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Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography (IC)–ICP-MS

Fast, sensitive, and accurate measurement of Cr(VI) using a Metrohm 940 IC coupled to the Agilent 7800 ICP-MS

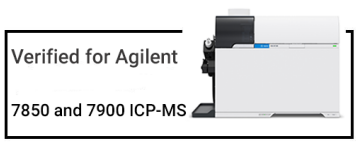
Authors

Yan Cheung[1], Jayesh Gandhi[2], Lori Allen[3], Amy Furreness[2], Matthew Natschke[3], Hannah Tangen[3], and Chris LeValley[3]

[1]Agilent Technologies, Wood Dale, Illinois, USA

[2]Metrohm USA, Riverview, Florida, USA

[3]University of Wisconsin-Parkside, Kenosha, Wisconsin, USA



Introduction

Chromium (Cr) is a metallic element that occurs naturally in rocks, soils, plants, and animals. There are two main forms or species of Cr: trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) is found in soil, water, vegetables, fruits, and meats, and is essential to human health as it helps to convert fat into energy. Hexavalent Cr also occurs naturally from erosion of Cr deposits, as well as being widely used in industrial process including tanning, stainless steel production, and metal finishing. In contrast to Cr(III), Cr(VI) is toxic and carcinogenic (*1*). Species interconversion between Cr(III) and Cr(VI) is pH dependent and can occur naturally or during sample storage and processing, as documented in the literature (*2–4*).

The variable speciation of Cr in waters and the lack of routine methods to independently measure the different forms have made it difficult for regulators to set specific limits for Cr(VI). As a result, many regulators have taken the practical approach of setting a limit for total Cr. The US Environmental Protection Agency (EPA) has established a permitted level of 100 µg/L (ppb) for total Cr in drinking water. Many US states have established lower limits of 50 µg/L, but there is currently no separate EPA limit for Cr(VI) (*5*). The World Health Organization (WHO) has set a provisional Guideline Value (pGV) of 50 µg/L total Cr in drinking water (*6*). The same 50 µg/L total Cr level is defined in the European Communities (Drinking Water) Regulations 2020, with a lower limit of 25 µg/L to be met by 2036 (*7*). In 2011, the California Office of Environmental Health Hazard Assessment (OEHHA) published a Public Heath Goal document setting a limit of 50 µg/L for total Cr and 0.02 µg/L for Cr(VI) in drinking water (*8*). As more regulations are likely to be updated to include specific limits for Cr(VI) in the future, simple routine analytical methods are needed to meet the limit requirements.

ICP-MS can be used for the measurement of Cr at low concentration levels. ICP-MS can also be coupled to a chromatographic separation technique such as high performance liquid chromatography (HPLC) to provide specific detection and quantification of Cr(III) and Cr(VI).

In this study, ion chromatography (IC) was coupled to ICP-MS for separation and low-level detection of Cr(III) and Cr(VI). Compared to HPLC, IC has some advantages for routine Cr speciation, as the IC pump is relatively low cost, and the IC sample path is metal-free. The metal (e.g. stainless steel) parts of a standard HPLC system can be replaced with metal-free components, but this adds further cost. A metal-free IC system coupled to an ICP-MS provides a cost-effective solution for routine, low-level analysis of the individual Cr species.

This study evaluated the method detection limits (MDLs) that could be achieved for Cr(III) and Cr(VI) by IC-ICP-MS. The IC-ICP-MS method was based on the established EPA Method 218.7 for Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV-Visible Spectroscopic Detection (*9*). Method 218.7 was used to guide sample preparation and statistical analysis of the new method's performance. To demonstrate the performance and robustness of the method for the analysis of drinking water, a spike recovery check was run for two tap water samples.

Experimental

Sampling and sample preservation

All standards were spiked with EDTA (Reagent Grade, Thermo Fisher Scientific) to give a final concentration of 2 mM to help with the preservation of Cr(VI). For the preservation of Cr species in the tap water samples, ammonium sulfate/ammonium hydroxide buffer (trace metal grade, Thermo Fisher Scientific) and EDTA (with final solution concentration of 2 mM) were added to the samples on collection.

