Cr(VI) MW: 52.00 (Cr); 99.99 (CrO_3) CAS: 18540-29-9 RTECS: GB6262000

METHOD: 7600, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
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OSHA : 0.1 mg/m^3 (as CrO_3)
NIOSH: 0.001 mg/m^3/10 h; carcinogen
ACGIH: 0.050 mg/m^3 (as Cr, soluble); some insoluble chromates are human carcinogens

PROPERTIES: oxidizing agent

SYNONYMS: vary depending upon the compound

SAMPLING

SAMPLER: FILTER (5.0-µm PVC membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 8 L @ 0.025 mg/m^3
-MAX: 400 L

SHIPMENT: routine

SAMPLE STABILITY: analyze within 2 weeks [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.05 to 0.2 mg/m^3 [2] (22-L samples)

BIAS: - 5.48%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.084 [2]

ACCURACY: ± 18.58%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: CrO_4^{2-}-diphenylcarbazide complex

EXTRACTION SOLUTION: 0.5 N H_2SO_4 or 2% NaOH-3% Na_2CO_3 (see steps 4 and 5)

WAVELENGTH: 540 nm; 5-cm path length

CALIBRATION: standard solutions of K_2CrO_4 in 0.5 N H_2SO_4

RANGE: 0.2 to 7 µg per sample

ESTIMATED LOD: 0.05 µg per sample

PRECISION ($\hat{S}_r$): 0.029 @ 0.3 to 1.2 µg per sample [3]

APPLICABILITY: The working range is 0.001 to 5 mg/m^3 for a 200-L air sample. This method may be used for the determination of soluble Cr(VI) (using 0.5 N H_2SO_4 as extraction solution or insoluble Cr(VI) (using 2% NaOH - 3% Na_2CO_3) [3].

INTERFERENCES: Possible interferences are iron, copper, nickel, and vanadium; 10 µg of any of these causes an absorbance equivalent to about 0.02 µg 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: This method combines and replaces P&CAM 169 [1], S317 [2] and P&CAM 319 [3]; the Cr(VI) criteria document [4] contains a method similar to P&CAM 169. Method 7604 is also specific for hexavalent chromium, using ion chromatography for measurement.

REAGENTS:

1. Sulfuric acid, conc. (98% w/w).
2. Sulfuric acid, 6 N. Add 167 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
3. Sulfuric acid, 0.5 N. Add 14.0 mL conc. H_2SO_4 to water in a 1-L flask; dilute to the mark.
4. Sodium carbonate, anhydrous.
5. Sodium hydroxide.
6. Potassium chromate.
7. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 mL acetone and 100 mL water.
8. Cr(VI) standard, 1000 µg/mL. Dissolve 3.735 g K_2CrO_4 in deionized water to make 1 L, or use commercially available solution.*
9. Calibration stock solution, 10 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:100 with deionized water.
10. Filter extraction solution, 2% NaOH-3% Na_2CO_3. Dissolve 20 g NaOH and 30 g Na_2CO_3 in deionized water to make 1 L of solution.
11. Nitrogen, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder (FWSB [MSA] or VM-1 [Gelman] or equivalent).
   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, plastic.
5. Spectrophotometer, UV-visible (540 nm), with cuvettes, 5-cm path length.
6. Filtration apparatus, vacuum.**
7. Beakers, borosilicate, 50-mL.**
8. Watchglass.**
9. Volumetric flasks, 25-, 100- and 1000-mL.**
10. Hotplate, 120 to 400 °C.
11. Micropipettes, 10-µL to 1-mL.
12. Centrifuge tubes, 40-mL, graduated, with plastic stoppers.**
13. Buchner funnel.**
14. Pipettes, TD 5 mL.**

** Clean all glassware with 1:1 HNO_3 and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Insoluble chromates are suspected human carcinogens [4]. All sample preparation should be performed in a hood.

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 8 to 400 L. Do not exceed 1 mg total dust loading on the filter.
3. Remove the filter from the cassette within 1 h of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with forceps. Discard the backup pad.

SAMPLE PREPARATION:

NOTE: There are two sample preparation techniques outlined below. For soluble chromates or chromic acid, follow step 4; for insoluble chromate or Cr(VI) in the presence of Fe, Fe^{2+} or other reducing agents, follow step 5.

4. Sample preparation for soluble chromates and chromic acid.
   a. Remove the blank and sample filters from the vials, then fold and place them into centrifuge tubes.
   b. Add 6 to 7 mL 0.5 N H_2SO_4 to each tube, cap, and shake to wash all surfaces of the filter. Allow filter to remain in tube 5 to 10 min [6].
   c. Remove the filter from the tube with plastic forceps, carefully washing all surfaces with an

additional 1 to 2 mL 0.5 N H_2SO_4. Discard the filters. Start reagent blanks at this point.

d. Filter the solution through a moistened PVC filter in a Buchner funnel to remove interferences from suspended dust. Collect the filtrate in a clean centrifuge tube. Rinse the bottle, which contained the filter, with 2 to 3 mL 0.5 N H_2SO_4 and pour into the funnel. Rinse the funnel and filter with 5 to 8 mL 0.5 N H_2SO_4.

e. Add 0.5 mL diphenylcarbazide solution to each centrifuge tube. Bring the total volume in each centrifuge tube to 25 mL with 0.5 N H_2SO_4. Shake to mix and allow color to develop (at least 2 min but no longer than 40 min. [6]). Transfer the solution to a clean 5-cm cuvette and analyze within 40 min of mixing (steps 9 through 11).

