Application Note: 40837

The Determination of Trivalent and Hexavalent Chromium in Mineral and Spring Water using HPLC Coupled to the XSERIES 2 ICP-MS with CCT

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Key Words

- CCT
- Chromium
- EDTA
- HPLC-ICP-MS
- Environmental Waters

Introduction

The extensive use of chromium in various industrial processes and the erosion of chromium from natural sources have resulted in its widespread occurrence in the environment. Monitoring of chromium in environmental compartments, and food and water sources is central in assessing the potential risk from exposure. The US Environmental Protection Agency (EPA) and the European Union have specified maximum admissible concentrations of 0.1 and 0.05 mg/L for total chromium under their respective drinking water directives.

However, due to significant differences in toxicity, reactivity and bioavailability, it is also vital to distinguish between the trivalent (Cr^{III}) and hexavalent (Cr^{VI}) valence states of chromium. Cr^{III} is essential for glucose, protein and fat metabolism whereas Cr^{VI} on the other hand is highly toxic due to its strong oxidising properties. To assess human health risks from environmental exposure to chromium and chromium species, an accurate analytical method comprising highly sensitive and specific detection is needed.

This application note describes the use of the HPLC-ICP-MS instrument package from Thermo Electron Corporation for the determination of chromium species in aqueous matrices. The HPLC reversed phase methodology employed complexation of Cr^{III} with EDTA to improve separation. Due to the carbon containing mobile phase, optional collision cell technology (CCT^{ED}) was optimized for the prevention of the polyatomic interference $^{40}Ar^{12}C^{+}$ on ^{52}Cr. The CCT additionally suppresses interference from matrix in the water samples. The analytical methodology was validated using a CRM (BCR CRM-544, lyophilized water) and method limits of detection (LOD) were determined from 3 times the standard deviation of species concentrations found in the blank (n = 5).

HPLC-ICP-MS configuration

A fully inert Thermo Scientific SpectraSYSTEM™ HPLC pump with AS3500 autosampler was coupled to the Thermo Scientific XSERIES 2 ICP-MS using the Thermo Scientific HPLC-ICP-MS Coupling Pack (P/N 4600485) and SpectraSYSTEM HPLC Wiring Harness (P/N 4600488). The XSERIES 2 was operated under standard hot plasma conditions using a one-piece quartz torch with 1.5 mm ID injector and PlasmaScreen™ option. The spray chamber was cooled to 2 °C with the optional Peltier cooling device. Thermo Scientific PlasmaLab and Xcalibur software packages were used in conjunction with the External Trigger Card (P/N 4600261) to enable automated HPLC accessory control using bi-directional communications and intelligent peak integration facilities. The associated HPLC parameters and analytical conditions for HPLC-ICP-MS are shown below in Table 1.

Column	Hypersil GOLD™ (150 x 4.6 mm, 5µm)
Injection volume	Range: 50 - 200 µL
Flow rate	0.8 mL min^{-1}
Isocratic elution	2 mM Ethylenediamenetetraacetic acid (EDTA) 0.25 mM Tetrabutylammonium phosphate (TBAP) pH 6.9
Forward Power	1300 W
Nebulizer Gas Flow	0.88 L min^{-1}
Auxilliary Gas Flow	0.85 L min^{-1}
Cool Gas Flow	13 L min^{-1}
Data Acquisition Mode	PlasmaLab Transient Time Resolved Analysis (TRA)
Isotopes (dwell times, ms)	^{52}Cr (200 ms)
	^{50}Cr, ^{51}V, ^{53}Cr, ^{54}Cr (50 ms)
Channels per AMU	1
Timeslice duration	407 ms
Transient acquisition time	400 s
Spray chamber	Glass impact bead
Nebulizer	Glass concentric
Cones	Xt
Collision Cell gas	8 % H_2 in He at 4 mL/min
Energy Discrimination Barrier	2 V
Focus	12.5 V

Table 1: HPLC-ICP-MS parameters

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Sample Preparation

Daily working standards were prepared by diluting the appropriate quantity of the commercially available stock solutions (1000 µg.mL^{-1}) of each chromium standard (chromium (III) and chromium (VI)) in the HPLC mobile phase. The stock solutions were kept at 4 °C in the dark.

The CRM BCR-544 (lyophilized water) was extracted according to the method outlined in the certification report supplied with the CRM. The sample was reconstituted with 20 mL HCO^-_3/H_2CO_3 buffer at pH 6.4. Aliquots of the reconstituted CRM were diluted 1:1 in 20 mM EDTA, 2.5 mM TBAP.

