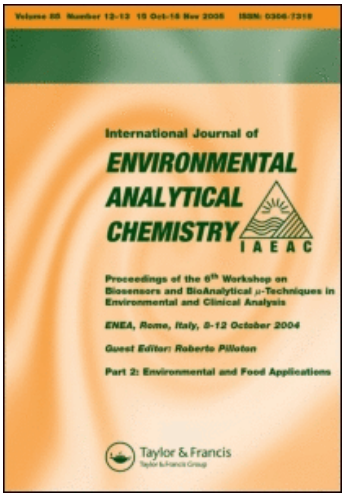

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Frank Sacher[a]; Brigitte Raue[a]; Josef Klinger[a]; Heinz-Jürgen Brauch[a]
[a] DVGW-Technologiezentrum Wasser, Karlsruhe, Germany

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SIMULTANEOUS DETERMINATION OF Cr(III) AND Cr(VI) IN GROUND AND DRINKING WATERS BY IC-ICP-MS

FRANK SACHER*, BRIGITTE RAUE, JOSEF KLINGER and HEINZ-JÜRGEN BRAUCH

DVGW-Technologiezentrum Wasser, Karlsruher Straße 84, 76139 Karlsruhe, Germany

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The coupling of ion chromatography (IC) and inductively-coupled plasma mass spectrometry (ICP-MS) provides a powerful tool for the simultaneous determination of Cr(III) and Cr(VI) in water samples. The experimental set-up of the technique is described in detail and performance data are given, whereby detection limits of 0.1 µg/l could be achieved for both chromium species without preconcentration. With this method, a complete analysis can be done in less than 3 minutes. In order to improve the repeatability of the method, Rh(III) as internal standard is used. Stability of the two chromium species in water turned out to be a major problem and optimal conditions for storage were determined. For real water samples storage at 4 °C in the dark at neutral pH and analysis as fast as possible is recommended. The application of the IC-ICP-MS technique to real water samples and the comparison to another, more time-demanding and less sensitive method proves the capacity of the method.

Keywords: Chromium; speciation; ion chromatography; ICP-MS; stability of samples

INTRODUCTION

In natural aqueous matrices, chromium is mainly found in two different oxidation states. In acid solutions, Cr(III) is the most stable form, at higher pH values, however, Cr(III) is easily oxidized to Cr(VI), which is found as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) in aqueous solutions. Depending on the ambient conditions, in ground waters both oxidation states of chromium can be present.

The toxicity of chromium strongly depends on its oxidation state. Cr(VI) is classified as carcinogenic and highly toxic even at very low concentrations,

* Corresponding author. Fax: +49-721-9678104. E-mail: sacher@TZW.de.

whereas Cr(III) is nontoxic and at low concentration levels even essential [1,2]. Hence, for a complete assessment of the chromium concentration levels in ground and drinking waters the separate determination of both chromium species is of special importance, although the limiting values in both, the German Drinking Water Regulation and the proposal for the New European Directive concerning the quality of water intended for human consumption, refer to the total amount of chromium and not to the concentration of individual species. If removal of chromium during drinking water treatment is necessary, the oxidation state is of interest again. Cr(III) can be easily removed by flocculation with iron salts or by lime softening [3], whereas Cr(VI) removal is difficult and reduction to Cr(III) prior to the removal step, e.g. by addition of iron(II) salts, seems to be the favorite technique.

Different analytical methods for the speciation of chromium are described in literature, based either on a colorimetric detection of chromium complexes or on the coupling of chromatographic separation techniques with spectrometric detection methods [4–20]. However, most of these methods are quite time-demanding and not very sensitive, so that additional preconcentration steps are necessary. Furthermore, coupling techniques often need outstanding technical equipment and, hence are not suitable for routine analysis. On the other hand, many colorimetric methods are restricted by the problem of interferences.

In this paper a method is presented which combines the separation of the inorganic chromium species by ion chromatography (IC) and the detection by inductively-coupled plasma mass spectrometry (ICP-MS). It will be shown that this coupling technique can be easily used for routine analysis, whereby the method is very fast (one complete speciation analysis in less than 3 minutes) and sensitive (detection limit of 0.1 µg/l for both chromium species without preconcentration). Special importance will be attributed to the convenient evaluation of the acquired data sets and to the stability of samples under different conditions of storage.

