

Low Range Hexavalent Chromium

(For use with DR1900, DR2800, DR3800, DR3900, DR5000 AND DR6000 Hach Spectrophotometers)

Hexavalent Chromium Method 8023

Scope and Application: Low Range Measurement in Drinking Water

Hexavalent Chromium, CrVI, is used in many industrial applications, including the production of stainless steel, textile dyes, and in anti-corrosion coatings. Hexavalent chromium is a human carcinogen through inhalation and the consumption of contaminated drinking water. Drinking and ground water systems can become polluted with CrVI from contaminated industrial waste that leaches into the system. A number of areas within the United States are now monitoring this contaminant or evaluating the potential for monitoring low-level hexavalent chromium due to its impact of public health.

The EPA has announced an intent to regulate CrVI (they currently only regulate total chromium), but has not set a MCL or established a promulgated reference method for drinking water. Therefore, monitoring of drinking water or ground water sources is not regulatory driven at this time. Any testing conducted now would likely be to meet state or local level requirements (if any local-level rules exist, check with your local regulatory authority on acceptable methods), or to understand if an issue exists before any potentially new federal regulations take effect.

Hach offers a hexavalent chromium method for the spectrophotometers using the ChromaVer 3 reagent (1,5-Diphenylcarbohydrazide). However; Hach's current method has low end reporting limit of 10 µg/L Cr⁶⁺, which is higher than some local state regulatory agencies require. This application note will describe how to achieve a low-end reporting limit of 0.5 µg/L Cr⁶⁺, with a calculated statistical method detection limit (MDL) of 0.125 µg/L Cr⁶⁺.

Equipment needed for this application:

- 1) Hot plate - Hach PN 2881500 (7x7 inch).
- 2) Erlenmeyer flasks, 125 mL – Hach PN 2089643 (pkg of 6, with screw caps).
- 3) 50-mL beaker - Hach PN 50041H.
- 4) Top loading balance, 500 g capacity or greater - Hach PN 2937101.
- 5) Deionized water - Hach PN 27256 (4L bottle).
- 6) 5-cm sample cell (glass) - Hach PN 2629250 or 5-cm sample cell (quartz) Hach PN 2624450).
- 7) ChromaVer 3 reagent powder pillows - Hach PN 12710-99
- 8) Parafilm - Hach PN 251764 (used to cover flasks if not using flasks with screw caps).
- 9) Alltech cation exchange cartridges, order directly from Alltech - Alltech PN 30256 for IC-H plus (for high conductivity samples or iron concentrations greater than 1 mg/L). To order contact Grace Davidson Discovery Sciences, E-mail: DiscoverySciences@grace.com, Telephone: 847-948-1078. *Used for high conductivity samples or iron concentrations greater than 1 mg/L, see

'Getting Started' section.

- 10) 10 cc syringe - Hach PN 2202400. *Used for high conductivity samples or iron concentrations greater than 1 mg/L, see 'Getting Started' section.

Enter User Program:

Follow the DR spectrophotometer's user manual to set up a user-entered program.

Enter these values into the user enter program:

Units = $\mu\text{g/L}$

Wavelength = 540 nm

Resolution = 0.01

Chemical Form 1 = Cr^{6+}

Calibration: select enter formula – select the quadratic formula ($C = a + bA + cA^2$),

a = -0.304, b = 23.4, c = 0.671

Timer 1 = 5.0 minutes

Getting Started:

Prior to pre-concentrating the sample, analyze the sample using Chromium, Hexavalent Method 8023 using ChromaVer 3 Reagent to ensure that the sample is below the $<10 \mu\text{g/L Cr}^{6+}$. The concentration range of the LR application is 0.5 to $50 \mu\text{g/L Cr}^{6+}$. The pre-concentration boiling procedure will increase the concentration by approximately 10 fold.

If your sample is colored, you will need to zero the spectrophotometer with the concentrated sample prior to adding the ChromaVer 3 reagent powder pillow.

If the sample has high conductivity (higher than 1 mS/cm for drinking water) or an iron concentration higher than 1 mg/L Fe; pass the 10 mLs of sample through the Alltech cation ion exchange cartridge prior to analysis to remove the interfering cations. This procedure is used to concentrate the CrVI , but will also concentrate the iron and background conductance by a factor of 8 to 10 fold (a good estimate of what the pre-concentrated conductivity will be is to divide the sample's conductivity by 0.11). Aspirate the 10 mLs of pre-concentrated sample into a 10 cc plastic syringe; attach the cation exchange cartridge to the syringe. At no more than two drops per second, force about 1 mLs of sample to waste and collect the remaining sample in a 50-mL beaker. Collect as much of the sample as possible for the colorimetric reaction. The minimum amount of sample needed to take a measurement in the 5-cm cell is 6 mLs (See the Effects of Conductivity section for more information).

Procedure:

To achieve this lower concentration range, the sample and standards need to go through a pre-concentration boiling step. (1 milliliter of water = 1 gram of water)

Collect as many clean 125-mL Erlenmeyer flasks and 50-mL beakers as samples or standards to be analyzed. Tare the balance and weigh each dry flask; writing the weight of the flask on the flask itself or record the flask's weight. After the dry flasks have been weighed, pour 100 g (mLs) of sample into the flask and bring to a boil on a hot plate. Continue to boil the sample until the volume below 10 mLs, do not allow the sample to boil dry. Once the volume in the flask gets below ~ 25 mLs, pay close attention not allowing the flask to boil dry. After allowing the flasks to cool down, weigh the flasks to ensure that

the volume is at 10 mLs or less. Once the volume is at 10 mLs or less, bring the sample volume back to 10 mLs (g).

