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Determination of Chromium Species using Ion Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry

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The goal of this report is to highlight a simple method to separate and quantify both major Cr species, Cr (III) and Cr (VI) in drinking water.

Keywords: Chromium speciation, Drinking water, Hexavalent Cr, IC-ICP-MS, IonPac AG7 column.

INTRODUCTION

Chromium is found naturally in rocks, soil, plants and animals, but can also be introduced into the environment as a result of human activity. Like many elements, chromium is found in multiple oxidation states, which can vary significantly in their toxicity, nutritional value, bioactivity, and environmental mobility. In trace amounts, trivalent chromium (Cr (III)) is considered an essential nutrient that promotes insulin, sugar, and lipid metabolism. In contrast, hexavalent chromium (Cr (VI)) is toxic and can lead to respiratory tract, stomach, and intestinal irritation, anemia, and is known to be a human carcinogen.[1] Cr (VI) can leach into drinking water sources naturally, but drinking water can also be contaminated by industrial processes such as wood treatment with copper dichromate, leather tanning with chromic sulfate, and stainless steel cookware. Because of the varying toxicity attributable to the different oxidation states of chromium, simply knowing the total chromium concentration in a solution is not sufficient to determine its true toxicity following exposure, and therefore speciation analysis is required. While inductively coupled plasma mass spectrometry (ICP-MS) can readily determine the total amount of an element present, chromatographic separation prior to the ICP-MS system is required to separate the different elemental species. Because Cr (III) and Cr (VI) have different charges, ion chromatography (IC) using anion exchange is the ideal separation method for analysis of these species.

One of the challenges with chromium speciation is that Cr (VI) can be degraded to Cr (III) and Cr (III) can be converted to a precipitate ($Cr(OH)_3$), depending on the solution pH.[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.[3]

In this application note, the Thermo Scientific™ Dionex™ Aquion™ Ion Chromatography system was coupled with the Thermo Scientific™ iCAP™ RQ ICP-MS to determine the concentration of Cr (III) and Cr (VI) in drinking water.

MATERIALS AND METHODS

Sample preparation

The tap water was acidified with 10 µL of concentrated nitric acid per 10 mL aliquot to yield a pH of around 4. A fortified sample was spiked with 0.1 mL of a standard solution containing 10 µg L^{-1} of both Cr species to 10 mL of the sample to give a final concentration of 0.1 µg L^{-1}.

Instrument configuration

The ion chromatography system used for this work consisted of a Dionex Aquion IC system and a Thermo Scientific™ Dionex™ AS-AP autosampler. All components of the IC system were controlled using the ChromControl plug-in for Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ Software. The system was purged and equilibrated prior to the start of sample analysis on each day. Data evaluation was accomplished using the tQuant virtual evaluation module of Qtegra Software. The chromatographic method was developed and published elsewhere,[4] in brief, an isocratic separation using 0.3 mol L^{-1} nitric acid was used to separate both Cr species using a Thermo Scientific™ Dionex™ IonPac™ AG7 anion exchange guard column. Using a guard column alone (length of only 5 cm) effectively reduces the analysis time per sample and therefore increases sample throughput. At the same time, the chromatographic resolution and sample capacity are sufficient for the analysis.

The iCAP RQ ICP-MS was operated using the conditions summarized in Table 1. After optimization of the instrument using the autotune routines delivered with the Qtegra ISDS Software, the outlet of the column was directly connected to the PFA-LC nebulizer using a zero dead volume connector. The instrument was operated using kinetic energy discrimination (KED) with He as a collision gas to effectively eliminate all potential polyatomic interferences on Cr.

Table 1. Instrument configuration

Ion Chromatography	
Column	Dionex IonPac AG7, 2 x 50 mm
Flow rate	0.4 mL min^{-1}
Eluent	0.3 mol L^{-1} Nitric Acid
Injection volume	25 µL
ICP-MS	
Spray chamber	Quartz cyclonic, chilled at 2.7 ºC
Nebulizer	PFA-LC
Injector	2.5 mm I.D., quartz
Interface	Nickel sampler and skimmer cone High matrix skimmer cone insert
Forward power	1550 w
Nebulizer gas	1.12 L min^{-1}
Collision cell gas	He at 4.5 mL min^{-1}
KED voltage	3 V
Dwell times	0.1 s
Total acquisition time	3 min 20 sec

RESULTS AND DISCUSSION

The second chromatogram (from top to bottom) in Figure 1 shows the separation of a solution containing Cr (III) and (VI) at a concentration of 0.1 µg L^{-1}. Both species are completely separated and complete elution is achieved within 120 s. To assure complete elution if a much higher concentration of Cr (III) is present in a sample, the total runtime of the method was extended to 200 s. For calibration of the system,

a three-point calibration curve was generated using standard solutions containing both Cr species at concentrations between 0.1 and 10 µg L^{-1}. The analytical figures of merit obtained are shown in Table 2. The stability of retention times was verified using 10 injections of tap water spiked with 0.1 µg L^{-1} of both species. The attainable detection limits were calculated based on the standard deviation of the peak area observed in the peak area of repeated injections (N = 15) of unspiked tap water. This allows for a rather conservative and realistic assessment of this parameter.