5. Sample preparation for insoluble chromates and for Cr(VI) in the presence of iron or other reducing agents:

NOTE: If significant amounts of Cr(III) are expected to be present, degas the sample solution by bubbling nitrogen through it for 5 min. before proceeding and purge the headspace above the solution during step 5.a.

a. Remove the PVC filter from the bottle, place it in a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH/3% Na_2CO_3. Start reagent blanks at this point. Purge the headspace above the solution with nitrogen throughout the extraction process to avoid oxidation of any Cr(III). Cover the beaker with a watchglass and heat it to near the boiling point on a hotplate with occasional swirling for 30 to 45 min. Do not boil the solution or heat longer than 45 min. Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost owing to reaction with the PVC filter. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

b. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask, keeping the total volume about 20 mL.

NOTE: If the solution is cloudy, filter it through a PVC filter in a vacuum filtration apparatus using distilled water rinses.

c. Add 1.90 mL 6 N sulfuric acid to the volumetric flask and swirl to mix.

CAUTION: CARBON DIOXIDE WILL BE EVOLVED CAUSING INCREASED PRESSURE IN THE FLASK. LET THE SOLUTION STAND FOR SEVERAL MINUTES UNTIL VIGOROUS GAS EVOLUTION CEASES.

d. Add 0.5 mL diphenylcarbazide solution, dilute to the mark with distilled water and invert several times to mix thoroughly. Pour out about one-half of the contents of the flask, stopper the flask and shake it vigorously several times, removing the stopper each time to relieve pressure.

NOTE: This step releases bubbles of carbon dioxide which otherwise would cause high and erratic readings.

e. Transfer an aliquot of the solution remaining in the flask to a 5-cm cuvette and analyze (steps 9 through 11).

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards. Transfer 6 to 7 mL 0.5 N H_2SO_4 to each of a series of 25-mL volumetric flasks. Pipet 0 to 0.7 mL of 10 µg/mL calibration stock solution into the volumetric flasks. Add 0.5 mL diphenylcarbazide solution to each and sufficient 0.5 N H_2SO_4 to bring the volume to 25 mL. These working standards contain 0 to 7 µg Cr(VI).
7. Analyze the working standards together with blanks and samples (steps 9 through 11).
8. Prepare a calibration graph [absorbance vs. µg Cr(VI)].

MEASUREMENT:

9. Set wavelength on the spectrophotometer to 540 nm.
10. Set to zero using a 0.5 N H_2SO_4 reagent blank.
11. Transfer sample solution to a cuvette and record the absorbance.

NOTE 1: A sample containing 1.5 µg Cr(VI)/25 mL gives ca. 0.2 absorbance.

NOTE 2: If the absorbance values for the samples are higher than the standards, dilute using 0.5 N H_2SO_4, repeat this step, and multiply the resulting absorbance by the appropriate dilution factor.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

P&CAM 169 and S317 are essentially the same method and are suitable for soluble chromate and chromic acid. Method S317 was validated with generated samples of chromic acid mist [2,6], and P&CAM 169 was tested with field samples [1,7]. P&CAM 319 was developed because a method was needed to analyze for insoluble chromates [3]. This method was tested with insoluble chromates in matrices such as paints, primer and ceramic powders [3].

Precision, analytical range, recovery data, etc., for the three methods pooled are as follows:

Total $\hat{S}_{rT}$:	0.084
Measurement $\bar{S}_r$ [1-3]:	0.02 to 0.04
Range [3]:	0.5 to 10 $\mu g/m^3$
Collection Efficiency [5]:	94.5%
Sampling Rate [1,3]:	1.5 to 2.5 L/min
Stability (two weeks) [1]:	96% recovery
Acceptable Filters [3]:	FWSB (MSA); VM-1 (Gelman).

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 169, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[2] Ibid, V. 3, S317, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Ibid, V. 6, P&CAM 319, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).
[4] NIOSH (1975) Criteria for a Recommended Standard: Occupational Exposure to Chromium (VI). Cincinnati, OH: U.S. Department of Health, Education, and Welfare, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 76-129.
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards. Occupational Health Guidelines for Chromic Acid and Chromates. U.S. Department of Health and Human Services (NIOSH) Publication No. 81-123 (1981).
[6] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[7] Abell, M. T. and J. R. Carlberg. A Simple Reliable Method for the Determination of Airborne Hexavalent Chromium, Am. Ind. Hyg. Assoc. J., 35, 229 (1974).

METHOD REVISED BY:

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