(Original weight of flask = 85.6 g, flask with boiled down sample = 92.5 g. Add DI water until flask with boiled down sample weighs 95.6 g.)

Cap or parafilm the flasks, swirl the flask well to ensure that the all of the droplets along the sides are in solution. Pour the 10 mLs of re-constituted sample into a 50-mL beaker and add one ChromaVer 3 powder pillow to the sample and swirl to mix. Allow the reagent to react for 5 minutes before analyzing. If the sample has back ground color after the pre-concentration step, zero the colored concentrated sample prior to adding the ChromaVer 3 reagent.

After the 5 minutes reaction period has expired, pour 10 mLs of DI water (or the concentrated sample) into the 5-cm sample cell and zero the cell. Discard the DI water blank and pour the reacted sample into the 5-cm sample cell and allow the spectrophotometer take the reading (the reading will be automatic with the user entered program). If the measurement is above 50 $\mu\text{g/L}$, dilute the sample accordingly with DI water and pre-concentrate the sample again.

Support Data:

Precision Study

Standard	Average	Standard Deviation	% RSD
10 µg/L	9.94 µg/L	0.24	2.40
20 µg/L	19.69 µg/L	0.25	1.26

Ten replicates were analyzed

MDL Study

Standard	Average	Standard Deviation	MDL
0.5 µg/L	0.48 µg/L	0.04	0.125

Seven replicates were analyzed

Drinking Water Spikes

Sample	Unspiked	Spiked Concentration (20 µg/L)	% Recovery
Drinking Water 1	0.025	19.9	99.38
Drinking Water 2	0.26	18.69	92.15
Drinking Water 3	0.04	20.1	100.3

Two replicates of drinking water spiked samples were analyzed along with one unspiked drinking water sample

ERA Samples

Standard	Average	Standard Deviation	% Recovery
25 µg/L	24.88 µg/L	0.058	99.52%

Three replicates were analyzed

ERA QC Standard WasteWatR Chromium VI, Catalog No. 984, Lot No. PO95505
ERA, Arvada, Colorado, US Phone: 303-431-8454
Mean Determined Concentration: **24.88 µg/L Cr⁶⁺**
Known Concentration: 630 µg/L Cr⁶⁺



**ENVIRONMENTAL
RESOURCE
ASSOCIATES**
The Industry
Standard™

Interlaboratory Acceptance Range: 518 – 746 µg/L Cr⁶⁺
Diluted standard from 630 µg/L Cr⁶⁺ to produce 25 µg/L Cr⁶⁺ = 99.52% Recovery

Effects of Conductivity:

Due to the pre-concentration of the sample for the LR application, the conductivity of the sample will increase between 8 to 10 fold. To determine if the sample will need to be pre-treated by the cation exchange cartridges, spike a known concentration of CrVI into a sample and proceed with the pre-concentrate step. Measure the resulting conductivity and analyze the spiked sample to determine the % recovery. If the % recovery of the spiked sample is low, then the sample will need to be pre-treated by passing the pre-concentrated sample through the cation exchange cartridge. If the samples conductivity is still too high to produce an acceptable spike recovery after passing the sample through the cartridges, the sample will need to be diluted to reduce the ion concentration in the sample.

Drinking Water

Sample Conductivity (µS/cm)	Spike Recovery (20 µg/L)	Sample Conductivity (µS/cm) after CEC*	Spike Recovery after CEC* (20 µg/L)
116	20	4800	20
122	20	7370	13.4
1000	20		
8857	0.14		

*Cation Exchange Cartridge

HIS Reagent Water*

Sample Conductivity (µS/cm)	Spike Recovery (20 µg/L)	Sample Conductivity (µS/cm) after CEC	Spike Recovery after CEC (20 µg/L)
1700	20	5197	19
2116	20	6407	19
3982	20	9809	18
6407	20	10,240	18
7514	20	19,000	18
13,980	8.25	31,410	15

*High Ionic Strength Water, 1700 µS/cm conductivity.

Formulation = 1.4 g NaHCO₃, 1.48 g Na₂SO₄, 1.54 g NaCl, diluted to 4 L with DI water.

IC-H plus Cartridges:

Cation exchange cartridges (IC-H plus) retain CrIII and the CrVI pass through. The pH of the sample should be between 2 and 11 so that all of the dissolved CrVI is present as either the anion hydrogen chromate (HCrO₄⁻) or chromate (CrO₄²⁻) will pass through the cartridge. Other divalent cations such as iron and molybdenum will also be retained by the cartridges resin; which will interfere with the ChromaVer 3 chemistry. The IC-H plus has a bed size of 1.5 mL and an internal volume of 1.5 mL. The cartridge contains 2.0 milliequivalents of H⁺ which under ideal conditions will remove an equal amount of polyvalent cations from the sample. Where possible adjust the sample size to use 50% or less of the cartridge's capacity.

Cartridge Preconditioning:

Pass 5 to 10 mL of DI water through the device. This removes interstitial contaminants and wets the packed bed.

Cartridge Regeneration:

The IC-H plus cartridge can be cleaned for reuse by passing 7 mLs of 2M HCl, then passing 10 mLs of DI water through the cartridge.

References:

Water Analysis Handbook, fifth edition, Hach Method 8023, Hexavalent Chromium 1,5-Diphenylcarbohydrazide.

Ball, James. W, McCleskey, R. Blain., 2003, A New Cation-Exchange Method for Accurate Field Speciation of Hexavalent Chromium: U.S. Geological Survey, Water-Resources Investigations Report 03-4018.

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

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To locate the HACH office or distributor serving you, visit: www.hach.com

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