

Ion Chromatography Method for the Determination of Trace Levels of Chromium(VI) in Water

R. Michalski

Institute of Environmental Engineering of the Polish Academy of Science
M. Skłodowska-Curie Street 34, 41-819 Zabrze, Poland

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Abstract

Chromium exists usually in the (III) or (VI) oxidation states. In contrast to Cr(III), which is essential to mammalian systems, Cr(VI) is dangerous for humans due to its toxicity and carcinogenic properties. Cr(VI) compounds are highly soluble, mobile and bioavailable compared to Cr(III) species. Chromium is usually analyzed using instrumental methods such as AAS or ICP, which are accurate and sensitive, but allow determination of only the total content of chromium in a sample. Determination of Cr(VI) still represents a formidable challenge in analytical chemistry.

This paper describes sensitive and selective determination of Cr(VI) in water samples on $\mu\text{g L}^{-1}$ levels using an ion chromatography system with UV detector, without any sample preconcentration method. The detection limits achieved were less than $0.1 \mu\text{g L}^{-1}$ in deionized water and $0.2 \mu\text{g L}^{-1}$ in rainwater and drinking water, respectively. The method was applied to determination of Cr(VI) in rainwater and water extracts from galvanic sediments.

Keywords: chromium(VI), ion chromatography, water analysis.

Introduction

The growing interest in the development of analytical techniques for chromium determination originates from widespread industrial use of this element and by the fact that its two main oxidation states have fundamentally various influences on humans [1,2].

The uncomplexed trivalent chromium species are the chromic ion Cr(III), and while it is soluble in acidic solutions, it typically precipitates as the hydroxide in alkaline solutions. Due to the slow ligand exchange kinetics Cr(III) is not toxic and in low concentrations is essential to mammalian systems [3].

The hexavalent species of chromium exists primarily as chromic acid (H_2CrO_4) and its salts, hydrogen chromate (HCrO_4^-) and chromate (CrO_4^{2-}) ions depend on sample pH. The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is a dimer of HCrO_4^- , which forms when the concentration of chromium exceeds approximately 1 g L^{-1} .

Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to sparingly soluble trivalent chromium species [4]. Cr(VI) is a strong oxidizing agent and therefore harmful to biological systems. This fact warrants its regulation in the environmental.

According to European [5] and Polish [6] regulations, the maximum allowable concentration of total chromium in drinking water is $50 \mu\text{g L}^{-1}$. Additionally, Polish regulations distinguish between total chromium and Cr(VI), whose concentration cannot exceed $3 \mu\text{g L}^{-1}$.

The analytical determination of metal ions at low concentration levels has received considerable attention in the last few years [7]. The determination of heavy metals, including chromium, has traditionally been carried out by atomic absorption spectrometry (AAS) [8] or inductively coupled plasma (ICP) [9]. These instrumental methods are precise and sensitive but allow determination of total chromium only. The concentration of Cr(VI) is estimated from the difference of total chromium content and Cr(III),

which can be analyzed using photometric methods. This so-called "difference method" causes inaccurate calculated concentrations of Cr(VI).

The United States Environmental Protection Agency (US EPA) recognizes four methods for determination of Cr(VI): co-precipitation [10], colorimetric with diphenylcarbazide [11], chelation/extraction [12] and differential pulse polarography [13].

One of the main powerful analytical tools available for analyzing heavy metals ions is high-performance liquid chromatography (HPLC) in its different technical modes such as: ion chromatography (IC), chelation-ion chromatography (CIC), reversed-phase liquid chromatography (RP-LC) or ion-interaction chromatography (IIC) [14]. From among these techniques the most often applied is ion chromatography.

The ion chromatography method with UV detection was published by Dionex [15]. It concerns the determination of Cr(VI) in water, wastewater and solid waste extracts and is based on post-column derivatization with diphenylcarbazide at 520 nm.

Hyphenated techniques such as IC-ICP-MS or IC-AAS are very sensitive and after pre- or post-column derivatization steps allow determination of chromium species [16-18]. These techniques use rather complex and expensive instrumentation. Such an instrumental feature constitutes a strong limitation, especially for laboratories which are still using either former or standard ion chromatography instrumentation.

