Chromium Speciation in Drinking Water by LC-ICP-MS

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Introduction

Chromium is a transition metal which may be present in the environment in various forms depending on the sample type and origin. Hexavalent chromium, Cr(VI) is well known to be highly toxic, while the other stable oxidation state, trivalent chromium, Cr(III) is an essential element for humans. Various regulations around the world exist to minimize the risk of exposure to dangerous levels of Cr(VI). More recently, permissible levels of Cr(VI) in drinking water have been re-evaluated and significantly lower limits have been proposed.

In this study, an isocratic separation of Cr(III) and Cr(VI) using HPLC coupled to ICP-MS is used to quantify ultra-trace levels of both Cr(III) and Cr(VI) in highly mineralized waters in less than 4 minutes. Data is presented to highlight the improved analytical capability for these species in waters and the applicability of the method to the determination of Cr species in food and environmental samples.

LC-ICP-MS

Figure 1. Agilent 7700 Series ICP-MS and HPLC

The separation and detection of the two Cr species is important because the total chromium concentrations does not provide adequate information on toxicity. The anionic, hexavalent form of Cr is toxic, while in its cationic trivalent oxidation state, chromium is an essential element for human nutrition. Hence separating the forms (or species) is necessary before quantifying using ICP-MS as a detector. LC-ICP-MS enables Cr species to be separated and measured with high accuracy and good sensitivity.

Experimental

HPLC conditions: An Agilent 1200 liquid chromatograph equipped with a binary HPLC pump, autosampler and vacuum degasser were used in this study. The HPLC system was connected to the ICP-MS using the Agilent LC connection kit. An anion exchange column (4.6 mm i.d.x 30 mm polyhydroxymethacrylate base resin) was used for separation. The column temperature was maintained at ambient for all experiments. The bio-compatibility kit was installed for sample delivery line. The detail of operating conditions are written in Table 2.

ICP-MS: An Agilent 7700x ICP-MS was used for detection. Instrument operating conditions are shown in table 1.

Initially, the removal of the interferences on m/z 52 was evaluated. The use of collision/reaction cell technology with ICP-MS allows Cr to be measured with good accuracy and sensitivity, with removal of the primary matrix-based interferences due to ArC and ClOH. The relationship between He gas flow and analyte signal is shown in Figure 2. From this graph, the best flow rate for He gas was 3-5mL/min. For simplicity, the center value, 4mL/min was applied in this method. H_2 gas was also evaluated, however it showed no significant difference compared with He.

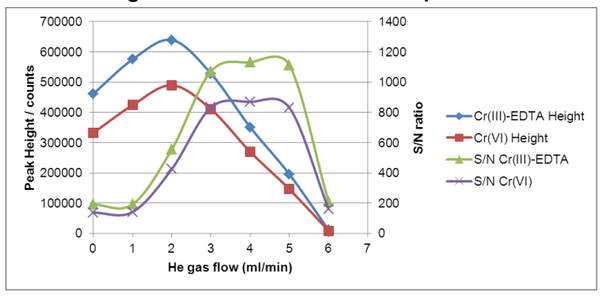

Figure 2. Peak Height and Signal to Noise ratio vs He gas flow

Table 1. Height and S/N for Cr species with different He flow rate.

He gas flow mL/min	0	1	2	3	4	5	6
Cr(III)-EDTA Height	461582	575026.5	639270	528348.5	351199	195695	11111.5
Cr(VI) Height	332757	423882	489734	410468	269922	146298	8605.5
Noise	2413.5	2987.5	1152.5	493	310.5	176	53.5
S/N Cr(III)-EDTA	191.25	192.48	554.68	1071.70	1131.08	1111.90	207.69
S/N Cr(VI)	137.87	141.89	424.93	832.59	869.31	831.24	160.85

Results and Discussion

Table 2. Operating parameters of ICP-MS and HPLC

ICP-MS Parameters	
RF power	1550 W
Sample depth	8 mm
Carrier gas	1.05 L/min
Dwell time	0.5 sec
Isotope monitored	^{52}Cr, ^{53}Cr
Cell gas	He
Flow rate of cell gas	4mL/min
HPLC Parameters	
Column	Agilent anion exchange column, G3268-80001: 4.6mm x 30mm id
Mobile phase	5mM EDTA (2Na) / 5mM NaH_2PO_4/15mM Na_2SO_4 pH=7.0 adjusted by NaOH
Flow rate	1.2mL/min
Temperateure	Ambient
Injection volume	100uL

