Low-level speciated analysis of Cr(III) and Cr(VI) using LC(IC)-ICP-MS

Application note

Environmental

Authors

Mina Tanoshima[1], Tetsushi Sakai[1], Craig Jones[2]

1. Agilent Technologies
Tokyo, Japan

2. Agilent Technologies
Santa Clara, CA, USA

Introduction

Chromium (Cr) is used in stainless steel and other alloys, and is commonly used to provide a corrosion-resistant coating to steel and other metals. Cr is also widely used in dyes, preservatives and the tanning industry. Cr typically exists in one of two common oxidation states, Cr(III), also known as Cr^{3+} or trivalent chromium, and Cr(VI), Cr^{6+} or hexavalent chromium. These two oxidation states differ markedly in their properties, in that Cr(III) is an essential trace dietary nutrient for humans, while Cr(VI) is a known carcinogen. As a result, Cr is monitored and regulated in many sample types, including the environment, food, drinking water, pharmaceutical products and consumer goods. Worldwide, Cr is typically regulated in drinking water at a maximum allowable level of around 50 to 100 µg/L (ppb), but the Office of Environmental Health Hazard Assessment (OEHHA) of the California EPA has recently published a draft Public Health Goal proposing a “negligible

risk" limit more than 1000x lower at 0.02 µg/L (20 ng/L or ppt) Cr(VI) in drinking water. The US EPA is expected to follow suit. Cr(VI) is also regulated in waste products, for example under the European Union Restrictions on Hazardous Substances (RoHS) regulations, which control certain harmful substances (including Cr(VI)) in electrical and electronic goods. Occupational exposure to Cr(VI) is strictly controlled in many industries; recent studies have also indicated a health risk from chronic exposure to low levels of Cr(VI) by ingestion. As a result, there is a need for a routine, highly sensitive method to determine both Cr(III) and Cr(VI) in a wide range of sample types. An HPLC-ICP-MS method using collision/reaction cell ICP-MS operated in helium cell mode is described below.

Experimental

The Agilent 7700 Series ICP-MS with the Octopole Reaction System (ORS^3) collision/reaction cell (CRC) provides sensitive and specific analysis of chromium (Cr) in the presence of multiple interferences. These interferences arise from carbon (ArC) and chloride (ClO) and can affect the two major isotopes of Cr at mass 52 and 53. Operating the ORS^3 in helium mode removes the matrix-based polyatomic interferences from both Cr isotopes, allowing data to be internally validated by comparing the measured results for both isotopes. However, to directly measure Cr(VI), it must be separated from Cr(III), typically by anion exchange liquid chromatography (LC) or ion chromatography (IC), prior to the ICP-MS measurement. LC/IC-ICP-MS is a routine, well-established speciation technique. Measurement of Cr(VI) alone is simple, but the determination of both Cr species is more difficult, because Cr(III) is cationic and Cr(VI) is anionic in solution. In real sample analysis, the measurement can also be compromised by mineral elements in the sample competing for binding sites in the column, leading to low recovery and retention time shifts. A newly developed method overcomes these challenges.

HPLC conditions

An Agilent 1200 high performance liquid chromatograph (HPLC) equipped with a binary pump, autosampler and vacuum degasser was used in this study. The LC was fitted with the Agilent LC bio-compatibility kit (part number 5065-9972), which replaces the metal components in the LC sample path with inert materials such as PEEK. The HPLC system was connected to the ICP-MS using the Agilent LC connection kit. An anion exchange column (4.6 mm internal diameter x 30 mm polyhydroxymethacrylate base resin) was used for separation. The column was maintained at ambient temperature for all experiments. Details of the operating conditions are reported in Table 1.

ICP-MS conditions

An Agilent 7700x ICP-MS was used for Cr detection, and instrument operating conditions are shown in Table 1. The ORS^3 was operated in helium mode to remove the matrix-based interferences ArC and ClOH on the primary Cr isotope at m/z 52 and ClO on the secondary isotope at m/z 53. ^{53}Cr, was measured in addition to the primary ^{52}Cr isotope to give confirmation of the results at the primary isotope. He mode is universal (works for all polyatomic species), so the same He mode conditions could be used for both Cr isotopes.

