

# CHROMIUM, HEXAVALENT, by Field-Portable Spectrophotometry

7703

Cr[VI]      MW: 52.00 (Cr) 99.99 (CrO<sub>3</sub>) CAS: 18540-29-9      RTECS: GB6262000

**METHOD:** 7703, Issue 1

**EVALUATION:** FULL

**Issue 1:** 15 March 2003

**OSHA:** C 0.1 mg/m<sup>3</sup> (as CrO<sub>3</sub>)

**PROPERTIES:** oxidizing agent

**NIOSH:** 0.001 mg/m<sup>3</sup>/10 h (carcinogen)

**ACGIH:** 0.050 mg/m<sup>3</sup> (water-soluble compounds);  
0.010 mg/m<sup>3</sup> (insoluble compounds)

**SYNONYMS:** vary depending on the compound; chromate commonly used

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (5.0-µm PVC membrane [1,2]; 0.8-µm MCE or 1.0-µm PTFE acceptable for field analysis [3]).	<b>TECHNIQUE:</b>	FIELD-PORTABLE VISIBLE SPECTROPHOTOMETRY
<b>FLOW RATE:</b>	1 to 4 L/min	<b>ANALYTE:</b>	Cr[VI] - diphenylcarbazone complex
<b>VOL-MIN:</b>	10 L (2 L/min for 5 min)	<b>EXTRACTION:</b>	10 mL 0.05 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> / 0.05 M NH <sub>4</sub> OH (pH = 8 ± 0.5), ultrasonic extraction 30 min
<b>-MAX:</b>	1200 L (2 L/min for 600 min)	<b>Cr[VI] ISOLATION:</b>	Strong anion exchange solid phase extraction
<b>SHIPMENT:</b>	refrigerant pack at 4 ± 2 °C (optional)	<b>ELUTION SOLUTION:</b>	0.5 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> / 0.1 M NH <sub>4</sub> OH
<b>SAMPLE STABILITY:</b>	analyze within 24 hours; if applicable, keep samples at 4 ± 2 °C.	<b>WAVELENGTH:</b>	540 nm, 1-cm path length
<b>BLANKS:</b>	One per twenty field samples, minimum of 2 per set.	<b>CALIBRATION:</b>	standard solutions of K <sub>2</sub> CrO <sub>4</sub> in 0.5 M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> / 0.1 M NH <sub>4</sub> OH
<b>ACCURACY</b>		<b>RANGE:</b>	1 to 400 µg per sample
<b>RANGE STUDIED:</b>	0.045 to 1146 µg/m <sup>3</sup> (~20 to ~200-L samples) [3, 4]	<b>ESTIMATED LOD:</b>	0.08 µg Cr[VI] per sample [3]
<b>BIAS:</b>	-1.00% [3]	<b>PRECISION (s,):</b>	0.035 @ 3 to 400 µg per sample [3]
<b>OVERALL PRECISION (Ŝ<sub>r,t</sub>):</b>	0.080		
<b>ACCURACY:</b>	± 15.7%		

**APPLICABILITY:** The working range is (at least) 0.05 to 1000 µg/m<sup>3</sup> for a 200 to 500-L air sample. This method may be used for the determination of soluble forms of Cr[VI]. Insoluble Cr[VI] requires modification of the method using ultrasonic extraction with carbonate buffer.

**INTERFERENCES:** Interferences from reducing agents such as Fe<sup>2+</sup> are minimized to the extent possible by the alkaline ultrasonic and solid phase extraction procedures. Interferences from other metal cations are eliminated by solid phase extraction [5]. Some reduction can occur on the filter during sampling, and is usually due to the presence of Fe<sup>2+</sup>, organic material, and/ or acidic conditions [6]. Reduction of Cr[VI] can occur over time on any filter type, and is especially problematic on MCE filters [7]. However, the use of MCE and PTFE filters has been found to be acceptable for field use, where performance has been found to be equivalent to that of PVC filters [3]. During ultrasonic extraction, oxidation of Cr[III] in solution to Cr[VI] is prevented by the use of an ammonium buffer [8].

