SRM 1643d, which contains filtered and acidified water and 26 elements. The chromium content is 18.53 ± 0.20 µg/L, where the latter value denotes expanded uncertainty, whose level of confidence is ca. 95%.[21] The found average of twelve ICP MS measurements was 18.66 ± 0.35 µg/L of total Cr, where the interval ± 0.35 means the confidence interval with 95% probability. A simple comparison of the received result with the reference value reveals that the ICP MS method provides true results.

The second way of the trueness evaluation was made by means of the *recovery* study. The apparent recovery, *R*, is the ratio of the concentration found by the considered method, *c*, versus the reference value, c_{ref}, and can be calculated as:[22]

$$R = (c/c_{ref}).100 \qquad (1)$$

This expression is valid when the analyte is spiked to matrix blanks. We performed this task by various dilution of the SRM 1643d preparing in this way eight solutions with four different concentration in the range ca. 1–10 μg/L. For all reference samples obtained in this way, first the apparent recovery was calculated, then the mean $\bar{R}$ and the standard deviation s(R) were found. Trueness was finally assessed by comparing the found mean apparent recovery $\bar{R}$ with 100% using the *t*-test:

$$t = |100 - \bar{R}| \cdot \sqrt{n} / s(R) \qquad (2)$$

With the found $\bar{R}$=100.68 and $s(R)/\sqrt{n}$ = 2.53 the calculated *t*- value was 0.2702, which was much less then the critical $t(0.05, 7)$ = 2.3646, so that the true results were confirmed also in this way.

Precision

Precision expresses the closeness of agreement between independent test results obtained under stipulated conditions[20,22] and should be obtained by using the standard reference material or fortified sample blanks at different concentrations across working range. The most common way to express precision is in a form of standard deviation, however, it can be expressed also as a variance (squared standard deviation) or a coefficient of variation (relative standard deviation in per cents).

The key problem is definition of experimental conditions, which depend on several factors (e.g. the operator, the equipment, the laboratory, day of measurement). The calculated precision depends on the changed factors. One extreme case of precision is repeatability when no factor is changed and experiments are made without a break. The second extreme is reproducibility when all the important factors are changed; such a kind of precision can be reached only by inter-laboratory tests. However, there exist some kinds of within-laboratory precision where one or more factors are changed except the change of the laboratory. They are called intermediate precision,[22] inter-day repeatability (when only the day is changed) and within-laboratory reproducibility, as well. When calculating the intermediate precision it has to be known, which factor(s) is/are changed. We have calculated the intra-day repeatability (no factor changed) and the inter-day repeatability (only time changed), performing the Cr analyses in the same day and in three consecutive days, respectively.

Although the repeatability can be calculated separately, it is possible to achieve simultaneously the intra-day and inter-day repeatabilities by the Analysis of Variance (ANOVA) applying a two-factor fully nested experimental design.[22,23] For this purpose we have used Nant d'Avril environmental sample without and with a chromium spike.

Table 1. Scheme of the spreadsheet calculation of the repeatability variance s_r^2.

D	x_{11}			
a	x_{12}			
y	.	$\overline{x}_1$	$S_1 = \sum_{i=1}^{n}(x_{1i} - \overline{x}_1)^2$	
	.			
1	x_{1n}			
D	$x_{1,2}$			
a	x_{22}			
y	.	$\overline{x}_2$	$S_2 = \sum_{i=1}^{n}(x_{2i} - \overline{x}_2)^2$	$s_r^2 = \frac{\sum_{j=1}^{p} S_j}{p(n-1)}$
	.			
2	x_{2n}			
D	x_{31}			
a	x_{32}			
y	.	$\overline{x}_p$	$S_p = \sum_{i=1}^{n}(x_{pi} - \overline{x}_1)^2$	
	.			
p	x_{pn}			

The experimental design is shown schematically in Table 1 - ten replicate measurements (n=10) were made in each run, one run was made in each of three days (p=3). The found grand mean is 1.757 µg/L Cr, the repeatability standard deviation is 0.043 µg/L and the corresponding coefficient of variation is 2.45%.

Using the same experimental design and the expressions described in Table 2 the within-laboratory precision was calculated as the variance s_w^2, standard deviation s_w=0.123 µg/L and the coefficient of variation $s_w / \overline{x}_G$ = 6.99%.