Table 1. Operating parameters of HPLC and ICP-MS

HPLC parameters	
Column	Agilent anion exchange, p/n G3268-80001 4.6 mm x 30 mm
Mobile phase	5 mM EDTA (2Na)* – 5 mM NaH_2PO_4/15 mM Na_2SO_4, pH = 7.0 adjusted with NaOH
Flow rate	1.2 mL/min
Temperature	Ambient
Injection volume	100 µL
ICP-MS parameters	
RF power	1550 W
Sample depth	8 mm
Carrier gas	1.05 L/min
Dwell time	0.5 s/isotope
Isotopes monitored	^{52}Cr, ^{53}Cr
Cell gas	He at 4 mL/min

* High-purity Na-EDTA (Dojindo Laboratory, Japan) was used for this work and no problem of trace metal contamination was encountered.

Results and discussion

Under the conditions described above, detection limits (DLs) of <200 ng/L for both ^{52}Cr(III) and ^{52}Cr(VI) were obtained. DLs were calculated as three times the peak-to-peak signal to noise. The DLs obtained with injection volumes ranging from 5 µL to 100 µL are shown in Table 2.

Drinking water analysis

This method was applied to the determination of both Cr(III) and Cr(VI) species in spiked and unspiked mineral water samples. The three samples evaluated were a Japanese mineral water (Water A), and two French mineral waters referred to as Water B and C. The drinking waters selected covered a range of typical mineral water compositions. Water C was very highly mineralized (over 450 ppm Ca and over 1000 ppm sulfate). The major element composition of the water samples is shown in Table 3.

Figure 1 shows the chromatograms obtained from mineral water A: unspiked and also spiked with 10 µg/L of both Cr(III) and Cr(VI). Table 4 shows the summary results for the long-term analysis of all 3 water samples (8 hours, n=30 for each sample). The excellent long-term stability and the accurate recovery of ppb-level spikes for both Cr species validates the effectiveness of the optimized method, and is especially impressive considering the high matrix level of Water C. RSDs for Cr(VI) and Cr(III) peak area and concentration were all <2.5%, demonstrating the stability and reproducibility of the method for use in routine labs. Furthermore, adding EDTA to form Cr(III)-EDTA prevented interconversion between Cr(III) and Cr (VI), demonstrated by good spike recovery for both species.

Table 2. DLs for Cr species as a function of injection volume

Injection vol. (µL)	Peak height/counts		Noise	Area/counts		DL (µg/L)	
	^{52}Cr(III)	^{52}Cr(VI)		^{52}Cr(III)	^{52}Cr(VI)	^{52}Cr(III)	^{52}Cr(VI)
5	32621	24233	204	514586	503778	1.88	2.53
20	130764	97934	314	2101007	2007572	0.72	0.96
50	323593	241948	300	5154321	4970771	0.28	0.37
100	632808	475244	274	10204281	9796463	0.13	0.17

Table 3. Major element composition for three different mineral waters

Element	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

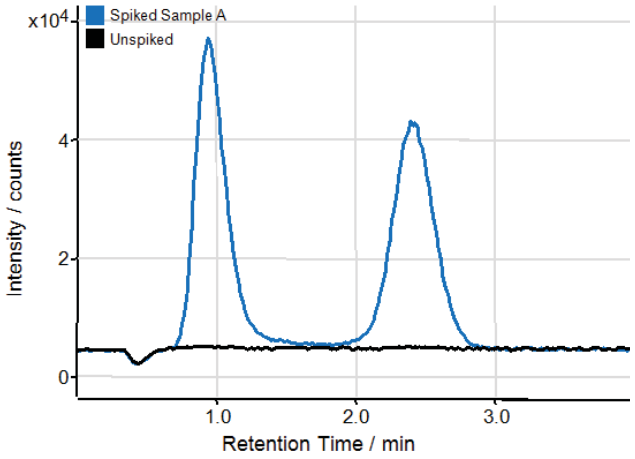

Figure 1. Overlaid chromatograms for Mineral Water A — unspiked (black) and spiked with 10 µg/L Cr species (blue). Cr(III) elutes at ~1 min, Cr(VI) at ~2.5 min.