The IC sample vials (Metrohm) were fitted with polypropylene septa, which are free from rubber or silicon. A previous study found that rubber septa interfere with the ability of EDTA to chelate and stabilize the Cr species (*10*).

Instrumentation

This work was run on an Agilent 7800 ICP-MS, but the method is also compatible with the Agilent 7850 ICP-MS or Agilent 7900 ICP-MS models. The ICP-MS was coupled to a Metrohm 940 Professional IC fitted with a Metrosep ASUPP4 250/4.0 column. Cr was measured at its major isotope, ^{52}Cr (83.79% abundance), to ensure the best signal in the ICP-MS.

The EDTA present in the IC mobile phase could lead to the formation of a significant level of $^{40}Ar^{12}C$ polyatomic ions, which would contribute to the background signal at *m/z* 52. However, Agilent ICP-MS systems include the ORS^4 collision/reaction cell (CRC) that uses helium (He) collision mode with kinetic energy discrimination (KED) to control common polyatomic ions, including carbon-based interferences. When the cell is pressurized with He, polyatomic ions such as ArC^+ are filtered out effectively, while analyte ions such as Cr^+ are transmitted through the cell. He mode therefore minimizes the background signals from ArC polyatomic ions, allowing Cr to be measured at low concentrations at mass 52. Chromatographic data was collected using Time Resolved Analysis (TRA) mode with an integration time of 0.5 s per point. The total acquisition time was 6 minutes. IC and ICP-MS operating parameters are given in Tables 1 and 2.

Table 1. IC operating parameters.

Parameter	Setting
Column	Metrosep ASUPP4 250/4.0
Flow Rate (mL/min)	1.0
Injection Volume (µL)	250
Mobile Phase	10 mM ammonium nitrate (ACS Certified grade, Thermo Fisher Scientific) with 2 mM EDTA adjusted to pH 10 with ammonium hydroxide (Trace Metal Grade, Thermo Fisher Scientific)

Table 2. ICP-MS operating parameters.

Parameter	Setting
RF Power (W)	1550
Sample Depth (mm)	8
Nebulizer Gas (L/min)	1.07
He Cell Gas Flow Rate (mL/min)	10
KED Bias (V)	7
Isotope Monitored	^{52}Cr
Integration Time (s)	0.5
Acquisition Time (min)	6.0

Calibration standards and calibration curves

Eight calibration standards ranging from 0.01 to 10 ppb for both Cr(III) and Cr(VI) were used to create the calibration curves. Figure 1 shows the overlaid chromatograms for the lowest six of these calibration standards.

Both Cr species eluted within four minutes and the total sample-to-sample time was less than 10 minutes, including rinsing and loop loading. If higher sample throughput is required, the run time could be reduced by adjusting the mobile phase pH, rinse and stabilization times between injections, and column length, for example.

Baseline separation of Cr(III) and Cr(VI) species ensured the accurate measurement of both species at low concentrations in water samples. The method also provided low background, good sensitivities of the Cr ion signals, and good retention time (RT) stability.

The calibrations for both Cr species demonstrated excellent linearities (R = 1.0000) over single and sub-ppb concentrations, as shown in Figure 2.