Since its inception in 1975 [19], ion chromatography has developed into a mature and highly developed analytical technique for separation and determination of inorganic ions. Because the most common mode of detection has been conductivity, this technique was usually applied to determination of common anions (F^- , Cl^- , NO_3^- and SO_4^{2-}) and cations (Na^+ , K^+ , Mg^{2+} and Ca^{2+}), which are present in environmental samples on $mg\ L^{-1}$ concentration levels.

Recent developments such as the use of higher capacity columns, larger loop injection, more complex sample preparation and detection schemes have been incorporated into new approved methods to allow the determination of ionic contaminants such as bromate, perchlorate and some metal species [20-22].

The present work reports a direct, sensitive and selective determination of Cr(VI) in different types of waters on $\mu g\ L^{-1}$ levels using ion chromatography with UV detection. Limit of quantification calculated from peak area and peak height as well as some statistical parameters were estimated according to appropriate standards [23, 24]. The described method was applied to determination of Cr(VI) in environmental samples such as rainwater and extracts from galvanic sediments.

Experimental Procedures

Chemicals

Analytical grade K_2CrO_4 , pyridine-2,6-dicarboxylic acid (PDCA) and NH_4OH used for preparation of stan-

dard solutions and eluent were obtained from Merck (Germany). Eluent was degassed with helium.

All other chemicals (KF , HCl , $MgCl_2$, KBr , KNO_3 , Na_2SO_3 , H_2SO_4 , $NaNO_3$, $MgSO_4$, $Ca(NO_3)_2$, $Cr(NO_3)_3$, $CrCl_3$) used to check their influence on Cr(VI) determination were also purchased from Merck.

Water used in the experiments was purified using Millipore equipment (Bedford, USA) and had a electrical conductivity $< 0.05\ \mu S\ cm^{-1}$.

Apparatus

Ion chromatographic separation was performed on Dionex DX-500 ion chromatograph system (Sunnyvale, CA, USA) consisting of: gradient pump (GP 40), UV detector (AD 20), rear-loading Rheodyne injection valve, autosampler ASM-2 (Dionex) and Chromeleon Workstation (version 6.3).

A new generation of ion-exchange columns from Dionex IonPac CG 5A (guard column) and IonPac CS 5A (analytical column) containing mixed anion and cation beds with sulfonic acid and alkanol quaternary ammonium functional groups were used in this work.

These high-resolution ion-exchange columns are recommended for the determination of transition and lanthanide metals with visible absorbance detection. The CS5A column has a unique bilayer latex structure consisting of both anion- and cation-exchange retention mechanisms, thus ionic species can be separated using either anion- or cation or cation-exchange chromatography. Selected parameters of anion exchange latex particles are: 76 nm (diameter), 2% (crosslinking) and 40 μg /column (capacity), whereas cation exchanges are: 140 nm (diameter), 10% (crosslinking) and 20 μg /column (capacity), respectively. The column is chemically compatible with typical HPLC solvents up to 50%.

Preparation of Calibration Solutions

A 1000 $mg\ L^{-1}$ chromium(VI) stock standard solution had been prepared by dissolving potassium dichromate in deionized water and then stored in a refrigerator at 2°C to 8°C.

10 calibration solutions of Cr(VI) in the range 1-10 $\mu g\ L^{-1}$ prepared in deionized water, drinking water and rainwater by diluting the stock standard solution to the required concentration just before use.

Deionized water obtained from Millipore device, drinking water collected at Agency of Environmental and Geology at Wiesbaden (Germany) on 23.07.2002 and rainwater were sampled at the industrial area of Cologne (Germany) in the middle of July 2002.

Analytical Conditions

The selection of analytical conditions was based on Dionex Technical Note no.24 [25], published in July 1991 and withdrawn from use a few years later. The significant difference was the use of modern analytical columns and detection

Table 1. Peak area and peak height of Cr(VI) in calibration solutions and selected statistical data.

Concentration of Cr (VI) in calibration solution [$\mu\text{g L}^{-1}$]	Deionized water		Tap water		Rainwater	
	Peak area	Peak height	Peak area	Peak height	Peak area	Peak height
1	0.013	0.101	0.026	0.105	0.053	0.095
2	0.039	0.215	0.048	0.265	0.064	0.156
3	0.054	0.339	0.062	0.316	0.088	0.289
4	0.074	0.422	0.083	0.480	0.106	0.463
5	0.092	0.524	0.112	0.522	0.119	0.542
6	0.118	0.621	0.133	0.638	0.131	0.629
7	0.135	0.737	0.145	0.771	0.155	0.780
8	0.149	0.819	0.159	0.886	0.168	0.894
9	0.171	0.912	0.179	0.967	0.184	0.946
10	0.186	0.995	0.196	1.113	0.214	1.127
Standard deviation [$\mu\text{g L}^{-1}$]	0.15	0.14	0.26	0.24	0.27	0.26
Coefficient of variation [%]	2.78	2.65	4.84	4.42	4.95	4.78
Limit of quantification [$\mu\text{g L}^{-1}$]	1.21	1.15	2.04	1.87	2.08	2.01

Table 2. Method precision and recovery.