Table 4. Concentration data for 10 µg/L spiked mineral water and stability test data (8 hours, n=30)

Sample		^{52}Cr(III)-EDTA		^{52}Cr(VI)	
		Area	Conc. µg/L	Area	Conc. µg/L
Water A	Average	906410	10.4	913019	10.3
	%RSD	1.4	1.4	2.1	2.1
Water B	Average	933560	10.7	920154	10.3
	%RSD	1.0	1.0	2.3	2.3
Water C	Average	900775	10.3	879234	9.9
	%RSD	0.8	0.8	1.4	1.4

Quantification of Cr(VI) at ultra-trace levels

While the new method was developed to measure both Cr(III) and Cr(VI) in drinking water, the state of California in the US has recently (2009) proposed a new "Public Health Goal" of 0.02 µg/L for Cr(VI) in drinking water. To meet this goal, the method was optimized for higher sensitivity and selectivity for Cr(VI) alone. The same column was used for separation, but the method was modified with a larger injection volume and lower concentration of EDTA(2Na) in the mobile phase. With these modifications, Cr(III) could not be quantified because of interference from the water dip due to the large injection volume.

Using the larger injection volume and modified mobile phase, the detection limit for Cr(VI) was reduced to single ng/L (ppt). Although high concentration anions are present in drinking water, no peak shape change or retention time shift occurred, as illustrated in the chromatograms for a 50 ng/L standard and 3 California waters shown in Figure 2. Calibration linearity was better than 0.9995 for Cr(VI) (calibration range 0.05–1.00 µg/L) as shown in Figure 3. The Cr(VI) detection limit (3x peak-to-peak signal to noise) was calculated at 0.008 µg/L.

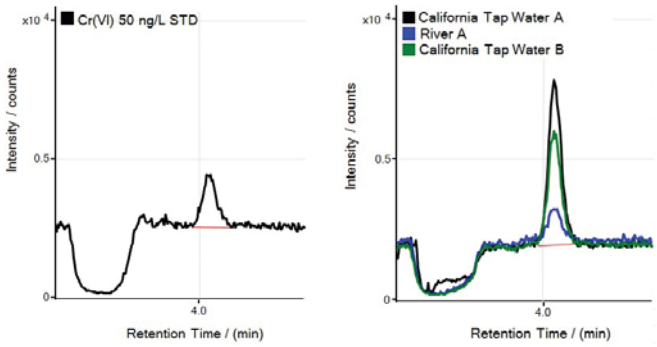

Figure 2. Chromatograms of a 50 ng/L Cr(VI) standard solution (left) and three different waters (unspiked) from the state of California (right)

