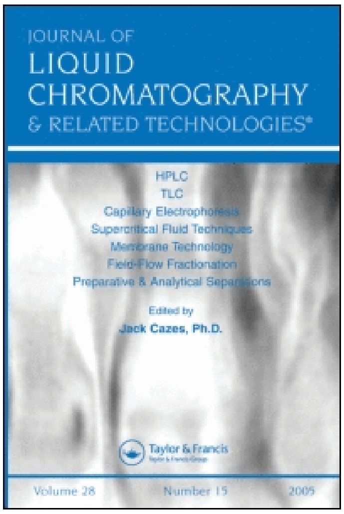

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Trace Level Determination of Cr(III)/Cr(VI) in Water Samples Using Ion Chromatography with UV Detection

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Abstract: In the present research, a method of simultaneous determination of Cr(III) and Cr(IV) with mixed bed ion-exchange column was carried out. Cr(III) is oxidized to Cr(VI) in post-column derivatization reaction, then both ions are detected by a UV detector, at wavelength $\lambda = 365\,\mathrm{nm}$.

The performance characteristics of the method were established by determining the following validation parameters: precision and accuracy, linearity, limit of detection, and limit of quantification. The influence of sample pH and selected inorganic ions on chromium species analyses has been checked. The method was applied for simultaneous determination of Cr(III)/Cr(VI) in environmental samples such as, rainwater and galvanic sediments.

Keywords: Chromium species, Ion chromatography, Water analysis

INTRODUCTION

The growing awareness of the strong dependence of the toxicity of selected heavy metals upon their chemical forms has lead to an increasing interest in the qualitative and quantitative determination of specific metal species.

One of the most interesting examples is chromium, which has numerous applications in the industry, including production of steel and other alloys, bricks, dyes, pigments, leather tanning, and wood preserving. Chromium enters into the air, water, and soil, mostly as chromium(III) and chromium(VI),

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as a result of natural processes and anthropogenic activities. Because of its widespread and long-term use, contamination of soil and groundwater with chromium is worldwide.[1]

Biochemical and toxicological investigation has shown that, for living organisms, the chemical form of a specific element, or the oxidation state in which that element is introduced into the environment is essential.[2] The chromium species most frequently found in water are chromium(VI) (i.e., chromate—CrO_4^{2-}), cationic chromium(III) hydroxo compounds—$Cr(OH)^{2+}$, $Cr(OH)_2^+$, and organically bound and colloidally sorbed Cr(III)).[3]

The probability of occurrence of ions Cr(III) as free cations in environmental samples is insignificant, because they easily form complexes with different substances present in the sample and in samples with pH over 7 they form insoluble $Cr(OH)_3$.

Cr(III)/Cr(VI) species differ with regards to their biological, chemical, and toxicological properties. Cr(III) compounds are essential in the human body, playing a vital role in the metabolism of glucose, while Cr(VI) is toxic and carcinogenic.

Consequently, attempts have been made to distinguish between Cr(III) and Cr(VI). There are several methods available for chromium speciation in environmental samples. However the most efficient and promising seems to be ion chromatography separation and detection using appropriate detectors.

Ion chromatography is more effective and demonstrates less interference than spectrometric methods. The object of analysis is usually chromium(VI) because of its carcinogenity. The methods of Cr(VI) analysis in water and in sewage are mostly based on separation on anion-exchange columns, and determination of Cr(VI) after post-column derivatization reaction with 1,5-diphenylcarbazide, in UV detectors at 520 nm.[4–6]

The chemistry of chromium is complex, because depending on sample pH and its matrix, chromium occurs as different forms. This is the reason that for species analysis of chromium various detection methods are employed, such as: laser-enhanced ionization,[7] on-line thermal lens spectrometric detection,[8] thermal ionization isotope mass spectrometry,[9] inductively coupled plasma mass spectrometry with hydraulic high pressure nebulization,[10] chemiluminescence detection,[11] or the most popular atomic absorption spectroscopy,[12,13] and inductively coupled plasma mass spectrometry detection.[14,15]

These methods are very sensitive; however, in view of complex procedures, as well as price of instruments, their applications in routine laboratories are limited. There is a need to work out a simple and reliable simultaneous method for Cr(III) and Cr(IV) determination on trace level concentration.

