HSE
Health and Safety Executive

Hexavalent chromium in chromium plating mists

Colorimetric field method using 1,5-diphenylcarbazide and spectrophotometry or colour comparator

MDHS52/4

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1 This method describes a field procedure for the measurement of time-weighted average concentrations of hexavalent chromium (Cr(VI)) originating from chromium plating mist. The method is suitable for static measurements adjacent to chromium plating baths to aid in assessing efficacy of measures to control emissions of chromium plating mist.

2 The method is not suitable for measurement of personal exposure as these are usually substantially lower than the lower limit of the working range of this method when adequately controlled. A procedure for the measurement of personal exposure to Cr(VI) is described in BS ISO 16740[1] or alternatively it can be assessed by measurement of total chromium.[2, 3] The limitations of the total chromium approach are outlined in Appendix 1.

Summary

3 A measured volume of air is drawn through a membrane filter mounted in an inhalable sampler. The filter is then desorbed with dilute sulphuric acid and the soluble Cr(VI) compounds are derivatised by the addition of 1,5-diphenylcarbazide solution. After colour development, quantification is carried out using a spectrophotometer at 540 nm or semi-quantitatively using a colour comparator.

4 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

5 A minimum sampling period of 15 minutes at 2 $l.min^{-1}$ is recommended when analysis is carried out using spectrophotometry.

6 When using a colour comparator a minimum 1 hour sampling time at 2 $l.\ min^{-1}$ is recommended; a 2 hours sampling duration (120 litres ±10% air sample) is required in order to make direct comparison of colour formation with Cr(VI) concentration.

Prerequisites

7 Users of this method will need to be familiar with the content of MDHS14.[4]

Safety

8 Users of this method should be familiar with standard laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

9 Inhalable dust sampler with protective cover as described in MDHS14.[4]

10 Personal sampling pumps that meet the requirements of BS EN 1232.[5]

11 Binder-free, sodium-hydroxide-treated polyvinylidine fluoride membrane filters, with pore size of 5 µm or less. Filters should have a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter. Prepare the filters by soaking overnight in 1 M sodium hydroxide solution and dry in a clean environment.

12 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

13 Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes to transport samples to the laboratory. For fixed point sampling above or adjacent to plating baths, a suitable adjustable clamp stand is required to enable the sampler to be located in the test position above the exhaust plane or surface of liquid.

Laboratory apparatus and reagents

14 During the analysis, use only reagents of a recognised analytical grade.

15 Water: complying with the requirements of ISO 3696 grade 2 water (electrical conductivity less than 0.1 $m.S.m^{-1}$ and resistivity greater than 0.01 MΩ.m at 25 °C).[6]

16 Sodium hydroxide pellets: The concentration of hexavalent chromium shall be less than 10 $\mu g.kg^{-1}$.

17 Sodium hydroxide solution (1M): dissolve 4 g of sodium hydroxide pellets in 50 ml of water, allow to cool and make up to 100 ml with water.

18 Sulphuric acid (H2SO4): concentrated, ρ about 1.84 $g.\ ml^{-1}$, mass fraction about 98%.

19 Sulphuric acid 0.25 M. Caution: Do not add water to acid as the reaction is very exothermic, ensure appropriate controls and personal protective equipment are used according to the risk assessment. Add approximately 500 ml of water to a 1 litre volumetric flask. Carefully add 14 ml of concentrated sulphuric acid and mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

20 1,5-diphenylcarbazide solution, 0.25% (m/v) in 50% (v/v) acetone: Dissolve 0.25 g of 1,5-diphenylcarbazide in 50 ml of acetone. Quantitatively transfer to a 100 ml volumetric flask, dilute to the mark with water, stopper and mix thoroughly. This solution has a limited shelf life. When prepared it should be of a light straw

colour; it should be discarded immediately if any pink coloration or darkening is observed. It is good practice to make the solution up daily.

21 Stock standard hexavalent chromium solution, 1000 µg.ml^{-1} of Cr(VI): Use a commercially available standard solution at a concentration of 1000 µg.ml^{-1}. Observe the manufacturer's expiry date and storage conditions.

22 Working standard hexavalent chromium solution, 100 µg.ml^{-1} Cr(VI): Accurately pipette 10.0 ml of stock standard hexavalent chromium solution into a 100 ml volumetric flask, and dilute to the mark with water, stopper and mix thoroughly. This solution should be stable for up to one year.