**OTHER METHODS:** This method is designed to be used in the field, but can also be utilized in the fixed-site laboratory. It is an alternative to laboratory methods such as NIOSH method 7605 or OSHA method ID-215 (hot plate digestion and ion chromatography). NIOSH method 7600 is a similar procedure, but no separation step is used. A field method not involving a Cr[VI] isolation step, MDHS method 61, has been promulgated by the British Health and Safety Executive [9].

**REAGENTS:**

1. Ammonium sulfate, reagent grade.
2. Ammonium hydroxide, reagent grade.
3. Water, distilled or deionized.
4. Hydrochloric acid (37%), reagent grade.
5. Acetonitrile, reagent grade.\*
6. 1,5-Diphenylcarbazide (DPC), reagent grade.
7. Methanol, reagent grade.
8. Extraction solution (extraction buffer): 0.05 M  $(\text{NH}_4)_2\text{SO}_4$  / 0.05 M  $\text{NH}_4\text{OH}$ , 1 L, aqueous in distilled or deionized water.  
NOTE: Modification of method by using carbonate buffer (e.g., sodium carbonate) is required for extraction of insoluble Cr[VI].
9. Elution solution (elution buffer): 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  / 0.1 M  $\text{NH}_4\text{OH}$ , 250 mL, in distilled or deionized water.
10. Cr(VI) standard (as potassium chromate),\* 1000  $\mu\text{g}/\text{mL}$ .
11. Calibration stock solution, 100  $\mu\text{g}/\text{mL}$ : Dilute 1000  $\mu\text{g}/\text{mL}$  Cr(VI) standard 1:10 with extraction buffer. (Solution is stable for a month.)
12. Diphenylcarbazide complexation solution (20 mM): Measure 0.48 g DPC powder and place in a 100-mL volumetric flask. Add ~80 mL of acetonitrile and dissolve the DPC. Bring up to the mark with additional acetonitrile and mix thoroughly.

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Samplers: 5- $\mu\text{m}$  pore size polyvinylchloride (PVC), 0.8- $\mu\text{m}$  pore size mixed cellulose ester (MCE), or 1.0- $\mu\text{m}$  polytetrafluoroethylene (PTFE) filters, 37-mm diameter, with backup pads, in polystyrene cassette filter holder, 2- or 3-piece.  
NOTE: MCE filters, and some PVC filters, promote reduction of Cr[VI] on a timescale of a few days. However, either filter type is acceptable for field use if the samples are to be analyzed within 24 h of collection.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Ultrasonic bath (sonicator), 100 W minimum power.
4. Solid phase extraction manifold, 12- or 24-port.
5. Portable vacuum pump with pressure metering valve.
6. Portable visible spectrophotometer, sample path length 1 cm with Quartz cuvette(s).
7. Strong anion exchange solid phase extraction (SPE) cartridges, 10-mL, disposable; loaded with 500 or 1000 mg quaternary amine bonded silica, capacity ~1 meq/g.
8. Pipettors, mechanical, assorted volumes (e.g., 1 to 10 mL) with disposable tips.
9. Micropipettors, mechanical, assorted volumes (e.g., 10 to 100  $\mu\text{L}$ ) with disposable tips.
10. Centrifuge tubes, plastic, 15-mL, with screw caps.
11. Scintillation vials, 20-mL, glass, with PTFE-lined screw caps.
12. Assorted beakers (and possibly Erlenmeyer flasks), various volumes.
13. Volumetric flasks, 25-, 100-, 250-, and 1000-mL.
14. Forceps, PTFE-coated.
15. Glass or plastic rods.
16. Disposable gloves, plastic or latex.
17. Laboratory wipes.
18. Portable power generator (if necessary).  
NOTE: If no power supply is available at the field site, electric power can be provided by means of a portable, gasoline (or other) generator.

