COMPARISON OF THE ANALYTICAL PERFORMANCE OF TWO COLUMNS USED FOR DETERMINATION OF CHROMIUM(VI) IN WATER

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SUMMARY

In the different compartments of the environmental chromium occurs mainly in the oxidation states (III) and (VI). Although Cr(III) is an essential trace element for humans, Cr(VI) is highly cancerogenic and mutagenic. It is, therefore, necessary for risk assessment not only to determine total chromium, but also to determine chromium species, especially Cr(VI). Hexavalent chromium can be determined as chromate (CrO_4^{2-}) by ion chromatography. In recent years ion chromatography has became a powerful technique for determination of ions, including inorganic and organic anions and cations.

In the work discussed in this paper an ion-chromatographic method using ion-exchange columns and direct UV detection for determination of Cr(VI) in water samples has been validated. The analytical performance of Dionex IonPac AS7 and CS5A columns has been compared and method linearity and sensitivity, limit of determination, and limit of quantification calculated from peak area and peak height are given.

INTRODUCTION

Interest in analysis of chromium in the environment originates from widespread use of this metal in a variety of industries, for example metallurgical, chemical, and refractories. The different toxicity and bioavailability of chromium(III) and chromium(VI) are well-known and, because they are a public-health concern, require strict monitoring. Chromium(III) is essential for humans whereas Cr(VI) compounds are highly toxic and cancerogenic [1]. Chromium is usually analysed by use of instrumental techniques such as AAS or ICP [2,3]. These methods are precise and sensitive but enable determination of total chromium only. According to

European [4] and Polish [5] regulations the maximum permissible concentration of total chromium in drinking water should not exceed 50 μg L^{-1}. Polish regulations also distinguish between total chromium and Cr(VI), the concentration of which should not exceed 3 μg L^{-1}. The concentration of Cr(VI) is usually estimated from the difference between the total chromium content and the concentration of Cr(III), which is analysed by means of photometric methods. One consequence of this so-called 'difference method' is that calculated concentrations of Cr(VI) are not accurate, especially when the Cr(VI)/Cr(III) ratio is less then 1:100. Thus, species analyses including simultaneous separation of Cr(III) and Cr(VI) is desirable. If this is not possible, more interesting toxicologically is determination of Cr(VI) only, because of its cancerogenic properties.

One of the best methods available for determination of ions in water samples is ion chromatography [6]. This well-established analytical method was initially used mainly for determination of common anions and cations. Recently a new generation of analytical columns, larger loop injection, and more complex sample preparation and detection techniques have been incorporated into new approved methods to enable species analyses and determination of ionic contaminants at trace concentrations [7,8]. Application of ion chromatography to the analysis of chromium species in environmental samples is possible using different detectors, for instance ICP–MS [9], UV [10–12], or chemiluminescence [13]. The most popular in ion chromatography conductivity detector is not sufficiently sensitive for determination of chromium ions. Cr(VI) analyses in water samples are usually based on separation using a suitable ion-exchange column, post-column derivatisation, and UV detection [14,15]. These methods are sensitive and accurate, with limits of determination below 0.1 μg L^{-1}, but, because a post-column device is necessary, are more complex than direct methods. An alternative is simple and selective determination of Cr(VI) in water by ion chromatography with direct UV detection with a limit of quantification at the μg L^{-1} level [16].

The objective of the work discussed in this paper was application of ion chromatography with UV detection to the determination of Cr(VI) ions in water samples, including comparison of the analytical performance of two ion-exchange columns used for separation and determination of Cr(VI) in water samples. The Dionex IonPac AS7 analytical column in combination with an AG7 guard column was designed for analysis of a wide range of anions including fluoride, chloride, polyphosphates, nitrite, bromide, cyanide, sulphate, nitrate, iodide, and chromate. Dionex [14] and

the US EPA [15] recommend this anion-exchange column for analysis of Cr(VI) using post-column derivatisation. The Dionex IonPac CS5A column (used in combination with a CG5A guard column) was designed to separate a broad range of chelated metal complexes (transition metals and lanthanides) by anion and/or cation-exchange chromatography. The CS5A column contains a 55% cross-linked, microporous, hydrophobic resin core agglomerated with two layers of permeable latex particles. The latex particles carry the cation and anion-exchange functionality. The first layer is fully sulphonated latex for cation exchange and the second is fully aminated layer for anion exchange. For both columns the method was validated by determination of linearity, accuracy, and limits of determination and quantification.

EXPERIMENTAL

Chemicals

Analytical grade K_2CrO_4, used for preparation of standard solutions of Cr(VI), and $MgSO_4$, used for eluent preparation, were obtained from Merck (Germany). Eluents were degassed with helium before use. Water used in the experiments was purified by use of Millipore (Bedford, USA) equipment; its electrical conductivity was <0.05 μS cm^{-1}.

Apparatus

Ion chromatography was performed with a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph consisting of a gradient pump (GP 40), UV detector (AD 20), rear-loading Rheodyne injection valve, autosampler (ASM-2), and Chromeleon Workstation (version 6.3). A Perkin–Elmer 100 atomic absorption spectrometer was used for determination of total chromium. The analytical conditions used (Table I) were based on those used in other work [17].

Preparation of Calibration Solutions

Chromium(VI) stock standard solution (1000 mg L^{-1}) was prepared by dissolving of potassium dichromate in deonized water. It was stored under refrigeration at 2 to 8°C. To exclude possible interferences from the matrix, ten calibration solutions containing Cr(VI) in the range 1.0–10.0 μg L^{-1} were prepared in deonized water or tap water by diluting the stock standard solution to the required concentration immediately before use.