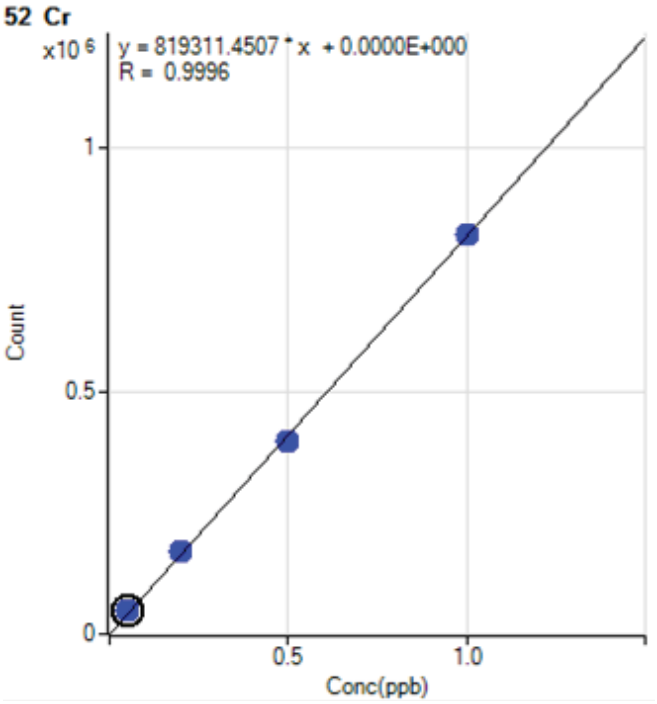

Figure 3. Calibration plot for Cr(VI) using modified method

Table 5 shows the analysis and spike recovery data for the two drinking waters (tap water A and B) and the river water (river water A) from California. The measured concentration of Cr(VI) in all three samples exceeded the proposed California regulation of 0.02 ppb. Overlaid chromatograms for tap water A (unspiked and spiked with 0.5 µg/L Cr(VI)) are shown in Figure 4.

Table 5. Analysis and spike recovery data (0.5 µg/L Cr(VI)) for three different water samples. Units: µg/L.

	Tap water A			Tap water B			Tap water C		
	Non-spiked	Spiked	Recovery (%)	Non-spiked	Spiked	Recovery (%)	Non-spiked	Spiked	Recovery (%)
1	0.1840	0.6335	90.58	0.1203	0.6198	99.12	0.0411	0.5231	96.27
2	0.1772	0.6470	93.28	0.1281	0.6222	99.60	0.0423	0.5282	97.30
Average	0.1806	0.6403	91.93	0.1242	0.6210	99.36	0.0417	0.5256	96.79

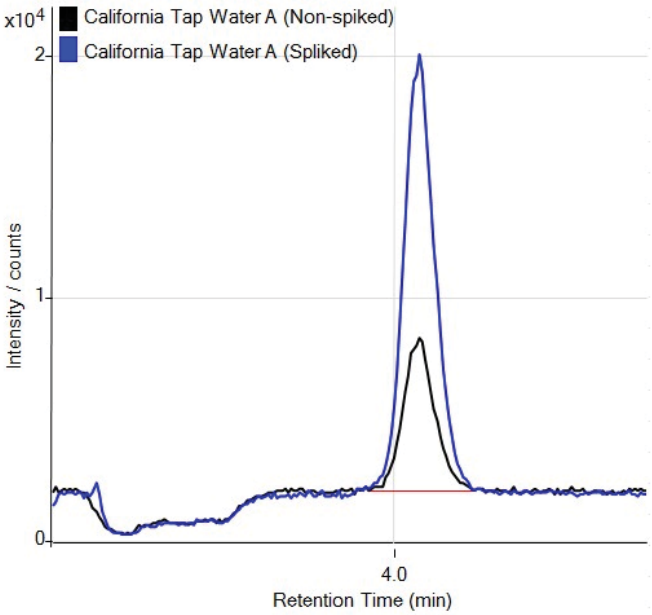

Figure 4. Chromatograms of Cr(VI) for spiked (0.5 µg/L) and unspiked tap water A

Conclusions

Accurate, sensitive determination of chromium species in highly mineralized waters was demonstrated using anion exchange chromatography after conversion of Cr(III), which is cationic, to its anionic form by complexing with EDTA. Analysis is rapid, taking only about 3 minutes, and is capable of measuring both species at concentrations less than 200 ng/L. To improve Cr(VI) sensitivity further, the method was modified by adjusting the mobile phase and increasing the injection volume. While this prevents the simultaneous measurement of Cr(III), the detection limit for Cr(VI) was improved to ~0.008 µg/L (8 ppt), which is well below the draft Public Health Goal of 0.02 µg/L proposed by the state of California.

www.agilent.com/chem

Published January 23, 2012
Publication number: 5990-9366EN

Agilent Technologies