Mineral and spring water samples were diluted 9:1 in 20 mM EDTA, 2.5 mM TBAP.

Spikes of Cr^{III} and Cr^{VI} were added to the reconstituted CRM and the mineral water samples prior to dilution with the EDTA solution. Both the standards and samples were placed in a heated water bath at 70 °C for 1 h to accelerate complexation of the Cr^{III} with EDTA.

Results and Discussion

The chromatographic data is displayed automatically in the XSERIES 2 PlasmaLab software package following analysis. An example of the chromatographic separation of chromium-containing standards at a concentration of 1 µg. L^{-1} is shown in Figure 1 (a.). The HPLC methodology using EDTA as complexation agent allowed the baseline separation of Cr^{III} and Cr^{VI} with retention times of 215 s and 260 s respectively.

External calibration curves were generated in PlasmaLab using a blank and Cr^{III} and Cr^{VI} calibration standards of 0.1, 0.2, 0.5, 1, 2, 5 and 10 µg.L^{-1}. Quantification of Cr^{III} and Cr^{VI} species was achieved in several samples using the external calibration curves presented in Figure 2 and fully quantitative data processing was achieved using PlasmaLab's automated peak integration tools.

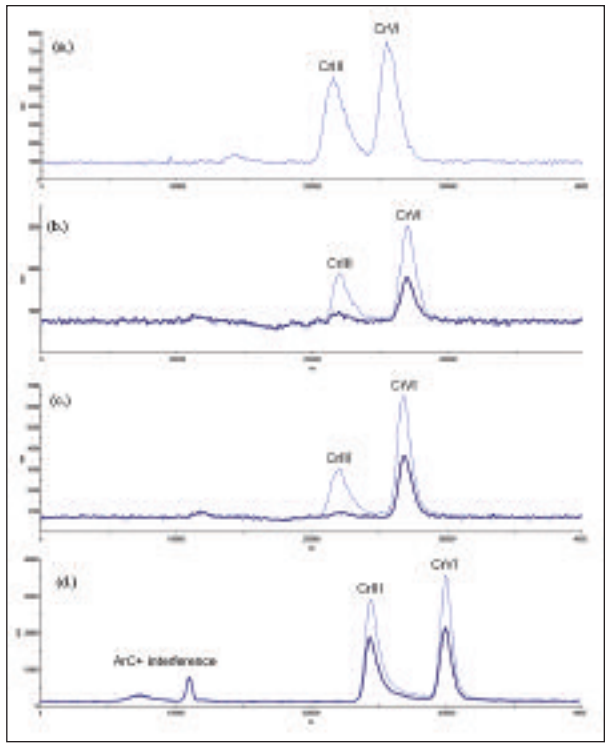

Figure 1: HPLC-ICP-MS chromatograms at *m/z* 52 of (a.) a Cr^{III} and Cr^{VI} standard at 1 µg.L^{-1}; (b.) mineral water D (dark blue) and mineral water D with a spike of Cr^{III} and Cr^{VI} at 0.19 µg.L^{-1} (light blue); (c.) mineral water E (dark blue) and mineral water E with a spike of Cr^{III} and Cr^{VI} at 0.46 µg.L^{-1} (light blue); (d.) reconstituted CRM 544 (dark blue) and reconstituted CRM 544 with a spike of Cr^{III} and Cr^{VI} at 10.1 µg.L^{-1} (light blue)
(a.)-(c.) : 200 µL injection
(d.) : 50 µL injection

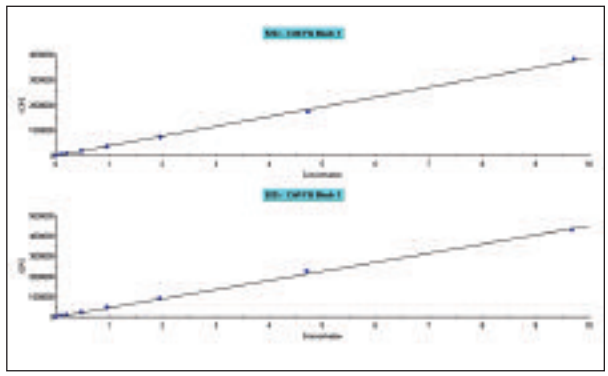

Figure 2: Fully quantitative calibration curves for Cr^{III} and Cr^{VI}

The mineral water samples analyzed were selected from a local supermarket. The samples were analyzed in triplicate. Their mineral content and the quantitative data for Cr^{III} and Cr^{VI} are presented in Table 2. The chromatograms for sample D and E are presented in Figure 1 (b.) and (c.) respectively. All the samples contained Cr^{VI} as the major species with concentrations varying between 0.054 and 0.409 µg.L^{-1}. Three of the five water samples contained Cr^{III} at levels above the limit of detection (but just above or below the quantification limit). Due to the low levels of chromium species in these samples, the detection and quantification limits of the

