

CHROMIUM and compounds, as Cr

7024

Cr	MW: 52.00 (Cr)	CAS: 7440-47-3 (Cr metal) 22541-79-3 [Cr(II)] 16065-83-1 [Cr(III)]	RTECS: (Cr) GB420000 Cr(II) GB6260000 Cr(III) GB6261000
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METHOD: 7024, Issue 2

EVALUATION: FULL

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<p>OSHA : 1.0 mg/m³ (metal); 0.5 mg/m³ [Cr(II), Cr(III)]</p> <p>NIOSH: 0.5 mg/m³ [Cr metal, Cr(II), Cr(III)]</p> <p>ACGIH: 0.5 mg/m³ [Cr metal, Cr(II), and Cr(III)]; see Method 7600 for Cr(VI)</p>	<p>PROPERTIES: metal; d 7.14 g/cm³; MP 1890 °C; valences +1 to +6 in salts</p>
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SYNONYMS: vary depending on the compound

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER (0.8-µm cellulose ester membrane)</p> <p>FLOW RATE: 1 to 3 L/min</p> <p>VOL-MIN: 10 L @ 0.5 mg/m³</p> <p>-MAX: 1000 L</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: stable</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: ATOMIC ABSORPTION, FLAME</p> <p>ANALYTE: chromium</p> <p>ASHING: conc. HCl, 9 mL; 140 °C conc. HNO₃, 9 mL; 400 °C</p> <p>FINAL SOLUTION: 5% HNO₃, 20 mL</p> <p>FLAME: nitrous oxide-acetylene, reducing</p> <p>WAVELENGTH: 357.9 nm</p> <p>CALIBRATION: standard solutions of Cr in 5% HNO₃</p> <p>RANGE: 5 to 250 µg per sample [2,3]</p> <p>ESTIMATED LOD: 0.06 µg per sample [4]</p> <p>PRECISION (\hat{S}_r): 0.04 to 0.06 [5]</p>
ACCURACY	
<p>RANGE STUDIED: 0.4 to 1.8 mg/m³ (insoluble) 0.3 to 1 mg/m³ (soluble) [1] (90-L samples)</p> <p>BIAS: - 0.64%</p> <p>OVERALL PRECISION (\hat{S}_{rT}): 0.076 (insoluble) [1] 0.085 (soluble) [1]</p> <p>ACCURACY: ± 20.91%</p>	

APPLICABILITY: The working range is 0.05 to 2.5 mg/m³ for a 100-L air sample. This is an elemental analysis for total Cr, not compound specific. Some compounds of Cr may not be dissolved by this method. Aliquots can be analyzed separately for approximately four additional metals.

INTERFERENCES: Interferences from iron and nickel are minimized by using a high temperature flame (reducing nitrous oxide-acetylene or oxidizing air-acetylene).

OTHER METHODS: This method combines and replaces P&CAM 173 [4], P&CAM 152 [5], S323 [2], and S352 [3]. Method 7300 (Elements by ICP-AES) is an alternate analytical method. Hexavalent chromium, sampled on PVC filters, may be determined colorimetrically by Method 7600 or Method 7604.

REAGENTS:

1. Nitric acid, conc.
2. Hydrochloric acid, conc.
3. Nitric acid, 5%. Add 50 mL conc. HNO_3 to water; dilute to 1 L.
4. Calibration stock solution, 1000 $\mu\text{g/mL}$ Cr. Dissolve 3.735 g K_2CrO_4 or 2.829 g $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled or deionized water to make 1 L solution.
5. Distilled or deionized water.
6. Nitrous oxide.
7. Acetylene.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8- μm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with a nitrous oxide-acetylene burner head and chromium hollow cathode lamp.
4. Regulators, two-stage, for nitrous oxide and acetylene.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.*
6. Volumetric flasks, 100-mL.*
7. Graduated centrifuge tubes, 15-mL.*
8. Assorted volumetric pipets, as needed.*
9. Hotplate, surface temperature to 140 °C.

* Clean all glassware with nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a sample size of 10 to 1000 L. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [2,3]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be necessary for some samples, especially if several metals are to be determined on a single filter.

3. Open the cassettes and filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HCl, cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HCl.
NOTE: Start reagent blanks at this step.
5. Add 3 mL conc. HNO_3 , cover with a watchglass, heat on hotplate (140 °C) until the volume is reduced to ca. 0.5 mL. Repeat two more times using 3 mL conc. HNO_3 .
6. Cool solution and dissolve the residues in 1 mL conc. HNO_3 .
7. Transfer the solution quantitatively to a 15-mL graduated centrifuge tube.
8. Dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate with at least six working standards. Add known amounts of calibration stock solution, covering the range 0 to 1000 µg Cr (0 to 200 µg Cr per sample) to 100-mL volumetric flasks and dilute to volume with 5% HNO₃.
10. Analyze the working standards together with the blanks and samples (steps 15 and 16).
11. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check instrument drift.
13. Check analytical recoveries with at least one spiked media blank per 10 samples.
14. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

15. Set spectrophotometer as recommended by the manufacturer and to conditions on page 7024-1. NOTE: Air-acetylene flame may also be used. In a fuel-lean air-C₂H₂ or reducing (fuel-rich) N₂O-C₂H₂ flame, interference by Fe or Ni is minimized or eliminated, but sensitivity for Cr is reduced. A reducing air-C₂H₂ flame provides the best sensitivity, but the greatest susceptibility to interference [5].
16. Aspirate standards and samples. Record absorbance readings
NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute the solutions with 5% HNO₃, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

17. Using the measured absorbances, calculate the corresponding solution concentrations (µg/mL) of chromium in the sample, C_s, and average media blank, C_b, from the calibration graph.
18. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration of chromium, C (mg/m³), in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Lab testing with spiked filters and generated atmospheres of soluble chromium (potassium dichromate) was done at one-half, one and two times the OSHA standard for chromium compounds other than Cr(VI) of 0.5 mg/m³. The range studied was 0.28 to 0.95 mg/m³. The precision was 0.082 and a bias was not observed [1,2].

Lab testing with spiked filters and generated atmospheres of insoluble chromium, (produced from thermal decomposition of chromium hexacarbonyl) was done at one-half, one and two times the OSHA standard for chromium metal of 1.0 mg/m³ [1,3]. Collection efficiency was 1.00 and analytical recoveries averaged 98% in the range 45 to 190 µg Cr per sample.

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S323, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[3] Ibid, S352.

[4] Ibid, V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).

[5] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer (1976).

METHOD REVISED BY:

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