The repeatability was finally determined also for the chromium(III) spiked *Nant d'Avril* sample but this time in only one run (p=1). The found mean concentration, the repeatability standard deviation and the coefficient of variation values are 10.84 µg/L,

0.131 µg/L and 1.21%, respectively. The found value of the repeatability coefficient of variation is here significantly smaller than its value for the unspiked sample, on the other hand the repeatability standard deviation is significantly larger. Even though no special variance homogeneity study was performed, the found behaviour testifies that the variance is not homogeneous and is moderately growing with the chromium concentration.

Limits of detection and quantification

A special calibration experiment was designed for determining the limit of detection (LOD) and the limit of quantification (LOQ). Ten replicate measurements were made for the blank as well as eight standard solutions so that altogether 90 signal measurements were performed. The upper limit approach to the LOD and LOQ calculations is described in detail in Ref. 16 and 17, and is depicted in Figure 1 which brings the magnified part of the calibration – only first calibration points located in the vicinity of both limits are shown. The LOD and LOQ calculation was made as follows:[16,17]

Table 2. Calculation of different kinds of the precision variances.

Variance	Way of calculation	f *)	Equation number
Repeatability, s_r^2	$\frac{\sum_{j=1}^{p}\sum_{i=1}^{n}(x_{ji}-\bar{x}_j)^2}{p(n-1)}$	$p(n\text{-}1)$	(3)
Total, s_G^2	$\frac{n\sum_{j=1}^{p}(\bar{x}_j-\bar{x}_G)^2}{p-1}$ *)	p-1	(4)
Between run, s_b^2	$\frac{s_G^2-s_r^2}{n}$	p-1	(5)
Intermediate precision (within-laboratory), s_w^2	$s_b^2+s_r^2$	pn-1	(6)

*) f denotes the number of degrees of freedom; $\bar{x}_G$ denotes the grand mean, $\bar{x}_G = (\sum_{j=1}^{p}\bar{x}_j)/p$.

$$\mathrm{LOD} = \{\, t(\nu, 1\text{-}\alpha)\, s_{yx} / q_1 \,\} [1 + 1/n + \bar{c}^2 / \sum_{i=1}^{n}(c_i - \bar{c})^2]^{1/2} \quad (7)$$

$$\mathrm{LOQ} = 3\{\, t(\nu, 1\text{-}\alpha)\, s_{yx} / q_1 \,\} [1 + 1/n + \bar{c}^2 / \sum_{i=1}^{n}(c_i - \bar{c})^2]^{1/2} \quad (8)$$

where q_1 denotes the slope, s_{yx} is the residual standard deviation (the standard error of regression), $\bar{c}$ and c_i is the mean calibration standard concentration and the i-th calibration standard concentration, respectively. The found LOD is 0.0297 µg/L and the LOQ is 0.0892 µg/L.

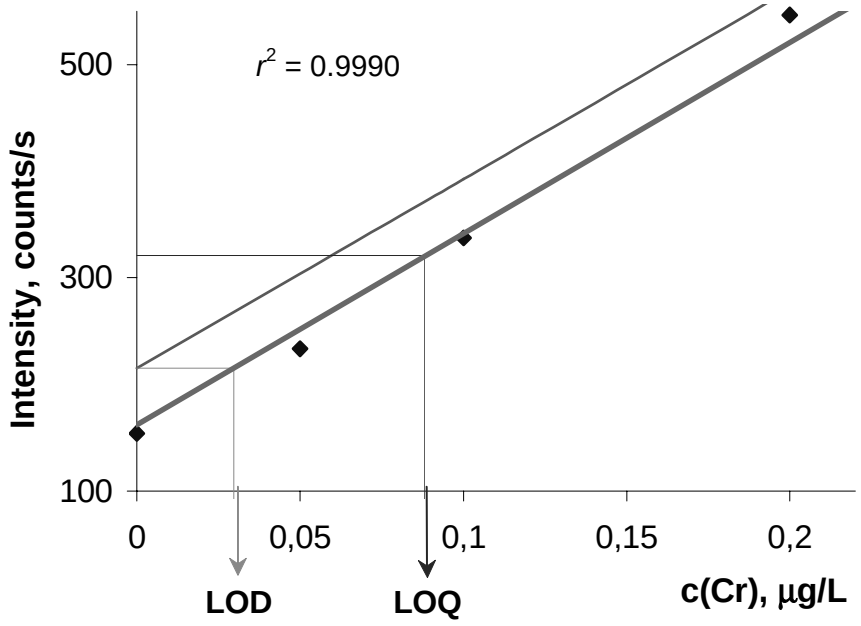

Figure 1. First part of the calibration line for the chromium determination in acidified water by ICP MS (Cr^{53} isotope was measured). The upper line (thin) above the calibration line (thick) limits the one-sided upper confidence band constructed for 99% probability level. Each point represents the mean of ten replications. The intensity axis expresses the gross signal (no blank correction).