23 Laboratory detergent solution: A laboratory grade detergent suitable for cleaning of samplers and laboratory glassware, diluted with water according to the manufacturer's instructions.

24 Borosilicate laboratory glassware (suitable plastic beakers may also be used): including beakers; watch glasses; measuring cylinders; and volumetric flasks complying with the requirements of BS ISO 3585:1998.[7] Cleaned before use with laboratory detergent and laboratory washing machine followed by soaking in 0.25 M sulphuric acid for at least 24 hours. Finally rinsing with water. Chromic acid must not be used for cleaning any glassware and it is recommended that a set of glassware be reserved for the analysis of hexavalent chromium.

25 Positive displacement micropipettes complying with the requirements of BS EN 8655-6:2002.[8]

26 Spectrophotometer or colour camparator: A spectrophotometer capable of measuring in the region of 540 nm, with matched cells (10 mm path length) or colour comparator with 'Chromium (VI)' comparator disc. The comparator disc has nine colour standards representing 0.00, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, and 0.1 mg.m^{-3} of Cr(VI) for the recommended sample volume of 120 litres of air.

Preparation and sampling

27 The presence of reducing agents or dust in the workplace air can lead to an underestimation of Cr(VI). If it is possible that there could be significant interference, follow the procedure given in Appendix 2 to assess whether the method is suitable for use under the test conditions.

28 Locate the samplers depending on the type of process as outlined in Appendix 3.

29 Preparation of samplers and sampling should be carried out in accordance with the procedures described in MDHS14[4] for inhalable dusts.

30 Set aside a minimum of three unused samplers as blanks, or for batches of more than 30, one blank for every ten samples collected. Ensure that the blank samplers are handled in the same way as the samples but draw no air through them.

31 After sampling, remove the filter from each sampler and place in a labelled filter transport cassette. Alternatively, transport the sample filters to the laboratory in the samplers with their protective cover in place in a suitable container.

32 For samplers which have an internal filter cassette, remove the filter cassette from each sampler and fasten with its lid or transport clip before transport.

Calibration solutions for spectrophotometry

33 Accurately dispense 0, 20, 40, 60, 80 and 100 µl of the working standard hexavalent chromium solution into separate 50 ml beakers.

34 Accurately add 8 ml of 0.25 M sulphuric acid and proceed as for sample analysis below from the addition of 2 ml of 1,5-diphenylcarbazide solution (paragraph 39).

Sample analysis

35 Proceed with the analysis immediately after sampling. If this is impracticable, store filters in an airtight container in a cool, dark location until analysis is possible. Analysis can be delayed for up to four weeks after sampling when using sodium hydroxide-treated filters.

36 Transfer the sample and blank filters to individual 50 ml beakers using flat-tipped tweezers.

37 Accurately add 8 ml of 0.25 M sulphuric acid to each filter and stand for twenty minutes to allow dissolution of the sample, swirling occasionally. If the sampler used was of the type in which airborne particles deposited on the internal surfaces of the filter cassette constitute part of the sample, wash any particulate material adhering to the internal surfaces into the beaker using an aliquot of the 8 ml 0.25 M sulphuric acid.

38 Accurately add 2 ml of 1,5-diphenylcarbazide solution to the calibration, blank or sample solutions and swirl to mix. Stand for ten minutes, swirling occasionally, then analyse the solutions using the spectrophotometer or colour comparator.

39 When analysing a large batch of samples, measurement may take place up to 30 minutes after addition of 1,5-diphenylcarbazide solution provided that the beakers are covered to prevent the evaporation of acetone.

Absorbance measurement using spectrophotometer

40 Measure the absorbance of the magenta chromagen at 540 nm for the calibration solutions and the samples according to the instrument manufacturer's instructions, using water as the reference solution.

41 A linear calibration graph should be obtained for 0 to 1 $\mu g.ml^{-1}$ Cr(VI).

42 Rinse the cell with water between each blank, sample, or calibration solution, then rinse the cell with each sample solution before refilling and recording the absorbance.

Absorbance measurement using comparator

43 Determine the Cr(VI) in air concentration in blanks and samples by visual comparison of colour intensity with standard colour discs, according to the manufacturer's instructions using water as the reference.

44 The apparent concentration of Cr(VI) in air read from the comparator disc is based on a sample volume of 120 litres. If the sample volume was 120 litres (±10%)

and no blank correction is required, then the apparent concentration of hexavalent chromium in air read from the comparator disc will be the actual concentration of hexavalent chromium in air.

