Chromium Speciation in Drinking Water using LC(IC)-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.

Experimental

Figure 1. Agilent 7700 Series ICP-MS and HPLC

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

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 Agilent's bio-compatibility kit (Part # 5065-9972) was installed for sample delivery line. The details of the operating conditions are reported in Table 1.

ICP-MS: An Agilent 7700x ICP-MS was used for Cr detection. Instrument operating conditions are shown in Table 1.Initially, the removal of interferences on the primary Cr isotope at 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, 4mL/min flow rate was applied in this method. H_2 gas was also evaluated, however it showed no significant improvement compared with He.

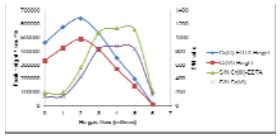

Figure 2. Peak Height and Signal to Noise ratio vs He gas flow

Table 1. Operating parameters of ICP-MS and HPLC

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

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 height to height of 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 2.

Results and Discussion

Table 2. DLs for Cr species to injection volume

Injection volume	Peak Height / counts		Area / conuts		DL	
	52Cr(III)	52Cr(VI)	52Cr(III)	52Cr(VI)	52Cr(III)	52Cr(VI)
5 µL	32620.5	24233	514586	503778	**1.88**	**2.83**
20 µL	130764	97933.5	2101007	2007572	**0.72**	**0.98**
50 µL	323692.5	241948	5154321	4970770.5	**0.28**	**0.37**
100 µL	632807.5	475244	1E+07	9796463	**0.13**	**0.17**

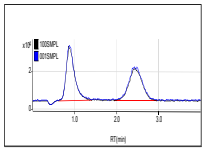

Figure 3. 8 hours stability test using 5ug/L standard solution (n=100)

The long-term stability was evaluated using a Cr standard solution. Figure 3 shows good reproducibility over 8 hours (n=100) using 5ug/L standard solution. The RSDs for both ^{52}Cr(III)-EDTA and ^{52}Cr(VI) were less than 5%.

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 compositions, 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. The major composition of the water samples

	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

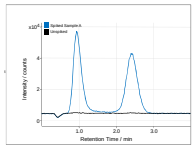

Figure 4. Chromatogram for spiked (blue) and unspiked (black) mineral water A

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

Sample		52 Cr(III)-EDTA		52 Cr(VI)	
		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) were avoided through the selection of an appropriate pH for the samples and mobiles phase, and the use of EDTA in the mobile phase.

Applying bio-inert LC pump

The possibility to lower the background using Agilent 1260 Infinity Bio-inert pump was also evaluated. The metal-free components in the sample flow-path and the absence of iron and steel in solvent delivery was expected to help achieve lower detection limit when quantifying Chromium. Mobile phase and 1% HNO_3 (EL grade) and 0.1% HCl were quantified after passing through the bio-inert pump and also conventional pump. Ultra Pure Water (Millipore), 5mM EDTA, 5mM $NaHPO_4$, and $NaSO_4$ were also quantified for the reference of the background. The results are shown in Table 6.

Table 6. Results of Cr concentration and background

With conventional LC pump

	52 Cr	
	Conc. [ppb]	CPS
Mobile phase	0.46	6781.3
1%HNO3	0.81	11838.4
0.1% HCl	0.51	7532.8

With Bio-inert LC pump

	52 Cr	
	Conc. [ppb]	CPS
Mobile phase	0.31	4659.5
1%HNO3	2.70	38835.5
0.1% HCl	0.43	6405.6

	52 Cr	
	Conc. [ppb]	CPS
UPW	<0.000	142.2
5mM EDTA	0.04	795.6
5mM NaHPO4	0.21	3139.2
15mM Na2SO4	<0.000	180.0

When comparing between conventional and bio-inert pump, the solution which passed through bio-inert pump showed slightly lower background. When quantified the each component of the solution. the background of 5mM $NaHPO_4$ showed relatively high. In order to achieve lower background and lower detection limit, applying higher purified $NaHPO_4$ might help.

Results and Discussion

Quantification of Cr(VI) at ultra-trace levels

While we have developed the method to measure both Cr(III) and Cr(VI)in drinking water simultaneously, the State of California in the US has recently proposed (2009) setting a new "public health Goal" for Cr(VI) in drinking water of 60ng/L. To meet this goal, another method for higher sensitivity and selectivity for Cr(VI) quantification was developed. The method is outlined in Table 7. The same column was used for separation but the injection volume was increased to 1500ul. In this method, Cr(III) was not quantified because with large injection volume, the water dip will cover the peak of Cr(III)and also in order to quantify Cr(III), EDTA will be added to the sample solution and this EDTA, anion, might help excess of the capacity of the column, causing peak shape change or retention time delay. From these reasons, only Cr(VI) was focused to measure.

Table 7. Operating parameters of ICP-MS and HPLC

HPLC Parameters		ICP-MS Parameters	
Column	Agilent anion exchange column,	RF power	1550 W
	G3268-80001: 4.6mm x 30mm id	Sample depth	8 mm
Mobile phase	1mM EDTA (2Na) / 5mM NaH_2PO_4/15mM Na_2SO_4	Carrier gas	1.05 L/min
	pH=7.0 adjusted by NaOH	Dwell time	0.5 sec
Flow rate	1.2mL/min	Isotope monitored	^{52}Cr, ^{53}Cr
Temperateure	Ambient	Cell gas	He
Injection volume	1500uL	Flow rate of cell gas	4mL/min

By applying a larger injection volume (1500 ul), DLs in the region of ng/L for Cr(VI) became achievable. Although other high concentration anions exist in drinking water besides Cr(VI), no peak shape change nor retention time delay occurred. The calibration linearity showed good correction coefficient which was better than 0.9995 in the low level: Cr(VI) {1000~50ng/L}. Detection limit calculated by S/N was about 8ng/L.

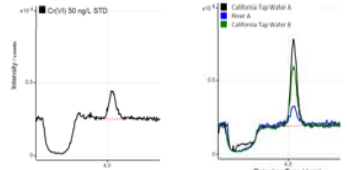

Figure 5. Chromatograms of Cr (V) for standard solution and various waters from the State of California, USA. The left chromatograph shows 50ng/L standard solution and the right shows non-spiked chromatographs of three water samples.

Table 8 shows the spike recovery test for tap water from two different places and river water sample from California. Chromatograms are shown in Figure 5. While the amount of Cr(VI) for River Water A was calculated below this published health limits, the results for both Tap Water A and B are above the proposed goal.

Table 8. Results of 500ng/L spike recovery test for three different water samples.

	Tap Water A			Tap Water B			River Water A		
	Non spiked	Spiked	Recovery (%)	Non spiked	Spiked	Recovery (%)	Non spiked	Spiked	Recovery (%)
1	0.1840	0.6335	90.59	0.1203	0.6198	99.12	0.0411	0.5231	96.27
2	0.1772	0.6470	93.39	0.1281	0.6222	99.68	0.0423	0.5282	97.35
Average	0.1806	0.6403	91.93	0.1242	0.6210	99.36	0.0417	0.5256	96.78

Conclusions

Cr(III)-EDTA and Cr(VI) were successfully separated and quantified using LC(IC)-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

Cr(VI) was successfully quantified at much lower levels, using high volume injection, achieving 8ng/L of DL.

The applying the bio-inert LC pump may expect the better DL with lower background. Also applying higher purified $NaHPO_4$ might help.