For the sake of comparison, the LOD and LOQ values were calculated also by the traditional way – using the threefold and tenfold blank standard deviation approach. This way of computing has led to very low results; the found LOD is 0.0042 µg/L and the LOQ is 0.014 µg/L. The most probable explanation is a very low blank standard deviation, s_b. The mean signal of ten replicate ICP MS measurements of the chromium free solution was 154.3 counts/s and the corresponding s_b = 2.48 counts/s. Details of a possible failure in the traditional way of the LOD/LOQ determination are discussed in.[16]

Taking into account the LOQ obtained by the ULA and excellent linearity of all calibration lines (mentioned in *Analytical calibration*) it can be concluded that the linear range for the ICP MS chromium determination is between 0.090 and 20 µg/L (or more).

Speciation

The speciation analysis of chromium occurring in environment (including the determination of organic Cr(III) complexes) is extremely important because of a great difference of Cr(VI) and Cr(III) in the toxicity and bioavailability of these forms. The most serious problem encountered in chromium speciation is to elaborate an analytical procedure, which does not change the ratio of the chromium oxidation states. In acidic solutions, especially in the presence of dissolved organic compounds and sulfides, the risk of the Cr(VI) to Cr(III) reduction exists. In an alkaline medium on the contrary, the Cr(III) oxidation may occur. Hence, the selection of an appropriate analytical method should take into consideration the type of matrix (natural water, effluents, sediments, biological materials, etc.), the concentration level of the chromium forms and the presence of substances, which may disturb the chemical equilibrium between the chromium oxidation states.

Determination of Cr(VI) by spectrophotometry.

Higher concentrations of chromium(VI) can be effectively determined with DPC, which in acidic media of 0.1 to 0.2 mol/L H_2SO_4 forms with Cr(VI) a highly coloured violet complex.[7] At the absorption band maximum 546 nm, we have found the molar absorption coefficient ε = 41700 L mol^{-1} cm^{-1}. Using the ULA approach, the found LOD and LOQ in a 1 cm cuvette are 41.5 µg/L and 125 µg/L Cr(VI), respectively. In the concentration region 40–950 µg/L the calibration lines exhibited a very good linearity (r^2 = 0.9986); the same linear range was confirmed also by inspecting residuals.

With regard to speciation aspects it is important that chromium(III) does not interfere but all possible Cr(III) oxidants do interfere.

Catalytic adsorption stripping voltammetric determination of Cr species.

The CAdSV method couples the adsorptive in-situ preconcentration of the Cr(III)-DTPA complex on the electrode surface with the utilization of the catalytic action of nitrate ions, i.e. a catalytic reaction between reduced Cr(III)-DTPA complex and nitrate ions. This combined effect enables the enhancement of sensitivity and a considerable decrease in the limit of quantification of Cr determination.[8,24] The faradaic current, I_f, as the final analytical signal, is the product of a dual amplification effect: an interfacial

accumulation and a catalytic reaction, so that I_f = [adsorptive enrichment] × [catalytic enhancement].

We confirmed, as was earlier observed,[8] that the CAdSV peak current vs. time dependences obtained for two solutions containing the same concentration Cr(VI) or Cr(III) in 0.1 mol/L acetic buffer (pH 5.8) and 0.01 mol/L DTPA are very different. The decay of the Cr(VI) signal was rather small, about 15% per hour only, whereas the Cr(III) signal completely vanished after 30 min. It is evidenced that the complex Cr(III)-DTPA, which is formed by Cr(III)* in statu nascendi as a product of the electrochemical Cr(VI) reduction, is more electrochemically active (with regard to further reduction producing a Cr(II) complex) than the Cr(III)-DTPA obtained spontaneously. The suggested mechanism of the reactions taking place in the bulk phase and the electrode surface, respectively, is schematically presented in Figure 2.

In the presence of nitrate ions the reoxidation process occurs and the Cr(III)-DTPA complex is regenerated. The Cr(III)-DTPA complex formed spontaneously in the solution exhibits lower adsorption and catalytic activity, its signal rapidly decreases with time and finally disappears as a result of a slow structural change. The kinetically and perhaps also thermodynamically stable Cr(III) complexes with organic ligands are nearly completely voltammetrically inactive in the presence of DTPA and nitrate ions.

