



Authors: C. Derrick Quarles, Jr., Scott Smith, Patrick Sullivan, Jordyn Blake, Nick Bohlim, and Daniel R. Wiederin
Derrick.Quarles@icpms.com

Evaluation of Drinking Water for Hexavalent Chrome and Total Metal Concentrations

Introduction

The amount of chromium in drinking water has been a controversial and debatable topic recently. The EPA set the federal drinking water maximum contaminant level (MCL) to be less than 100 ppb total Cr based on a study from 1991. However, the Safe Drinking Water Act (SDWA) requires the EPA to periodically review the level of contaminants in drinking water. In 2008, the EPA started to review the health effects associated with hexavalent chromium (Cr(VI)).

In contrast to the EPA, the state of California set 50 ppb total Cr as its limit for drinking water in the 1970's. In the year 2000, the issue reached a turning point when the film *Erin Brockovich* debuted, which shed light on a major utility company poisoning residents of Hinkley, CA. The film educated people on the dangers of hexavalent chromium in drinking water. The state of California set a public health goal of 0.02 ppb hexavalent chromium (2008), but settled for an MCL of 10 ppb of total chromium in drinking water (2014). In 2016, a statement released by the "Environmental Working Group" stated over

200 million Americans were being exposed to unsafe levels of hexavalent chromium. In May 2017, the Sacramento Supreme Court withdrew the 10 ppb MCL stating it was not economically feasible to reach these limits. The MCL for total chromium still remains at 50 ppb.

With all the attention focused on investigating and potentially lowering the MCL for hexavalent chromium, the instrumentation for analyzing it must be able to meet these standards. Total chromium analysis can be easily achieved by standard ICPMS methods, but in order to determine if hexavalent chromium is present in drinking water it requires a speciation method that usually involves a liquid chromatography (LC) system attached to an ICPMS. Most commercially available LC systems have metal-based components that will inherently lead to higher backgrounds. Having a metal-free LC system will allow for lower backgrounds and therefore lead to better detection limits.



Instrumentation

Trace metal laboratories are often required to speciate samples at frequencies that do not require a dedicated LC-ICPMS. As a result, costly LC systems need to be constantly attached and detached from the ICPMS. The prepFAST IC is a single platform capable of providing total elemental analysis and elemental speciation. The user can seamlessly switch between total metal analysis and speciation without having to change any hardware, solutions, or samples. In addition, the system can autocalibrate from single stock standards and auto-dilute samples for both total metal and speciation analysis.



- Completely metal-free system, including flow path and sample path
- Automated switching between total metal analysis and speciation analysis modes
- Automated switching between acid and basic matrices for total metals
- High pressure eluent delivery (HPLC)
- Gradient elution capability

Sample Collection

Drinking water was collected from various locations in or around Omaha, NE, USA. The drinking water was sampled from residential wells, residential taps, commercial taps, bottled water, and from the Missouri River. The water samples were collected in a 50 mL test tube and capped for transport back to ESI for testing. All samples were analyzed in their native state, utilizing the inline autodilution capabilities to dilute the samples prior to injection onto the column. The inline autodilution helps eliminate or minimize any species interconversion that is usually the result of manual sample preparation prior to analysis. The autocalibration feature allows the calibration curves for Cr(VI) and Cr(III) to be produced from a single stock standard solution (no need for a series of calibration standards to be prepared).

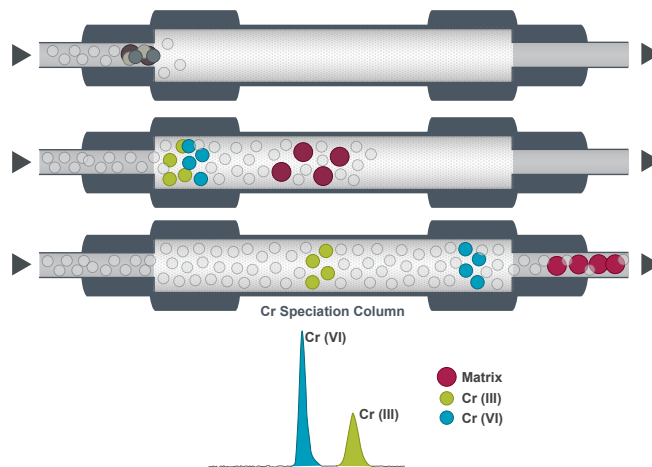


Figure 1. Illustration of the chromatographic separation of Cr (VI) and Cr (III) as they elute off of the anion exchange column.