Sample	Number of replicates	Mean concentration [$\mu\text{g L}^{-1}$]	RSD [%]	Recovery [%]
Deionized water	10	-	-	-
Deionized water spiked with 1 $\mu\text{g L}^{-1}$ Cr(VI)	10	1.06	6	106.0
Deionized water spiked with 1 $\mu\text{g L}^{-1}$ Cr(VI)	10	5.28	5.6	105.6
Deionized water spiked with 1 $\mu\text{g L}^{-1}$ Cr(VI)	10	10.45	4.5	104.5
Deionized water spiked with 1 $\mu\text{g L}^{-1}$ Cr(VI)	10	51.64	3.3	103.2

mode (direct UV detection at 365 nm instead of post column derivatization with diphenylcarbazide at 520 nm).

Separation conditions are described below:

Guard column	-	IonPac CG5A (4 x 50 mm)
Analytical column	-	Ion Pac CS5A (4 x 250 mm)
Eluent	-	10 mM L ⁻¹ PDCA + +148 mM L ⁻¹ NH ₄ OH
pH of eluent	-	9.8
Flow rate	-	0.8 mL min ⁻¹
Back pressure	-	75 bar
Injection volume	-	100 μL
Detection	-	UV
Wavelength	-	365 nm

Results

Peak area and peak height, as well as standard deviation, coefficient of variation and limit of quantification

calculated according to ISO 8466-1 and DIN 32 645 are shown in Table 1.

Method Performance and Validation

Precision and recovery experiments were performed by spiking deionized water with different levels of standard Cr(VI). The data obtained are shown in Table 2. Different experiments were conducted to study the potential interferences arising from the presence of various substances in environmental samples. Any significant interference originating from selected anions (F⁻, Cl⁻, NO₃⁻, Br⁻, SO₃²⁻ and SO₄²⁻) and cations (Na⁺, K⁺, Mg²⁺ and Cr³⁺) were observed.

Analysis of Real Samples

In order to be useful this method was used to determine Cr(VI) in environmental samples. Four samples

Table 3. Concentration of Cr(VI) in analyzed samples.

Sample	Total Cr content [$\mu\text{g L}^{-1}$] *	Concentration of Cr(VI) [$\mu\text{g L}^{-1}$]
Rainwater no.1	7.32	1.3
Rainwater no.2	3.62	0.8
Rainwater no.3	8.26	2.2
Rainwater no.4	5.05	1.1
Water extract from galvanic sediments no.4	80.58	15.1
Water extract from galvanic sediments no.12	112.46	22.8
Water extract from galvanic sediments no.23	40.87	7.7
Water extract from galvanic sediments no.24	80.64	14.3

*The total Cr content was determined by ICP-MS method.

of rainwater (originating from an industrial area) and 4 samples of water extracted from galvanic sediments were prepared. Rainwater after sampling was filtered using a $0.2 \mu\text{m}$ Sartorius filter.

100 g of dry galvanic sediments was placed into a 1 L plastic bottle and filled to 1 L volume with deionized water. After 24 hours of shaking the extract was filtered by $0.2 \mu\text{m}$ Sartorius filter before analysis. Table 3 shows data obtained for the rainwater and galvanic samples. Besides the concentration of Cr(VI), it also gives the total chromium content in analyzed samples determined by ICP-MS method. An example of chromatogram is given in Fig. 1.

The concentration of Cr(VI) in analyzed samples was determined by area measurement of the peaks representing this ion by comparison with standard peaks obtained from standard solutions of chromium(VI).