Table 2. Analytical figures of merit

	Cr (VI)	Cr (III)
Retention time (s)	36 ± 0.2	101 ± 1.2
Sensitivity (kcps/µg L^{-1})$^{-1}$	114	123
Detection Limit (ng L^{-1})	4.0	9.0

Next, the performance of the guard column was evaluated with a locally sourced drinking water. Drinking water typically contains a high amount of both different cationic (for example, alkaline and alkaline earth elements) as well as anionic species (for example carbonate, sulfate and chloride), leading to an increased column load and potentially compromising the separation efficiency for the species under investigation. As can be seen from the chromatograms in Figure 1, no difference in the elution profile is observed between the injection of a standard solution (in ultrapure water) or a spiked drinking water sample.

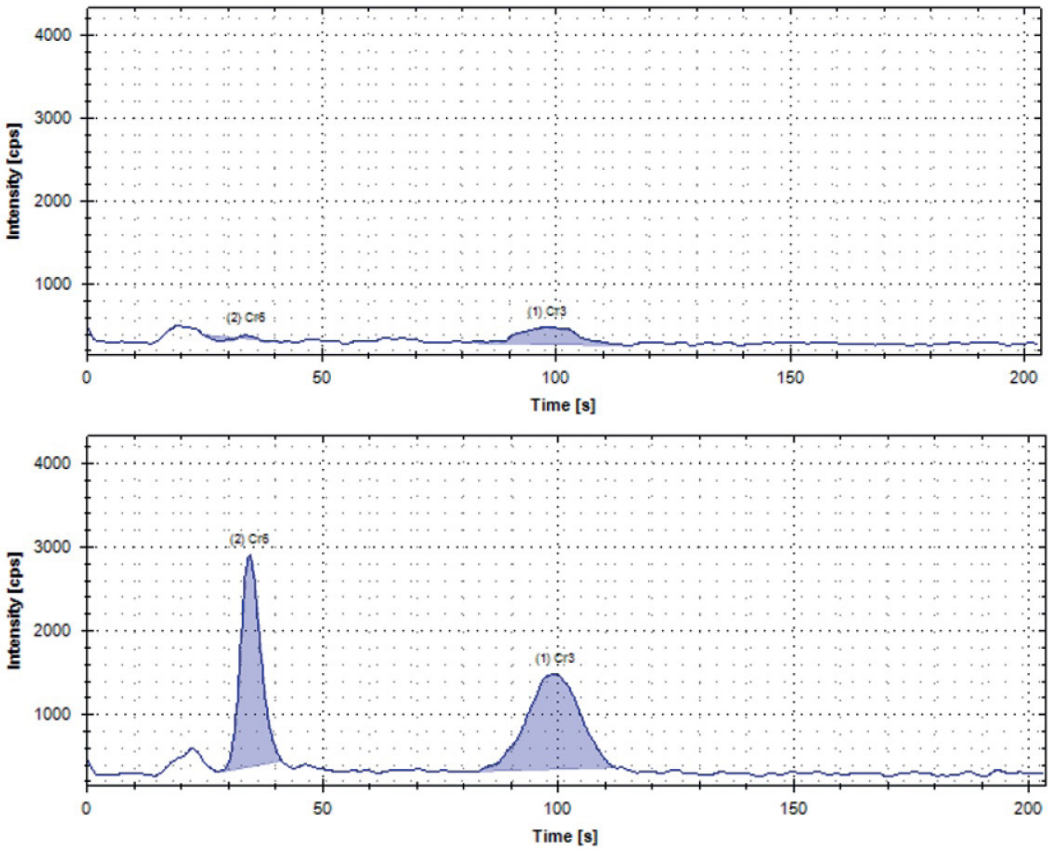

Figure 1. Chromatograms showing the injection of (from top to bottom) a blank, a standard solution containing 0.1 µg L^{-1} of both species (top), tap water, and spiked tap water (0.1 µg L^{-1}). For better comparability, all are scaled identically.