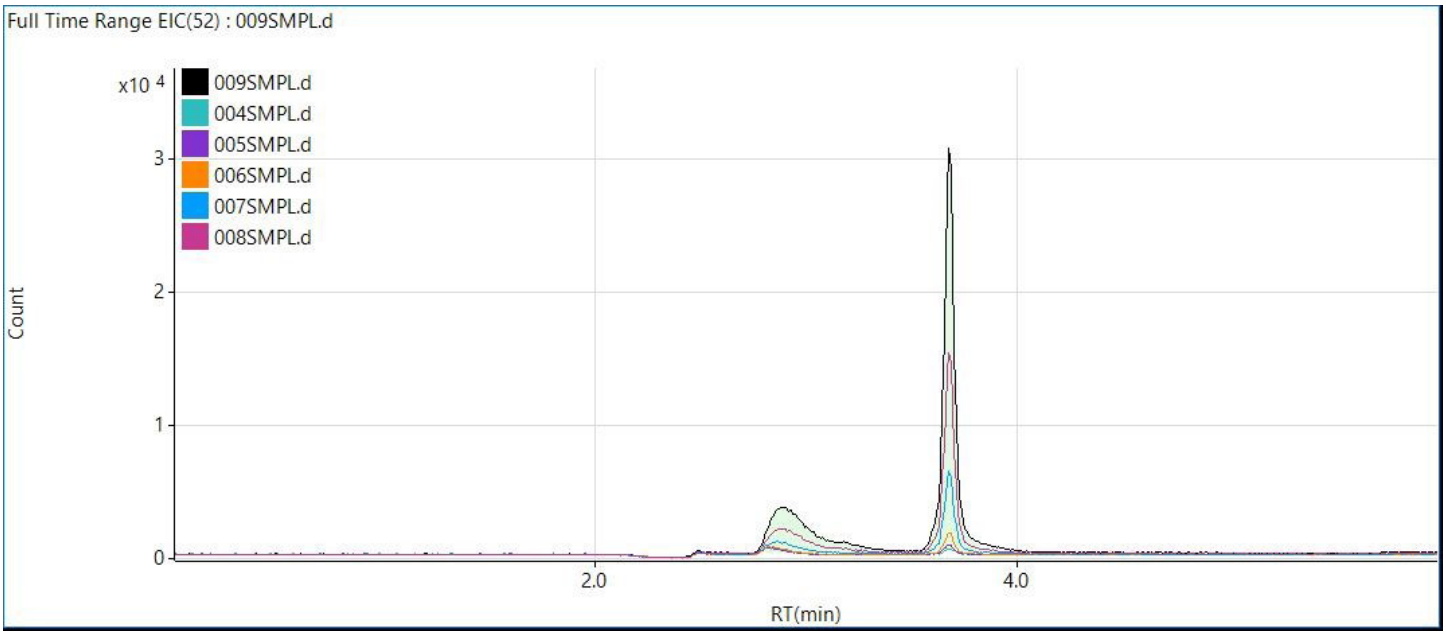


Figure 1. Overlaid chromatograms of six calibration standards at 0.01, 0.025, 0.05, 0.1, 0.5, and 1 ppb. An additional, higher level standard at 10 ppb was used in the calibration but has been excluded from the plot to allow the lower levels standards to be seen more clearly.