One of the methods is based on pre-column derivatization of Cr(III) with chelating agents such as pyridine-2,6-dicarboxylic acid (PDCA)[8,16] or ethylenediaminetetraacetate (EDTA)[6,14] and post-column derivatization of Cr(VI) with 1,5-diphenylcarbazide, which enable their simultaneous determination by means of UV detector.[8,16] Disadvantage of this method is slow kinetic formation of Cr(III) complex and its dependence on pH. Trojanowicz et al.[17] used ion pair chromatography with Cr(III) oxidation to Cr(VI) and spectrophotometric detection with diphenylcarbazide at 540 nm.

Present research describes simultaneous separation and determination of Cr(III)/Cr(VI) by means of ion-exchange column with mixed bed, oxidation of Cr(III) to Cr(VI), and next theirs detection at 365 nm in UV detector.

This method was applied by Heberling et al.[18] to species analysis of chromium(III) and chromium(VI), on mg L^{-1} level in plating solutions and wastewater using anion-exchange column.

Considering the progress in the introduction of new generations of ion-exchange resins in separation columns and the necessity of analysis of chromium species on trace levels, this method was developed for simultaneous determination of Cr(III)/Cr(VI) in environmental samples on μg L^{-1} level.

The influences of sample pH, common inorganic anions and cations, as well as sample matrix on chromium species analysis were checked. The method validation was performed and then the method was applied to simultaneous determination of Cr(III)/Cr(VI) in rainwater and water extracts from galvanic sediments.

EXPERIMENTAL

Reagents

Analytical grade K_2CrO_4, $CrCl_3$, $MgSO_4$, $Na_2S_2O_8$, $AgNO_3$ used for preparation of standard solution, eluent, and post column reagents were obtained from Merck (Merck, Germany). $HClO_4$ was purchased from Fluka (Fluka, Germany) and was analytical grade quality. All other chemicals (KF, NaCl, $MgCl_2$, KBr, K_3PO_4, Na_2SO_4, $NaNO_3$, and $Ca(NO_3)_2$) used to check the influence of inorganic ions on Cr species separation were purchased from Merck (Merck, Germany).

Cr(III) stock solution (1.000 g L^{-1}) was prepared by dissolving 5.124 g of $CrCl_3 \cdot 6H_2O$ in 1 L deionised water obtained from a Millipore water system (resistivity 18 MΩ cm, filtered through a 0.2 μm membrane filter). Cr(VI) stock solution (1.000 g L^{-1}) was prepared by dissolving 3.734 g of K_2CrO_4 in 1 L deionized water. Stock solutions of Cr(III) and Cr(VI) were stored in a refrigerator and were renewed every week. Analytical solutions of chromium(III) and chromium(VI) were prepared daily by diluting the stock solutions to obtain an adequate chromium concentration.

Post column reagents were prepared daily by diluting appropriate amounts of $Na_2S_2O_8$ and $AgNO_3$ in deionized water. All samples were kept at 4°C, protected from light, and were analysed on the day of preparation. The solutions were degassed under a stream of helium.

Instrumentation

A Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph consisting of: gradient pump (GP 40), UV detector (AD 20), rear-loading Rheodyne injection valve, post-column heater (PCH-2), autosampler (ASM-2), and Chromeleon Workstation (version 6.3) were used in this study.

Dionex, IonPac columns with mixed bed-CG5A (guard column, 50 × 4 mm I.D.) and CS5A (analytical column, 250 × 4 mm I.D.) containing unique bifunctional pellicular resins (mixed divinylbenzene-styrene copolymer with latex addition and sulfonic cation exchange and alkanol quaternary ammonium anion exchange functional groups) were used. These columns were successfully applied in previous studies for the determination of Cr(VI)[19] and Cr(III)/Cr(VI)[20] in water samples.

RESULTS AND DISCUSSION

Method Optimization

The chromatographic method used was adapted from a procedure proposed by Heberling et al.[18] who applied Dionex IonPac AS7 anion-exchange column to determination of Cr(III)/Cr(VI) on the $\mathrm{mg\,L^{-1}}$concentration level in plating solution.