- Automated, in-line sample dilution and syringe-driven sample loading
- Micro sample compatible with selectable sample loop loading
- Enclosed mobile station with optional ULPA filter preserves sample integrity
- Xceleri data reduction software

Cr Calibration Curve

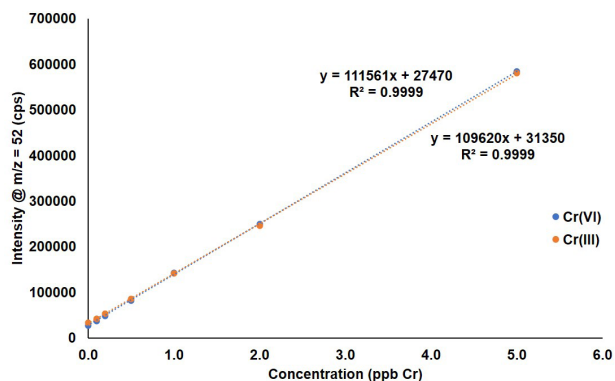
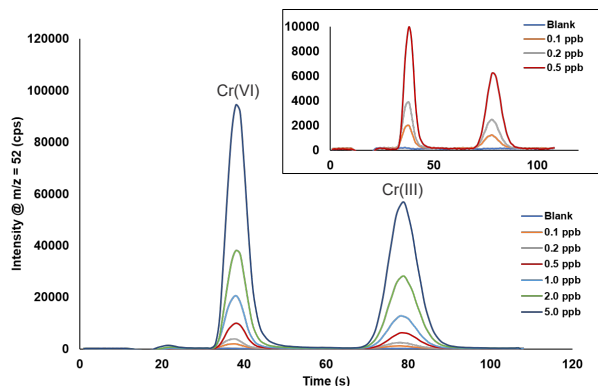


Figure 2. Cr(VI) and Cr(III) autocalibration prepared from a single stock calibration standard.

Speciation Standards



Drinking Water Sample

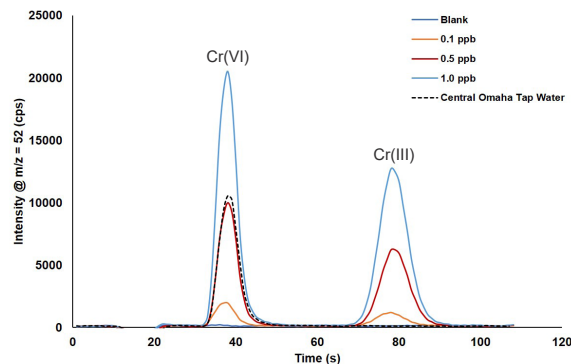


Figure 3. Chromatograms for the standards and samples showing the peaks eluting for Cr(VI), and Cr(III). The central Omaha tap water was analyzed using a 2x inline dilution.

Analytical Methodology

Table 1 displays the figures of merit for the chromium speciation method. The limits of detection (LOD) and limits of quantification (LOQ) are not only both below the maximum contaminant level (10 – 100 ppb Cr) but also the public health goal of 0.02 ppb Cr(VI) suggested by the state of California. Thus regardless of the limits that are determined in the future by the state of California or the Federal government, the chromium speciation method provided by ESI will easily provide the desired detection limits.

In order to have a good chromatographic method, the retention time of the species eluting must remain precise. Figure 2 displays the chromatograms for both the standards and some of the water samples analyzed.

The first peak is Cr(VI), which elutes at 38 seconds, and the second peak is Cr(III), which elutes at 79 seconds. The recovery of the method was evaluated using spiked samples at the beginning, middle, and end of the analysis (similar to QC samples). Both Cr(VI) and Cr(III) presented average recoveries of ~ 101% and 102%, respectively (Table 2).

Table 1. Limits of Detection & Quantification.

	LOD (ppt)	LOQ (ppt)
Cr (VI)	1.0	3.4
Cr (III)	1.5	5.1

LOD = $(3 \times \sigma_{\text{blank}}) / \text{slope}$
 LOQ = $(10 \times \sigma_{\text{blank}}) / \text{slope}$

Table 2. Recovery of spiked samples tested during analysis.

Sample	QC Position	Cr (VI)		Cr (III)	
		Concentration (ppb)	% Recovery	Concentration (ppb)	% Recovery
Water 1		0.034	-	0.020	-
Water 1 + 1 ppb spike	Beginning	1.066	103	0.960	94
Water 2		0.099	-	0.030	-
Water 2 + 1 ppb spike		1.110	101	1.101	107
Water 3	Middle	0.011	-	0.019	-
Water 3 + 1 ppb spike		1.071	106	0.990	97
Water 4	End	0.007	-	0.033	-
Water 4 + 1 ppb spike		0.989	98	1.174	114
Water 5		0.867	-	0.063	-
Water 5 + 1 ppb spike		1.827	98	1.043	98
Average Recovery		Cr (VI)	101 ± 3 %	Cr (III)	102 ± 8 %

Table 3. Drinking water samples tested using ESI's prepFAST IC instrument and chromium speciation method.

