

# CHROMIUM, HEXAVALENT by Ion Chromatography

7605

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

**METHOD:** 7605, Issue 1

**EVALUATION:** FULL

**Issue 1:** 15 March 2003

**OSHA :** 0.1 mg/m<sup>3</sup> (as CrO<sub>3</sub>)  
**NIOSH:** 0.001 mg/m<sup>3</sup>/10 h; carcinogen  
**ACGIH:** 0.050 mg/m<sup>3</sup> (as Cr, soluble); some insoluble chromates are human carcinogens

**PROPERTIES:** oxidizing agent

**SYNONYMS:** Vary depending upon the compound; chromate commonly used, "chrome six."

SAMPLING	MEASUREMENT
<p><b>SAMPLER:</b> FILTER (5.0-<math>\mu</math>m PVC membrane)</p> <p><b>FLOW RATE:</b> 1 to 4 L/min</p> <p><b>VOL-MIN:</b> 1 L @ 0.05 mg/m<sup>3</sup>  <b>-MAX:</b> 400 L</p> <p><b>SHIPMENT:</b> Routine. Can be shipped cold when deemed necessary.</p> <p><b>SAMPLE STABILITY:</b> Stable for 2 weeks at room temperature. Stable for 4 weeks if stored in refrigerator.</p> <p><b>BLANKS:</b> 2 to 10 field blanks per set</p>	<p><b>TECHNIQUE:</b> Ion chromatography with post-column derivatization and UV detection.</p> <p><b>ANALYTE:</b> CrO<sub>4</sub><sup>-2</sup>-diphenylcarbazide (DPC) complex</p> <p><b>EXTRACTION:</b> 5 mL 2% NaOH- 3% Na<sub>2</sub>CO<sub>3</sub>. Dilute to 25 mL after heating.</p> <p><b>INJECTION VOLUME:</b> 100 <math>\mu</math>L</p> <p><b>COLUMN:</b> Dionex NG1 Guard, HPLC- AS7 Separator or equivalent</p> <p><b>MOBILE PHASE:</b> 250 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> /100 mM NH<sub>4</sub>OH</p> <p><b>FLOW RATE:</b> 1.0 mL/min; 0.7 mL/min post column</p> <p><b>POST-COLUMN REAGENT:</b> 2.0 mM DPC + 10% MeOH +1N H<sub>2</sub>SO<sub>4</sub></p> <p><b>DETECTOR:</b> 540 nm</p> <p><b>CALIBRATION:</b> Standard solutions of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in NaOH-Na<sub>2</sub>CO<sub>3</sub> buffer</p> <p><b>RANGE:</b> 0.05 to 20 <math>\mu</math>g per sample</p> <p><b>ESTIMATED LOD:</b> 0.02 <math>\mu</math>g per sample [3]</p> <p><b>PRECISION (<math>\hat{S}_r</math>):</b> 0.015 @ 0.5 to 5 <math>\mu</math>g/sample [3]</p>
ACCURACY	
<p><b>RANGE STUDIED:</b> 0.05 to 120 <math>\mu</math>g Cr(VI) [1,2]</p> <p><b>BIAS:</b> -1.6% [2]</p> <p><b>OVERALL PRECISION (<math>\hat{S}_r</math>):</b> 0.07</p> <p><b>ACCURACY:</b> <math>\pm</math> 17.4% (0.6 - 960 <math>\mu</math>g/m<sup>3</sup>) [1]</p>	

**APPLICABILITY:** The working range is 0.00025 to 0.1 mg/m<sup>3</sup> for a 200-L air sample. This method can be used for the determination of Cr(VI) using 2% NaOH - 3% Na<sub>2</sub>CO<sub>3</sub> for extraction.

**INTERFERENCES:** Possible interferences are iron, copper, nickel, and vanadium; 10  $\mu$ g of any of these causes an absorbance equivalent to approximately 0.02  $\mu$ g Cr(VI) due to formation of colored complexes. Interference due to reducing agents (e.g., Fe, Fe++) is minimized by alkaline extraction (step 5).

**OTHER METHODS:** Method 7703 is a field portable method for Cr(VI). OSHA Method W4001 is for the measurement of Cr(VI) in wipe samples [4]. OSHA Method ID-215 is for measurement of Cr(VI) and employs precipitation to reduce Cr(III) oxidation. [5]. A similar air method is ISO 16740 [6]. EPA Method 218.6 is for water matrices [7]. Method 7604 is also specific for hexavalent chromium, using ion chromatography, but has a higher detection limit than 7605.

