Haihan Chen - hachen@shimadzu.com

Chromium Speciation of Drinking Waters by IC-ICP-MS

Haihan Chen, Jonathan Peters, Hui Guo, Craig Young, and Ruth Marfil-Vega. Shimadzu Scientific Instruments, 7102 Riverwood Dr, Columbia, MD 21046, USA

Introduction

The EPA has set a maximum contaminant level for total chromium in drinking water to be 100 ppb. Chromium in waters exists in two different oxidation states: trivalent [Cr(III)] and hexavalent [Cr(VI)]. While trivalent chromium is an essential human dietary element, hexavalent chromium is a carcinogen and a reproductive toxicant, and can cause other health issues. Despite the lack of Federal regulations specific for Cr(VI) in drinking water in the US, it is critical to develop robust and rapid methods speciating chromium due to the different toxicities of Cr(III) and Cr(VI).

Ion Chromatography (IC) coupled with Inductively Coupled Plasma Mass Spectrometer (ICPMS) has been developed for chromium speciation because ICPMS offers both multi-element and multi-isotope detection with high sensitivity. But the simultaneous separation of chromium is an unusual case since Cr(III) typically exists as cationic aqua-hydroxo complexes while Cr(VI) exists typically as an anionic chromate species. Typical methods to determine chromium speciation involve incubation of samples with complexing agents such as EDTA, which forms a complex with Cr (III) to allow a single chromatographic method to be used to separate Cr(III) and Cr(VI). It requires hours of sample preparation considering the time for adding complexing agent, as well as heating and cooling the samples.

In this study, we explore and discuss the combination of a Shimadzu Inductively Coupled Plasma Mass Spectrometer (ICPMS-2030) and a Shimadzu Prominence Ion Chromatography (IC) to determine chromium speciation in drinking water. A column to separate both cations and anions was used to avoid sample pretreatment with complexing agents, eliminate any possible risk of contamination as well as maximize sample throughput.

Experimental

Sample Preparation

Tap and well water sample were collected locally and analyzed directly without any pretreatment. Fortified samples were prepared by spiking 1000 µg/L Cr(III) and Cr(VI) stock standard solutions into the samples. A commercially available standard sample containing 4 µg/L of 22 different elements, including aluminum (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), selenium (Se), silver (Ag), sodium (Na), thallium (Tl), vanadium (V) and zinc (Zn), was also analyzed to estimate possible matrix effects on the quantification accuracy of chromium speciation.

Chromium standards were prepared by diluting 1000 mg/L stock solutions of trivalent and hexavalent chromium in deionized water. The mobile phase was made from trace metal grade concentrated nitric acid (HNO_3).

Samples and calibration standards were prepared and stored in deionized water with resistivity equal or greater than 18.0 MΩ-cm for species stabilization and avoiding possible contamination.

Instrumentation

All analyses were run on a Shimadzu Prominence IC coupled to a Shimadzu ICPMS-2030. The instrumental parameters are shown in **Table 1** and **Table 2**.

The IC was configured with an inert flow path. It consists of a system controller CBM-20, an online degassing unit DGU-403, a solvent delivery unit LC-20Ai, an autosampler SIL-20AC with PEEK valve and inert kit, and a column oven CTO-40C.

Table 1. Operating conditions of Shimadzu Prominence IC

Parameter	Setting	Parameter	Setting
Column	Shodex™ VC-50 2D	Separation Scheme	Isocratic
Mobile Phase	9mM HNO_3	Column Temp.	50°C
pH	2	Injection Volume	20 µL
Flow Rate	0.3 mL/min	LC Vials	Plastic, 1.5 mL

Table 2. Operating conditions of Shimadzu ICPMS-2030

Parameter	Setting	Parameter	Setting
Radio Freq. Power	1.20 kW	Mix Gas	0.00 L/min
Sampling Depth	5.0 mm	Cell Gas	6.0 mL/min
Plasma Gas	8.0 L/min	Cell Voltage	-21 V
Auxiliary Gas	1.10 L/min	Energy Filter	7.0 V
Carrier Gas	0.70 L/min	Chamber Temp.	5°C

The ICPMS is equipped with a collision cell that uses helium (He) to discriminate polyatomic interferences based on kinetic energy. Chromium was analyzed with He gas on. This allows chromium to be measured more accurately with better sensitivity, using the main isotope at 52 m/z, with removal of the primary polyatomic interferences such as ArC and ClOH. An LC fittings kit (Glass Expansion Inc.) was used to connect IC tubing directly to the nebulizer.

Results and Discussion

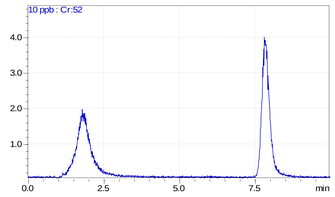

Figure 1. Chromatogram of 10 ppb Cr(III) and Cr(VI)

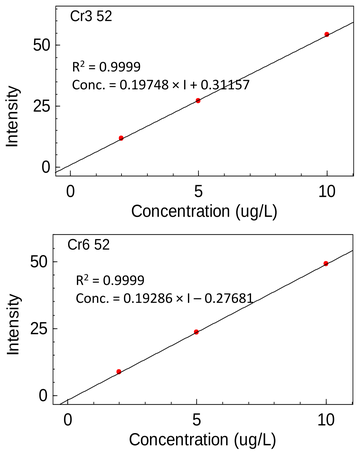

Figure 2. Calibration curves of Cr(III) and Cr(VI) in the range of 2-10 µg/L

A chromatogram of a mixed chromium standard is shown in **Figure 1**. Chromium species, Cr(III) and Cr(VI), are well separated and elute within 10 minutes.