	Drinking Water Source	Source Location	pH	Cr (VI) (ppb)	Cr (III) (ppb)	Cr (VI) + Cr (III) (ppb)
Residential	Investigator's Well	Honey Creek, IA	7.71	0.209	0.100	0.309
Residential	Investigator's Neighbor's Well	Honey Creek, IA	7.68	5.19	0.250	5.44
Residential	Missouri Valley Tap	Missouri Valley, IA	8.86	0.214	0.105	0.32
Residential	Fort Calhoun Tap	Fort Calhoun, NE	7.95	2.27	0.062	2.33
Residential	Central Omaha Tap	Omaha, NE	8.04	1.05	< DL	1.12
Residential	Bennington Tap	Bennington, NE	8.13	2.26	0.038	2.30
Commercial	Council Bluffs Tap 1	Council Bluffs, IA	7.92	1.74	0.104	1.85
Commercial	Council Bluffs Tap2	Council Bluffs, IA	7.98	1.62	0.052	1.68
Commercial	Blair Tap 1	Blair, NE	8.10	2.33	0.064	2.40
Commercial	Blair Tap 2	Blair, NE	8.03	2.37	0.034	2.40
Commercial	Northwest Omaha Tap 1	Omaha, NE	7.14	2.11	0.057	2.17
Commercial	Northwest Omaha Tap 2	Omaha, NE	7.54	2.25	0.037	2.29
Bottled	Water 1	France	7.96	0.061	0.195	0.255
Bottled	Water 2	USA	8.27	0.028	0.103	0.131
Bottled	Water 3	USA	8.48	0.237	0.486	0.723
Bottled	Water 4	USA	8.53	0.556	0.118	0.674
Bottled	Water 5	USA	8.04	0.327	0.289	0.616
Bottled	Water 6	-	8.21	<DL	0.179	0.179
Natural	Missouri River Location 1	Omaha, NE	8.10	0.025	0.039	0.064
Natural	Missouri River Location 2	Omaha, NE	8.15	0.026	0.037	0.064
Natural	Missouri River Location 3	Omaha, NE	8.14	0.026	0.037	0.062

Sample Analysis

The drinking water samples that were collected in or around Omaha, NE, USA were tested using the prepFAST IC chromium speciation method in combination with a PerkinElmer NexION 350d ICPMS. The samples were placed onto the autosampler rack with no sample preparation. The autodilution feature was used to make an inline 2x dilution of each water sample just prior to injection onto the column. The final results are shown in Table 3, along with source location, and pH at time of analysis. The total Cr in this experiment is the sum of Cr(VI) and Cr(III). However, it could have easily been done as a separate total analysis experiment. The pH ranged from 7.14 – 8.86 for all water samples tested. The analysis was completed within 48 hours of collecting the water samples.

Results

A water sample from one of the wells tested came back much higher than any of the other samples tested. Interestingly, the well water from the investigator's neighbor was high in Cr (VI), but the investigator's well water did not show high levels of Cr (III or VI). The two wells are believed to be from the same aquifer, located ~ 1300 feet apart from one another. The investigator's well water is housed in a newer model pressure tank that is lined with a silver ion infused polypropylene antimicrobial layer. The plumbing is made up of cross-linked polyethylene (PEX) water lines and has a sediment filter. The investigator's neighbor's well water is housed in a much older pressure tank with no liner. The plumbing is entirely copper tubing and has no in-line filter. It is believed that the plumbing lines, filter, and tank are the cause for the difference in Cr species detected (more on the well water in subsequent sections).

All of the tap water sampled, except for Missouri Valley was ~ 1–2 ppb Cr(VI) regardless if it was residential or commercial. The Missouri Valley tap water had the lowest amount of Cr(VI) tested (0.214 ppb). Missouri Valley receives its water from the Boyer River and is processed by the city of Missouri Valley. Omaha, Bennington, and Fort Calhoun receive water from the Missouri River and are processed by Metropolitan Utilities District. Blair and Council Bluffs both receive water from the Missouri River, but each city processes its own water.

