Application Note: 40807

Chromium Speciation in Cement Extracts and Airborne Particulates using HPLC Coupled with the XSeries^{II} ICP-MS

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Key Words

- Airborne Particulates
- Cement
- Chromium
- HPLC
- ICP-MS

Introduction

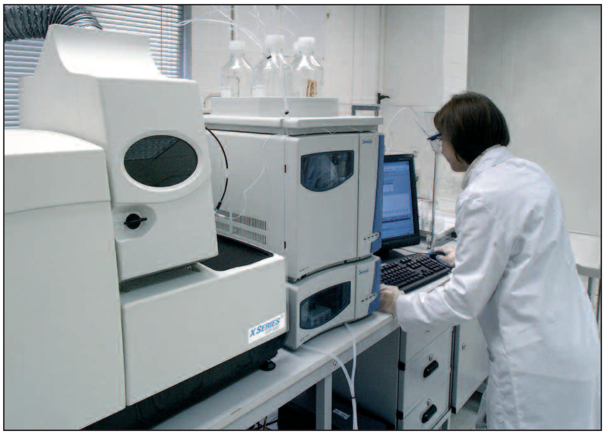
Oxidation state and chemical form are important factors which influence the toxicity, bioavailability and mobility of chromium. For example, trivalent chromium (Cr^{III}) is essential for many biochemical mechanisms in contrast to hexavalent chromium (Cr^{VI}) which is highly toxic due to its high oxidation potential and ability to attack the skin, respiratory and digestive systems. To date there is an increasing requirement for methodologies to enable sensitive, quantitative chromium speciation analyses in order to determine concentrations of toxic and/or non-toxic species and to better understand the implications of total chromium concentrations.

Chromium is employed in a number of industrial applications (e.g. chromium plating, stainless steel production, paint, pigment and cement manufacture) and occupational exposure issues have prompted the implementation of a number of directives for the protection of employees in the workplace. According to the European Commission (EC) directive 2003/53/EC, wet cement should contain no more than 2 ppm hexavalent chromium and according to the directive 2000/53/EC, no more than 2 g of hexavalent chromium can be used in anti-corrosion coatings on road vehicles. Additionally, the 'occupational health and safety administration' (OSHA) have recently proposed a permissible exposure limit of 0.5 µg/m^3 Cr^{VI} in workplace atmospheres (OSHA method number ID-215).

This application note describes the use of an HPLC-ICP-MS instrument package from Thermo Electron Corporation to enable the determination of chromium species in cement extracts and airborne workplace particulates. Chromium species were separated on-line prior to ICP-MS detection using a cation exchange stationary phase in conjunction with a 100 % aqueous acidic mobile phase. The HPLC-ICP-MS methodology was validated using a CRM (NIST CRM-545, welding dust). Method detection limits (MDLs) and limits of quantification (LOQ) were determined using the 3σ and 10σ models respectively based on repeat injections of the calibration blank (n=5).

HPLC-ICP-MS configuration

A Finnigan™ SpectraSYSTEM™ HPLC pump with AS3500 autosampler were coupled to the XSeries^{II} ICP-MS using the Thermo Electron HPLC-ICP-MS Coupling Kit (P/N 4600485) and Finnigan SpectraSYSTEM HPLC Wiring Harness (P/N 4600488). The XSeries^{II} 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. 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.



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Column	Dionex IonPac® CS5A (250 x 2.0 mm, 5µm)
Injection volume	20 µL
Flow rate	0.7 mL min^{-1}
Gradient elution	0.35 to 1.2 M HNO_3
Forward Power	1400 W
Nebulizer Gas Flow	0.9 L min^{-1}
Auxilliary Gas Flow	0.85 L min^{-1}
Cool Gas Flow	14.5 L min^{-1}
Data Acquisition Mode	PlasmaLab Transient Time Resolved Analysis (TRA)
Isotopes (dwell times, ms)	^{13}C (10 ms)
	^{51}V (10 ms)
	^{52}Cr (200 ms)
	^{53}Cr (10 ms)
Channels per AMU	1
Timeslice duration	263 ms
Transient acquisition time	450 s (per sample)
Spray chamber	Glass impact bead
Nebulizer	Glass concentric
Cones	Xt

Table 1. HPLC-ICP-MS conditions

Sample Preparation

Cement extracts were prepared according to the Technical Regulations for Dangerous Materials method TRGS 613 (Germany). 10.0 g of sample were mixed with 40 mL of water for 15 min at 300 rpm using a mechanical shaker. The extracts were centrifuged at 3000 rpm for 20 minutes and then filtered through a 0.45 µm filter. Samples were diluted appropriately with Milli-Q® water and aliquots then used for the speciation analysis.

