

Determination of Airborne Particulate Hexavalent Chromium

1. INTRODUCTION

Collection procedures are given for soluble and insoluble chromium compounds. Analytical procedures are given for the determination of hexavalent chromium, total chromium and a fusion technique for chromium ore.

Chromium, finding its way into the air from metallurgical operations, is probably in the trivalent or zero state. The toxicity of trivalent chromium has not been demonstrated. The most abundant form of airborne trivalent chromium is probably chromium sesquioxide, an extremely insoluble compound. Divalent chromium compounds are so easily oxidized that they cannot exist in ambient air. Hexavalent chromium in the air probably originates from the production of chromates and dichromates by the chemical industry. Hexavalent chromium compounds are extremely toxic.

2. FIELD OF APPLICATION

The method is applicable to the measurement of the levels of suspended particulate chromium found in either ambient or industrial atmospheres. Since levels of chromium in urban air are low and the possibility of contamination from chromium containing metals in the laboratory may be rather high, care must be taken to ensure that the chromium being measured is actually due to the air sample.

3. PRINCIPLE

In the method to be described, airborne particulates are collected by drawing air through dry filter media such as a silver membrane filter, by collection on acetate membrane filters, or by the use of an electrostatic precipitator. Suitably prepared samples or aliquots are assayed using *s*-diphenylcarbazide.

4. REACTIONS

The most important reactions relate to the complete dissolution of the particulate sample to form a homogeneous test sample. As microgram quantities of material may be involved, losses due to incomplete solution, volatility or adsorption must be avoided. If a portion of the airborne chromium to be measured is in the form of chromium trioxide, Cr_2O_3 , some difficulty may be encountered in solubilizing all the chromium.

5. REAGENTS

5.1 *Triple-distilled water*

Redistill double-distilled water in an all borosilicate-glass still. Triple-distilled water is used in all steps following the oxidation of chromium to the hexavalent form to avoid possible reduction which might occur from impurities in double-distilled water. In all subsequent references to the use of water, triple-distilled water is meant.

5.2 *Nitric acid, concentrated, redistilled*

Redistill reagent grade acid in an all borosilicate-glass still. Discard the first 50ml distillate.

5.3 *Sodium hydroxide solution, 0.1 N*

Dissolve 4gm sodium hydroxide in water and make up to 1 litre with water.

5.4 *Potassium permanganate, 0.1 N*

Dissolve 3.16gm reagent grade potassium permanganate in water and make up to 1 litre with water.

5.5 *Sodium azide, 5%*

Dissolve 5gm sodium azide in water and make up to 100ml with water. Store in refrigerator. Shelf life: 1 month.

5.6 *Sulfuric acid, 5 N*

Cautiously add 139ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.7 *Sulfuric acid, 2 N*

Cautiously add 54ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.8 *Sulfuric acid, 0.5 N*

Cautiously add 13.9ml concentrated sulfuric acid to about 800ml water. Add dilute (0.5%) potassium permanganate solution to the hot acid solution until a very faint pink color appears. Cool and dilute to 1 litre with water.

5.9 *Sodium dihydrogen phosphate buffer, 4 M*

Dissolve 138.01gm sodium dihydrogen phosphate monohydrate in water and make up to 250ml with water.

5.10 *Sodium bisulfate, 40%*

Dissolve 20gm sodium bisulfate in water and make up to 50ml with water.

5.11 *s-Diphenylcarbazide*

Dissolve 10.0gm of phthalic anhydride in 175ml redistilled 95% ethyl alcohol, warming to effect solution. Cool, add a solution of 0.625gm of s-diphenylcarbazide in about 50ml of redistilled 95% ethyl alcohol, and make up to 250ml with the ethyl alcohol. Keep in a brown bottle in the refrigerator. This solution is stable for several months.

5.12 *Stock hexavalent chromium solution (1ml \approx 80 μ g Cr)*

Dissolve 0.2263gm reagent grade potassium dichromate in water and make up to 1 litre with water.

5.13 *Standard hexavalent chromium solution (1ml \approx 2 μ g Cr)*

Dilute 5ml of stock hexavalent chromium solution to 200ml with water. Prepare fresh daily.