Under the conditions described above, ICP-MS detection using He gas mode yielded detection limits (DLs) of < 200 ng/L for both ^{52}Cr(III) and ^{52}Cr(VI) with injection volume of 100ul. The detection limits were calculated as three times the peak-to peak signal to noise as measured on standard chromatograms. However, increasing the injection volume should provide better DLs. The DLs with various injections volumes from 5ul-100ul are shown in Table 3.

Table 3. DLs for Cr species by LC-ICP-MS

Injection volume	Peak Height / counts		Noise	Peak Area / conuts		DL (conc. / µg/L)	
	Cr(III)-EDTA	Cr(VI)		Cr(III)-EDTA	Cr(VI)	Cr(III)-EDTA	Cr(VI)
5 µL	32621	24233	204	514586	503778	**1.88**	**2.53**
20 µL	130764	97934	314	2101007	2007572	**0.72**	**0.96**
50 µL	323593	241948	300	5154321	4970771	**0.28**	**0.37**
100 µL	632808	475244	273.5	10204281	9796463	**0.13**	**0.17**

The long-term stability was evaluated using a Cr standard solution. Figure 3 shows good reproducibility over 8 hours using 5ug/L standard solution. The RSDs for both ^{52}Cr(III)-EDTA and ^{52}Cr(VI) were less than 5%.

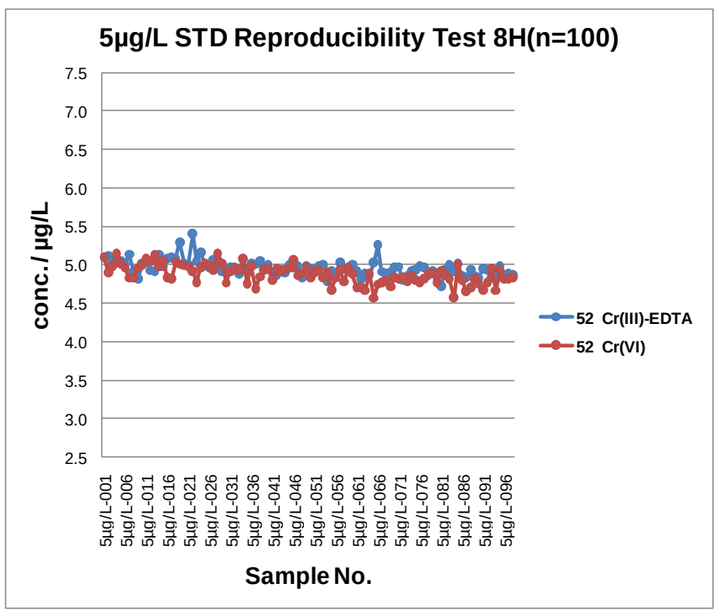

Figure 3. 8 hours stability test using 5ug/L standard solution

Drinking Water Analysis

In order to test the suitability of the method for these real-world sample types, the method was applied to the determination of both Cr species in both spiked and unspiked mineral water samples.

The three samples evaluated were a Japanese mineral water referred as Water A, and two French mineral waters referred as Water B and Water C. The drinking waters selected covered a wide range of typical mineral water composition, including Water C which is at the extreme end of highly mineralized drinking water (over 450ppm Ca and over 1000ppm sulfate). The major element composition of the water samples is shown in Table 4.

Table 4. Major element composition for three different mineral waters.

