

MIDHS

*Methods for the Determination of
Hazardous Substances*
Health and Safety Laboratory

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Total hexavalent chromium compounds in air

Colorimetric laboratory method using
1,5-diphenylcarbazide

March 1988

INTRODUCTION

Occurrence¹⁻²

1 Elemental chromium is not found free in nature and the only ore of importance is the spinel ore, chromite or chrome iron stone, ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$), which contains chromium sesquioxide (Cr_2O_3) along with variable quantities of other oxides. Only ores containing more than 40% Cr_2O_3 are used commercially. In the elemental form chromium is a hard steel-grey, brittle metal which is stable in air and water at room temperature and has a melting point of 1890°C . The principle source of the metal is by reduction of chromium sesquioxide with aluminium powder or by electrolysis. Chromium can have a valency of 2 (basic and unstable), 3 (amphoteric) or 6 (acidic), and a wide range of chromium alloys and inorganic chromium compounds are encountered in the workplace; in general, hexavalent chromium compounds are the most important industrially because of their acidic and oxidative properties. These compounds vary greatly in their toxic and carcinogenic effects; chromium and its inorganic compounds are, therefore, divided into a number of different groupings based on toxicological and epidemiological data. These groupings include:

Chromium metal and alloys

Divalent chromium compounds (Cr^{II}) (Chromous compounds)

Trivalent chromium compounds (Cr^{III}) (Chromic compounds)

Hexavalent chromium compounds (Cr^{VI})

2 Hexavalent chromium compounds include chromium trioxide (CrO_3) - the anhydride of chromic acid, chromates (eg Na_2CrO_4), dichromates (eg $\text{Na}_2\text{Cr}_2\text{O}_7$) and polychromates. These compounds are generally produced from sodium chromate (Na_2CrO_4) and sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), which are, in turn, produced from chromium sesquioxide by roasting with soda ash in a rotary furnace at 1100°C .

Uses of hexavalent chromium compounds¹⁻²

3 Soluble hexavalent chromium compounds, such as chromic acid and soluble chromates, are used extensively

as electrolytes in electroplating and in anodising. Sodium and potassium chromates are used as mordants or fixatives for the dyeing of textiles. Soluble hexavalent chromium compounds are also used in the manufacture of dyestuffs and as catalysts in the chemical industry.

4 Sparingly soluble and insoluble hexavalent chromium compounds (such as zinc chromates, calcium chromate, lead chromate, barium chromate, strontium chromate, and sintered chromium trioxide) are used principally as pigments in paints, varnishes, oil and water colours, printing fabrics, and rubber. Some are also used as corrosion inhibitors, in battery depolarization, and in oxidizing reactions.

5 Hexavalent chromium is also produced as a constituent of stainless steel welding fume in certain welding operations, notably in manual metal arc (MMA) welding and flux cored arc (FCA) welding. It is predominantly present in welding fume in a soluble form.

Toxicity¹⁻⁶

6 There is abundant evidence that soluble hexavalent chromium compounds may cause irritant and allergic contact dermatitis, skin ulcers and nasal irritation varying from rhinitis to perforation of the nasal septum. Historically, very high percentages of workers in the chromium plating industry had dermatitis or skin ulcers and perforated or ulcerated nasal septa⁷. Dermatitis from exposure to soluble hexavalent chromium compounds has been reported from groups of employees as varied as lithographers⁸⁻⁹, diesel repair shop workers¹⁰, leather workers¹¹, and in the cement industry¹². Soluble hexavalent chromium compounds are not generally believed to be carcinogens, although this remains a matter of some controversy⁴.

7 Insoluble hexavalent chromium compounds, and in particular those which are sparingly soluble in water, have been related to an increased incidence of lung cancer², and are therefore suspected carcinogens.

Precautions^{2,3,13}

8 Hexavalent chromium compounds should be handled, wherever possible, in enclosed plant. Where this is not possible, local exhaust ventilation of a high standard should be provided for processes where dust or mist is likely to be produced. Local exhaust ventilation by lip extraction or chemical/mechanical spray suppressants should be provided and used at chromium plating baths.