5.14 *Standard trivalent chromium solution (1ml \approx 2 μ g Cr)*

Pipet 5ml of stock hexavalent chromium solution into a Phillips beaker. Reduce the chromium by adding about 15mg sodium sulfite and 0.5ml of nitric acid. Evaporate to dryness gently as strong heating may reoxidize the chromium. Add 0.5ml nitric acid and again evaporate to dryness gently to destroy any excess sulfite. Dissolve in 1ml nitric acid with warming and make up to 200ml with water. Test a portion for the absence of hexavalent chromium by adding some diphenylcarbazide. This solution is stable for 2-3 days.

5.15 *Wash acid*

Carefully add 50ml concentrated nitric acid to 150ml concentrated hydrochloric acid, mix, and add to 200ml water.

5.16 *8-Quinolinol, 1.0% in chloroform*

Dissolve 10.0gm 8-hydroxyquinoline in 1 litre chloroform. Store in dark bottle in refrigerator. Shelf life: 3 months.

6. APPARATUS

6.1 *Spectrophotometer*

Able to cover the visible range including wavelength 540nm and with wavelength scale reading to 0.1nm.

6.2 *Laboratory shaking machine*

As available commercially.

6.3 *Muffle furnace*

As available commercially, preferably with temperature programming.

6.4 *Platinum crucibles*

10ml capacity or larger.

6.5 *Steam bath*

Usual laboratory equipment.

6.6 *Glassware*

Beakers, Griffin and Phillips type, volumetric flasks, and cuvettes for spectrophotometer.

6.7 *Silver membrane filters*

These are available from Selas Flotronics, Spring House, Pennsylvania, U.S.A.

6.8 *Acetate membrane filters*

These are available from Millipore Corporation, Bedford, Mass., U.S.A.

6.9 *Electrostatic precipitator*

A suitable instrument is available from Mine Safety Appliances, Pittsburgh, Pennsylvania.

7. SAMPLING AND SAMPLES

7.1 *Soluble chromium*

Particulates should be collected with silver membrane filters. A minimum air volume of 5 cubic feet should be sampled. The silver membrane filters may be submitted to the laboratory in field monitors or in plastic petri dishes. Blank filters should be submitted in duplicate.

7.2 *Insoluble chromium*

Particulates should be collected with acetate membrane filters or by electrostatic precipitator. A minimum volume of 5 cubic feet should be sampled. For submission to the laboratory, seal the ends of the collecting tubes before shipment. Plastic caps or aluminium foil may be used. Acetate membrane filters may be submitted in the field monitors or in plastic petri dishes. Submit filter or tube blanks in duplicate.

8. SAMPLE PREPARATION

8.1 *Glassware (used throughout these procedures)*

Glassware should be thoroughly cleaned with a detergent solution, rinsed well with tap water and then rinsed with "wash acid", followed by tap water and then triple-distilled water. To avoid contamination, chromic-sulfuric acid mixture is not used. When necessary, alcoholic potassium hydroxide is used to remove grease.

8.2 *Silver membrane filters*

Place silver membrane filter in clean wide-mouthed plastic bottle. Add 25ml of 0.1 N sodium hydroxide solution and fasten lid securely on bottle. Place on shaking machine and shake gently for 20 minutes. Extract blank filters with each batch of samples. Transfer extracts into a 50ml volumetric flask and make to volume with 0.1 N sodium hydroxide. Proceed with analysis as directed in Section 9.1.

8.3 *Electrostatic precipitator tubes or acetate membrane filters*

8.3.1 *Chromium compounds (other than chromium ore)*

Dissolve acetate membrane filter in nitric acid in a 250ml Phillips beaker and add 0.25ml of 40% sodium bisulfate solution. Evaporate to dryness at a moderate heat and ash by adding small amounts of nitric acid until a white ash is obtained. Rinse electrostatic precipitator tubes into clean beakers with 2% nitric acid solution containing a wetting agent. Transfer sample to 250ml Phillips beaker and add 0.25ml of 40% sodium bisulfate solution as for acetate filters. Ash with small amounts of nitric acid at a moderate heat until a white ash is obtained. In either case dissolve ash in redistilled nitric