The aim of this research was to develop this method with application of the mixed-bed column (Dionex IonPac CS5A) to species analysis of chromium of the concentration level of $\mu\mathrm{g\,L^{-1}}$ and to study the influence of pH on Cr(III)/Cr(VI) determination and recovery from environmental water samples.

The comparison study of applications of anion-exchange column (Dionex, IonPac AS7) and mixed bed column (Dionex, IonPac CS5A) to simultaneously separate and determine Cr(III)/Cr(VI) is described in a previous work.[20] As a result of these experiments the following conditions were chosen as optimal:

Guard column	IonPac CG5A
Analytical column	IonPac CS5A
Eluent	$40\,\mathrm{mM\,L^{-1}\ MgSO_4} + 30\,\mathrm{mM\,L^{-1}\ HClO_4}$
Flow rate (post column reagent)	$0.8\,\mathrm{mL\ min^{-1}}$ (eluent) + $0.5\,\mathrm{mL\ min^{-1}}$
Post-column reagent	$0.15\,\mathrm{M\,L^{-1}\ Na_2S_2O_8} + 0.23\,\mathrm{mM\,L^{-1}\ AgNO_3}$
Reaction coil temperature	80°C
Injection volume	100 μL
Detection	UV ($\lambda = 365\,\mathrm{nm}$).

The scheme of the system used is shown in Figure 1. The example of the chromatogram of a standard sample containing 100 μg L^{-1} of Cr(III) and 100 μg L^{-1} of Cr(VI), prepared in deionised water is shown in Figure 2.

Calibration and Method Validation

Validation based on ISO guidelines[21] was carried out on the ion chromatography method with responses for peak area collected and evaluated. In order to verify precision and accuracy, linearity, detection limits and quantification limits, 10 calibration solutions of Cr(III) and Cr(VI) in the range 10–100 μg L^{-1} prepared in demonized water were injected into the eluent stream. All calibration solutions were analysed in triplicate under optimalised chromatographic conditions.

The calibration curve covering the concentration range was obtained and the linear relationship between peak area and concentration were experimentally verified. The results of the calibration data are summarised in Table 1.

The Influence of the Sample Matrix on the Simultaneous Determination of Cr(III)/Cr(VI)

The following experiment has been done: 20 mL, 50 mL, and 80 mL of tap water was placed in 100 mL volumetric flasks, then appropriate volumes of stock solutions of chromium(III) and chromium(VI) solutions were added to obtain concentrations of 100 μg L^{-1} Cr(III) and Cr(VI), and finally diluted to volume with deionised water. Such prepared solutions were analysed three times each, immediately after preparation. The mean value of peak areas and peak heights of Cr(VI) and Cr(III) ions are shown in Figure 3. The pH of tap water used in this experiment was 7.31. The samples pH (with 20%, 50%, and 80% v/v of tap water) were 7.08, 7.15, and 7.25 respectively.

Subsequently, eight solutions containing 100 μg L^{-1} of Cr(III) and Cr(VI), each were prepared in 100 mL volumetric flasks. Next, to particular flasks 0.5 mL, 2.0, and 5.0 mL respectively, of stock solutions (1.0 g L^{-1} each) of: fluoride (as KF), chloride (as NaCl), bromide (as KBr), nitrate (as $NaNO_3$), phosphate (as K_3PO_4), sulphate (as Na_2SO_4), calcium (as $Ca(NO_3)_2$) and magnesium (as $MgCl_2$) were added. Then, samples were analysed in optimal analytical conditions.

Furthermore, in order to check the influence of sample matrix on the separation of Cr(VI) and Cr(III), samples were passed through RP_{18} cartridges or cartridges in Ag^+ form, as well as those treated with EDTA or etylenediamine before injection into the separation column and then analysed chromatographically.