**SPECIAL PRECAUTIONS:** Hexavalent chromium is a human respiratory carcinogen [10]. Efforts must be made to prevent aerosolizing chromate-containing compounds and solutions. All sample preparation should be carried out in a well-ventilated area (vacuum hood preferable); forced ventilation should be used if no hood is available. Acetonitrile solutions are flammable must be handled carefully, i.e., wearing of impermeable gloves, and avoidance of vapors. To the extent possible, solutions should be prepared in the laboratory before taking them to the field.

### **SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range of 1 to 4 L/min for a sample size of 100 to 1000 L. Do not exceed 2 mg of particulate loading on the filter. Label the filter cassette.
3. Don a fresh pair of disposable plastic or latex gloves (to prevent sample contamination).
4. With PTFE-coated forceps, remove filters from cassettes after completion of sampling, and place in separate plastic 15-mL centrifuge tubes for subsequent sample preparation. Discard cellulose backup pads and gloves.

### **SAMPLE PREPARATION:**

5. Add 10 mL of extraction solution (weak buffer) to each 15-mL centrifuge tube containing the filter sample. Ensure that the filter is covered by the extraction solution. If necessary, push the filter down with a clean glass or plastic rod to immerse the entire filter. Cap and label the tubes.
6. Place sample tubes in the ultrasonic bath (sonicator). The water level in the bath should be higher than the liquid level in the centrifuge tube. Sonicate for 30 minutes.  
NOTE: Numerous centrifuge tubes containing sample filters can be subjected to sonication at one time, depending upon the size of the ultrasonic bath. Ensure that the bath is warm (but  $\leq 40^{\circ}\text{C}$ ).
7. Set up the solid phase extraction manifold.
  - a. Place disposable solid phase extraction (SPE) cartridges in each port, and place scintillation vials beneath the cartridges. Label the cartridges.
  - b. Attach the vacuum pump to the SPE manifold.
  - c. To condition SPE cartridges, pipet 3 mL of methanol into each cartridge, and evacuate. Then pipet 3 mL of extraction solution into each cartridge, and evacuate. Repeat.
8. Extract Cr[VI] from sample solution.
  - a. Pipet 3 to 5 mL of each ultrasonicated sample solution from the centrifuge tubes into the disposable SPE cartridge. Dispose of the pipet tip.
  - b. Adjust the vacuum to obtain an extraction rate of about one drop per second (approximately 8" Hg; no more than 10" Hg). Manually tighten cartridges by twisting, if necessary, to slow down the rate of liquid dripping.  
NOTE 1: For samples in which the expected Cr[VI] concentration is high, smaller aliquots (1 to 2 mL) should be dispensed into the SPE cartridges to prevent breakthrough. High concentration of Cr[VI] can be assessed visually by its orange color.  
NOTE 2: For samples having low Cr[VI] concentration, additional 3 to 5 mL aliquots of ultrasonicated sample solution can be loaded onto SPE cartridges (step 8.a.). In this manner, the cartridge can be used to preconcentrate Cr[VI].
  - c. When it appears the solution has passed through all the cartridges, increase the vacuum to ensure that all solution passes through the cartridges. This step selectively binds Cr[VI] to the stationary phase of each cartridge.
  - d. To remove residue of Cr[III] and other potential interferences, turn the vacuum down (by turning counterclockwise) to 0" Hg. Add 1 mL distilled or deionized water to each cartridge, adjust vacuum to 1 drop per second (~8" Hg), then reduce to 0" when completed.
  - e. Remove the scintillation vials beneath the cartridges and discard.  
NOTE: This solution contains unwanted fractions that should contain no Cr[VI].
9. Place clean, labeled scintillation vials beneath correct cartridges in the SPE manifold.
  - a. Add 9 mL of the elution solution (elution buffer) to each cartridge to elute Cr[VI], and repeat steps 8.b. through 8.d.
  - b. Remove the scintillation vials, and cap them. Dispose of the used SPE cartridges.  
NOTE: The scintillation vials now contain extracted and isolated Cr[VI], which is ready for subsequent analysis.
10. Uncap each scintillation vial containing extracted and isolated Cr[VI], and add 100  $\mu\text{L}$  HCl.
11. Add 2 mL DPC complexation solution, recap vials, and mix thoroughly. Allow to stand for at least 5 min for complete color development.

### CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with at least 6 working standards over the range of 0 to 2 µg/mL of Cr[VI] per standard.
  - a. To 10-mL volumetric flasks containing ~5 mL of elution solution (strong buffer), pipet known volumes (20 to 300 µL) of Cr[VI] calibration stock solution (100 µg/mL) to produce concentrations of 0.1, 0.2, 0.5, 1.0, and 2.0 µg/mL. Add 100 µL of HCl and 2 mL of diphenylcarbazide (DPC) complexation solution to each. Dilute to the mark with elution solution and mix thoroughly.  
NOTE: A minimum of two of the concentration levels (e.g., 0.1 and 1.0 µg/mL) should be run at least in triplicate.
  - b. Prepare a blank by pipetting 100 µL of HCl and 2 mL of DPC complexation solution into 10-mL volumetric flask containing ~5 mL of the elution solution (elution buffer); dilute to the mark with elution solution and mix thoroughly.
  - c. Analyze the calibration solutions and the blank (steps 15 to 20).
13. Analyze at least two field blanks, one field blank per twenty samples (steps 10, 11 and 15 to 20). Also analyze at least three of the calibration solutions in triplicate.
14. Prepare a calibration graph of absorbance vs. Cr[VI] concentration.  
NOTE: As an alternative to steps 12 to 14, the standard addition approach can be used [11].

### MEASUREMENT:

15. Turn on the spectrophotometer, and allow for an appropriate warm-up period.
16. Set the spectrophotometer to 540 nm. Set portable spectrophotometer parameters according to the manufacturers instructions and the conditions on page 7703-1.
17. Rinse the quartz cuvette three times with distilled or deionized water, then rinse with blank solution.
18. Measure the blank. Adjust the spectrometer to zero absorbance.
19. Uncap the scintillation vial containing the sample solution to be analyzed.
  - a. Condition the cuvette by filling with the solution to be analyzed, and discard the solution.
  - b. Refill the cuvette with the sample solution to be analyzed.
  - c. Place the cuvette in the spectrophotometer.  
NOTE: Wipe any extra moisture or liquid off the sides of the cuvette with a dry laboratory wipe, and take care to handle the cuvette only by the frosted sides.
20. Analyze samples, standards, and blanks. Record the absorbance.  
NOTE: If the absorbance value is greater than 2 absorbance units, dilute the solution to be analyzed with elution solution (strong buffer) and reanalyze.

### CALCULATIONS:

21. From the calibration graph, determine the mass of Cr[VI] in each sample,  $W$  (µg), and in the average field blank,  $B$  (µg).  
NOTE: If standard addition method was used, make appropriate adjustments from the calibration graph obtained [11].
22. Calculate the concentration,  $C$  (mg/m<sup>3</sup>), of Cr[VI] in the air volume sampled,  $V$  (L):

$$C = \frac{(W - B)}{V}, \text{mg} / \text{m}^3$$

NOTE: If samples were diluted during sample preparation, be sure to account for the dilution factor in the calculation.

**EVALUATION OF METHOD:**

This method was evaluated in the laboratory with spiked filters [3-5] and a certified reference material containing a known loading of Cr(VI) [4]. This certified reference material (CRM) is European Commission, Institute for Reference Materials and Measurements (EC/IRMM) CRM 545, Cr(VI) and Cr(total) in welding dust loaded on a glass fiber filter [12]. The method has also been evaluated in the field, where samples collected during aircraft maintenance operations were analyzed on-site [3, 4]. The accuracy was estimated using the protocol summarized in a NIOSH technical report [13].

Alternative filter types can also be used, e.g., PTFE, binder-free glass fiber filters, or quartz fiber filters. Filter materials should be tested before use to ensure Cr(VI) stability. Filters can be pretreated with base to minimize Cr(VI) reduction during sampling in high-iron or acidic environments [6].

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