Discussion of Results

1. Chemical speciation of Cr(VI) in environmental samples is essential to fully understand its toxicity and bioavailability. The method described is sensitive and selective and allows determination of Cr(VI) on $\mu\text{g L}^{-1}$ levels in different water samples.
2. Ion chromatography with UV detection after post col-

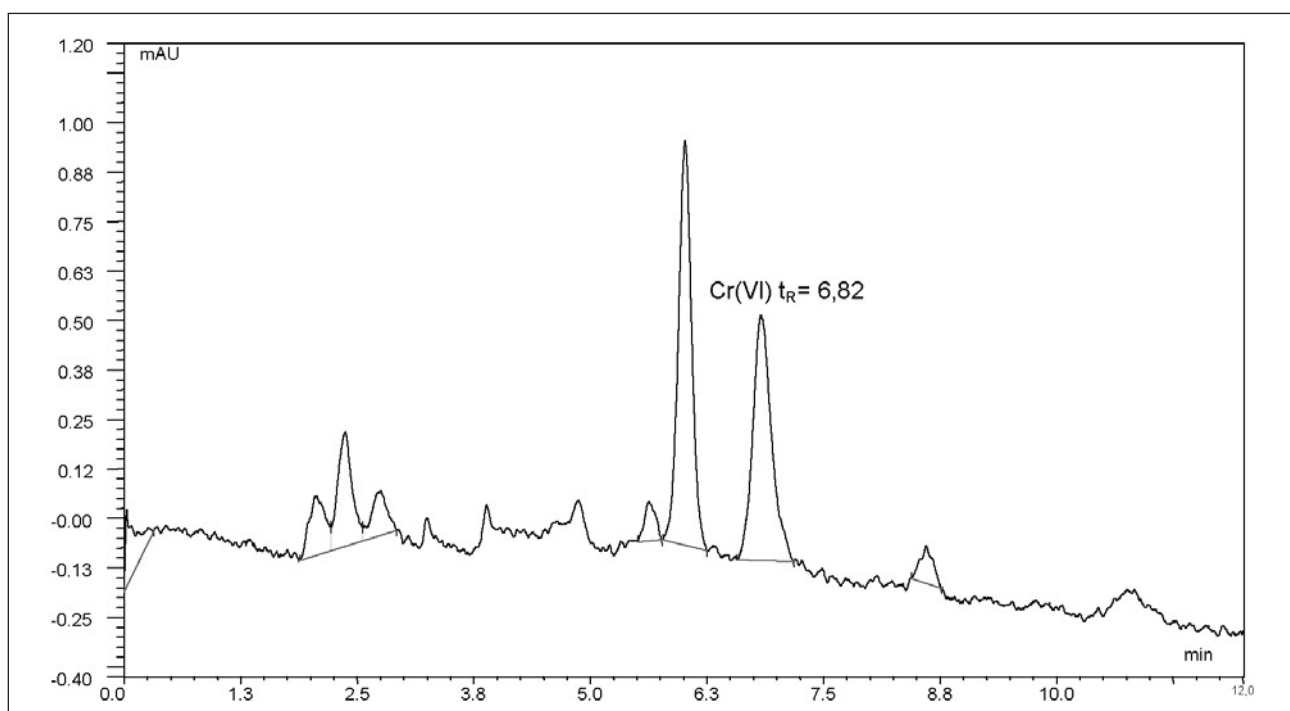


Fig. 1. An example chromatogram of water extract of galvanic sediments no.23. (Analytical conditions as described in Experimental).

umn derivatization was used so far, but compared to described direct method the old one until now used is more complicated due to the necessity of using a post column device.

3. Chromium(III) is not retained on column in described analytical conditions, because of the slow kinetics of ligand exchange with PDCA.
4. A comparison of results for deionized water, drinking water and rainwater samples (Table 1) affirmed that there are no significant differences if some statistical data are calculated from peak area or peak height. The limit of quantification calculated from peak height is lower than the calculated from peak area, but the difference is less than 5%.
5. Common anions and cations usually present in environmental samples have no influence on separation and analysis of Cr(VI).
6. Detection limits, precision and recovery (Table 2) are quite satisfactory for environmental proposes. Only methods requiring much more sophisticated instrumentations than ion chromatography with UV detector provide better detectability.
7. A comparative study of different analytical methods was not carried out, thus the information result from Table 3 is that Cr(VI) amounted to about 20% of total chromium content in these environmental samples.
8. Because of the application of classic UV detector – in comparison to other instrumental techniques such AAS or ICP, this method is relatively cheap and readily available in typical laboratories.

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