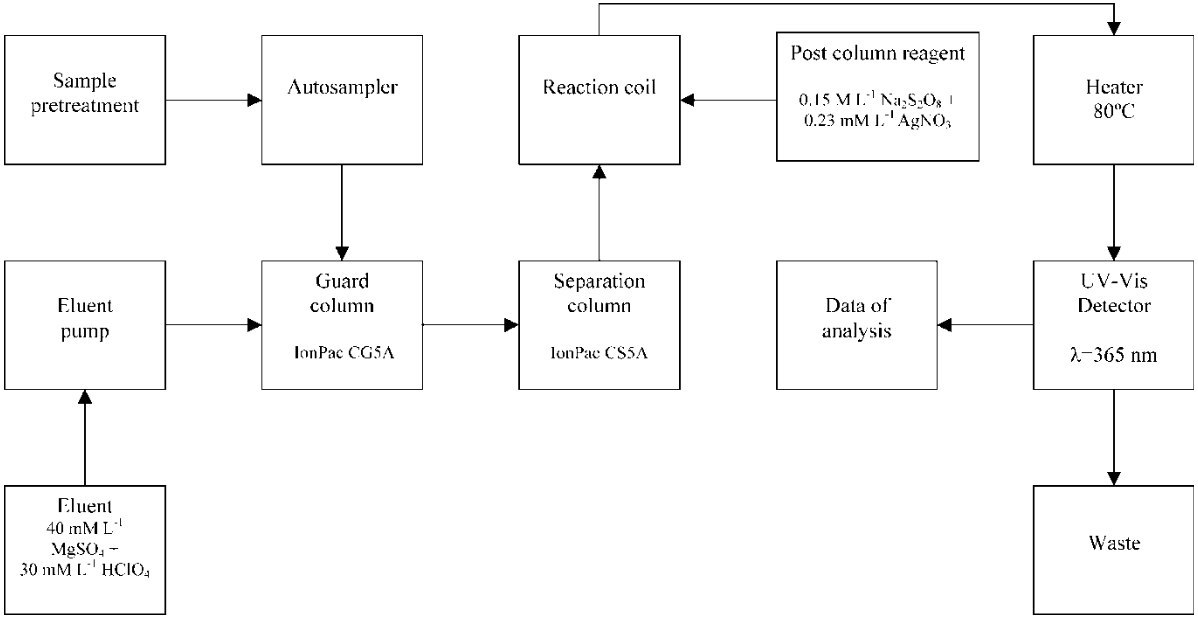

Figure 1. The diagram of analytical system used.

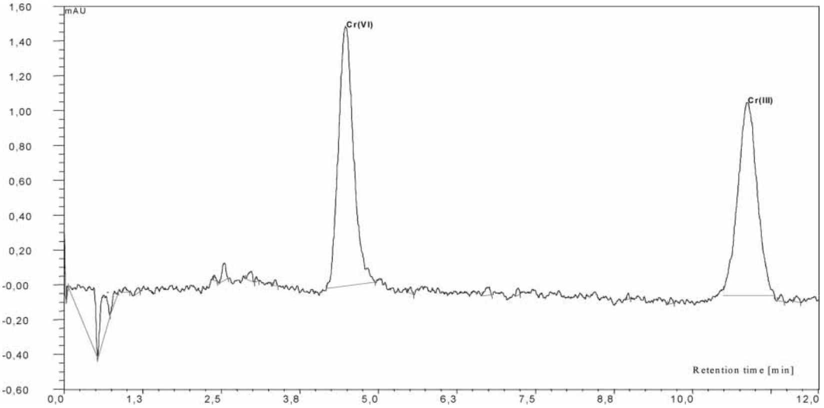

Figure 2. Chromatogram of sample containing 100 μg L^{-1} of Cr(VI) and Cr(III) each.

Influence of pH and Chromium Recovery

On chromatograms of standard samples prepared in deionised water, two peaks appeared which were equivalent to Cr(VI) and Cr(III). If sample pH was over 7 only one peak of Cr(VI) was observed on the chromatogram. The size of this peak did not suggest oxidation of Cr(III) to Cr(VI).

In the next part of the experiment, two series of samples containing 100 μg L^{-1} of Cr(III) and Cr(VI) each, were prepared in tap water. In the first set of samples, pH was adjusted to: 3, 5, 7, 9, and 11, respectively, by means of 0.01 M L^{-1} HCl or 0.01 M L^{-1} NaOH, before addition of a standard solution of Cr(III)/Cr(VI). In the second set, pH was adjusted after addition of Cr(III)/Cr(VI).

Increasing the sample pH from 3 to 7 has caused the decreasing of the peak area and peak height of Cr(III). At pH 9 and above the peak has totally disappeared.