methodology were improved with a 200 µL sample loop, rather than a 50 or 100 µL sample loop (figures of merit are presented in Table 3). The method was validated for the mineral and spring water samples by determining the recovery of Cr^{III} and Cr^{VI} standards added to the samples prior to the complexation step (data presented in Table 2). The recovery determined for the five samples analyzed fell between 90 and 105 %, even for spikes at levels as low as 0.1 µg.L^{-1} of each chromium species.

Further method validation was performed through duplicate analyses in two independent bottles of CRM BCR-544 (lyophilized solution). A chromatogram of reconstituted BCR-544 is presented in Figure 1 (d.). Due to the higher levels of chromium species in this CRM, a sample loop of 50 µL was used for the fully quantitative calibration and sample. The chromatogram shows that Cr^{III} and Cr^{VI} were found in the CRM and that carbon based matrix eluting close to the void volume creates a $^{40}Ar^{12}C+$ interference on *m/z* 52. This is most likely due to the high carbonate concentration (0.042 %) in the reconstituted sample. The associated quantitative data is presented in Table 2 and there is satisfactory agreement between the measured and certified values for Cr^{III} and Cr^{VI}. However, the pH of the reconstituted solution is critical for preventing hydrolysis of the Cr^{III} species and the solution should be complexed or analyzed as soon as possible after the recommended purge with CO_2 (refer to the certification report of CRM 544 for further details).

Sample Loop /µL		Cr^{III} / µg.L^{-1}	Cr^{VI}/ µg.L^{-1}
50	BEC	0.096	0.026
	LOD	0.039	0.017
	LOQ	0.131	0.056
200	BEC	0.018	0.002
	LOD	0.017	0.009
	LOQ	0.055	0.029

Table 3: Figures of merit for the HPLC-ICP-MS methodology

Summary

The Thermo Scientific External Trigger Card and PlasmaLab software features permit automated instrument operation and integration for the routine speciation of chromium using HPLC-ICP-MS. The above described methodology provides a validated solution for rapid, accurate and sensitive determination of Cr^{III} and Cr^{VI} species.

	Mineral content and characteristics / mg.L^{-1}										Quantative data / µg.L^{-1}		Recovery / %	
	Na	Ca	Mg	K	CO_3	SO_4	NO_3	Cl	pH	Residue	Cr^{III}	Cr^{VI}	Cr^{III}	Cr^{VI}
A	2.8	1.2	0.2	0.4	4.9	3.3	2.3	3.2	6	19	n.d.	0.054 ± 0.003	110	104
B	11.6	11.5	8	6.2	71	8.1	6.3	13.5	7	130	n.d.	0.149 ± 0.008	92	98
C	13	63	23	1.8	300	14	2	11	7.4	290	0.045 ± 0.008	0.125 ± 0.013	90	106
D	5	78	24	1	357	10	3.8	4.5	7.2	309	0.036 ± 0.006	0.159 ± 0.002	100	105
E	35	49	12	1	186	17	5	54	7.8	288	0.060 ± 0.005	0.409 ± 0.002	105	98
BCR 544					4200			905			24.57 ± 2.56	23.94 ± 0.43	*92	*105

Table 2: Mineral water characteristics and fully quantitative and recovery data for Cr^{III} and Cr^{VI} in commercially available mineral and spring water samples and BCR CRM 544

* Measured chromium species data as a percent of the certified value

MDL and LOQ Data for Cr Species

MDLs and LOQs for Cr^{III} and Cr^{VI} species were determined in accordance with the 3σ and 10σ models respectively using fully quantitative analyses of method blanks (n = 5) and the associated figures of merit for sample injection volumes of 50 and 200 µL are presented in Table 3.

Plasma Capabilities from Thermo Fisher Scientific

The use of an Inductively Coupled Plasma source (ICP) is the accepted and most powerful technique for the analysis and quantification of trace elements in both solid and liquid samples. Its applications range from routine environmental analyses to the materials industry, geological applications to clinical research and from the food industry to the semiconductor industry.

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Thermo Scientific iCAP ICP

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Thermo Scientific ELEMENT2 HR-ICP-MS

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