



CHROMIUM, HEXAVALENT

7600

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

METHOD: 7600, Issue 3

EVALUATION: FULL

Issue 1: 15 May 1989

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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 upon the compound

| SAMPLING | MEASUREMENT |
|---|---|
| <p>SAMPLER: FILTER (5.0 µm PVC membrane)</p> <p>FLOW RATE: 1 L/min to 4 L/min</p> <p>VOL-MIN: 34 L @ 0.005 mg/m³ -MAX: 400 L</p> <p>SHIPMENT: Routine</p> <p>SAMPLE STABLE: Analyze within 2 weeks [1]</p> <p>FIELD BLANKS: 2 to 10 field blanks per set</p> | <p>TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY</p> <p>ANALYTE: Chromium-diphenylcarbazone complex</p> <p>EXTRACTION SOLUTION: 0.25 mol/L sulfuric acid or solution of 20 g/L sodium hydroxide and 30 g/L sodium carbonate (see steps 4 and 5)</p> <p>WAVELENGTH: 540 nm; 5 cm path length</p> <p>CALIBRATION: Standard solutions of potassium chromate in 0.25 mol/L sulfuric acid</p> |
| ACCURACY | <p>RANGE: 0.2 µg to 7 µg per sample</p> |
| <p>RANGE STUDIED: 0.05 mg/m³ to 0.2 mg/m³ [2] (22 L samples)</p> <p>BIAS: -5.48%</p> <p>OVERALL PRECISION ($\hat{S}_{\overline{r}}$): 0.084 [2]</p> <p>ACCURACY: ±18.6%</p> | <p>ESTIMATED LOD: 0.05 µg per sample</p> <p>PRECISION (\bar{S}): 0.029 @ 0.3 µg to 1.2 µg per sample [3]</p> |

APPLICABILITY: The working range is 0.00042 mg/m³ to 3.6 mg/m³ for a 400 L air sample. This method may be used for the determination of soluble hexavalent chromium (using the acidic extraction solution) or insoluble hexavalent chromium (using the basic extraction solution) [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 hexavalent chromium due to formation of colored complexes. Interference due to reducing agents (e.g., elemental iron, divalent iron) is minimized by alkaline extraction (step 5).

OTHER METHODS: This method combines and replaces NIOSH methods P&CAM 169 [1], S317 [2], and P&CAM 319 [3]; the hexavalent chromium criteria document [4] contains a summary of more recent methods for air analysis, wipe analysis, and biological monitoring.

REAGENTS:

1. Sulfuric acid,* concentrated (98% mass fraction), reagent grade.
2. Sulfuric acid, 3 mol/L. Add 167 mL concentrated sulfuric acid to water in a 1 L flask; dilute to the mark.
3. Acidic extraction solution, sulfuric acid, 0.25 mol/L. Add 14.0 mL concentrated sulfuric acid to water in a 1 L flask; dilute to the mark.
4. Sodium carbonate, anhydrous, reagent grade.
5. Sodium hydroxide,* reagent grade.
6. Potassium chromate,* reagent grade.
7. Diphenylcarbazide solution. Dissolve 500 mg sym-diphenylcarbazide in 100 mL acetone and 100 mL water.
8. Hexavalent chromium standard,* 1000 µg/mL. Dissolve 3.735 g potassium chromate in deionized water to make 1 L, or use commercially available solution.
9. Calibration stock solution,* 10 µg/mL. Dilute 1000 µg/mL hexavalent chromium standard 1:100 with deionized water.
10. Basic extraction solution. Dissolve 20 g sodium hydroxide and 30 g sodium carbonate in deionized water to make 1 L of solution.
11. Glassware cleaning solution.* Add a volume of concentrated nitric acid to an equal volume of deionized water.
12. 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.
NOTE: Some PVC filters promote reduction of hexavalent chromium. Check each lot of filters for recovery of hexavalent chromium standard.
2. Personal sampling pump, 1 L/min 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. Watch glass.[†]
9. Volumetric flasks, 25 mL, 100 mL, and 1000 mL.[†]
10. Hotplate, 120 °C to 400 °C.
11. Micropipettes, 10 µL to 1 mL.
12. Centrifuge tubes, 40 mL, graduated, with plastic stoppers.[†]
13. Büchner funnel.[†]
14. Pipettes, TD, 5 mL.[†]

[†]Clean all glassware with the glassware cleaning solution and rinse thoroughly before use.

