



CHROMIUM, HEXAVALENT, by Field-Portable Spectrophotometry

7703

Cr(VI) AW: 52.00 CAS: 18540-29-9 RTECS: GB6262000
CrO₃ MW: 99.99 CAS: 1333-82-0 RTECS: GB6650000

METHOD: 7703, Issue 2

EVALUATION: FULL

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OSHA: 0.005 mg/m³ (1910.1026); C 0.1 mg/m³ as CrO₃
(exceptions to 1910.1026)

PROPERTIES: Oxidizing agent

NIOSH: 0.0002 mg/m³ (8 h); carcinogen

SYNONYMS: Vary depending on the compound; chromate commonly used

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER (5.0 µm PVC membrane [1,2]; 0.8 µm MCE or 1.0 µm PTFE acceptable for field analysis [3])</p> <p>FLOW RATE: 1 L/min to 4 L/min</p> <p>VOL-MIN: 54 L (2 L/min for 27 min) -MAX: 1200 L (3 L/min for 400 min)</p> <p>SHIPMENT: Refrigerant pack at 4 °C ± 2 °C (optional)</p> <p>SAMPLE STABILITY: Analyze within 24 h; if applicable, keep samples at 4 °C ± 2 °C</p> <p>BLANKS: One per twenty field samples, minimum of 2 per set</p>	<p>TECHNIQUE: FIELD-PORTABLE VISIBLE SPECTROPHOTOMETRY</p> <p>ANALYTE: Chromium-diphenylcarbazone complex</p> <p>EXTRACTION: 10 mL 0.05 mol/L ammonium sulfate / 0.05 mol/L ammonium hydroxide (pH = 8 ± 0.5), ultrasonic extraction 30 min</p> <p>Cr(VI) ISOLATION: Strong anion exchange solid phase extraction</p> <p>ELUTION SOLUTION: 0.5 mol/L ammonium sulfate / 0.1 mol/L ammonium hydroxide</p> <p>WAVELENGTH: 540 nm, 1 cm path length</p> <p>CALIBRATION: Standard solutions of potassium chromate in elution solution</p> <p>RANGE: 1 µg to 400 µg per sample</p> <p>ESTIMATED LOD: 0.08 µg hexavalent chromium per sample [3]</p> <p>PRECISION (\bar{S}_r): 0.035 @ 3 µg to 400 µg per sample [3]</p>
ACCURACY	
<p>RANGE STUDIED: 0.045 µg/m³ to 1146 µg/m³ (about 20 L to 200 L samples) [3,4]</p> <p>BIAS: -1.00% [3]</p> <p>OVERALL PRECISION (\hat{S}_{rr}): 0.080</p> <p>ACCURACY: ±15.7%</p>	

APPLICABILITY: The working range is 0.22 µg/m³ to 333 µg/m³ for a 1200 L air sample. This method may be used for the determination of soluble forms of hexavalent chromium. Insoluble hexavalent chromium requires modification of the method using ultrasonic extraction with carbonate buffer.

INTERFERENCES: Interferences from reducing agents such as divalent iron 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 divalent iron, organic material, and/or acidic conditions [6]. Reduction of hexavalent chromium 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 trivalent chromium in solution to hexavalent chromium 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 hexavalent chromium isolation, 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% mass fraction),* reagent grade.
5. Acetonitrile,* reagent grade.
6. 1,5-Diphenylcarbazide (DPC), reagent grade.
7. Methanol,* reagent grade.
8. Extraction solution (extraction buffer): 0.05 mol/L ammonium sulfate / 0.05 mol/L ammonium hydroxide, 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 hexavalent chromium.
9. Elution solution (elution buffer): 0.5 mol/L ammonium sulfate / 0.1 mol/L ammonium hydroxide, 250 mL, in distilled or deionized water.
10. Potassium chromate,* reagent grade.
11. Hexavalent chromium standard,* 1000 µg/mL. Dissolve 3.735 g potassium chromate in deionized water to make 1 L, or use commercially available solution.
12. Calibration stock solution,* 100 µg/mL: dilute 1000 µg/mL hexavalent chromium standard 1:10 with extraction buffer. (Solution is stable for a month.)
13. Diphenylcarbazide complexation solution (20 mmol/L): Measure 0.48 g DPC powder and place in a 100 mL volumetric flask. Add about 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 µm pore size polyvinylchloride (PVC), 0.8 µm pore size mixed cellulose ester (MCE), or 1.0 µm 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 hexavalent chromium 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 L/min to 4 L/min, with flexible connecting tubing.
3. Ultrasonic bath (sonicator), 100 W minimum power.
4. Solid phase extraction manifold, multi-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 mg or 1000 mg quaternary amine bonded silica, capacity about 1 mmol/g of singly charged anion.
8. Pipettors, mechanical, assorted volumes (e.g., 1 mL to 10 mL) with disposable tips.
9. Micropipettors, mechanical, assorted volumes (e.g., 10 µL to 100 µL) 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 mL, 100 mL, 250 mL, 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: NIOSH considers all hexavalent chromium compounds to be suspect occupational carcinogens [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. Methanol and acetonitrile solutions are flammable and 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. Concentrated hydrochloric acid is highly corrosive and ammonium hydroxide is a respiratory irritant. All work with these compounds should be performed in a hood. Use proper protective clothing including gloves, safety glasses, and laboratory coat. Potassium chromate is a strong oxidizer with risk of fire and explosion upon contact with combustible substances and reducing agents.