45 If the Cr(VI) concentration of a sample solution is found to be over-range, ie greater than 0.1 $mg.m^{-3}$, dilute the sample solution by a suitable factor with 0.25 M sulphuric acid and 1,5-diphenylcarbazide solution that have been pre-mixed in the ratio 4:1. Do this without delay, and immediately carry out the measurement on the diluted solution. Record the dilution factor.

Calculations

46 Concentration ($mg.m^{-3}$) of hexavalent chromium, ρ(CrVI), in air using spectrophotometry:

$$\rho(CrVI) = \frac{[\rho(CrVI)_1 \times V_1\ DF_1] - [\rho(CrVI)_0 \times V_0\ DF_0]}{V}$$

where:

$\rho(CrVI)_1$ = concentration of Cr(VI) in the sample, in $\mu g.ml^{-1}$

$\rho(CrVI)_0$ = mean concentration of Cr(VI) in the blanks, in $\mu g.ml^{-1}$

V_1 = volume of the sample solution, in ml

V_0 = volume of the blank solutions, in ml

DF_1 = dilution factor for the sample solution (if required)

DF_0 = dilution factor for the blank solutions (if required)

V = volume of the air sample, in litres.

47 For normal use the volume of sample and blank solutions is 10 ml and the dilution factor for sample and blank measurements is 1, so that the equation reduces to:

$$\rho(CrVI) = \frac{[\rho(CrVI)_1 - \rho(CrVI)_0] \times 10}{V}$$

Concentration ($mg.m^{-3}$) of hexavalent chromium in air, ρ(CrVI), using colour comparator:

$$\rho(CrVI) = [\rho(CrVI)_1 \times DF_1 - \rho(CrVI)_0 \times DF0] \times 120/V$$

where:

$\rho(CrVI)_1$ = apparent concentration of Cr(VI) in air from the sample solution measurement, in $mg.m^{-3}$

$\rho(CrVI)_0$ = mean apparent concentration of Cr(VI) in air of the blank solution measurements, in $mg.m^{-3}$

DF_1 = dilution factor for the sample solution

DF_0 = the dilution factor for the blank solution

120 = volume of air for which the comparator disc readings apply, in litres

V = volume of the air sample, in litres.

48 For normal use the dilution factor for sample and blank measurements is 1, and typically there will be no measurable blank, so that the equation reduces to:

$\rho(CrVI) = \rho(CrVI)_1 \times 120/V$

Appendix 1: Use of total chromium as a surrogate for hexavalent chromium

1 Measurement procedures for total chromium in air[2,3] can be used to estimate personal exposure to hexavalent chromium, if it is assumed that all the chromium sampled is in the hexavalent state. This will normally be the case when only hexavalent chromium plating processes are being used in the workplace, but exposure could be overestimated if trivalent chromium plating is also being carried out.

2 If measurements of total chromium in air are used to estimate personal exposure to hexavalent chromium in such circumstances, they should therefore be regarded as worst case scenario.

Appendix 2: Procedure for assessing the effect of possible reducing agents and dust on hexavalent chromium measurements

1 Hexavalent chromium plating baths may be sited close to operations that release reducing agents into the air, or in areas with high levels of air pollution. In such cases, Cr(VI) in air concentrations could be underestimated. The following procedure may be used to estimate whether extraneous material collected on the filters has the capacity to reduce Cr(VI).

2 Collect a sample of background air in the workplace in which Cr(VI) in air measurements are to be made. The sampling position should be remote from the plating baths, so that it is unlikely that a significant amount of chromium plating mist will be collected. Sample the air for 2 hours using the type pf filter that will be used in the test method.

3 Place the sample filter and an unused filter into separate 50 ml beakers. Dispense 60 µl (6.0 µg of Cr(VI)) of working standard hexavalent chromium solution into each beaker, which is equivalent to a sample collected at the lower limit of the working range for a sampling time of two hours.

4 Analyse the spiked sample and blank filters Cr(VI) and compare the results. If no reducing agents have been collected, the results will be the same. If the result obtained for the spiked sample filter is less than 80% of that obtained for the spiked blank filter, it implies that the method will not comply with the overall uncertainty requirements of BS EN 482.[9]

5 Under such circumstances it is recommended, where possible, that personal exposure to Cr(VI) is assessed by measuring total chromium.[2,3]

Appendix 3: Sampler position

Manual baths

1 Position the sampler within the open space above the bath, the boundary of which is defined by the vertical planes through the edges of the bath. Where local exhaust ventilation is used to control emission of chromium plating mist, position the sampler 300 mm above the exhaust plane of the extraction system, with the filter in the vertical position. Where spray suppression is used without extraction ventilation, position the sampler 300 mm above the surface of the electrolyte, with the filter in the vertical position.