Table 1. Method validation parameters

Parameter	Cr(III)	Cr(VI)
Concentration range (μg L^{-1})	10.0–100.0	
Standard deviation (μg L^{-1})	0.90	0.99
Accuracy (R.S.D) (%)	3.64	3.80
Limit of detection (μg L^{-1})	2.03	2.23
Limit of quantification (μg L^{-1})	6.06	6.69
Linearity (r^2)	0.9986	0.9991

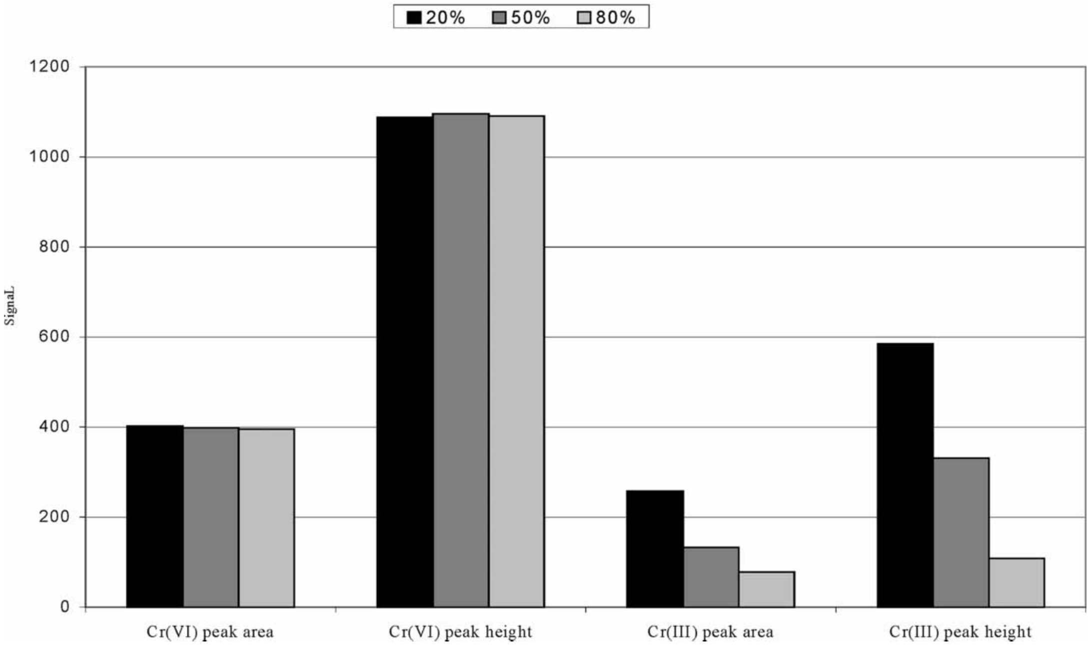

Figure 3. Peak area and peak height changes of Cr(III) and Cr(VI) in dependence of tap water volume added.

To check the chromium recovery, four samples containing 20 μg L^{-1} or 100 μg L^{-1} of Cr(III) and Cr(IV) each, were prepared in tap water and rainwater. Next, the pH of samples was set to pH = 5 and samples were analyzed 10 times each. The mean results of determination are shown in Figure 4. Total chromium content was determined by the AAS method.

Cr(III)/Cr(VI) Determination in Environmental Samples

The method was applied to simultaneous determination of Cr(III)/Cr(VI) in real samples such as rainwater and galvanic sediments. Rainwater was collected at an industrial area close to a cement plant, and galvanic samples originated from a galvanic waste landfill site. The samples were not stabilised (by using e.g., strong acids) before analysis.

100 g of dry galvanic sediments was placed into a 1 L plastic bottle and filled up to volume with deionised water. After 24 hours of shaking, the extract was diluted with deionised water (1 : 10 v/v) and filtered by a 0.2 μm Sartorius filter before analysis. In Table 2 are shown data obtained for rainwater and galvanic samples, including uncertainty of measurements calculated according to Guide to the Expression of Uncertainty in Measurement.[21]

To check chromium species recovery from analysed environmental water samples, 5.0 μg L^{-1} of Cr(III) and Cr(VI) were added to analyzed rainwater. To each water extract from galvanic sediments, 20 μg L^{-1} of Cr(III) and Cr(VI) were added, and then each sample was analyzed in triplicate. The mean results along with uncertainty of measurement are given in Table 2.