Table I

Analytical conditions used for determination of chromium(IV)

Guard column	Dionex IonPac: AG7 or CG5A
Analytical column	Dionex IonPac: AS7 or CS5A
Eluent	80 mmol L^{-1} MgSO$_4$
Flow rate	0.8 mL min^{-1}
Injection volume	100 μL
Detection	UV (λ = 365 nm)

RESULTS AND DISCUSSION

Both sets of columns (Dionex IonPac AG7 + AS7 and CG5A + CS5A) were used for separation of Cr(VI) in ten calibration solutions in the range 1.0–10.0 μg L^{-1}, prepared in two series in deonized water and tap water.

Table II

Summary of method validation results, on the basis of peak areas and peak heights, for both sets of columns (the calibration solution was prepared in deionized water)

	Sample matrix	AG7 + AS7		CG5A + CS5A	
		Calculated from peak area	Calculated from peak height	Calculated from peak area	Calculated from peak height
Linearity	Deionized water	$y=0.021x-0.001$	$y=0.116x-0.010$	$y=0.019x-0.006$	$y=0.097x+0.022$
	Tap water	$y=0.020x+0.006$	$y=0.095x+0.019$	$y=0.019x-0.008$	$y=0.109x-0.040$
Relative standard deviation (%)	Deionized water	3.14	3.05	3.65	4.03
	Tap water	3.63	4.44	4.32	3.91
Standard deviation (μg L^{-1})	Deionized water	0.17	0.17	0.17	0.22
	Tap water	0.20	0.24	0.24	0.21
Limit of determination (μg L^{-1})	Deionized water	0.52	0.50	0.52	0.66
	Tap water	0.59	0.73	0.71	0.64
Limit of quantification (μg L^{-1})	Deionized water	1.36	1.32	1.37	1.72
	Tap water	1.88	1.72	1.83	1.67

The calibration solutions prepared in tap water enabled estimation of the effects of common anions (fluoride, chloride, nitrite, and sulphate) and cations (sodium, potassium, calcium, and magnesium) on the separation and determination of Cr(VI). The peak areas and peak heights obtained for Cr(VI) ions were used to test the homogeneity of the variation, the linearity, and calibration and method characteristics in accordance with ISO 8466-1 [18]. A comparative study of the two columns using ISO 16489 [19] was also conducted. A summary of results from method validation, including linearity, standard deviation, relative standard deviation, limit of determination, and limit of quantification, calculated on the basis of peak areas or peak heights for both sets of columns, and their dependence on the sample matrix (deonized or tap water) is given in Table II. All samples were analysed three times and mean values were used in calculations.

The method was applied to the determination of Cr(VI) in drinking water and rain water. The data obtained from three original samples and the same samples spiked with Cr(VI) are given in Table III.

Table III

Results from determination of Cr(VI) in drinking water and rainwater

Sample matrix	Sample number	Total Cr ($\mu g\ L^{-1}$)	Concentration of Cr(VI) ($\mu g\ L^{-1}$)		Recovery (%)	
			AG7 + AS7	CG5A + CS5A	AG7 + AS7	CG5A + CS5A
Drinking water	1	< 1.00	< 0.50	< 0.05	–	–
	2	2.47	0.74	0.83	–	–
	3	12.62	0.96	1.12	–	–
Drinking water spiked with 5 $\mu g\ L^{-1}$ Cr(VI)	1	6.38	4.91	5.23	103	98
	2	8.76	5.60	6.01	97	103
	3	17.07	6.07	6.16	102	101
Rain water	1	6.27	1.84	1.96	–	–
	2	20.41	9.62	9.35	–	–
	3	7.85	2.61	2.17	–	–
Rain water spiked with 5 $\mu g\ L^{-1}$ Cr(VI)	1	11.85	6.92	7.06	101	109
	2	25.90	14.37	14.82	98	103
	3	13.22	7.98	7.67	104	107

The method is clearly suitable for determination of Cr(VI) at $\mu g\ L^{-1}$ levels in environmental water samples–the limit of quantification and the

linearity are satisfactory for determination of Cr(VI) in drinking water and other water with low contamination. Only methods that require more sophisticated instrumentation provide better detectability.

The different ion-exchange resins used in the Dionex IonPac AS7 and CS5A columns lead to different retention times of the Cr(VI) ion–4.5 min on the AS7 column and 6.3 min on the CS5A column under the conditions used in this work. Despite this difference the columns gave comparable results–limits of determination and quantification of Cr(VI) were not significantly different for the different columns, so the method is robust not only with regard to the eluent applied and its flow-rate but also with regard to the separation column used. Use of peak area or peak height for calculations also resulted in no significant differences. Comparable results were obtained from determination of Cr(VI) in drinking water and rainwater using the AS7 and CS5A columns. Recovery of chromium(VI) from samples spiked with 5 μg L^{-1} Cr(VI) was in range 98–109%.

The tap water sample matrix had no effect on the method. In general, slightly better limits of determination and quantification were obtained when Cr(VI) calibration solutions were prepared in deonized water.

Because of the use of $MgSO_4$ as eluent and UV detection, the method is less expensive than other instrumental techniques, for example ICP–MS; it is, therefore, suitable for routine use in all laboratories.

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