9 Employees should be provided with, and be required to use, suitable protective clothing. In particular, where there is a possibility that employees may be exposed to solids or liquids containing soluble hexavalent chromium compounds, then aprons and bibs of impervious material should be worn, together with loose fitting rubber gloves, rubber boots or other waterproof footwear, face shields (eight inch minimum), and any other appropriate protective clothing necessary to prevent skin contact. If accidental skin or eye contact occurs, affected areas must be thoroughly washed without delay. Where soluble hexavalent chromium compounds are used, facilities for quick drenching of the body, and an eye-wash fountain should be provided within the immediate work area for emergency use. As a further precaution a supply of a suitable barrier cream (3:1 soft paraffin BP/lanolin) should be applied to the uncovered skin before starting work.

10 Although nasal ulceration is usually due to airborne mist, spray or dust, a good standard of personal hygiene is important in avoiding the production of nasal symptoms from direct transfer of hexavalent chromium to the nasal mucosa, particularly in the electroplating industry, but also in industries handling soluble chromate and dichromate salts^{12,14}.

First aid^{2,13}

11 First aid for ulceration is seldom necessary, but any breaches of the skin should be cleaned immediately and covered with a sterile dressing, which is in turn covered completely with a waterproof adhesive plaster. The use of a chelating disodium calcium edetate ointment will speed up healing of the indolent ulceration. In severe cases medical attention should be sought.

Determination of total hexavalent chromium-in-air concentrations

12 This is not a reference method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte (eg other methods in the MDHS series). With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided they have accuracy and reliability appropriate to the application.

PRINCIPLE¹⁵⁻¹⁷

13 The method described is based upon the spectrophotometric determination of the magenta chromogen formed when 1,5-diphenylcarbazide reacts with hexavalent

chromium in dilute sulphuric acid solution. The hexavalent chromium dust or fume is collected on a PVC/A filter, or an alkali-treated PVC/A filter for chromic acid mist, and extracted with a leach solution of 2% (m/v) sodium hydroxide / 3% (m/v) sodium carbonate. The solution is filtered, acidified, the colorimetric reagent added, and the absorbance measured at a wavelength of 540nm using a spectrophotometer.

14 The procedure described separates hexavalent chromium in solution from trivalent chromium, trivalent iron, and interfering divalent iron etc, which are all precipitated under alkaline conditions. The principle has been described by various workers¹⁵⁻¹⁷, and has been incorporated into methods published by NIOSH¹⁸ and BSI¹⁹.

SCOPE

15 This method is suitable for the determination of concentrations of total hexavalent chromium in workplace atmospheres. The method is suitable for sampling over periods in the range 1 to 8 hours.

16 MDHS 52²⁰ gives details of a simplified colorimetric field method for soluble hexavalent chromium compounds in air, and this can be used when compounds which undergo redox reactions with hexavalent chromium (eg Fe^{II} compounds) are known to be absent from the test atmosphere (eg for sampling of chromic acid mists).

17 The lower analytical limit, defined as ten times the standard deviation of a blank determination, is approximately 0.001mg Cr^{VI}/m³ for samples of the minimum 120 litres of air.

Precision

18 The precision of the method²¹ is expected to be better than 10%, measured as a coefficient of variation, for samples of the minimum 120 litres of air which are in the range 0.025 to 0.1 Cr^{VI}/m³.

Interferences

19 Vanadium is the only interferent, but under the test conditions given, this is minimal.

REAGENTS

20 During the analysis, use only reagents of recognised analytical reagent grade and only distilled water of equal purity. Do NOT pipette by mouth.

Water

21 Distilled or de-ionized water should be used. Its electrical resistance must be greater than 0.5megohm/cm or the electrical conductance less than 2µmho/cm.

1m sodium hydroxide

22 Dissolve 4g of sodium hydroxide pellets in 50ml of de-ionized water (para 21). Cool, and dilute to volume in a 100ml volumetric flask. Mix thoroughly.

Leach solution (2% (m/v) sodium hydroxide / 3% (m/v) sodium carbonate)

23 Dissolve 20g sodium hydroxide pellets and 30g anhydrous sodium carbonate in de-ionized water (para 21), and dilute to volume in a 1 litre volumetric flask. Mix thoroughly.

4.5N Sulphuric acid

24 Carefully add 62.5ml of concentrated sulphuric acid (relative density approximately 1.84g/ml, about 98% (m/m) solution), to 250ml of de-ionized water (para 21). Cool, dilute to volume in a 500ml volumetric flask. Mix thoroughly.

1,5-Diphenylcarbazide

25 Dissolve 0.25g 1,5-diphenylcarbazide in 50ml of acetone. Dilute to 100ml with de-ionized water (para 21), and mix thoroughly.

