Speciation analysis of Cr (III) and Cr (VI) in drinking waters using anion exchange chromatography coupled to the Thermo Scientific iCAP Q ICP-MS

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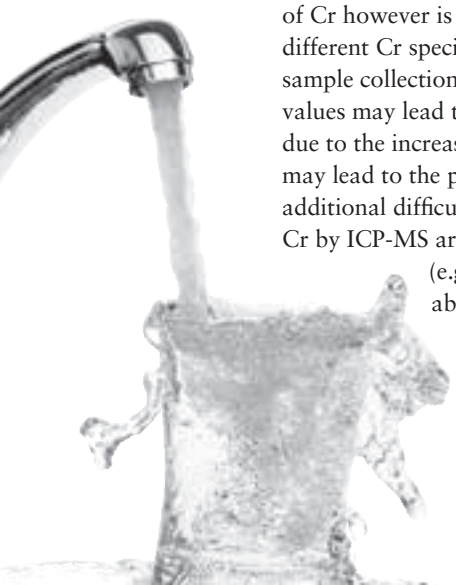
Key Words
iCAP Q, Cr speciation, Ion chromatography, Drinking water, ICS-5000

Goal

To develop a sensitive, robust and high throughput method for the trace level analysis of Cr (III) and Cr (VI) species in natural waters using IC-ICP-MS.

Introduction

Due to it widespread use in industrial applications such as chromium plating, dye manufacturing and preservation of wood and leather materials, chromium concentrations in environmental samples are monitored on a routine basis. Both the United States EPA and the European Union have specified maximum admissible chromium concentrations in their respective drinking water directives. As with many other trace elements, chromium (Cr) is typically found in more than one chemical form, each of which with different chemical properties and behavior, such as bioavailability and toxicity. For chromium, Cr (III) is essential to human beings and involved in different processes in the body while Cr (VI) is highly toxic. Total Cr content therefore in, for example, a drinking water sample does not provide sufficient information to evaluate potential hazards to populations exposed to it. In order to provide this critical information a supporting speciation analysis is required to determine the amounts of the different Cr species in the sample. The speciation analysis of Cr however is a challenging task, since the stability of different Cr species is easily affected by conditions during sample collection and treatment[1]. For example, low pH values may lead to the degradation of Cr (VI) to Cr (III) due to the increased redox potential, while high pH values may lead to the precipitation of Cr (III) as $Cr(OH)_3$[2]. An additional difficulty in the accurate speciation analysis of Cr by ICP-MS are the numerous spectral interferences (e.g. $^{35}Cl^{16}O^{1}H^{+}$ or $^{40}Ar^{12}C^{+}$) on the most abundant chromium isotope, ^{52}Cr.



Sample and calibration solution preparation

Daily working standards were prepared by diluting the appropriate quantity of commercially available stock solutions (1000 µg/mL) of each chromium standard in a 0.1 mol/L ammonium nitrate solution adjusted to a pH of 4. Drinking water was collected in a PFA bottle previously rinsed with high purity nitric acid. The water was analyzed directly without dilution or pH adjustment in order to keep the species unchanged before analysis.

Instrument configuration

Chromatographic separations were carried out using the Thermo Scientific Dionex ICS-5000 ion chromatography system. Due to its completely metal-free solvent pathway, this system is non-contaminating and is therefore perfectly suited for elemental speciation studies at the trace levels required by this application. For the separation of the two Cr species, a Thermo Scientific Dionex AG-7 anion exchange column (2 x 50mm) was used throughout this study. Although this column is designed to be used as a guard column, its highly effective separation medium contains capacities for the separation of both cationic and anionic species[3] and it is therefore able to completely separate both Cr species in less than three minutes. A Thermo Scientific iCAP Qc ICP-MS was used as a high performing elemental detector of the Cr species eluted from the ICS-5000. Due to the use of flatapole technology in the Thermo Scientific QCell collision cell, the iCAP Q series of ICP-MS instruments offer the selectivity to suppress spectral interferences while maintaining the high sensitivity for trace metal detection in coupled applications such as IC-ICP-MS.