Automatic and semi-automatic processes

2 Placing the sampler over the bath is impracticable on safety grounds. In most cases, access to the bath is restricted by solid or wire-mesh safety barriers. These can be used as support for a permanent sampling point, to which the sampler can be conveniently attached. Locate the sampling point halfway along the bath and 300 mm above the edge, where it is as near as possible to the sources of chromium plating mist emissions, and not remote from them. Position the sampler at the sampling point, with its inlet orientated toward the centre of the bath and with the filter in the vertical position.

Enclosed processes

3 Enclosed systems are usually provided with access points to the chromium plating bath for process control purposes. Locate the sampling point as near as possible to the access point, and not further than 300 mm away from the opening. Position the sampler at the sampling point, with its inlet orientated toward the centre of the bath and with the filter in the vertical position.

Appendix 4: Method performance

Limit of detection for spectrophotometry

1 The qualitative and quantitative detection limits for Cr(VI), defined as three times and ten times the standard deviation of the blank determination, are typically around 0.04 µg and 0.14 µg. For the minimum air sample volume of 30 litres, this corresponds to airborne concentrations of Cr(VI) of 0.0015 $mg.m^{-3}$ and 0.005 $mg.m^{-3}$, respectively.

2 However, field trials have shown that recovery of Cr(VI) is affected by the presence of dust or reducing agents in the sampled air. In such circumstances, the lower limit of the working range of the method can increase from 0.005 $mg.m^{-3}$ to as much as 0.05 $mg.m^{-3}$. Nevertheless, a more usual value for the lower limit of the working range, which will apply under most circumstances, is 0.025 $mg.m^{-3}$. This is adequate for making fixed point measurements above or adjacent to chromium plating baths, but is of limited use for making personal exposure measurements.

Overall uncertainty

3 The mean analytical recovery for 90 filters spiked with between 0.3 µg and 24.0 µg of Cr(VI) has been determined to be 98.4 ±4.4%. The overall uncertainty, as defined by BS EN 482 20069, and based on this data for spectrophotometry measurements, has been estimated to be less than 40%, for samples in the range 0.15 µg to 6.0 µg, and less than 23%, for samples in the range 0.75 µg to 24.0 µg.

4 The precision of measurements made with a comparator has not been determined, but is less precise than with spectrophotometry.

Interferences

5 Reducing agents and dust present in the sampled air can lead to low results by causing reduction of the Cr(VI) collected on the filter. Agents which could interfere include metal dust, ferrous compounds, carbonaceous urban particulate and sulphur dioxide.

6 Field trials indicate that the maximum negative bias observed is typically around 0.005 mg.m^{-3} of Cr(VI). However, dust generated by grinding metal components in preparation for plating has been found to lead to serious underestimates of Cr(VI) in air concentrations.

It has been estimated that in order for the method performance to comply with BS EN 482[9] for overall uncertainty, the bias of the analytical method should be no greater than 10%. On this basis, potential interference by reducing agents and dust can increase the lower limit of the working range from to 0.005 mg.m^{-3} to 0.05 mg.m^{-3} of Cr(VI). In this situation, the measurement procedure falls outside the accuracy for compliance with standard.

7 Vanadium is the only known substance to interfere with the spectrophotometric method, but under the test conditions given, this interference is insignificant.

References

1 BS ISO 16740:2005 *Workplace air – Determination of hexavalent chromium in airborne particulate matter – Method by ion chromatography and spectrophotometric measurement using diphenyl carbazide* British Standards Institution

2 BS ISO 30011:2010 *Workplace air – Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry* British Standards Institution

3 BS ISO 15202-3: 2004 *Workplace air – Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry. Analysis* British Standards Institution

4 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 (Fourth edition) HSE 2014 www.hse.gov.uk/pubns/mdhs

5 BS EN 1232:1997 *Workplace atmospheres: Pumps for personal sampling of chemical agents Requirements and test methods* British Standards Institution

6 BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and test methods* British Standards Institution

7 BS ISO 3585:1998 *Borosilicate glass 3.3. Properties* British Standards Institution

8 BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution

9 BS EN 482:2006 *Workplace atmospheres: general requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

You should use the most current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

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