The Cr (III + VI) measured in all bottled water samples was below 0.73 ppb, with Bottled Water 4 having the highest amount of Cr (VI) (0.556 ppb) and Bottled Water 3 having the highest amount of Cr (III) (0.486 ppb). Bottled Water 6 had the lowest amount of Cr (VI), which was below the detection limits of the method (LOD = 0.001 ppb Cr (VI)). All of the water samples mentioned so far in this study were treated/processed. Thus 3 samples were collected from the Missouri River at Dodge Park to have a comparison to a natural source of water. The results showed levels of 0.025 ± 0.001 ppb for Cr (VI) and 0.038 ± 0.001 ppb for Cr (III) from the Missouri River. These results show that regardless of the location where the samples were collected, the amount of Cr remained constant. The natural water had the lowest amount of Cr, suggesting that most of the Cr that is in our drinking water comes from transportation or processing.

To further investigate the high Cr (VI) found in the neighbor's well, additional samples were collected (> 30 days after original testing). Samples were collected from before the pressure tank, after the pressure tank, and after the hot water heater from the investigator's well to see if there was any variation in Cr. Unfortunately, the neighbor's well had no way to collect samples from before and after the pressure tank without cutting the piping, so samples were taken after the pressure tank only. The additional well water testing

confirmed the original results showing high Cr (VI) for the neighbor's well water. The four well water samples were repeated 6 times to show repeatability of the method (Table 4). In addition, the results from samples analyzed during initial testing were compared to those analyzed 34 days later (Table 5).

As mentioned in the instrument section, the prepFAST IC was switched into total metals analysis mode for the additional well water samples. The presence of elements such as Mn (Mn-oxidizing bacterium) or Cl (chlorination of water) have been linked to oxidizing Cr (III) to Cr (VI).¹⁻⁴ Thus the four samples collected were analyzed according to EPA guidelines for water testing in hopes of better understanding why the neighbor's well had high Cr (VI) levels. Comparing the investigator's well water to the neighbor's well water, As, Cr, Co, Cu, Pb, Mn, V, and Zn resulted in considerable differences (Table 6). The neighbor's well had higher amounts for the aforementioned elements except for Co and Mn, which were lower than the investigator's well. The high Cu detected in the neighbor's well can be attributed to the copper piping, while the other elements are most likely attributed to the older tank/filter system being employed. It was noticed that the neighbor's well had higher amounts of Cl displayed in Fig. 2 (not quantified), which could be contributing to the conversion of the Cr (III) into Cr (VI).

The current EPA methods all report the total Cr in drinking water. Therefore it is important that the speciation method be accurate with respect to total metals analysis for Cr. Table 7 displays the comparison of Cr (VI) + Cr (III) to total Cr (obtain from total metals analysis). The % bias between the methods was $\leq 10\%$ for the 4 well water samples tested. Having the ability to switch between speciation and total metals allows for greater analytical flexibility while maintaining the desired accuracy for these types of analyses.

Table 4. Additional testing for the well water samples (n = 6) using both the Cr speciation and total Cr methods.

		Cr (VI)		Cr (III)	
		Average	% RSD	Average	% RSD
Investigator's Neighbor's Well	After Pressure Tank	4.96 ± 0.09	1.9	0.197 ± 0.016	8.3
Investigator's Well	After Pressure Tank	0.185 ± 0.003	1.5	0.129 ± 0.005	4.0
Investigator's Well	After Hot Water Heater	0.167 ± 0.003	1.8	0.113 ± 0.004	3.1
Investigator's Well	Before Pressure Tank	0.168 ± 0.005	3.1	0.118 ± 0.006	4.9

Table 5. Comparison of Cr speciation results from two separate days. Day 34 represents a water sample being taken 34 days after the initial sample (day 1) was taken and analyzed.

	Cr (VI)		Cr (III)	
	Day 1	Day 34	Day 1	Day 34
Investigator's Neighbor's Well	5.19	4.96	0.250	0.197
Investigator's Well	0.209	0.185	0.100	0.129

Table 6. Total metals analysis for the additional well water samples (n = 6) using EPA guidelines.

Element	Investigator's Neighbor's Well	Investigator's Well		
	After Pressure Tank (ppb)	After Pressure Tank (ppb)	After Hot Water Heater (ppb)	Before Pressure Tank (ppb)
⁹ Be	<DL	<DL	<DL	<DL
²⁷ Al	0.987	1.01	2.88	1.69
⁵¹ V	1.77	0.123	0.128	0.140
⁵² Cr	4.84	0.337	0.254	0.296
⁵⁵ Mn	0.042	169	132	59.9
⁵⁹ Co	0.035	0.135	0.301	0.071
⁶⁰ Ni	0.293	0.365	0.503	0.351
⁶³ Cu	208	14.3	2.96	2.01
⁶⁶ Zn	13.5	1.93	1.37	0.974
⁷⁵ As	0.405	0.049	0.042	0.044
⁸² Se	4.16	4.71	4.80	4.76
⁹⁸ Mo	0.827	1.57	1.58	1.56
¹⁰⁷ Ag	<DL	<DL	<DL	<DL
¹¹¹ Cd	0.004	0.035	0.013	0.010
¹²¹ Sb	0.076	0.030	0.030	0.042
¹³⁸ Ba	238	225	213	221
²⁰² Hg	<DL	<DL	<DL	<DL
²⁰⁵ Tl	<DL	0.059	0.067	0.083
²⁰⁸ Pb	1.68	0.105	0.057	0.028
²³² Th	<DL	<DL	<DL	<DL
²³⁸ U	4.64	6.12	5.48	6.46