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General analytical conditions

The iCAP Qc ICP-MS was equipped with a peltier cooled PFA spray chamber and a PFA-LC nebulizer (Elemental Scientific, Omaha, NE, USA). The PFA-LC nebulizer has a very low dead volume and is compatible with LC fittings making it ideal for chromatographic analyses. The demountable torch was equipped with a 2 mm I.D. injector. For interference-free detection of $^{52}Cr^{+}$ and $^{53}Cr^{+}$, all measurements were carried out in a single collision cell mode, with kinetic energy discrimination (KED), using pure He as collision gas.

The instrument was operated using the following parameters:

Parameter	Value
Forward power	1550 W
Nebulizer gas	0.80 L/min
Injector	2 mm I.D.
Cell gas flow / KED voltage	4.8 mL/min He / 2V
Dwell time	100 ms

Table 1: iCAP Q operating parameters.

Chromatographic separations on the ICS-5000 were carried out using the parameters summarized in Table 2. For the elution of the different Cr species, anion exchange chromatography was chosen using isocratic elution with nitric acid. Although the two species have different charges, (Cr (III) is present predominantly as $[Cr(H_2O)_6]^{3+}$ and Cr (VI) as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$ depending on the pH), the Dionex AG-7 column can elute both due to its capacities for the separation of both cations and anions3. In contrast to other techniques based on reversed phase ion pairing chromatography, no prior incubation with complexing agents such as EDTA is required with the method described. Sample pre-treatment is therefore no longer required, eliminating any possible risk of contamination as well as maximizing sample throughput. Under the applied conditions, complete separation of Cr (III) and Cr (VI) is accomplished in less than 150 s.

Column	Dionex AG-7 (2 mm i. D., 50 mm length)
Elution	Isocratic
Mobile phase	0.4 mol/L HNO_3
Flow rate	400 µL/min
Injection volume	20 µL
Duration	150 s

Table 2: ICS-5000 operating parameters

Coupling between instruments was achieved by direct connection of the column outlet to the nebulizer. Bi-directional communication was established by using a trigger cable that attached to the I/O panel next to the iCAP Q's sample introduction system. All quantification (evaluation of peak areas and concentrations etc) were achieved using the tQuant features of the Thermo Scientific Qtegra control software.

Results and Discussion

For initial method development, a mixture containing 5 ng/g of each Cr species was separated using different mobile phases. The resulting chromatograms are shown in Figure 1 as screenshots from the Qtegra™ software package. While the Cr (VI) was easily eluted from the column with all the mobile phases tested, Cr (III) was strongly retained and only eluted as a distinguishable peak at nitric acid concentrations higher than 0.3 mol/L. At even higher concentrations, however, the redox potential of Cr (VI) is increased and could potentially lead to its reduction and therefore possible loss. For this reason, a compromise nitric acid concentration limited to 0.4 mol/L was used for the elution of both Cr species in this study. At this concentration, cycle times of under 150 s were achieved for a complete separation of Cr (III) and Cr (VI).