A surface area (static) dust sample and filters containing airborne particulate matter collected from a stainless steel manufacturing plant were prepared according to ISO 16740:2005, which specifies a method for the determination of the time-weighted average mass concentration of Cr^{VI} in workplace air. Sequential sample preparation methods are specified for the extraction of soluble and insoluble hexavalent chromium. The surface area dust sample and filters (Teflon) were firstly extracted with 10 mL $(NH_4)_2SO_4$ - NH_4OH buffer (0.5 M) at pH 8 for 1 hour at ambient temperature. The first extractant was decanted into a clean dry vial and the samples were subsequently extracted with 6 mL 2 % NaOH – 3 % Na_2CO_3 for 1 hour in an ultrasonic bath. The second extractant was decanted into a clean dry vial. All extracted samples were diluted appropriately with Milli-Q® water prior to analysis. The CRM BCR-545 (welding dust) was extracted according to the method outlined in the certification report supplied with the CRM. The filter was leached with 10 mL 2 % NaOH – 3 % Na_2CO_3 buffer for 30 min in an ultrasonic bath heated at 70 °C. The sample was then centrifuged for 2 min at 2500 rpm and diluted with Milli-Q® water prior to analysis.

Results and Discussion

The HPLC methodology enabled separation of Cr^{VI} and Cr^{III} species with retention times of 90 and 395 seconds respectively (Figure 1 (a.)). External calibration curves were generated in PlasmaLab using a blank and Cr^{VI} and Cr^{III} calibration standards at 0.5, 1, 2, 10 and 25 ng/g (Figure 2). Quantification of Cr^{VI} and Cr^{III} 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. Method validation was performed through triplicate analyses of one extract of CRM BCR-545 (welding dust). The associated quantitative data is presented in Table 2 and there is good agreement between the measured and certified values for Cr^{VI} (40.2 mg/g).

Chromium containing species were determined in six cement extract samples. Figure 1(b.) presents data derived from a cement sample that contains no reducing agents and Figure 1(c.) presents data for a cement extract known to contain lignin sulphonate as a reducing agent.
The chromatographic peak observed in the void volume ($^{52}M^+$, Figure 1(c.)) was attributed to the formation of the $^{52}ArC^+$ polyatomic species and this is confirmed by the overlay of the peak observed for ^{13}C. All of the cement samples analyzed were found to contain Cr^{VI}. However, the reducing agents in cement samples 5 and 6 were found to maintain the level of the water-soluble Cr^{VI} concentration below the maximum permitted value of 2 mg/kg.

Chromatograms for the dust sample extracted following the ISO 16740 protocol for soluble and insoluble Cr are presented in Figure 1(d.) and Figure 1(e.) respectively. A chromatographic peak was observed in the void volume for the extract prepared for soluble Cr^{VI} analysis when examining the $^{52}M^+$ data. However, concomitant peaks were also observed at $^{51}M^+$ and $^{53}M^+$ reflecting the natural isotopic ratio of ^{35}Cl and ^{37}Cl (i.e. as $^{51}ClO^+$ and $^{53}ClO^+$ polyatomic species). As a result of this, the $^{52}M^+$ peak was attributed to formation of the $^{52}ClOH^+$ species. A $^{52}M^+$ peak was also identified in the void volume for the extract prepared for analysis of insoluble Cr^{VI} although this peak was not attributed to the formation of $^{52}ArC^+$ or $^{52}ClOH^+$ species. Further work is required to confirm the origin of this chromatographic peak.