EXPERIMENTAL

Cr(III) was used as $Cr(NO_3)_3 \cdot 9\ H_2O$ and Cr(VI) as $K_2Cr_2O_7$. Both chemicals were of analytical grade and purchased from Merck (Darmstadt, Germany). Standard solutions were made in deionised water. All concentrations given in this paper refer to the amount of chromium. Rh(III) was used as a 1 g/l solution of $RhCl_3$ in 8% hydrochloric acid. This solution was available as ICP-MS standard from Merck. Nitric acid and a 25% aqueous solution of ammonia were of analytical grade and purchased from Merck, too. A scheme of the whole experimental set-up for the simultaneous determination of Cr(III) and Cr(VI) by IC-ICP-MS is

presented in Figure 1. As a rule, the sample is used without further pre-treatment. Sample injection takes place manually via a Rheodyne 6-port valve. Separation of the two chromium species is done on an anion exchange column (OmniPac PAX100 guard column from Dionex, Idstein, Germany) using a 0.05 mol/l nitric acid as eluent, which is adjusted to pH 2 with a 12.5% aqueous solution of ammonia. Cr(III) as a cation is not held back by this anion exchange column and elutes within the dead time of the column, whereas Cr(VI) as an anion is held back and elutes with a retention time of 1.4 min. Hence, the whole analysis can be done within less than three minutes.

For the sensitive detection an ICP-MS system ELAN 6000 (Perkin-Elmer, Überlingen, Germany) is used, whereby the effluent of the IC column is directly coupled to the nebulizer system of the ICP-MS unit. In order to test the performance of the ICP-MS for the determination of chromium certified reference materials (NIST Standard Reference Material 1643d "Trace Elements in Water" and SLRS-3 "Riverine Water Reference Material for Trace Metals" delivered by the National Research Council Canada) were regularly measured.

For the detection of the chromium species mass number 52 is used, which has a natural abundance of 83.8% and therefore provides the highest sensitivity. Interferences from $^{36}Ar^{16}O$ result in an increasing background noise for mass number 52 and, hence, in a loss of sensitivity. Nevertheless, this effect is not as important for the IC-ICP-MS technique as for pure ICP-MS without separation step.

Due to the chromatographic separation step in front of the ICP-MS system interferences of the two chromium species with $^{40}Ar^{12}C$ were not observed. In addition, blank values for chromium were very low and no contamination effects due to the equipment could be detected. Ion chromatographic conditions and ICP-MS parameters for the speciation of chromium are summed up in Table I. Figure 2 presents a chromatogram of a standard solution with both, 10 µg/l Cr(III) and Cr(VI) in drinking water. It can be seen that the peak width is smaller for Cr(III) than for Cr(VI) and, hence, the Cr(III) peak is a little bit taller.

A basic requirement for the acquisition of a chromatogram is the ability to acquire and to process time resolved data sets. This requirement is totally fulfilled by the ELAN 6000 software. But, as the ELAN ICP-MS software is no chromatographic software, it is unsuitable for a satisfactory evaluation of the acquired data. For example, setting of baselines or peak integration is not possible. Furthermore, the data format of the ELAN software is not legible by any common chromatographic software. Hence, for an easy and convenient data evaluation, the data sets acquired by the ELAN software have to be transformed into another, more suitable format. This can be done by an additional transformation software. At first, the ICP-MS data file is converted into a NetCDF format using the NT-file translator, which is a part of the ELAN software. This data format can then be transformed into a raw-data format using the convert program

which can be installed as additional feature of the Turbochrom software from Perkin-Elmer. Turbochrom is a common software for GC or HPLC applications. Finally, with the Turbochrom software and the transformed data sets peak labelling, manual and automatic baseline setting, peak integration as well as generation of calibration tables and automatic report generation can be done. For setting up calibration curves or calculating concentrations of real water samples, the peak areas of the Cr(III) and Cr(VI) signals were used.