SPECIAL PRECAUTIONS: NIOSH considers all hexavalent chromium compounds to be suspect occupational carcinogens [4]. Concentrated acids are highly corrosive, and sodium hydroxide is caustic. 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 the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 L/min to 4 L/min for a sample size of 34 L 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 hexavalent chromium in the presence of iron, divalent iron, 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 mL to 7 mL of acidic extraction solution to each tube, cap, and shake to wash all surfaces of the filter. Allow filter to remain in tube 5 min to 10 min [5].
 - c. Remove the filter from the tube with plastic forceps, carefully washing all surfaces with an additional 1 mL to 2 mL of acidic extraction solution. Discard the filters. Start reagent blanks at this point.
 - d. Filter the solution through a moistened PVC filter in a Büchner funnel to remove interferences from suspended dust. Collect the filtrate in a clean centrifuge tube. Rinse the bottle, which contained the filter, with 2 mL to 3 mL of acidic extraction solution and pour into the funnel. Rinse the funnel and filter with 5 mL to 8 mL of acidic extraction solution.
 - e. Add 0.5 mL diphenylcarbazide solution to each centrifuge tube. Bring the total volume in each centrifuge tube to 25 mL with acidic extraction solution. Shake to mix and allow color to develop (at least 2 min but no longer than 40 min [5]). Transfer the solution to a clean 5 cm cuvette and analyze within 40 min of mixing (steps 9, 10, and 11).

5. Sample preparation for insoluble chromates and for hexavalent chromium in the presence of iron or other reducing agents:

NOTE: If significant amounts of trivalent chromium 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 of basic extraction solution. Start reagent blanks at this point. Purge the headspace above the solution with nitrogen throughout the extraction process to avoid oxidation of any trivalent chromium. Cover the beaker with a watch glass and heat it to near the boiling point on a hotplate with occasional swirling for 30 min 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 of 3 mol/L 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, 10, and 11).

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards. Transfer 6 mL to 7 mL of acidic extraction solution to each of a series of 25 mL volumetric flasks. Pipet 0 mL to 0.7 mL of 10 µg/mL calibration stock solution into the volumetric flasks. Add 0.5 mL diphenylcarbazide solution to each flask and sufficient acidic extraction solution to bring the volume to 25 mL. These working standards contain 0 µg to 7 µg hexavalent chromium.
7. Analyze the working standards together with blanks and samples (steps 9, 10, and 11).

8. Prepare a calibration graph [absorbance vs. μg hexavalent chromium].

MEASUREMENT:

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

NOTE 1: A sample containing 1.5 μg hexavalent chromium in 25 mL gives about 0.2 absorbance.

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

CALCULATIONS:

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

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

NOTE: 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:

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 [2,5], and P&CAM 169 was tested with field samples [1,6]. 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}_r : | 0.084 |
| Measurement \bar{S}_r [1,2,3]: | 0.02 to 0.04 |
| Range [3]: | 0.5 $\mu\text{g}/\text{m}^3$ to 10 $\mu\text{g}/\text{m}^3$ |
| Collection efficiency [5]: | 94.5% |
| Sampling rate [1,3]: | 1.5 L/min to 2.5 L/min |
| Stability (two weeks) [1]: | 96% recovery |

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METHOD REVISED BY:

Martin T. Abell, NIOSH/DPSE; NIOSH method S317 validated under NIOSH Contract CDC-99-74-45.

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