**REAGENTS:**

1. Sulfuric acid, conc. (98% w/w).\*
2. Ammonium hydroxide, conc. (28%).\*
3. Ammonium sulfate monohydrate, reagent grade.
4. Sodium carbonate, anhydrous.
5. Sodium hydroxide, reagent grade.\*
6. Methanol, HPLC grade.\*
7. 1,5-Diphenylcarbazide, reagent grade.
8. Potassium dichromate or potassium chromate.\* Dry at 100 °C and store in a desiccator.
9. Post-Column Derivatizing Reagent:  
Diphenylcarbazide solution. Dissolve 500 mg 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. While stirring, add 500 mL water containing 28 mL of conc. sulfuric acid. Dilute to a final volume of one liter with water. This reagent is stable for 4 - 5 days. Prepare in one-liter quantities as needed.
10. Cr(VI) standard, 1000 µg/mL. Dissolve 2.829 g potassium dichromate in deionized water to make one liter, or use commercially available solution.  
NOTE: 3.731 g K<sub>2</sub>CrO<sub>4</sub> can also be used.
11. Calibration stock solution, 1.0 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:1000 with deionized water.
12. Filter extraction solution, 2% NaOH-3% Na<sub>2</sub>CO<sub>3</sub>. Dissolve 20 g NaOH and 30 g Na<sub>2</sub>CO<sub>3</sub> in deionized water to make one liter of solution.
13. Eluent (mobile phase); 250 mM ammonium sulfate/200 mM ammonium hydroxide. Dissolve 33 g ammonium sulfate in approximately 500 mL distilled water and add 6.5 mL conc. ammonium hydroxide. Dilute to one liter with distilled water and mix.
14. Nitrogen, pre-purified.

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder.  
NOTE: Some PVC filters promote reduction of Cr(VI). Check each lot of filters for recovery of Cr(VI) standard.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Vials, scintillation, 20-mL glass, PTFE-lined screw cap.\*\*
4. Forceps, nonmetallic.
5. Gloves, polypropylene or latex.
6. Liquid chromatography apparatus consisting of autosampler; pump; NG1 (Dionex Corp.) or equivalent guard column; HPIC-AS7, 4 x 250-mm (Dionex Corp.) separator column (or equivalent); post-column reagent delivery system, 2.2-m PEEK™ tubing mixing/reaction loop with 1 m in a water bath at 32 °C ± 3 °C; and UV detector.
7. Filtration apparatus, PTFE luer-lock filter (Gelman IC Acrodisc or equivalent)/syringe.
8. Beakers, borosilicate, 50-mL.\*\*
9. Watch glass.\*\*
10. Volumetric flasks, 25-, 100-, and 1000-mL.\*\*
11. Oven at 107°C, not to exceed 115°C.  
NOTE: Hot plate can be used. An ultrasonic bath can be used instead of oven or hot plate.
12. Micropipettes, 10-µL to 0.5-mL.
13. Pipettes, TD 5-mL.\*\*
14. Bagged refrigerant.

\*\* Clean all glassware with 1:1 HNO<sub>3</sub>:H<sub>2</sub>O and rinse thoroughly before use.

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**SPECIAL PRECAUTIONS:** Many chromate compounds are suspected human carcinogens [8]. All sample preparation should be performed in a hood. Concentrated acids and bases are toxic and corrosive. When working with concentrated acids and bases, wear protective clothing. Ammonium hydroxide is a respiratory irritant. Methanol is flammable and toxic.

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**SAMPLING:**

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 1 to 400 L. Do not exceed 1 mg total dust loading on the filter.

3. Filters can be left in the cassettes for shipping to the lab, but to minimize sample contamination during shipping, remove the filter from the cassette within one hour of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with gloved hands and nonmetallic forceps. Discard the backup pad. As a precaution, it is recommended to ship the samples with bagged refrigerant.

#### **SAMPLE PREPARATION:**

4. Don a clean pair of disposable plastic gloves (to prevent sample contamination). Using forceps, transfer the PVC filter to a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH/3% Na<sub>2</sub>CO<sub>3</sub>. Start media blanks at this point.

NOTE 1: If significant amounts of Cr[III] are expected to be present in the samples, either (a) degas the sodium hydroxide/sodium carbonate extraction solution by bubbling nitrogen through it for 5 min. before proceeding, or (b) use a precipitation reagent [1].