TABLE I IC conditions and ICP-MS parameters for the determination of chromium species

IC conditions:	
pump:	Perkin Elmer 200LC Bio pump
separation column:	Dionex OmniPac PAX100 guard column
eluent:	0.05 mol/l HNO_3
	(adjusted to pH 2 with NH_3 solution)
flow rate:	1 ml/min
sample volume:	100 µl
internal standard:	$RhCl_3$
ICP-MS parameters:	
ICP-MS:	Perkin Elmer Elan 6000
RF power:	1150 W
plasma gas:	argon
plasma gas flow:	15 l/min
auxiliary gas flow:	1 l/min
nebulizer gas flow:	0.975–1.050 l/min (cross-flow)
detector mode:	pulse counting
lens:	lens scan enabled
data acquisition:	
m/z(Cr):	52
m/z(Rh):	103
scanning mode:	peak hopping
measurement unit:	counts
sweeps/reading:	1
readings/replicate:	120
replicates:	1
dwell time:	1250 ms
integration time:	300000 ms

RESULTS

Performance data

For the calculation of the performance data, a calibration was carried out in spiked deionized water with ten concentration levels in the range of 0.4 to 4 µg/l Cr(III) and Cr(VI), respectively. Figure 3 presents the resulting calibration curves for the two chromium species. In Table II the limits of detection, identification and determination are given. Calculation of these parameters was done according to the German standard method DIN 32645[21]. As it can be seen, detection limits of about 0.1 µg/l can be achieved for both species without further preconcentration. Due to the better performance of the respective peak in the chromatogram, Cr(III) is more sensitive than Cr(VI).

TABLE II Limits of detection, identification and determination for the analysis of Cr(III) and Cr(VI) with IC-ICP-MS

Species	*Limit of Detection in ug/l*	*Limit of Identification in ug/l*	*Limit of Determination in ug/l*
Cr(III)	0.097	0.19	0.35
Cr(VI)	0.12	0.24	0.44

In Table III data for the repeatability of the method in different matrices are presented. For the determination of the repeatability a tenfold injection of one sample was done within a time period of one day. The experiments were carried out in deionized water and in drinking water at a concentration level of 10 µg/l for both, Cr(III) and Cr(VI).

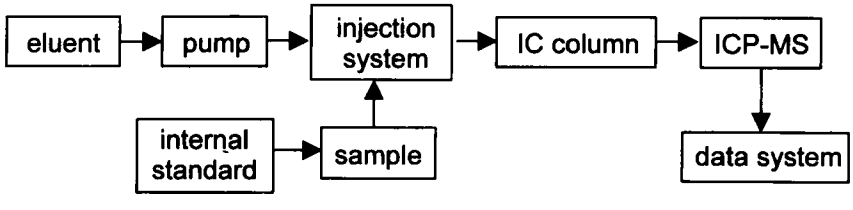

FIGURE 1 Experimental set-up for the simultaneous determination of Cr(III) and Cr(VI) by IC-ICP-MS

The data in Table III prove that the repeatability of the IC-ICP-MS method is excellent for deionized water. However, for drinking water the data, especially for Cr(III), are worse than for deionized water. A deeper analysis of the data shows that the sensitivity of the ICP-MS decreases with increasing number of measurements. This is mainly due to the contamination of the ICP-MS interface by calcium salts, which are present in drinking waters in the mg/l range. In order to improve the repeatability, 10 µg/l Rh(III) as internal standard were added to the samples prior to analysis. Rh(III) as a cation elutes like Cr(III) within the dead time of the anion exchange column and can be detected by mass number 103. Data evaluation for both, Cr(III) and Cr(VI) was done with respect to the Rh(III) peak area. When using the internal standard, the data for the repeatability in drinking water become as excellent as in deionized water as it can be seen from the last column in Table III (repeatability with internal standard).

TABLE III Repeatability for the analysis of Cr(III) and Cr(VI) with IC-ICP-MS in different matrices (c=10 µg/l, N=10)

species	*deionized water*	*drinking water (without internal standard)*	*drinking water (with internal standard)*
Cr(III)	1.7%	6.3%	1.8%
Cr(VI)	4.1%	4.2%	3.5%

Testing the IC-ICP-MS method with a certified reference material (CRM) is only possible when refering to the total chromium concentration as up to now no aqueous CRM is available for defined chromium species. When applying the method to the NIST Standard Reference Material 1643d "Trace Elements in Water" only Cr(III) was found which is not surprising as the CRM is stored under acid conditions. In a fivefold analysis the chromium concentration of the CRM was determined as (18.7 ± 0.5) µg/l whereby the certified value is (18.5 ± 0.2) µg/l.