Calibration curves were established with standards from 2-10 µg/L for both Cr(III) and Cr(VI). Quantification was based on integrated peak area. The calibration curves of Cr(III) and Cr(VI) are illustrated in **Figure 2**, each showing excellent linearity with correction coefficient (R^2) greater than 0.9999. The slopes of the calibration curves as shown in **Figure 2** match very closely (2.4% difference), demonstrating that the species of Cr(III) and Cr(VI) are stable and do not interconvert under the experimental conditions.

For this method, the detection limits for Cr(III) and Cr(VI) are 0.20 and 0.35 µg/L, respectively, two orders of magnitude lower than the current EPA maximum contaminant level of 100 ppb for total chromium. The detection limits can be further lowered by increasing injection volume, or using a column that have similar packing material but higher capacities.

With the separation established, a variety of samples were analyzed with the results shown in **Table 3**. The tap water sample does not contain detectable levels of Cr(III) and Cr(VI), while the well sample contains 0.738 ppb of Cr(VI). The commercial available standard, which contains 4 ppb of 22 different elements including Cr(III), was measured to have 3.92 ppb of Cr(III), with a recovery of 98%, indicating the co-existence of other elements do not interfere with chromium quantification.

To determine the accuracy of the results, all samples were spiked of 5 ppb of both chromium species. All spiked recovered within ±5% of the target values as shown in Table 3, further indicating the accuracy of the method.

Table 3. Concentrations of chromium species in µg/L in original and fortified samples as well as recovery yields in percent (n.d. = not detected)

Sample	Cr(III)	Cr(VI)
Tap water	n.d.	n.d.
Fortified tap water	5.05	5.16
Recovery (%)	101	103
Well water	n.d.	0.738
Spiked well water	5.15	5.61
Recovery (%)	103	97
Commercial Standard	3.92	n.d.
Fortified commercial standard	9.06	4.77
Recovery (%)	103	95

The long-term stability was also investigated. A mixture of both species with a concentration of 10 µg/L, was repeatedly injected into the system over 7.2 hours. The results are shown in **Table 4**. Variation of less than 1.4% for retention time and less than 2.6% for peak area were obtained, proving the stability of the standards, instrumentation and methodology.

Table 4. Retention time and peak area for multiple 20 µL injections of 10 µg/L Cr(III) and Cr(VI) Standard

Time of Inj. (hours)	Retention Time (min)		Peak Area (kilo counts)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0.00	7.818	1.795	67.85	56.94
0.48	7.843	1.840	69.08	56.97
0.96	7.817	1.819	69.55	56.14
1.27	7.839	1.904	66.25	56.95
1.45	7.809	1.856	68.11	58.30
1.63	7.771	1.843	68.65	57.75
1.82	7.804	1.828	69.71	59.70
2.01	7.823	1.855	69.53	61.08
2.20	7.769	1.822	67.83	59.67
2.38	7.808	1.840	71.91	58.18
2.57	7.770	1.823	70.37	58.26
2.75	7.797	1.812	72.47	59.03
2.93	7.782	1.801	71.00	60.99
3.12	7.809	1.862	71.41	58.21
3.30	7.768	1.830	70.97	60.33
3.74	7.784	1.805	67.30	60.79
4.17	7.777	1.843	66.32	60.68
4.60	7.751	1.814	67.48	58.34
5.04	7.771	1.831	68.71	58.50
5.47	7.783	1.856	68.32	58.15
5.90	7.789	1.809	68.49	58.02
6.08	7.764	1.829	68.58	60.87
6.27	7.749	1.877	69.07	57.03
6.45	7.794	1.841	67.40	61.64
6.64	7.770	1.831	68.88	58.31
6.82	7.770	1.851	68.11	59.10
7.01	7.771	1.857	69.84	60.40
7.18	7.735	1.829	66.07	58.16
Ave.	**7.787**	**1.836**	**68.90**	**58.88**
STD	**0.0267**	**0.0240**	**1.66**	**1.50**
RSD (%)	**0.34**	**1.31**	**2.40**	**2.55**

Conclusions

- Shimadzu ICPMS-2030 coupled with Prominence IC provides excellent sensitivity, precision, accuracy, stability, fast time response and high sample throughput for determination of chromium speciation in waters.
- The use of 9 mM nitric acid other than salt solutions as mobile phase reduces background signal and possible interference. The Shimadzu ICPMS-2030 equipped with a newly developed collision cell enables to effectively eliminate polyatomic interference, and achieve high-sensitive and low-interference analyses.
- The use of a column to separate both cations and anions enables fast separation of chromium speciation without any sample pretreatment with complexing agents. Eliminating sample preparation avoids any possible risk of contamination as well as maximizes sample throughput.

References

• "Practical Guide to ICP-MS", Robert Thomas , Marcel Dekker, Inc.