



Environmental

Sensitive determinations of hexavalent chromium in drinking water using a compact IC system

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Introduction

Chromate and dichromate have an oxidation state of +6 and therefore are colloquially known as hexavalent chromium, Cr(VI). Hexavalent chromium is a strong oxidizing, toxic, and potentially carcinogenic agent; therefore, it is a regulated compound. Total chromium as chromate is determined according to U.S. EPA Method 218.6 or slightly modified U.S. EPA Method 218.7 in Thermo Scientific Application Update 179: Sensitive determinations of hexavalent chromium in drinking water.^{1,2}

In this application proof note, the same application is demonstrated using a Thermo Scientific™ Dionex™ Inuvion™ ion chromatography system.

Method

Reagents, standards, and solutions

The following reagents are needed for this application proof note: ASTM Type I deionized water (>18 MΩ·cm resistivity), ammonium sulfate, diphenylcarbazide, methanol, potassium dichromate, and concentrated ammonium hydroxide, sulfuric acid, and nitric acid. Sodium or potassium salts of chloride, sulfate, carbonate, phosphate, and nitrate are needed to create a High Ionic Water (HIW) matrix.

Prepare 2 L of eluent (250 mM ammonium sulfate, 100 mM ammonium hydroxide), 100 mL of sample adjustment buffer (250 mM ammonium sulfate, 1,000 mM ammonium hydroxide), and 1 L of post-column reagent (PCR) (2 mM diphenylcarbazide, 10% methanol, 1 N sulfuric acid), according to Application Update 179 (AU179). Degas the eluent and PCR in an ultrasonic water bath with applied vacuum. End-line filters (P/N 045987) were added to the tubing inside the eluent and PCR containers to aid in pump damping. Replace the eluent and PCR every 3 or 4 days. The PCR is UV-sensitive and should be contained in an amber bottle.

Prepare a 1,000 mg/L chromate stock standard, intermediate standard, and working standards described in AU179. Dispose of chromate waste according to local and federal waste regulations.

Samples

- Municipal drinking water
- HIW matrix (100 mg/L chloride, carbonate, and sulfate as S, 10 mg/L nitrate as N and phosphate as P, and 1 mg/L fluoride, 0.1 mg/L nitrite, and 0.02 mg/L bromide)

One mL of sample adjustment buffer was applied to 99 mL of the sample.

Instrument method parameters

Instrument	Dionex Inuvion IC system, including column heater, and pump degas module
Autosampler	Thermo Scientific™ Dionex™ AS-DV autosampler with 5 mL Thermo Scientific™ Dionex™ PolyVials™ and filter caps (P/N 038141)
Columns	Thermo Scientific™ Dionex™ IonPac™ AS7, 2 mm column set (P/N 063099, 063097)
Eluent	250 mM ammonium sulfate and 100 mM ammonium hydroxide
Flow rate	0.36 mL/min
Inj. volume	1,000 µL
Column temp.	30 °C
Post-column reagent (PCR)	2 mM diphenylcarbazide, 10% methanol, 1 N sulfuric acid
PCR flow rate	0.12 mL/min by Thermo Scientific™ Dionex™ AXP-MS auxiliary pump (P/N 060684) with backpressure tubing to 1,200–1,800 psi
PCR knitted reaction coil	125 µL (P/N 053640); 2 mm PEEK mixing tee (Fisher Scientific P/N 06-611-699)
Detector	Thermo Scientific™ Dionex™ ICS-Series VWD Variable Wavelength Detector (P/N 069116 or 069117) or Thermo Scientific™ UltiMate™ 3000 Diode Array Detector (DAD) (P/N 5082.0010)
Detection	Visible absorbance, 530 nm
Flow cell	PEEK analytical flow cell, 11 µL, P/N 6074.0200 (VWD) or 13 µL P/N 6082.0400 (UltiMate 3000 DAD)
Background absorbance	18–100 µAU
Background noise	~35 µAU
System backpressure	1,300–1,500 psi (100 psi = 0.6894 MPa)
Run time	14 min
Software	Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) 7.3.2