26 This solution has a strictly limited shelf life. When prepared it should be a light straw colour. It should be discarded immediately. If any pink colouration is observed, and also once the solution darkens noticeably. It is advisable to make the solution up daily.

Standard hexavalent chromium solution (1000(µg/ml)

27 Dissolve 2.828g of dried potassium dichromate ($K_2C_2O_7$) in de-ionized water (para 21). Dilute to volume in a 1 litre volumetric flask. Mix thoroughly.

'Working' standard chromium solution (100µg Cr/ml)

28 Pipette 10.0ml of standard hexavalent chromium solution (para 27) into a 100ml volumetric flask, and dilute to volume with water. Mix thoroughly.

APPARATUS

Sampling head

29 The filter holder should preferably be of the enclosed head type, as described in MDHS14²². This head is designed to take a 25mm diameter filter, and has an end cap with seven 4mm diameter inlet orifices in it.

30 A 25mm open face filter holder should be used for the determination of chromic acid mist, since the only commercially available closed head types are fabricated in metal, and are therefore not suitable for this purpose.

31 BS6691¹⁹ recommends the use of a 37mm open face filter holder for the determination of total hexavalent chromium in welding fume, but this does not preclude the use of other filter holders or filter sizes.

32 The filter and sampling head should not give leakage of dust, or have any electrostatic or other properties that could influence representative air sampling.

Filter

33 The filter used must be compatible with subsequent analytical procedures, and in particular it must be suitable for collection of stable samples of hexavalent chromium, which has a tendency to be reduced by many filter materials. A Gelman DM800 PVC/A filter of an appropriate diameter (paras 29-31) is suitable, and is recommended. This is a PVC acrylic co-polymer filter, and in addition to its suitability for collection of hexavalent chromium, it also has good properties with regard to weight stability, which are necessary if total inhalable dust or fume is to be determined.

34 Determination of hexavalent chromium in chrome plating mists should be carried out using a 25mm diameter PVC/A filter which has been treated with 1M sodium hydroxide solution (para 22) by soaking overnight then drying in a chromium free environment. By neutralising the mist collected and establishing an alkaline environment, this treatment greatly reduces the tendency of hexavalent chromium to become reduced through oxidation of the filter material.

35 The PVC/A filters recommended are chromium free (ie contain less than 0.0µg of chromium, extractable under the conditions of the test), have a pore size of 0.8µm, and give more than 95% filtration efficiency at 0.3µm at a flow rate of 2 litres/min.

Pump

36 A pump is required that is capable of being worn by a person while carrying out his normal work, and capable of running continuously for 8 hours at 2 litres/min. The pump rate should be stable within (±5%, and the total volume of air sampled by the pump over sampling periods up to 8 hours should be within (±10% of the calculated volume²³.

Glassware

37 A selection of standard laboratory glassware is required, such as beakers and standard volumetric flasks. These will need to be specially cleaned and kept specifically for use in trace metal analysis.

NOTE: Chromic acid should not be used for cleaning any glassware associated with this method.

Spectrophotometer/colorimeter

38 A filter or grating spectrophotometer or colorimeter that is capable of measuring in the region of 540nm is required, together with appropriate matched cells or measuring tubes (path length 10-13mm).

Microlitre pipettes

39 An adjustable microlitre pipette, capable of being used in the range 20µl to 200ul, is recommended for preparation of standard solutions. Bottletop dispensers and/or additional pipettes are recommended for reagent addition.

PROCEDURE

Calibration of sampling pumps

40 The sampling volume may be a significant source of error in the final calculation of the total hexavalent chromium-in-air concentration. Each pump, with a representative filter in the sampling head, should be calibrated against an external flowmeter. Pump flow rates should be checked against an external flowmeter both before and after sampling and, unless operating experience proves it unnecessary, at least once during the sampling period. The flow indicator on the pump, if fitted, should be used as an indication that the equipment is working effectively²³.

Collection of samples

41 To minimise contamination, the filter should be loaded into the sampling head, unloaded and analysed in an area free from chromium contamination. The loaded sampling head should be covered with a protective cap during transportation through chromium contaminated areas. At the sampling site, draw a measured volume of at least 120 litres of the atmosphere through the filter at 2 litres/min. Remove the apparatus from the test atmosphere. Either transport the filter holder intact to the laboratory or area set aside for analysis or, using flat-tipped forceps, transfer the filter to a suitable container for transport.

42 A sample blank should be prepared by using a filter identical to that used for sampling, and subjecting it to the same handling procedure as the sample filter, except that no air is drawn through it.