The different behaviour of three mentioned species, i.e. Cr(VI), $Cr(III)_{active}$ and $Cr(III)_{inactive}$ can be utilized for the speciation study. Since in surface water the total Cr(III) is usually organically bound, the speciation procedure involves (1) a direct determination of Cr(VI), and (2) a total Cr determination after a previous oxidation of Cr(III) to Cr(VI) by UV irradiation.

Using the CAdSV method the working range is shifted down, as it can be seen from Figure 3 where voltammetric curves of Cr(VI) are well shaped in the concentration range 1×10^{-10}–1×10^{-9} mol/L; the corresponding calibration plot is linear with a high value of the coefficient of determination and no significant intercept value.

The CAdSV response increases linearly with concentration up to 4.2 μg/L Cr(VI) (Figure 3). The limits of detection and quantification calculated by means of the ULA method are 2.36 ng/L and 7.08 ng/L, respectively.

The mentioned values were obtained for ten standard solutions of Cr(VI) and for seven replicate current measurements for each standard; the mean values were used for

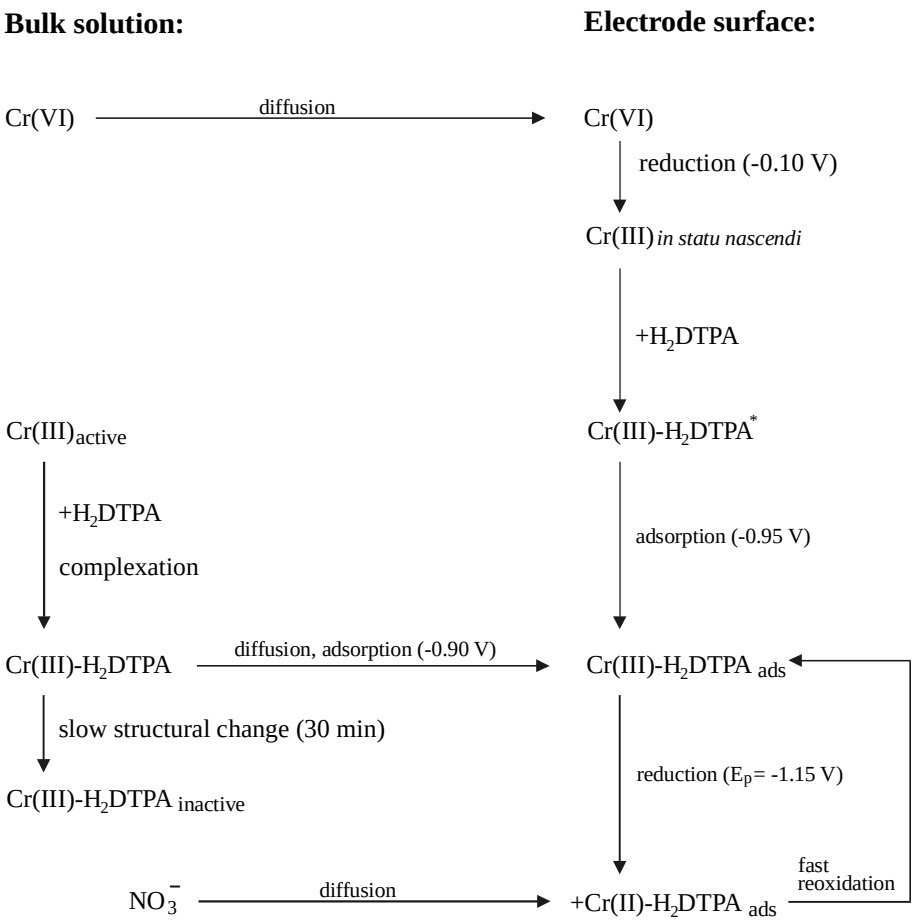

Figure 2. General scheme of bulk phase and electrode reactions for Cr(VI)-DTPA and Cr(III)-DTPA species. Subscript "inactive" refers to the ability of electrochemical reduction of Cr(III) to Cr(II).

