

# CHROMIUM, HEXAVALENT

7604

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

**METHOD:** 7604, Issue 2

**EVALUATION:** FULL

**Issue 1:** 15 May 1989

**Issue 2:** 15 August 1994

**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 according to the compound.

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (5.0-µm PVC membrane)	<b>TECHNIQUE:</b>	ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION
<b>FLOW RATE:</b>	1 to 4 L/min	<b>ANALYTE:</b>	chromate ion
<b>VOL-MIN:</b>	100 L @ 0.1 mg/m <sup>3</sup>	<b>EXTRACTION:</b>	5 mL 2% NaOH/3% Na <sub>2</sub> CO <sub>3</sub>
<b>-MAX:</b>	1000 L	<b>INJECTION VOLUME:</b>	50 µL
<b>SHIPMENT:</b>	routine	<b>ELUENT:</b>	7.0 mM Na <sub>2</sub> CO <sub>3</sub> /0.5 mM NaOH, 2.0 mL/min
<b>SAMPLE STABILITY:</b>	at least 2 weeks at 25 °C	<b>COLUMN:</b>	Dionex HPIC-AG5 guard, HPIC-AS5 separator, and anion suppressor, or equivalent
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>DETECTOR:</b>	1 µS full scale
<b>ACCURACY</b>		<b>CALIBRATION:</b>	standard solutions of Cr(VI) in 0.4% NaOH/0.6% Na <sub>2</sub> CO <sub>3</sub>
<b>RANGE STUDIED:</b>	0.05 to 0.15 µg/m <sup>3</sup> (400-L samples)	<b>RANGE:</b>	10 to 250 µg per sample [1]
<b>BIAS:</b>	+ 0.08%	<b>ESTIMATED LOD:</b>	3.5 µg per sample [1]
<b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b>	0.066 [1]	<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.043 @ 22 to 62 µg per sample [1]
<b>ACCURACY:</b>	± 13.0%		

**APPLICABILITY:** The working range is 0.01 to 4 mg/m<sup>3</sup> for a 500-L air sample. This method is less sensitive than method 7600 (colorimetric), but it contains fewer sample preparation steps and was found free from interferences when used for samples of five chromate-containing paints. This method may be used for the determination of insoluble or soluble Cr(VI).

**INTERFERENCES:** Interferences from reducing agents (e.g., Fe, Fe<sup>++</sup>) are eliminated by alkaline extraction. Cations of metals, interfering with the colorimetric method, do not interfere with this method. Inadequately-cleaned glassware may create a negative bias.

**OTHER METHODS:** This method is an alternative to NIOSH Method 7600 (colorimetric).

**REAGENTS:**

1. Sodium carbonate, anhydrous.
2. Sodium hydroxide, reagent grade.
3. 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 1 L of solution.
4. Eluent, 7.0 mM Na<sub>2</sub>CO<sub>3</sub>-0.5 mM NaOH. Dissolve 2.97 g Na<sub>2</sub>CO<sub>3</sub> in 4 L deionized water. Add 20 mL of 0.1 M NaOH (8 g/L).
5. Suppressor regenerant, 0.025 N H<sub>2</sub>SO<sub>4</sub>. Dilute 2.8 mL of conc. H<sub>2</sub>SO<sub>4</sub> in deionized water to 4 L.
6. Cr(VI) standard, 1000 µg/mL.
7. Calibration stock solution, 100 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:100 with distilled or deionized water.
8. Nitrogen, purified.
9. Water, distilled or deionized.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter (FWSB [MSA] or VM-1 [Gelman], or equivalent) with backup pad 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. Ion chromatograph, with conductivity detector, columns, suppressor (p. 7604-1).
4. Vials, scintillation 20-mL glass, PTFE-lined screw cap.
5. Forceps, plastic.
6. Syringe, 10-mL, with in-line membrane filter 0.45-µm pore size.
7. Beakers, borosilicate, 50-mL.
8. Watchglasses.
9. Volumetric, flasks, 25-, 100-, and 1000-mL.
10. Hotplate, 120 to 400 °C.
11. Micropipette, 20-µL, and other sizes.
12. Centrifuge tubes, 40-mL, graduated, with plastic, screw caps.