43 Analysis should proceed as soon as *possible* after sampling. If immediate analysis is impracticable the filter and holder, with protective cap in place, or the filter in a suitable container, should be stored in a cool dark location until analysis is possible; in any case delay should not exceed 3 days.

Analysis

44 Using flat-tipped forceps, place the PVC/A sample filter in a 50 ml squat-form beaker and accurately add 5ml of leach solution (para 23). Cover the beaker with a watch glass, and warm to near boiling point for 30 to 45 minutes. Do not allow the solution to boil; do not heat for longer than the specified period; and do not allow the solution to evaporate to dryness, because hexavalent chromium may be lost due to reaction with the filter material. If it is known that all hexavalent chromium present in the test atmosphere is soluble, eg in chromic acid mists, then there is no need to heat to effect dissolution.

45 Allow the solution to cool, and filter through a small diameter cellulose filter (a 7cm diameter Whatman 42 grade filter is suitable), pre-washed with leach solution (para 23), into a 25ml volumetric flask. Rinse the beaker and PVC/A filter thoroughly with two 2.5ml aliquots of leach solution (para 23), and pour the washings through the filter paper to combine them with the original filtrate.

46 Add 5ml 4.5N sulphuric acid (para 24) to the volumetric flask, and swirl to mix. Care is needed as the

mixture will evolve carbon dioxide and froth. Let the solution sit for several minutes until vigorous gas evolution ceases.

47 Pipette 1ml of 1,5-diphenylcarbazine solution (para 25) into the volumetric flask, dilute to volume with deionized water (para 21), and invert several times to mix, removing the stopper as necessary to relieve pressure. The solution prepared is approximately 0.5N wrt sulphuric acid.

48 Discard about one-half the contents of the volumetric flask, stopper the flask and shake it several times, removing the stopper each time to relieve pressure. This procedure releases dissolved carbon dioxide.

49 Wait 10 minutes, and then measure the absorbance (paras 52-54) of the solution as soon after that time as possible, since the colour fades with time.

Preparation of standard solutions

50 Pipette 0, 25, 50, 100, 150 and 200 μ l of the 'working' standard chromium solution (para 28) separately into each of six 25ml volumetric flasks. Add 10ml leach solution (para 23) and 5ml 4.5N sulphuric acid (para 24) to each flask, and swirl to mix. Care is needed as the mixture will evolve carbon dioxide and froth. Let the solutions sit for several minutes until vigorous gas evolution ceases, and then proceed as for sample solutions (para 47-49).

51 The standard solutions contain from 0, 0.1, 0.2, 0.4, 0.6, and 0.8(g Cr^{VI}/ml respectively.

Absorbance measurements

52 Set up the spectrophotometer or colorimeter as recommended in the manufacturer's handbook. It is recommended that the measurements be made at a wavelength of 540nm as this corresponds to the maximum absorbance of the magenta chromogen. At this wavelength the sensitivity (concentration giving an absorbance measurement of 0.0044 units) for chromium is about 0.006 μ /ml, assuming that 10mm path-length cells are used. A linear calibration graph is obtained for standards from 0 to 0.8 μ /ml.

53 Adjust the spectrometer zero with the zero standard in the optical beam, and then determine the absorbances of the remaining standards. It is recommended that these standard solutions are measured in increasing order of concentration. Plot a calibration graph of absorbance against concentration.

54 Measure the absorbance readings of the blank solution and the sample solutions, and obtain the concentrations of hexavalent chromium in these solutions from the calibration graph.

55 If the hexavalent chromium concentration of a sample solution is greater than 0.8 μ /ml, carry out an appropriate dilution with zero standard solution (para 50), and repeat the absorbance measurement.

Calculation

56 Let:

C_s = concentration of chromium in the sample solution ($\mu\text{g/ml}$)

C_b = concentration of chromium in the blank solution ($\mu\text{g/ml}$)

V_s = volume of sample solution (ml), normally 25ml (para 47)

V_a = volume of air sampled (litres)

d = dilution factor (para 55)

Then

$$\text{Concentration of total hexavalent chromium in air (mg Cr}^{VI}\text{/m}^3\text{)} = \frac{(C_s \times d - C_b) \times V_s}{V_a}$$

ADVICE

Advice on this method and the equipment used may be obtained from the Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, 403-405 Edgware Road, London NW2 6LN (Telephone 01-450 8911).

The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

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