System installation

This hexavalent chromium application was installed on the Dionex Inuvion system as described in AU179 and detector module manuals.^{2,3-5} The eluent leaving the column with the separated hexavalent chromium is mixed with the post-column reagent in the 2 mm PEEK mixing tee and 125 μ L reaction coil, where it enters the absorbance detector and is detected at 530 nm. To minimize pump noise and prevent degassing during analysis, yellow PEEK (0.003 in i.d., 0.008 cm i.d.) tubing coils (3 rated at 1,000 psi at 0.5 mL/min) to achieve 1,300 to 1,500 psi were installed between the Dionex AXP-MS pump and the PEEK mixing tee. Additionally, 5 ft (152 cm) of green PEEK (0.030 in i.d., 0.076 cm i.d.) tubing were installed between the Dionex AXP-MS pump and the backpressure tubing for pulse damping. Two feet (61 cm) of red PEEK (0.005 in i.d., 0.013 cm i.d.) tubing were installed on the cell outlet, per the detector manual.^{3,4}

Results

The synthetic HIW matrix sample and the municipal water samples were analyzed. To quantify the hexavalent chromium concentrations, the responses of hexavalent chromium to concentration were measured using four replicate injections of 0.01, 0.02, 0.05, 0.10, 0.15, and 0.20 μ g/L hexavalent chromium. The response plot was linear without forcing through zero, with a coefficient of determination (r^2) = 0.9989. The method detection limit was determined by the Student's *t*-test factor of 3.14 multiplied by the standard deviation of the average of 0.01 μ g/L, $n = 7$ replicate injections. The calculated MDL of 5.6 ng/L (0.0056 μ g/L), is comparable to that reported in EPA Method 218.7 (5.4 ng/L), and well below the California Public Health Goal of 0.020 μ g/L (20 ng/L).

Figure 1 compares the chromatograms of 0.10 μ g/L standard in DI water, HIW matrix sample, and HIW matrix with added 0.10 μ g/L hexavalent chromium. Hexavalent chromium was present in one of the reagents used to make the HIW matrix sample. As a result, the HIW matrix had 0.14 μ g/L hexavalent chromium with a 99.5% recovery ($n = 4$) of 0.10 μ g/L added hexavalent chromium. This application proof note demonstrates

the determination of 10 ng/L to 200 ng/L hexavalent chromium in a municipal drinking water sample and a synthetic HIW sample, which approximates the composition of a typical municipal water sample, according to modified U.S. EPA Method 218.7 and AU179 on a Dionex Inuvion IC system.

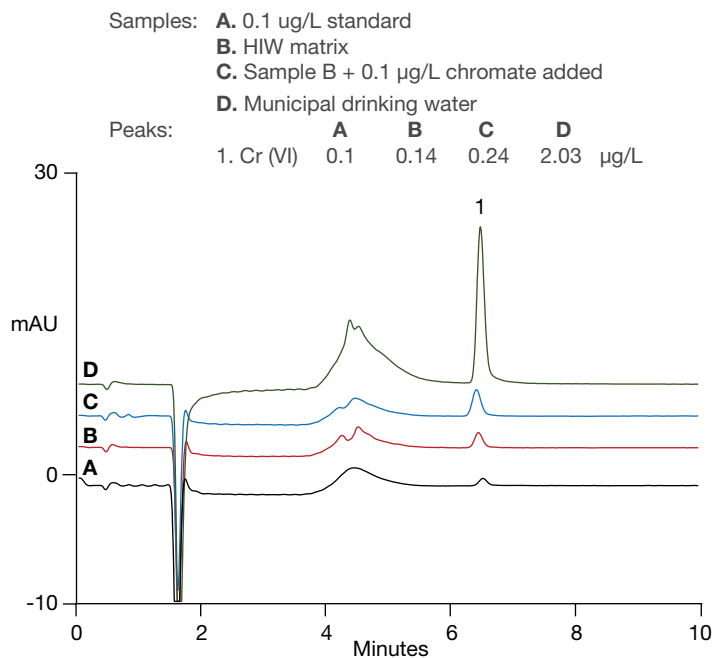


Figure 1. Hexavalent chromium in (A) 0.1 μ g/L standard in DI water, (B) High Ionic Water (HIW), (C) Sample B with 0.1 μ g/L chromate added, and (D) municipal drinking water sample.

References

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