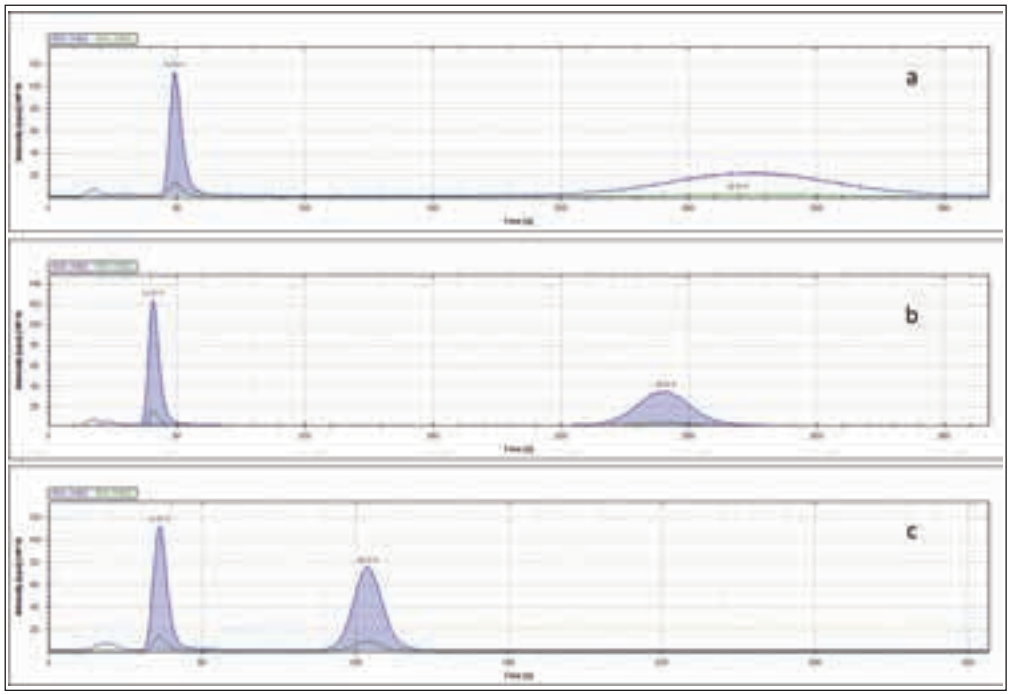

Fig. 1: Cr (III) and Cr (VI) chromatograms obtained using 0.2 (a), 0.3 (b) and 0.4 (c) mol/L nitric acid as mobile phase. Please note that the x-axis in (c) has been shortened to 300 s.

In order to determine the effect of any degradation of Cr (VI) to Cr (III) at these conditions, a linear calibration between 0.75 ng/g and 15 ng/g of each species was performed. The resulting calibration curves are shown in Figure 2. As can be seen, the detection sensitivity was determined to be 220 kcps / ng/g for both species, showing them to be unaffected by the HNO_3 matrix used. Detection limits (LOD) of 0.20 pg/g for Cr (VI) and 0.38 pg/g for Cr (III) were calculated from these calibrations.

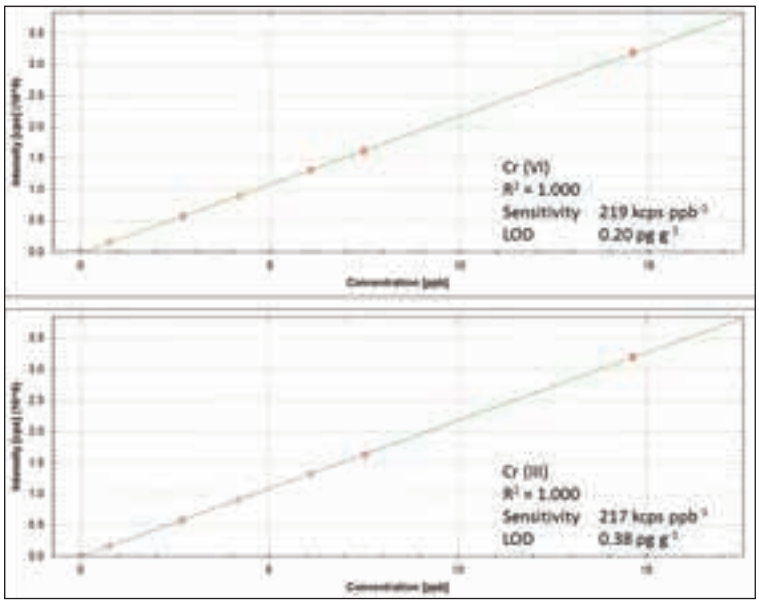

Figure 2: Calibration graphs for Cr (VI) and Cr (III).

As additional proof of the effectiveness of the proposed chromatographic separation, mixtures of both species were quantified against these calibrations in a spike recovery test. Each sample was analyzed in triplicate. The results obtained are shown in Table 3:

Conc. spiked [ng/g]	Cr (VI)		Cr (III)	
	Found (ng/g)	Recovery (%)	Found (ng/g)	Recovery (%)
2.34 of each	2.31 ± 0.01	99 ± 1	2.35 ± 0.02	100 ± 1
6.03 Cr (VI); 1.90 Cr (III)	6.01 ± 0.02	100 ± 1	2.00 ± 0.01	105 ± 1
1.87 Cr (VI); 6.20 Cr (III)	1.85 ± 0.01	99 ± 1	6.15 ± 0.03	99 ± 1

Table 3: Recovery of Cr (VI) and (III) species

These values indicate that recovery for both species is quantitative and therefore both species reach the plasma in their original chemical form. Furthermore, the achieved precisions indicate the excellent stability of the chromatographic separation.