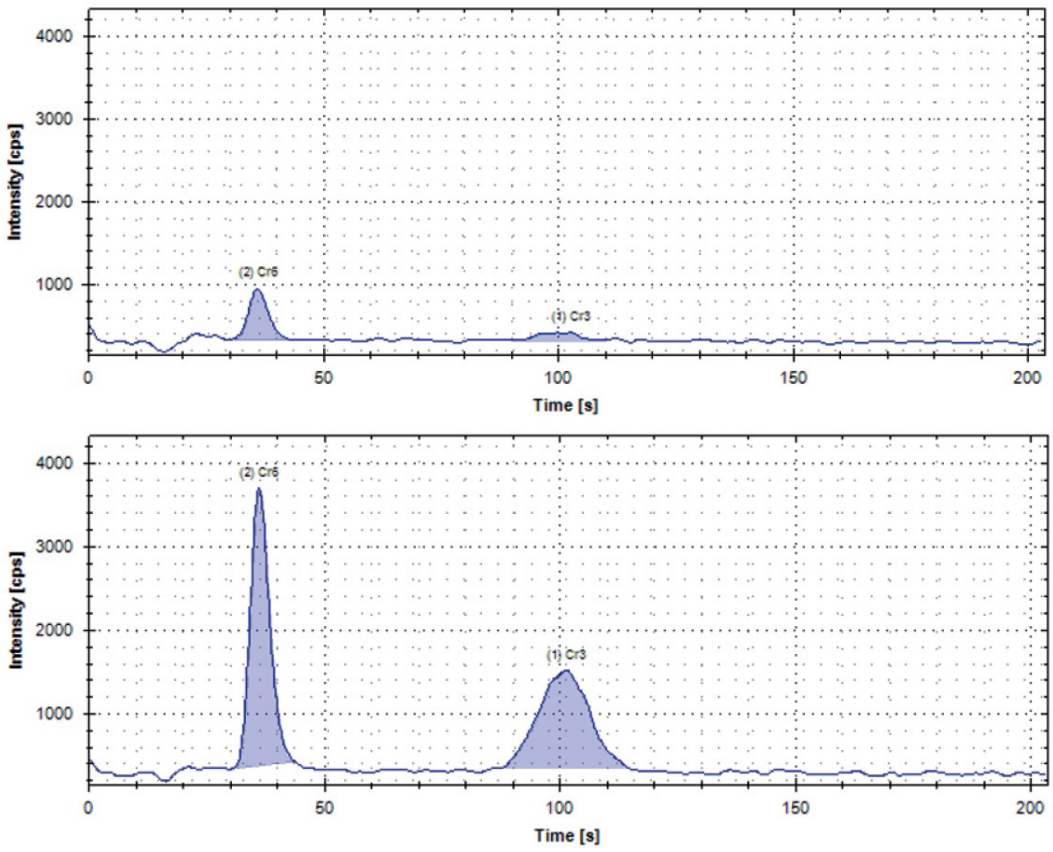

Figure 1. Chromatograms showing the injection of (from top to bottom) a blank, a standard solution containing 0.1 µg L^{-1} of both species (top), tap water, and spiked tap water (0.1 µg L^{-1}). For better comparability, all are scaled identically. (Continuation)

As can be seen, the blank did contain very low amounts of Cr (III) (approximately 20 ng L^{-1}) and the tap water sample contained a very low amount of Cr (VI), which was quantified to be approximately 25 ± 1 ng L^{-1}. To address the accuracy of the method, a sample was spiked with both Cr species at a concentration of 0.1 µg L^{-1} and the spike recovery was determined. In all cases, the spiked amount was recovered accurately with a recovery of 93 ± 1% for Cr (III) and 113 ± 5% for Cr (VI). The lower deviation for Cr (III) can be explained by the absence of naturally occurring Cr (III) in the samples, so that the recovery is based on the spiked amount only and excludes any variation from the actual content of water sourced from different taps.

CONCLUSION

In this application note, a method was outlined that coupled the Dionex Aquion IC system with the iCAP RQ ICP-MS system, which demonstrated linear calibrations over three orders of magnitude, good stability (based on multiple injections), and suitable accuracy and Limits of Detection (LOD). The use of a guard column alone is sufficient for this application and allows reduction of runtimes to around 3 min and therefore improves sample throughput. With an eluent ideally suited to ICP-MS, superior column chemistry specifically designed to provide both anion and cation exchange sites, and dedicated hardware for ion chromatography, that completely eliminates trace metal contamination, IC-ICP-MS is the optimal combination for chromium speciation.

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4. Thermo Fisher Scientific – Application Note 43098.

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