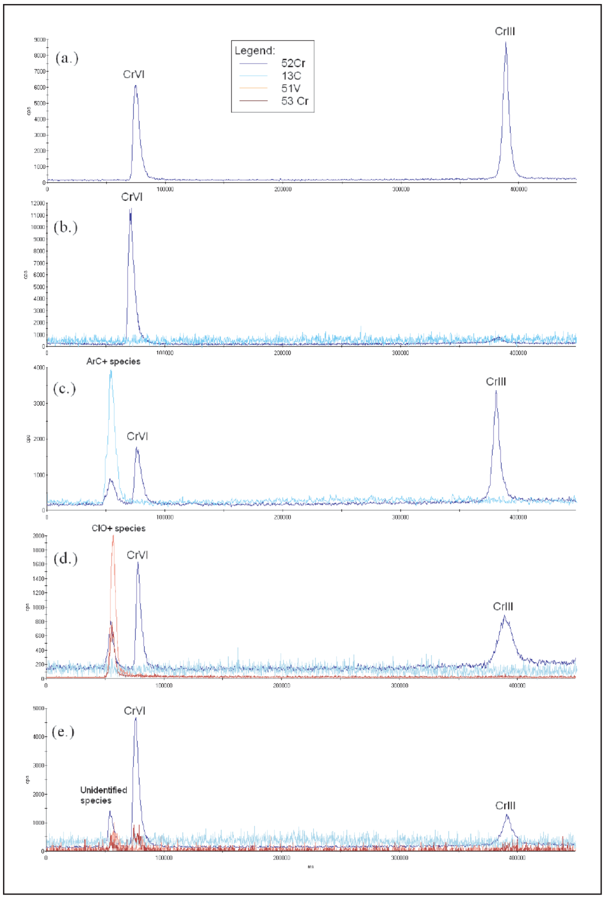

Figure 1.
(a.) commercially available Cr^{VI} and Cr^{III} standards at 5 ng g^{-1};
(b.) cement extract 3 (x200 dil.);
(c.) cement extract 6 (undiluted) - contains lignin sulphonate reducing agent;
(d.) extracted surface area dust (x2 dil.) - soluble Cr^{VI};
(e.) extracted surface area dust (x20 dil.) - insoluble Cr^{VI}.

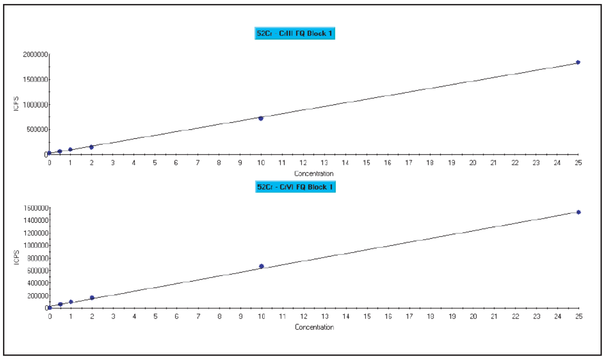

Figure 2. Calibration curves for Cr^{VI} and Cr^{III} calibration standards.

A series of spike recovery samples were prepared to validate the analytical methodology and ensure that there is no reduction of Cr^{VI} to Cr^{III} due to interactions with the polymeric media in the filters or during extraction process. Spikes of 100 ng Cr^{VI} were added to a filter extract during the extraction process and also to two filters prior to the extraction. The associated spike recovery data is presented in Table 2 and the complete recovery of the spiked concentrations confirms the accuracy of the methodology.

CRM 545 WELDING DUST (40.2 ± 0,6 g/kg Cr^{VI})	**Cr^{VI} (g/kg)**	**Cr^{III} (g/kg)**
Mean of three replicate analyses of one extract	39.8 ± 0.5 g/kg	-
CEMENT	**Cr^{VI} (mg/kg)**	**Cr^{III} (mg/kg)**
1	5.21	-
2	7.07	-
3	14.53	-
4	11.16	-
5	0.011	0.013
6	1.20	1.80
SURFACE AREA DUST	**Cr^{VI} (µg/kg)**	**Cr^{III} (µg/kg)**
Extraction of soluble Cr^{VI}	70	13
Extraction of insoluble Cr^{VI}	1544	156
FILTERS - SPIKE RECOVERIES (100 ng Cr^{VI})	**Cr^{VI} (ng)**	**Cr^{III} (ng)**
Filter 1 spiked prior to extraction	105	-
Filter 2 spiked prior to extraction	90	-
Filter 3 spiked during extraction	97	-

Table 2. HPLC-ICP-MS fully quantitative sample data

MDL and LOQ Data for Cr Species

MDLs and LOQs for Cr^{VI} and Cr^{III} 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 are presented in Table 3.

	Cr^{VI} µg/kg	**Cr^{III} µg/kg**
MDL (3σ)	0.10	0.64
LOQ (10σ)	0.35	2.13

Table 3. MDL and LOQ Data

Summary

The 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 and accurate determination of Cr^{VI} and Cr^{III} species, addressing the current requirement for assessment of occupational exposure and monitoring the workplace environment.

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