	Water A (ppm)	Water B (ppm)	Water C (ppm)
Na	6.5	11.6	9.4
Ca	9.7	11.5	468
Mg	1.5	8	74.5
K	2.8	6.2	2.8
Sulfate	–	–	1121

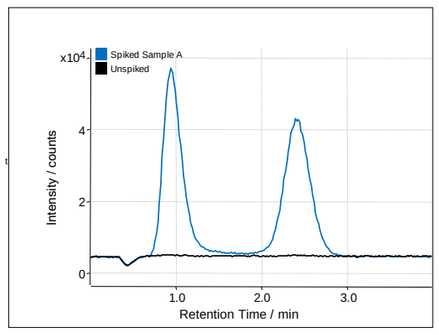

Figure 4. Chromatogram for spiked (blue) and unspiked (black) mineral water A

Table 5. Results of 10 ul/L mineral water stability test (8 hours, n=30/each water)

		52 Cr(III)-EDTA		52 Cr(VI)	
Sample		Area	Conc. [µg/L]	Area	Conc. [µg/L]
Sample A	**AVG**	906410	10.4	913019	10.3
	STD	12878	0.148	18745	0.211
	RSD %	**1.4**	**1.4**	**2.1**	**2.1**
Sample B	**AVG**	933560	10.7	920154	10.3
	STD	8958	0.103	21331	0.240
	RSD %	**1.0**	**1.0**	**2.3**	**2.3**
Sample C	**AVG**	900775	10.3	879234	9.9
	STD	6808	0.078	12490	0.140
	RSD %	**0.8**	**0.8**	**1.4**	**1.4**

The ability to recover low concentration spikes for both Cr species in the high matrix Water C indicates the effectiveness of the optimized method for sample stabilization. Furthermore the accurate recovery of low concentration spikes of both species indicates that potential problems of species interconversion, such as reduction of Cr(VI) to Cr(III) was avoided through the selection of an appropriate pH for the samples and the mobiles phase, and the use of EDTA in the mobile phase.

Septum Issue

During the long-term stability experiment as shown in Table 5, we found that the rubber septum could cause chemical changes in Cr species. As shown in Figures 6, with multiple injections from the same vial with a rubber septum, the Cr(VI) disappears and the Cr(III)-EDTA increases. It is speculated that a reducer or light stabilizer in the rubber septum caused this effect. To ensure species stability, it is necessary to avoid rubber septa for this application, as illustrated in Figure 7, which shows the same comparison from a vial with a solid polyethylene septum.

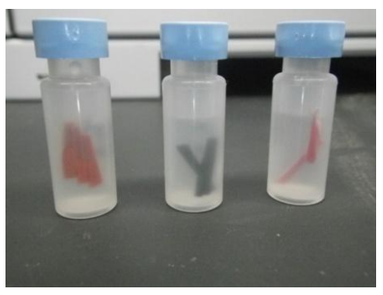

Fig 5. (left) Septa were added to 5µg/L Cr(III) and Cr(VI) STD

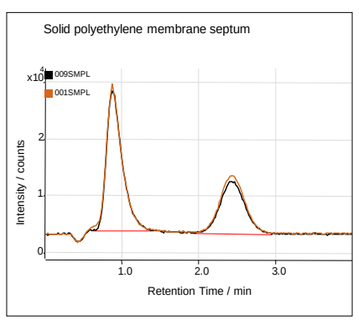

Figure 6. Chromatograms using Red Rubber septum (in black) and without any septum (in brown)

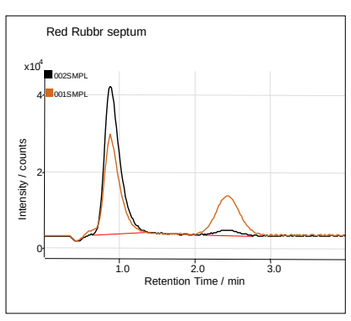

Figure 7. Chromatograms using Solid polyethylene membrane septum (in black) and without any septum (in brown) Solid polyethylene membrane septum

Table 6. Counts of Cr species after added different septums in 5ug/L std

	52 Cr (III)	52 Cr (VI)	52 Cr (III)	52 Cr (VI)	
Material of the septum	Count	Count	%	%	Judge
Red Rubber septum	553001	27722	160	12	bad
Black Viton Septum	725454	1060	210	0	bad
Teflon disc	378492	195816	109	86	good
Polyethylene membrane septum	352510	207741	102	91	good

Conclusions

Cr(III)-EDTA and Cr(VI) were successfully separated and quantified using LC-ICP-MS in natural, high matrix water samples:

- with good detection limits for both species
- with good long stability (8 hours)
- with good reproducibility within different columns

It is important not use the rubber septa when analyzing Cr by LC-ICP-MS