acid, and add 10ml water. Heat to dissolve if necessary. If there is no residue, make to volume of 25ml. Take out aliquot of 20ml and evaporate to dryness on steam bath. Proceed with analysis as directed in Section 9.2. If an insoluble residue is present, filter through Whatman 42 filter paper. Rinse until acid-free with distilled water. Combine filtrate with washings and set aside to be combined later with the leach of melt from the fusion of the residue. Place filter containing residue in platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter paper is completely ashed. To the residue add 0.05-0.01gm fusion mixture (4 parts by weight magnesium oxide mixed with 1 part by weight sodium carbonate, which is dried and stored in an air-tight container). Stir the residue into fusion mixture with glass rod. Cover crucible and place in muffle furnace. Raise temperature slowly to 900°C and hold there for 1-2 hours. Dissolve cooled melt with hydrochloric acid and water and heat if necessary. Examine leach for unfused particles. If present, they must be filtered and fused again. Filter leachings and combine with acid soluble portions (filtrate plus washings) and adjust to volume of 25ml. Take aliquot of 20ml and evaporate to dryness on the steam bath. Proceed with analysis as directed in Section 9.2.

8.3.2 Chromium ore

8.3.2.1 ORE SAMPLES COLLECTED ON ELECTROSTATIC PRECIPITATOR TUBES

Rinse electrostatic precipitator tubes with 10% hydrochloric acid solution. It may be necessary to rinse the tubes with alcohol to facilitate the acid rinse. If alcohol is used, then it must be evaporated from the acid solution before proceeding. Filter through Whatman 42 filter paper and wash with distilled water until acid-free. Combine filtrate with washing and set aside to be combined later with the leach of the melt from the fusion of the residue. Place filter containing residue in platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter paper is completely ashed. Proceed with fusion of residue as described in Section 8.3.2.3.

8.3.2.2 ORE SAMPLES COLLECTED ON ACETATE MEMBRANE FILTERS

Wrap filter in a Whatman 42 filter paper and place in a platinum crucible. Place uncovered crucible in muffle furnace and slowly raise temperature to 550°C. Hold at this temperature until filter papers are completely ashed. Proceed with fusion of residue as described in Section 8.3.2.3.

8.3.2.3 FUSION

To the residue add 0.2-0.3gm fusion mixture (4 parts by weight magnesium oxide mixed with 1 part by weight sodium carbonate which is dried and

stored in an air-tight bottle). Stir residue into fusion mixture with glass rod. Cover crucible, and place in muffle furnace. Raise temperature slowly to 900°C and hold there for 1-2 hours. Dissolve cooled melt with hydrochloric acid and water and heat if necessary. Examine leach for unfused particles. If present, they must be filtered and fused again. Combine leachings with acid soluble portions of ore samples and make to 100ml volume (or greater if necessary). Take aliquot for analysis and evaporate to dryness on steam bath. Proceed with analysis as described in Section 9.2.

9. PROCEDURE

9.1 *Silver membrane filters*

9.1.1 Hexavalent chromium

Place 20ml aliquot of the alkaline extract in a small Erlenmeyer flask. At the same time initiate a reagent blank of 20ml of 0.1 N sodium hydroxide. To both sample and blank, add 1.4ml 5 N sulphuric acid. Centrifuge if necessary, or filter through an alundum crucible. Decant supernatant into a 25ml volumetric flask. Add 1ml *s*-diphenylcarbazide reagent. Mix and make to volume with water. Read absorbance of the solution at 540nm on the spectrophotometer using 1cm cells, against the reagent blank. Colors too intense to read may be diluted to larger volumes using reagents in proportion, or alternatively, take the remaining 5ml aliquot of the original alkaline extract and proceed as described for the 20ml aliquot, except for adding 1.1ml 5 N sulfuric acid instead of 1.4ml.