Table 7. Comparison between Cr speciation and total Cr methods.

		Cr (VI) + Cr (III)	Total Cr	% bias
Investigator's Neighbor's Well	After Pressure Tank	5.16	4.84	6.6%
Investigator's Well	After Pressure Tank	0.314	0.337	-6.8%
Investigator's Well	After Hot Water Heater	0.280	0.254	10.3%
Investigator's Well	Before Pressure Tank	0.286	0.296	-3.3%

Conclusions

We at Elemental Scientific strive not only to provide a reliable method for today's standards, but also meet tomorrow's standards. The chromium speciation method using the prepFAST IC is capable of measuring Cr (VI) in drinking water far below the MCL listed by the EPA (100 ppb) or the state of California (50 ppb). Furthermore, this application would allow researchers the ability to measure below the public health goal of 0.02 ppb Cr (VI). The drinking water tested in this study shows that the source of chromium is not coming from the natural sources, but most likely from processing/transportation to the homes and businesses. The bottled drinking water is the lowest source of Cr in this study, whereas the drinking water from the investigator's neighbor's well was by far the highest. The total metals analysis showed that neighbor's well water was not only high in Cr (VI) but also As, Cr, Co, Cu, Pb, Mn, V, and Zn.

References

1. Murray, K.J., Mozafarzadeh, M.L., Tebo, B.M., Cr(III) oxidation and Cr toxicity in cultures of the manganese(II)-oxidizing *Pseudomonas putida* strain GB-1, *Geomicrobiology Journal*, 2005, 22, 151-159.
2. Murray, K.J., Tebo, B.M., Cr(III) is indirectly oxidized by the Mn(II)-oxidizing bacterium *Bacillus* sp. Strain SG-1, *Environ. Sci. Technol.*, 2007, 41, 528-533.
3. Lindsay, D.R., Farley, K.J., Carbonaro, R.F., Oxidation of Cr(III) to Cr(VI) during chlorination of drinking water, *J. Environ. Monit.*, 2012, 14, 1789-1797.
4. Nico, P.S., Zasoski, R.J., Importance of Mn(III) availability on the rate of Cr(III) oxidation on MnO₂, *Environ. Sci. Technol.*, 2000, 34, 3363-3367.

For more content regarding the Cr speciation method please see our article published in the *Journal of Analytical Atomic Spectrometry*.



A fully automated total metals and chromium speciation single platform introduction system for ICP-MS

Abstract

Measuring chromium species in drinking water has become of particular interest due to daily environmental contamination that is caused by industrial processes. Agencies such as the US Environmental Protection Agency and the European Union continue to investigate the maximum to which Cr(VI) contaminant levels should be set; thus laboratories must seek more efficient ways of performing routine analyses. In this work a single platform, automated speciation and total metals method is presented for chromium speciation in drinking water, waste water, industrial waters, and recipient waters, and for total metals in sludges, soils, organic waste, ashes, biological samples, or paint. Samples were measured using a prepFAST IC system for Cr(III) and Cr(VI) and the results were compared to the HPLC results. In addition, samples from the aqua regia total method were compared to those of the total metals method performed using the prepFAST IC. Sample comparisons resulted in linear regression plots with very good correlations, greater than 0.97 for total metals over a dynamic range of 0.010–100 000 $\mu\text{g L}^{-1}$ for 63 elements and greater than 0.98 for Cr(VI) speciation. The limits of detection for Cr(VI) and Cr(III) using the prepFAST IC and ICP-MS combination are 7 ng L^{-1} and 12 ng L^{-1} , respectively. The new method resulted in an ~43x improvement in detection limits as compared to the previous method employed in our laboratory. The accurate results for quality control samples of Cr(VI) were in good agreement with the historical values collected using the old method.



© Elemental Scientific | 7277 World Communications Drive | Omaha, NE 68122
Tel: 1-402-991-7800 | sales@icpms.com | www.icpms.com

17201-2