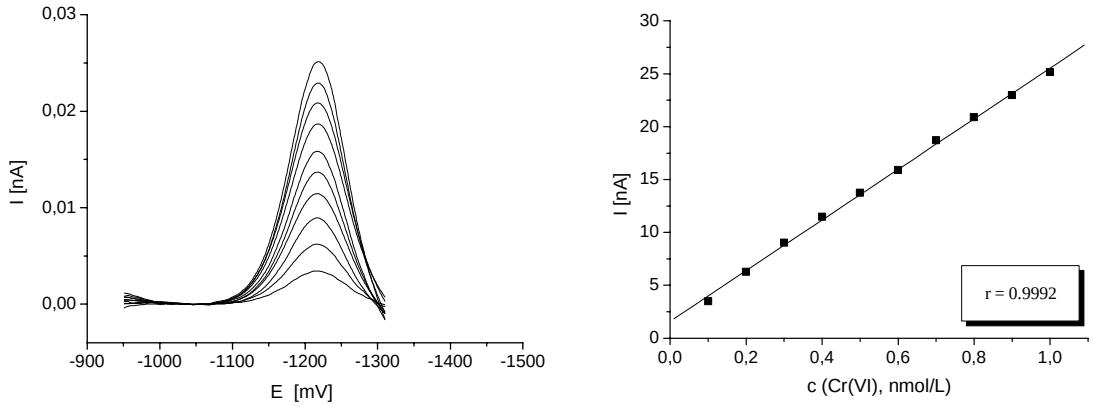

Figure 3. CAdSV curves and calibration plot for Cr(VI) at very low concentration level. Curves for $(1\text{-}10)\cdot10^{-10}$ mol/L Cr(VI) in $1\cdot10^{-2}$ mol/L DTPA, 0.25 mol/L KNO_3 and 0.05 mol/L acetic acid; pH = 6.2, E_{acc} = –0.950 V, t_{acc} = 60 s; the signal was corrected for the background.

the LOD and LOQ calculations (number of degrees of freedom = 8). A very good linearity in the range 7–52 ng/L was confirmed by the coefficient of determination r^2=0.9984 as well as by inspection of residuals. The found LOD and LOQ values are significantly lower compared to the detection and quantification limits found for the ICP MS measurements. Further decrease of the LOD and LOQ values in CAdSV is possible by prolonging the accumulation period.

The CAdSV method was validated with the use of the samples from the mountain river Białka spiked with known amounts of Cr(VI) and Cr(III). The recovery of Cr(VI) and Cr(III) spiked to the river water samples ranged from 100% to 106% for Cr(VI) and from 96% to 103% for Cr(III). Obtained CAdSV and ICP MS results for total Cr in the selected water samples were in a very good agreement.

Conclusions

For analysis of chromium traces present in water samples sensitive and selective instrumental methods were applied and tested such as inductively coupled plasma mass spectrometry, catalytic adsorptive stripping voltammetry and spectrophotometric method with 1,5-diphenylcarbazide. In case of CAdSV it was required to develop an analytical procedure comprising the preparation of samples for analysis, optimization of the determination conditions, as well as the assessment of sensitivity, accuracy, detection and quantification limits.

The CAdSV method with adsorptive preconcentration of the Cr(III)-DTPA complex on the HMDE enables speciation trace analysis with extremely low quantification limit. This method is cheap since it does not require the use of expensive equipment as it is in the case with spectrometric methods.

The ICP MS method is characterized by high sensitivity, sufficiently low quantification limit, good accuracy and can be successfully applied in routine analysis of total Cr in water samples. The examined spectrophotometric method using diphenylcarbazide has considerably higher quantification limit for Cr than ICP MS or CAdSV, and therefore it is not always sensitive enough for Cr analysis in the river water samples. However, it is suitable for Cr determination in the samples of severely polluted river water or wastewater, mainly on account of its simplicity and satisfactory accuracy. Moreover, it enables speciation between Cr(VI) and Cr(III).

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Povzetek

Primerjali smo karakteristike naslednjih analiznih metod za določanje sledov kroma v vzorcih vode: masne spektrometrije v povezavi z induktivno sklopljeno plazmo, absorpcijske spektrofotometrije in katalitske adsorpcijske inverzne voltametrične analize. Izračunali smo naslednje metrološke parametre: pravilnost, točnost, območje linearnosti, mejo zaznavnosti in mejo določitve. Meji zaznavnosti in določitve smo izračunali po metodi ULA, s katero upoštevamo negotovost parametrov umeritvene premice, pa tudi po ustaljeni metodi, z izračunom tri- in desetkratnika standardnega odklona določitev v slepem vzorcu.

Preverili smo tudi možnosti za raziskovanje speciacije obeh oksidacijskih stanj kroma, Cr(VI) in Cr(III). Uporabili smo metodo ICP MS za določitev vsebnosti skupnega kroma v vzorcih rečne vode. Katalistka adsorpcijska inverzna voltametrična tehnika z uporabo DTPA in nitrata pa je dovolj občutljiva za določanje sledov kroma v koncentracijah 0,01 do 0,1 μg/L in tudi za raziskave speciacije.