In a second experiment, the reproducibility of the method was investigated. For routine analysis, retention times and peak areas should remain constant to avoid repeated calibration blocks. To test this, a mixture of both species with a concentration of 5 ng/g was repeatedly injected into the LC system over 2.5 h (20 individual injections). Stabilities of < 1.5 % for retention time and < 0.3 % for peak area were obtained (Figure 3).

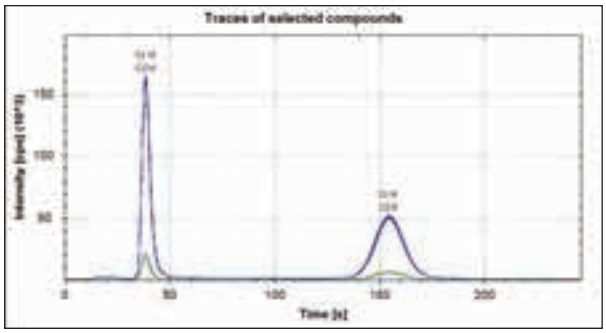

Figure 3: Overlay of 20 repeated injections of Cr (VI) and Cr (III)

Quantification of Cr (III) and Cr (VI) in tap water

Potable water was collected locally and analyzed using the proposed method. As can be seen from the chromatogram in Figure 4, only trace amounts of Cr (VI), at a retention time of ~40 s, could be detected in this sample. After external calibration, the amount of Cr (VI) observed was found to be 42.5 ± 1 pg/g. As an additional proof that the detected peak corresponds to Cr and is not affected by possibly co-eluting compounds causing spectral interferences (e.g. chlorine or carbon based polyatomic species), the isotope ratio $^{52}Cr^{+}/^{53}Cr^{+}$ was calculated and corresponds well to the theoretical value of 8.81).

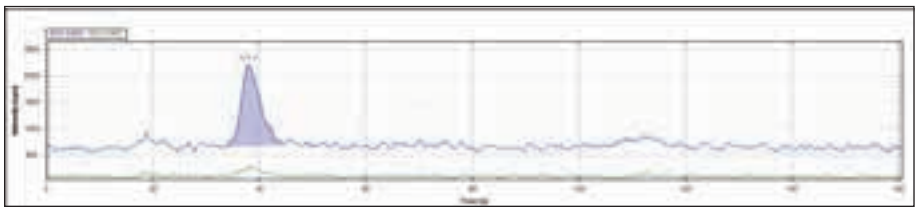

Figure 4: 52Cr and 53Cr chromatograms of a locally source potable water.

Conclusions

Through the combination of the ICS-5000 ion chromatography system with the iCAP Qc ICP-MS, a sensitive, robust method for the speciation analysis of trace levels of Cr (III) and Cr (VI) in natural waters has been developed. The method developed enables fast and reliable speciation analysis of both Cr (III) and Cr (VI) species in water samples without prior incubation steps and with high purity nitric acid as mobile phase. The short, but highly efficient Dionex AG-7 column, provides complete separation of both species in under 150 s, enabling high sample throughput for the routine analysis of water samples.

The new flatapole cell technology introduced in the iCAP Q ICP-MS provides interference-free detection of the ^{52}Cr and ^{53}Cr ions. Sub-ppt detection limits are achievable due to the completely metal free pathway of the ICS-5000 and the high instrumental sensitivity offered by the iCAP Q's He KED mode.

References

1. Séby, F., Charles, S., Gagean, M., Garraud, H., Donard, O. F. X., J. Anal. At. Spectrom. 18 (2003), 1386-1390

2. Xing, L., Beauchemin, D., J. Anal. At. Spectrom. 25 (2010), 1046-1055

3. Dionex homepage (http://www.dionex.com/en-us/products/columns/ic-rfic/specialty-packed/ionpac-as7/lp-73274.html)

Chemicals Used in this Note

Chemical	Fisher Scientific Catalogue Number
IonPac AG-7 Guard Column (2 x 50 mm)	063099
Fisher Optima grade nitric acid	A467-500

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