9.1.2 Total soluble chromium

The following procedure gives a measure of both hexavalent (9.1.1) and trivalent chromium compounds. Place a second 20ml aliquot of the 0.1 N sodium hydroxide extracts in a 125ml Phillips beaker. At the same time, initiate a reagent blank of 20ml of 0.1 N sodium hydroxide. To both sample and blank, add 1.4ml 5 N sulfuric acid. Add 0.5ml of 0.1 N potassium permanganate solution. Cover with a watch glass and heat on a steam bath for 20 minutes. If necessary, add more permanganate to maintain a slight pink color. Decolorize the permanganate by adding 5% sodium azide at the rate of 1 drop every 10 seconds, swirling after each drop. Three to five drops are usually required. Use sufficient azide to destroy any brownish tint of manganese dioxide but avoid excess. Solution may still be colored if interfering substances are present. Promptly cool to room temperature in a tray of cold water. Centrifuge, if necessary, or filter through an alumina crucible. If the supernatant is distinctly colored, extract at pH 4 with 8-quinolinol in chloroform. If solution is only slightly colored, proceed as follows. Decant supernatant into a 25ml volumetric flask. Add 1ml *s*-diphenylcarbazide reagent. Mix and allow 1 minute for color development. Add 2.5ml of 4 M phosphate buffer. Mix and dilute to mark with water.

Read absorbance (or transmittance) of the solution at 540nm using 1cm cells and against the reagent blank as reference. Colors too intense to read may be diluted to larger volumes using reagents in proportion or by taking the remaining 5ml aliquot of the original alkaline extracts and proceeding as described for the 20ml aliquot, adding, however, 1.1ml of 5 N sulfuric acid instead of 1.4ml.

9.2 *Electrostatic precipitator tubes or acetate membrane filters*

Samples taken by EP or acetate membrane filters are handled as follows:

9.2.1 Hexavalent chromium

No separate determination is made for hexavalent chromium because the ashing and/or fusion steps in sample preparation may alter the valence.

9.2.2 Total chromium

Total chromium is the sum of hexavalent and trivalent forms. Dissolve the residue, obtained from evaporation in the steam bath, in a few ml of water, adding a drop or two of 0.5 N sulfuric acid if necessary. The solution should be approximately pH 7 at this point. Adjust pH with 0.1 N sodium hydroxide in 0.1 N sulfuric acid as required. Initiate a reagent blank of 10ml water. Add 10ml 0.5 N sulfuric acid and 0.5ml 0.1 N potassium permanganate solution. Cover with watch glass and heat in a steam bath for 20 minutes. If necessary, add more permanganate to maintain a slight pink color. Decolorize the permanganate by adding 5% sodium azide at a rate of 1 drop every 10 seconds swirling after each drop. Three to five drops is usually required. Use sufficient azide to destroy any brownish tint of manganese dioxide but avoid excess. Solution may still be colored if interfering substances are present. Promptly cool to room temperature in a tray of cold water. Centrifuge, if necessary, or filter through an alundum crucible. If supernatant is distinctly colored, extract at pH 4 with 8-quinolinol in chloroform. If solution is only slightly colored continue as follows. Decant supernatant into a 25ml volumetric flask. Add 1ml *s*-diphenylcarbazide reagent. Mix and allow one minute for color development. Add 2.5ml of 4 M phosphate buffer. Mix and dilute to mark with water. Read absorbance (or percent transmittance) of the solution at 540nm using 1cm cells. For reference, use the reagent blank. Colors too intense to read may be diluted to larger volumes using reagents in proportion or take the remaining 5ml aliquot and proceed as described for the 20ml aliquot.

9.3 *Calibration*

9.3.1 Silver membrane samples

9.3.1.1 HEXAVALENT CHROMIUM

Standards in the range of 0 to 40 μ g hexavalent Cr are prepared by adding 0-1-2-5-10-20ml of standard hexavalent chromium solution, 2 μ g/ml, to a series of 25ml volumetric flasks. Add 10ml 0.2 N sodium hydroxide and proceed as directed in 9.1.1. Prepare a standard curve.

9.3.1.2 TOTAL SOLUBLE CHROMIUM

Standards in the range of 0 to 40 μ g chromium are prepared by adding 0-1-2-5-10-20ml of standard trivalent chromium solution; 2 μ g/ml, to a series of 125ml Phillips beakers. Add 10ml 0.2 N sodium hydroxide. Proceed as directed in 9.1.2. Prepare a standard curve.