Stability of chromium species

For the determination of the total amount of chromium, water samples are usually acidified by addition of nitric acid. Thereon, a significant decrease of the Cr(VI) concentration within a few days was observed, as it is illustrated in Figure 4. After 14 days nearly all Cr(VI) had disappeared. At the same time, the concentration of Cr(III) increased and therefore the total amount of chromium

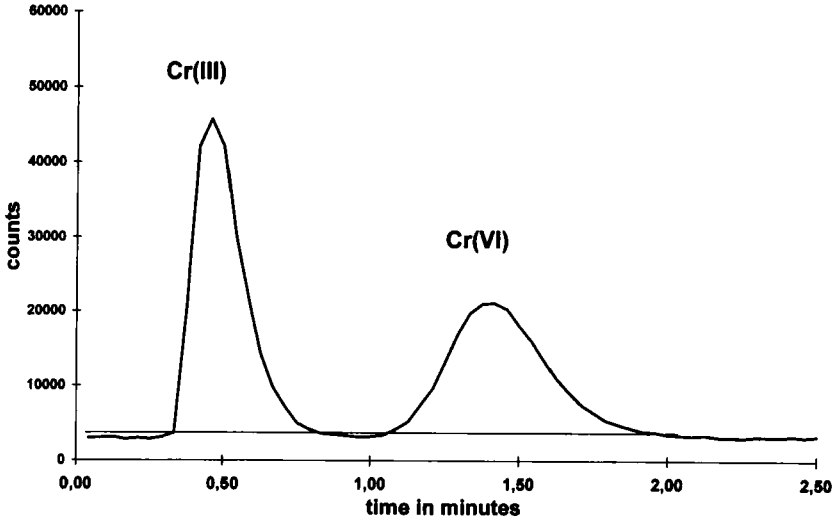

FIGURE 2 Chromatogram of a standard solution with 10 µg/l Cr(III) and Cr(VI) in drinking water

remained constant. This effect is already described in literature[22,23]. Additional experiments showed that the effect is faster at ambient temperature and slower in the cold and dark (see Figure 5). The only explanation for this result is that Cr(VI) is reduced to Cr(III) at low pH values. Repeating the same experiments in deionized water, the decrease of the Cr(VI) concentration was much slower. This result indicates that natural organic matter is involved in the reduction process. In Figure 5 the Cr(III) and Cr(VI) concentrations in deionized water are shown, too, whereby the samples were stored at ambient conditions. As Figure 6 illustrates, in drinking water at neutral pH Cr(VI) was stable over a time period of several days, whereas the Cr(III) concentration and hence the total amount of chromium continuously decreased. This effect can be attributed to the adsorption of Cr(III) ions onto the bottle's surface, especially when using glass bottles, but was also observed when using FEP bottles. Again the effect is slower in the cold and dark, but this time it is not affected by natural organic matter. The decrease of the Cr(III) concentration is in deionized water as fast as in drinking water.

Therefore, for speciation of chromium, sample storage at neutral pH in the cold (at least 4 °C) and dark and analysis as fast as possible is strongly recommended.