The concentration of Cr(III) and Cr(VI) in analysed samples was measured by peak area representing these ions by comparison with standard peaks obtained from standard solutions of Cr(III)/Cr(VI).

CONCLUSIONS

Chemical speciation of Cr(III)/Cr(VI) in environmental samples is essential to fully understand their toxicity and bioavailability. The method described is sensitive, selective, and allows determination of Cr(III) and Cr(VI) on μg L^{-1} levels in different water samples.

The influence of common inorganic anions and cations (up to 50 mg L^{-1}, each) on chromium ions separation was not observed. The area and the height of peaks and their retention times were the same as in samples without additives. Samples treated with EDTA or etylenediamine, as well as samples passed throughout RP$_{18}$ cartridges or cartridges in Ag^{+} form, have not shown any changes in separation of chromium species.

According to the data from Figure 3, the volume of tap water (20%, 50%, and 80% v/v) added to samples containing 100 μL^{-1} of Cr(III)/

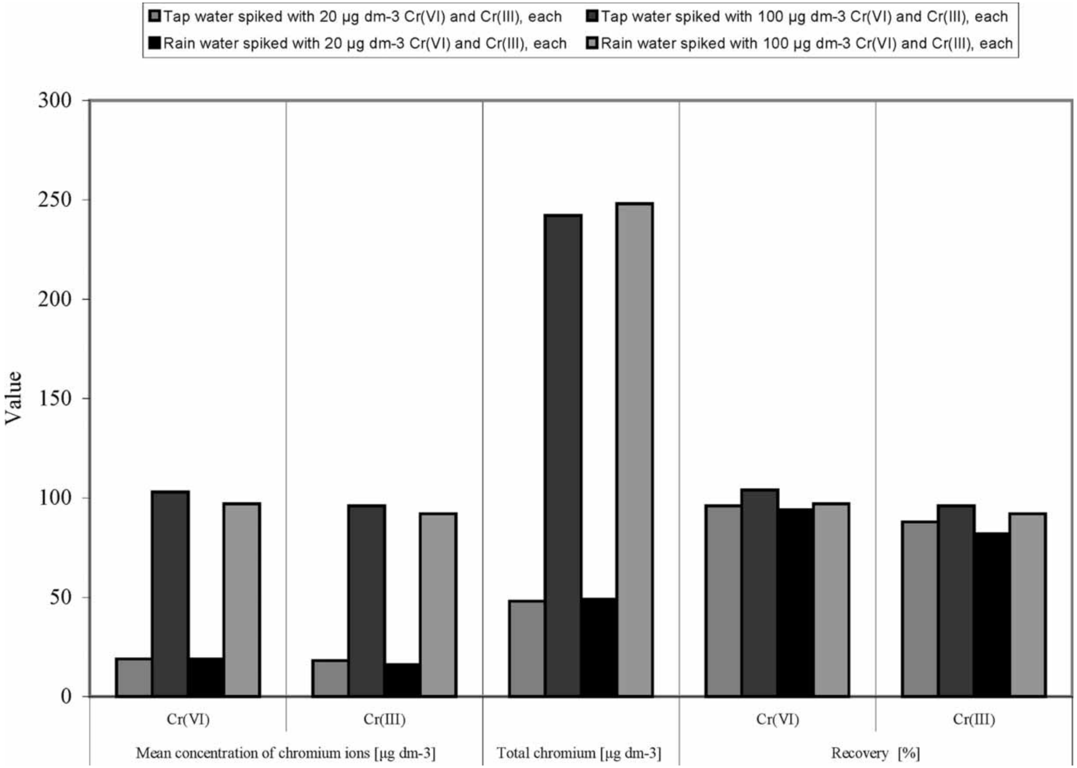

Figure 4. The concentration of Cr(VI)/Cr(III) and chromium recovery from tap water and rainwater samples, spiked with 20 or 100 $\mu g\,L^{-1}$ of Cr(III) and Cr(VI) each.