9.3.2 Electrostatic samples or acetate membrane filters

Standards in the range 0 to 40 μ g chromium are prepared by adding 0-1-2-5-10-20ml of standard trivalent chromium solution, 2 μ g/ml, to a series of small flasks. Add 0.25ml of 40% sodium bisulfate and evaporate to dryness. Proceed as directed under 9.2.2. Prepare a standard curve.

10. EXPRESSION OF RESULTS

10.1 After determining the amount of chromium in the sample or aliquot, from the standard curve, obtain the net amount by subtracting any reading obtained for the blanks. Make allowance for total number of aliquots taken.

10.2 *Silver membrane filters*

Report results as follows: Milligrams chromium trioxide (CrO₃) per cubic metre of air, calculated from hexavalent chromium and milligram soluble total chromium (Cr³ + Cr⁶) per cubic metre of air.

10.3 *Electrostatic samples or acetate membrane filters*

EP tubes or acetate membrane filters should be reported as milligrams total chromium (Cr³ + Cr⁶) per cubic metre of air.

11. NOTES ON PROCEDURE

11.1 *Collection efficiencies*

It is believed that the collection of chromium compounds is quantitative using any of the three sampling methods described.

11.2 *Temperature and pressure*

The effect of these sampling variables has been largely disregarded in the past. Since these factors have an effect upon the value of the measured air volume, it is recommended that these corrections be introduced routinely. There is increasing agreement, at the international level, that the standard conditions of temperature and pressure be 25°C and 760mm Hg.

11.3 *Solubility of chromium salts*

Chromium compounds that may be difficult to dissolve are chromium sesquioxide (Cr_2O_3) and elemental chromium (Cr). Elemental chromium is not found in nature and airborne chromium in the vicinity of electroplating or metallurgical plants is likely to be in the oxide form. The fluorides CrF_2 and CrF_3 have melting points above 1,000°C and loss of chromium during digestion of a glass fibre air sample does not occur on hydrofluoric acid digestion. Complete recovery of added trivalent ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and hexavalent (K_2CrO_4) chromium has been demonstrated (12.1).

11.4 *Interferences*

Iron and vanadium react with *s*-diphenylcarbazide to produce yellow-brown colors but the reaction is less sensitive than with chromium. Mercury produces a violet precipitate very slowly. Addition of a small amount of sodium chloride before *s*-diphenylcarbazide, forms mercuric chloride which eliminates this interference (12.2).

If a distinct color is noted after the oxidation of chromium to the hexavalent form, extraction with 8-quinolinol in chloroform at pH 4 will remove large amounts of iron, molybdenum and copper as well as vanadium. Extract excess 8-quinolinol with chloroform and then adjust pH to 1.0 with sulfuric acid before developing color. Nitrates are detrimental to the stability of the final color in 0.2 N sulfuric acid. It has been found that the interference can be greatly reduced by the addition of buffer to raise the pH to 2. The addition of the phosphate buffer before addition of the color reagent reduces the interference of iron. Fifteen minutes should be allowed for complete color development in this case.

It should hardly be necessary to mention that glassware should not be cleaned with the usual chromsulfuric acid cleaning solution. In fact, only new glassware should be used, which has never been cleaned in this way. Cleaning may be done with alcoholic potassium hydroxide or clean steam.

Care must be taken at all stages of sample preparation to avoid contamination from the stainless steel and chrome plated apparatus so omnipresent in modern laboratories.

11.3 *Sensitivity*

The limit of sensitivity should be so set that the analyst does not have to

work at the extreme lower portion of the calibration curve. A reasonable quantity is 1 microgram. Allowing for a 20/50 aliquot this would correspond to 0.02 milligrams chromium/m³ in a 5 cubic foot air sample.

12. REFERENCES

- 12.1 Determination of Chromium in Airborne Particulates by Atomic Absorption Spectrophotometry. Report EPS 4-AP-72-10, Environment Canada, Ottawa, December 1972.
- 12.2 Standard Procedure for Collection and Analysis of Chromium. Pennsylvania Department of Environmental Resources, Bureau of Occupational Health, P.O. Box 2063, Harrisburg, Pennsylvania, January 1973.