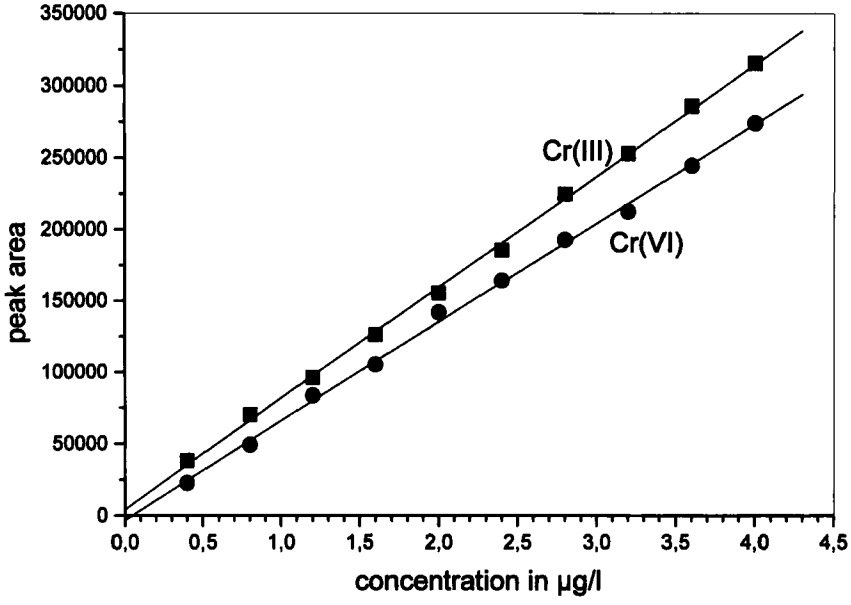

FIGURE 3 Calibration curves for Cr(III) and Cr(VI)

Comparison of methods

Table IV shows data for the chromium speciation in some ground water samples. Speciation was done with the IC-ICP-MS method presented in this paper as well as with an alternative method. Using the alternative method, at first the total amount of chromium is measured by ICP-MS. Then, the Cr(VI) concentration is determined colorimetrically[4] and afterwards the concentration of Cr(III) is calculated as difference between the total amount of chromium and the Cr(VI) concentration. The data prove that the total chromium concentrations calculated from the IC-ICP-MS data for Cr(III) and Cr(VI) correspond excellently to the total amount of chromium which was directly measured by ICP-MS. The correspondence between the Cr(VI) concentrations determined with the two different methods is very good, too. In addition, the data in Table IV clearly demonstrate the advantage of the IC-ICP-MS method. Due to its high sensitivity, the IC-ICP-MS technique is able to detect Cr(III) in concentrations of about 1 µg/l. Using the alternative method the Cr(III) concentration is calculated as difference between the total amount of chromium and the Cr(VI) concentration. As these two numbers have only a limited precision, the limit of detection for Cr(III) has to be set to 10 µg/l. Therefore, in all samples no Cr(III) could be detected with the alternative method.

TABLE IV Comparison of results for the chromium speciation in a ground water by IC-ICP-MS and an alternative method (all concentrations in µg/l)

	IC-ICP-MS			*alternative method*		
no.	*Cr(III)*	*Cr(VI)*	*Cr(total)**	*Cr(III)**	*Cr(VI)*	*Cr(total)*
1	1,3	62	63	< 10	62	64
2	< 0.1	65	65	< 10	62	64
3	<0.1	15	15	< 10	16	16
4	1.6	<0.1	1.6	< 10	< 10	1.6

*: calculated.