Table 2. Concentration of Cr(III) and Cr(VI) in analysed samples

Sample	Concentration of chromium species ($\mu g\,L^{-1}$) Cr(VI)	Concentration of chromium species ($\mu g\,L^{-1}$) Cr(III)	Total Cr content ($\mu g\,L^{-1}$)[a]
Rainwater no. 1 (pH = 4.91)	4.31 ± 0.74	5.74 ± 0.93	11.28 ± 0.41
Rainwater no. 1 spiked with 5.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	9.21 ± 0.58	10.23 ± 0.83	22.07 ± 0.55
Rainwater no. 2 (pH = 5.54)	6.18 ± 0.64	11.74 ± 2.11	23.08 ± 1.02
Rainwater no. 2 spiked with 5.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	11.48 ± 0.72	16.19 ± 1.83	44.12 ± 1.18
Rainwater no. 3 (pH = 5.23)	2.31 ± 0.54	7.74 ± 1.41	13.08 ± 0.52
Rainwater no. 3 spiked with 5.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	7.62 ± 0.39	12.31 ± 1.13	32.58 ± 0.70
Galvanic sediments no. 1	40.5 ± 6.90	75.1 ± 10.3	128.5 ± 5.7
Galvanic sediments no. 1 spiked with 20.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	61.3 ± 7.28	96.4 ± 11.5	170.1 ± 12.7
Galvanic sediments no. 2 (pH = 6.23)	68.4 ± 13.9	148.4 ± 24.1	228.4 ± 8.9
Galvanic sediments no. 2 spiked with 20.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	87.2 ± 11.4	166.1 ± 28.4	266.9 ± 10.3
Galvanic sediments no. 3 (pH = 6.44)	112.7 ± 19.5	228.2 ± 44.3	393.1 ± 13.8
Galvanic sediments no. 3 spiked with 20.0 $\mu g\,L^{-1}$ Cr(III) and Cr(VI)	133.4 ± 18.2	245.7 ± 38.3	431.7 ± 16.7

[a] The total Cr content was determined by AAS method.

Cr(VI) had no significant influence on changes of peak area and peak height of Cr(VI).

In contrast, increasing of sample pH to 7.26 (sample no. 3) caused disappearing of the Cr(III) peak.

If sample pH was strongly over 7, only one peak of Cr(VI) appeared on the chromatogram. Its size was the same as in samples prepared in deionised water containing appropriate concentration of Cr(VI). This indicates that Cr(III) was not oxidized to Cr(VI), but it forms insoluble $Cr(OH)_3$.

Simultaneous determination of Cr(III) and Cr(IV) in environmental samples have been possible on the level of $\mu g\,L^{-1}$, if samples pH is naturally below 7. If pH is over 7, sample pH has to be adjusted to pH around 5–7.

Chromium recovery from the tap water and rainwater samples spiked with Cr(III)/Cr(VI) is in the range, 82–104%, and is essentially less for Cr(III). The determined sum of Cr(III) and Cr(VI) concentration amounted about 64–70% of the total chromium content determined by the AAS method, which means that there are still some indefinite chromium species other than CrO_4^{2-} and Cr^{3+} (Figure 4).

This same chromium recovery value was observed in analysed rainwater and galvanic sediments spiked with 5,0 $\mu g\,L^{-1}$ Cr(III)/Cr(VI) or 20 $\mu g\,L^{-1}$ Cr(III)/Cr(VI), respectively.

The method was successfully applied to simultaneous determination of Cr(III) and Cr(VI) in rainwater and water extracts from galvanic sediments. The pH value of all tested environmental samples was below 7. Simultaneous determination of Cr(III)/Cr(VI) on $\mu g\,L^{-1}$ concentration level was possible, but these measurements characterised relatively high uncertainty (Table 2).

However, it should be emphasized that the problems of chromium species stability and possible oxidation by air oxygen were not the aim of this research. Furthermore, during the study, any certified reference material (e.g., BCR CRM 544) was not used. These should be done in further research, and can be helpful to explain why the total chromium content determined by the AAS method is less than the sum of Cr(VI) and Cr(III).

Nevertheless, only methods requiring much more sophisticated instrumentation than ion chromatography with UV detection provide better detectability.

The use of ion chromatography with mixed bed Dionex IonPac CS5A column, represents a new approach to the simultaneous determination of Cr(III)/Cr(VI) in environmental waters. This new approach, which is a modification of a method described by Heberling et al.[18] allows equivalent method performance with improved precision and method detection and method quantification limits.

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