NOTE 2: If only soluble chromates are of interest, use ammonium sulfate buffer in place of carbonate extraction solution [9, 10].

5. Cover the beaker with a watchglass and heat it to near the boiling point (100°C to 115°C) in an oven with occasional swirling for 45 min. Do not boil the solution. Longer heating times (up to 90 minutes) may be necessary for some samples (e.g., paint spray). Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost due to reaction with the PVC filter and/or co-collected aerosol constituents. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

NOTE: A hot plate, heater block, or ultrasonic bath can also be used for this step [9, 11].

- a. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask. Bring to volume with distilled water.

NOTE: If the solution is cloudy, filter an aliquot through a PTFE luer lock filter attached to a syringe.

- b. Transfer an aliquot of the solution to the appropriate vial for the chromatograph's autosampler and analyze (steps 9 through 13).

#### **CALIBRATION AND QUALITY CONTROL:**

6. Calibrate daily with at least six working standards. Transfer 5 mL of extraction solution to each of a series of 25-mL volumetric flasks. Pipet known volumes (0 to 5 mL) of calibration stock solution (1.0 µg/mL) into the volumetric flasks. For higher standards, pipet 10 - 20 µL of the 1000 µg/mL concentrated stock and bring the volume to 25 mL with distilled water. These working standards contain 0 to 20 µg Cr(VI) per sample.
7. Analyze the working standards together with blanks and samples (steps 9 through 13).
8. Prepare a calibration graph [instrument response vs. µg Cr(VI)].

#### **MEASUREMENT:**

9. Set wavelength on the detector to 540 nm.
10. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 7605-1. With a mobile phase flow rate of 1.0 mL/min., a post-column reagent flow rate of 0.7 mL/min., and a 2.2-m post-column tube, the derivative retention time should be approximately 3.7 - 4.7 minutes.  
NOTE: If the instrument response for the samples is higher than the standards, dilute using a 1:5 dilution of extraction solution:water to maintain a constant ionic strength; repeat the analysis; and multiply the measured concentration by the appropriate dilution factor. Alternatively, inject a smaller volume and multiply by the appropriate factor.
11. After the analysis is complete, flush the entire system with ASTM Type II water for at least one hour at 1.0 mL/min. with all columns on line. Remove the columns and continue flushing for an additional two hours. Flush the autosampler with several injections of water. Leaving the columns in line while the system is idle is not recommended.

**CALCULATIONS:**

12. From the calibration graph, determine the mass of Cr(VI) in each sample,  $W$  ( $\mu\text{g}$ ), and in the average blank,  $B$  ( $\mu\text{g}$ ).
13. Calculate concentration,  $C$  ( $\text{mg}/\text{m}^3$ ), of Cr(VI) in the air volume sampled,  $V$  (L):

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

NOTE:  $\mu\text{g}/\text{L} = \text{mg}/\text{m}^3$

**EVALUATION OF METHOD:**

This method was evaluated in the laboratory with spiked filters and a certified reference material containing a known loading of Cr(VI). 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]. This method was evaluated for extraction efficiency over the concentration range of 0.15 - 5  $\mu\text{g}/\text{sample}$  testing two brands of filters, SILICAL® and GLA-5000™[3]. In these experiments, test atmospheres were not generated; instead, Cr(VI) as the dichromate was fortified on the face of the sample filters, then 240 L of air with 35% relative humidity was pulled through at 1 L/min. A 30-day storage study using both types of filters was conducted at 1.5  $\mu\text{g}/\text{sample}$  (30x LOQ) at ambient room temperature and 4 °C. The average recovery of the stored samples was 94.8%. The estimation of the limit of detection and limit of quantitation (LOD/LOQ), were determined analyzing a series of liquid standards. The LOD and LOQ, 0.02  $\mu\text{g}/\text{sample}$  and 0.07  $\mu\text{g}/\text{sample}$  respectively were calculated by Burkart's method [13].

To fully evaluate this method, a field-study was conducted in which side-by-side samples were taken to measure exposures to Cr(VI) during spray-painting and electroplating operations. These samples were analyzed subsequently by 4 different methods (NIOSH Method 7605, 7703, 7300 and OSHA ID-215) [1]. NIOSH method 7300 was used to measure total chromium. The results from the other 3 methods correlated very well showing no statistical difference among the 3 methods. Recoveries of 98.4 ( $\pm 3.4$ ) % were obtained for CRM 545 ( $n = 6$ ) [2].

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