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 L/min to 4 L/min for a sample size of 54 L to 1200 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 min.

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 < 40 °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 hexavalent chromium from sample solution.
 - a. Pipet 3 mL 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 27 kPa or 203 mmHg; no more than 34 kPa or 254 mmHg). Manually tighten cartridges by twisting, if necessary, to slow down the rate of liquid dripping.

NOTE 1: For samples in which the expected hexavalent chromium concentration is high, smaller aliquots (1 mL to 2 mL) should be dispensed into the SPE cartridges to prevent breakthrough. High concentration of hexavalent chromium can be assessed visually by its orange color.

NOTE 2: For samples having low hexavalent chromium concentration, additional 3 mL 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 hexavalent chromium.

- 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 hexavalent chromium to the stationary phase of each cartridge.

- d. To remove residue of trivalent chromium and other potential interferences, reduce the vacuum to 0. Add 1 mL distilled or deionized water to each cartridge, adjust vacuum to obtain 1 drop per second (about 27 kPa or 203 mmHg), then reduce vacuum to 0 when completed.
 - e. Remove the scintillation vials beneath the cartridges and discard.
NOTE: This solution contains unwanted fractions that should contain no hexavalent chromium.
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 hexavalent chromium, and repeat steps 8.b, 8.c, and 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 hexavalent chromium, which is ready for subsequent analysis.
10. Uncap each scintillation vial containing extracted and isolated hexavalent chromium, and add 100 μ L hydrochloric acid.
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 μ g/mL to 2 μ g/mL of hexavalent chromium per standard.
- a. To 10 mL volumetric flasks containing about 5 mL of elution solution (strong buffer), pipet known volumes (10 μ L to 200 μ L) of hexavalent chromium calibration stock solution (100 μ g/mL) to produce concentrations of 0.1 μ g/mL, 0.2 μ g/mL, 0.5 μ g/mL, 1.0 μ g/mL, and 2.0 μ g/mL. Add 100 μ L of hydrochloric acid and 2 mL of 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 μ g/mL and 1.0 μ g/mL) should be run at least in triplicate.
 - b. Prepare a blank by pipetting 100 μ L of hydrochloric acid and 2 mL of DPC complexation solution into 10 mL volumetric flask containing about 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, 16, 17, 18, 19, and 20).
13. Analyze at least two field blanks, one field blank per twenty samples (steps 10, 11, 15, 16, 17, 18, 19, and 20). Also analyze at least three of the calibration solutions in triplicate.
14. Prepare a calibration graph of absorbance vs. hexavalent chromium concentration.
NOTE: As an alternative to steps 12, 13, and 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 manufacturer's 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 hexavalent chromium 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 , of hexavalent chromium in the air volume sampled, V (L):

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

NOTE 1: If samples were diluted during sample preparation, be sure to account for the dilution factor in the calculation.

NOTE 2: If the hexavalent chromium concentration is to be reported as chromic acid (CrO_3), multiply C by 1.92 (MW of chromic acid divided by AW of chromium).

EVALUATION OF METHOD:

This method was evaluated in the laboratory with spiked filters [3,4,5] and a certified reference material containing a known loading of hexavalent chromium [4]. This certified reference material (CRM) is European Commission, Institute for Reference Materials and Measurements (EC/IRMM) CRM 545, hexavalent chromium and total chromium 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 hexavalent chromium stability. Filters can be pretreated with base to minimize hexavalent chromium reduction during sampling in high-iron or acidic environments [6].

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