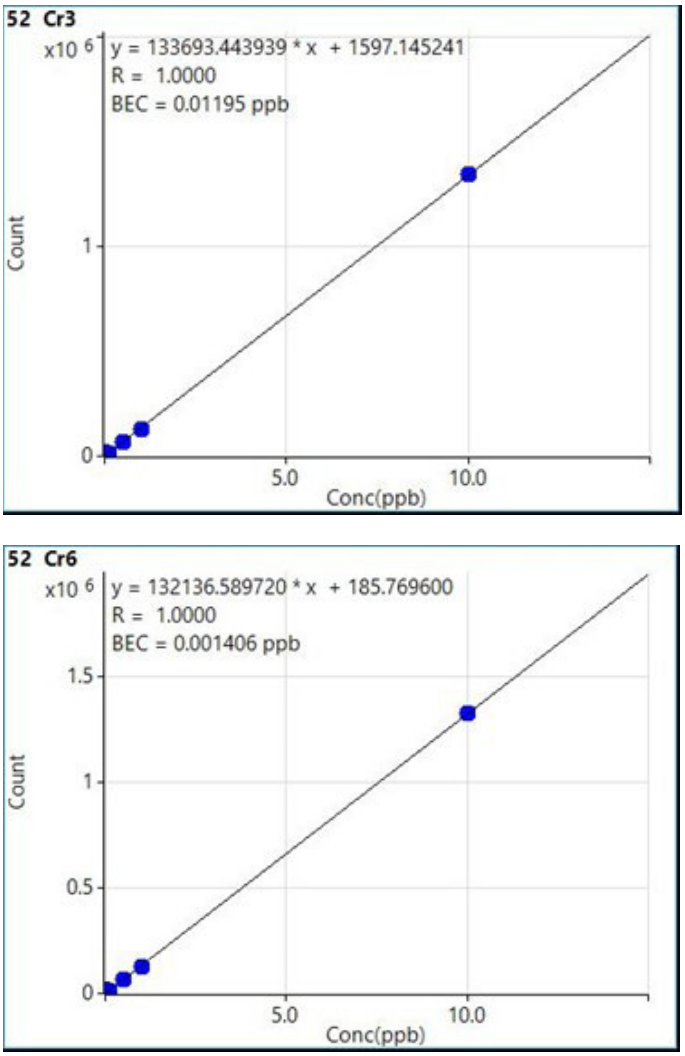


Figure 2. Calibration plots for Cr(III), top, and Cr(VI), bottom.

Determination of minimum reporting limit and method detection limits

Proposed Minimum Reporting Limits (MRLs) were established for the Cr species, and the proposed values were then confirmed experimentally using the IC-ICP-MS method. According to EPA method 218.7, the MRL is defined as "…the minimum concentration that can be reported by a laboratory as a quantified value…". The EPA method states that the proposed MRL concentration should not be lower than the lowest calibration standard. EPA 218.7 only defines an MRL for Cr(VI), but Cr(III) was included in this study to ensure that labs have a robust method to identify possible species interconversion. In the current study, MRL concentrations of 0.025 µg/L for Cr(III) and 0.020 µg/L for Cr(VI) were proposed and tests were performed to confirm these levels.

According to EPA 218.7, the MRL is confirmed if spikes at the MRL level can be recovered within the range of 50 to 150% with a probability of at least 99%. Compliance with the acceptable range for the MRL spike recovery is based on the Range for the Prediction Interval of Results (RPIR) at 99.5% confidence level. The range (upper and lower limit) of the PIR is calculated from the mean spike recovery at the MRL concentration ± the standard deviation (SD) multiplied by 3.963. The multiplication factor is calculated from the Student t value of 3.707 (for a 99.5% confidence level with at least seven replicates) multiplied by the square root of 1+(1/N) *(11)*.

For this work, the PIR limit values were therefore calculated from mean spike recovery + (SD x 3.963) for the upper PIR limit and mean spike recovery – (SD x 3.963) for the lower PIR limit. The calculated RPIR of the spike recoveries at the proposed MRL level should be within 50 to 150% recovery for the proposed MRL concentrations to be confirmed.

To confirm the proposed MRLs in this study, multiple reagent blank samples were fortified (spiked) with the Cr species at the proposed MRLs. These laboratory fortified blanks (LFBs) were analyzed over three days, with 10 replicates measured each day. The samples were freshly prepared each day and the replicates were analyzed as individual injections.

The mean and standard deviation were calculated for the Cr results in the 30 LFBs to allow the RPIR to be determined. The RPIR results showed that the spikes at the MRL levels could be recovered within the 50 to 150% range with 99.5% confidence. These results confirm the proposed MRLs of 0.025 µg/L for Cr(III) and 0.020 µg/L for Cr(VI) (Table 3). The confirmed MRLs ensure that any samples that exceed the California Public Health Goal requirement of 50 µg/L for total Cr or 0.02 µg/L for Cr(VI) can be reported with 99% confidence.

Table 3. LFB spike recovery results at MRL level from confirmation study on proposed Minimum Reporting Limits. Upper and lower RPIR must be within 150 and 50%, respectively.

(µg/L)	Cr III	Cr VI
Proposed MRL	0.025	0.020
Measured Mean	0.022	0.016
Measured SD	0.0020	0.0010
Calculated Upper RPIR	112%	99%
Calculated Lower RPIR	62%	58%
MRL Confirmed	Yes	Yes

Method Detection Limit (MDL)

MDL is defined as the minimum concentration that can be identified, measured, and reported with 99% confidence that the concentration is at least two to five times above the noise level. In chromatographic studies, detection limits are often quoted as the concentration that gives a signal-to-noise ratio (S/N) of 3 (DL = S/N = 3). Although EPA method 218.7 does not require labs to obtain or report an MDL, the value is a useful performance indicator and might be required by various regulatory bodies associated with compliance monitoring. The current study therefore included investigation of the MDLs for the two Cr species.