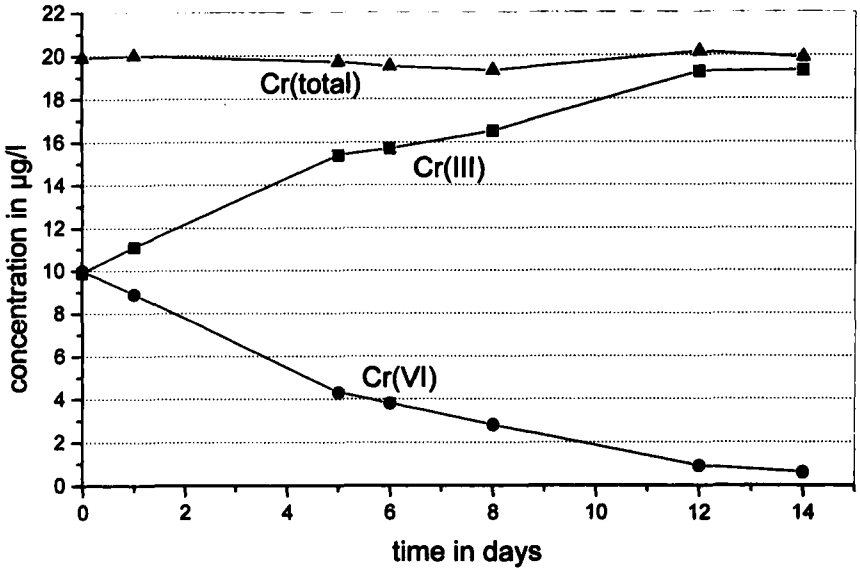

FIGURE 4 Stability of chromium in tap water at pH 2

Furthermore, due to the low sensitivity of the colorimetric method, the limit of detection for Cr(VI) is 10 µg/l. Thatś why in the case of sample no. 4 using the alternative method no decision can be made whether the total chromium concentration of 1.6 µg/l can be attributed to Cr(III) or Cr(VI). However, application of the IC-ICP-MS technique clearly shows that only Cr(III) is present in this sample.

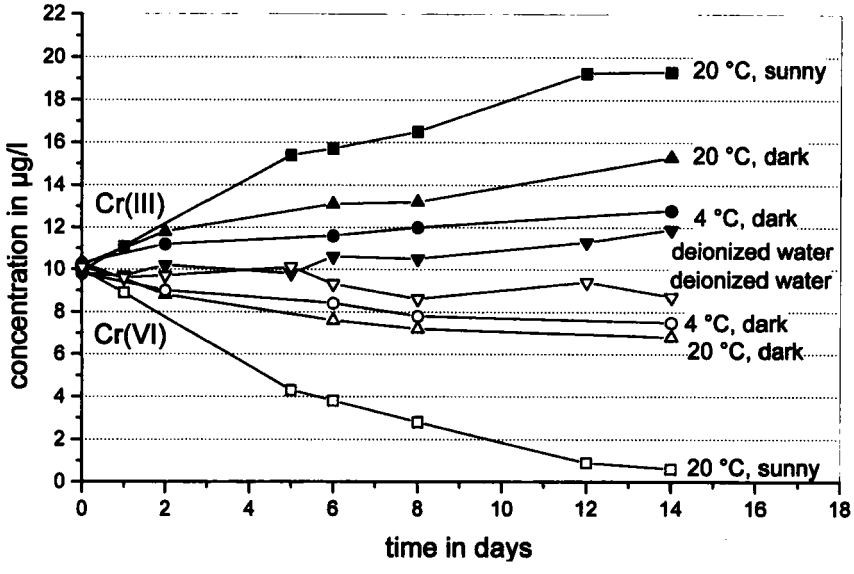

FIGURE 5 Stability of chromium in tap water and deionized water at pH 2

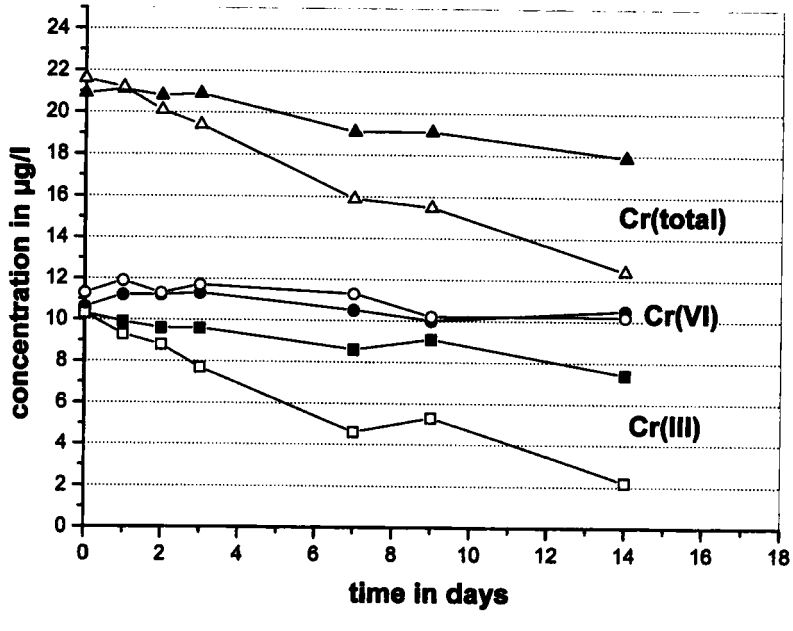

FIGURE 6 Stability of chromium in tap water at neutral pH (open symbols: sunny, 20 °C, solid symbols: dark, 4 °C)

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