**SAMPLING:**

1. Calibrate each personal 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 100 to 1000 L. Do not exceed 2 mg of particulate loading on the filter.
3. Remove the filter from the cassette within 1 hour of completion of sampling, and place it in a vial to be shipped to the laboratory. Handle the filters only with forceps. Discard the backup pad.

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**SPECIAL PRECAUTIONS:** Insoluble chromates are suspected human carcinogens [2]. All sample preparation should be performed in a hood.

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**SAMPLE PREPARATION:**

4. Place the filter face down in a 50-mL beaker, and add 5.0 mL extraction solution. Start reagent blanks at this point.  
NOTE 1: If significant amounts of Cr(III) are expected to be present, degas the extraction solution by bubbling a slow stream of nitrogen through it for 5 min before proceeding and purge the headspace above the solution with nitrogen during this step.  
NOTE 2: If only soluble chromates are of interest use distilled water in place of extraction solution.
5. Cover the beaker with a watchglass and place on a hotplate preheated to 135 °C. Heat the samples for 45 min with occasional swirling.  
NOTE 1: Do not allow the solution to boil or evaporate to dryness. Hexavalent chromium may be lost by reaction with the PVC filter, as indicated by a brown coloring in the filter.  
NOTE 2: Longer heating times, up to 90 min. may be necessary for some samples (e.g., paint spray [1]).
6. Cool the solution and transfer it quantitatively with distilled water rinses to a graduated

centrifuge tube. Adjust the final volume to 25 mL with distilled water.

#### CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range of 0 to 250 µg Cr (VI) per sample.
  - a. Pipet 0 to 2.5 mL calibration stock solution into each of a series of 25-mL volumetric flasks. Add 5 mL extraction solution to each flask and dilute to the mark with deionized water.
  - b. Analyze the working standards (steps 8 through 10).
  - c. Prepare a calibration graph [peak height vs. µg Cr(VI) per sample].

#### MEASUREMENT:

8. Set ion chromatograph according to manufacturer's recommendations and to conditions on page 7604-1. Set regenerant flow to 3 mL/min.
9. Inject 50 µL sample aliquot manually or with autosampler.  
NOTE: All samples and standards must be filtered before injection to avoid plugging columns and lines.
10. Measure peak height. (Retention time for Cr(VI) peak is approximately 12 min under these conditions.)

#### CALCULATIONS:

11. From the calibration graph, determine the mass of Cr(VI) in each sample, W (µg), and in the average blank, B (µg).
12. Calculate the concentration, C (mg/m<sup>3</sup>), of Cr(VI) in the air volume sampled, V (L):

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

#### EVALUATION OF METHOD:

This method was evaluated with three sets of 16 filter samples which were collected from a chromate-containing paint aerosol [2]. The average amount of Cr(VI) on the filter ranged from 24 to 62 micrograms. Half of the samples were analyzed by this method while the other half were analyzed by Method 7300 (ICP). The results were not significantly different at the 95% confidence level. To examine sample stability, selected members of a fourth set of filters were analyzed and the remainder were stored for two weeks under cover in a constant temperature and constant humidity environment. Comparison of the results of analysis before and after storage indicated that the amount of Cr(VI) did not change during this period.

#### REFERENCES:

- [1] Molina, D. and M. T. Abell. An Ion Chromatographic Method for Insoluble Chromium in Paint Aerosol. *Am. Ind. Hyg. Assoc. J.* 48:830-835 (1987).
- [2] NIOSH Testimony on the OSHA Proposal Rules on Air Contaminants, Docket #H-020, August 1, 1988.

#### METHOD REVISED BY:

Martin T. Abell, NIOSH/DPSE.