The same LFB spike recovery results used in the MRL confirmation study were used to calculate the MDLs. MDLs were obtained by multiplying the standard deviation of the 30 LFB replicates by 3.143 (the Student t value of at 99% confidence level with at least seven replicates). The MDLs in the current study were calculated as 0.006 µg/L for Cr(III) and 0.003 µg/L for Cr(V). The 30 LFBs gave an average peak-to-peak S/N of 9 for Cr(III) and 10 for Cr(VI).

Stability

Long term stability of the IC-ICP-MS system after multiple injections over multiple days was evaluated by the stability of the retention times for both Cr species. Repeated analysis of a quality control sample (0.1 µg/L standard) showed stable retention times for both Cr species with RSD of less than 1% for Cr(III) and 0.1% for Cr(VI). A summary of the analytical figures of merit is shown in Table 4.

Table 4. Analytical figures of merit for Cr(III) and Cr(VI).

	Cr(III)	Cr(VI)
Retention Time (min)	2.83 ± 0.03	3.67 ± 0.01
Peak-to-peak S/N @MRL	9	10
MDL (µg/L)	0.006	0.003
Sensitivity (cps/µg/L)	134,000	132,000

Tap water analysis and spike recovery

Two tap water samples from different sources were investigated. Both samples were measured unspiked and spiked with the Cr species at a concentration three to five times higher than their natural concentrations. Tap Water A was used in the low spike experiments, as it contained lower natural Cr content. Tap Water B was used in the high spike experiments due to its higher natural Cr concentration.

Species interconversion is a known issue for Cr speciation in natural water samples and can be caused by free chlorine and alkalinity (high pH). In this work, the interconversion issue was investigated by measuring spike recoveries in tap water samples with and without sample preservation. To prevent species interconversion, an ammonium sulfate/ammonium hydroxide buffer was added to the tap water samples per EPA 218.7. The ammonium ions in the preservative solution form complexes with free chlorine, while the hydroxide ions adjust the sample pH to form stable Cr complexes, preventing interconversion. Table 5 shows the percentage recoveries for Tap Water A with and without the addition of preservative. The results show that the over recovery of Cr(III) and under recovery of Cr(VI) were rectified by sample preservation.

Table 5. Spike recoveries for Cr(III) and Cr(VI) at low (0.15 µg/L) spike level in Tap Water A with and without preservatives, and at high (0.50 µg/L) spike level in Tap Water B with preservatives. (Note: due to laboratory conditions, Tap Water A without preservative was collected on a different day from Tap Water A with preservative).

		Cr(III)			Cr(VI)		
Sample	Concentration of Spike (µg/L)	Unspiked (µg/L)	Spiked (µg/L)	Recovery (%)	Unspiked (µg/L)	Spiked (µg/L)	Recovery (%)
Tap Water A (unpreserved)	0.150	0.00641	0.198	128	0.0368	0.144	72
Tap Water A (preserved)	0.150	0.028	0.173	97	0.0660	0.207	94
Tap Water B (preserved)	0.500	0.006	0.453	89	0.179	0.701	104

Conclusion

The sensitive and accurate determination of Cr(III) and Cr(VI) species in drinking waters was achieved using a Metrohm 940 IC system coupled to the Agilent 7800 ICP-MS. With both Cr species separated within four minutes, the IC-ICP-MS method is suitable for fast, routine measurement of the toxic Cr(VI) form in water samples, as increasingly required by regulatory bodies.

The sensitivity of the 7800 ICP-MS enabled both Cr species to be determined at low concentration levels. The Minimum Reporting Limits (MRLs) and Method Detection Limits (MDLs) calculated using the IC-ICP-MS method easily meet the EPA drinking water limit of 100 µg/L of total Cr. The new method also meets the California State Board Public Health Goal limits of 50 µg/L of total Cr and 0.020 µg/L of Cr(VI).

The spike recovery test showed that accurate results were obtained for Cr(III) and Cr(VI) in tap water samples when a preservative buffer was added to the samples during sample preparation.

The IC-ICP-MS method is simple, robust, stable, and easy to run by nonexpert analysts, making it useful for general analytical labs to use for the routine measurement of Cr(VI).

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