

# MDHS

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



# 52/3

## Hexavalent chromium in chromium plating mists

Colorimetric field method using  
1,5-diphenylcarbazide

April 1998

### INTRODUCTION

**Note 1:** This method updates and replaces MDHS 52/2.<sup>1</sup> The principal changes which have been made are (i) to recommend an additional filter suitable for sample collection, (ii) to incorporate information on the test procedure for monitoring emissions from electrolytic chromium processes, that was previously given in *Environmental Hygiene Series Guidance Note EH 6*,<sup>2</sup> (iii) to reduce the minimum sampling time from 1 hour to 15 minutes, except for measurements made with a comparator, and (iv) to withdraw the requirement to apply a factor to correct results for incomplete recovery of hexavalent chromium from the filter, which recent studies have shown to be unwarranted.

### Requirements of the Control of Substances Hazardous to Health (COSHH) Regulations 1994

#### General requirements of the COSHH Regulations

1 Those who carry out and supervise the procedures described in this MDHS could be exposed to various hazardous substances, and therefore should also be aware of the requirements of the COSHH Regulations.<sup>3</sup> These are designed to ensure that the exposure of people at work to substances that could cause health damage is either prevented, or where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who could be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

2 Guidance is given in the Approved Codes of Practices for the Control of Substances Hazardous to Health, the General COSHH ACOP, and the Control of Carcinogenic Substances, the Carcinogens ACOP, which are included in a single publication with the COSHH Regulations.<sup>4</sup>

### Requirements of the COSHH Regulations specific to electrolytic chromium processes

3 Regulation 10(2) of the COSHH Regulations<sup>3</sup> requires that, for the specific substances and processes listed in Schedule 4 of the Regulations, monitoring is carried out to demonstrate that control measures are properly used and maintained. 'Spray given off from vessels at which an electrolytic chromium process is carried out, except trivalent chromium' is one of the processes listed in Schedule 4, with a requirement that monitoring is to be carried out every 14 days.

4 Regulation 10(2) of the COSHH Regulations<sup>3</sup> may be complied with by using the method described in this MDHS to measure the concentration of hexavalent chromium in the air above or adjacent to chromium plating baths, and demonstrating that this is below 0.05 mg m<sup>-3</sup>. In such circumstances, personal exposure of chromium plating workers is assumed to be kept well below the maximum exposure limit (see paragraph 15). Provided that control measures are properly applied, used and maintained, they should be capable of keeping the concentration of hexavalent chromium in the air above or adjacent to chromium plating baths well below this level. An Engineering Information Sheet<sup>5</sup> gives guidance on how to control exposure to chromium plating mist.

### Occurrence, properties and uses

5 Occurrence, properties and uses of chromium and its inorganic compounds, including hexavalent chromium compounds, are fully covered in HSE Guidance Note EH 2.<sup>6</sup> Soluble hexavalent chromium compounds, and in particular chromium trioxide, are used extensively as electrolytes in electroplating and anodising. In these processes the bursting of small bubbles of gases generated by electrolysis causes the formation of mists composed of fine droplets of electrolyte. These are commonly referred to as chromium plating mists.

## Health effects

6 The health effects of chromium and its inorganic compounds, including hexavalent chromium compounds, are summarised in HSE Guidance Note EH 2<sup>6</sup> and are fully covered in HSE Toxicity Review TR 21.<sup>7</sup>

7 Hexavalent chromium compounds may be absorbed into the body following inhalation exposure, although the extent of absorption depends on solubility. Some absorption may also occur following ingestion and there is also some absorption of hexavalent chromium across the skin. Once absorbed, hexavalent chromium binds to red blood cells, and may remain in the body for several weeks, before elimination as chromium (III), mainly in the urine.

8 Hexavalent chromium compounds are very toxic following single inhalation exposure; the principal effects involve severe irritancy to the eyes and respiratory tract. Hexavalent chromium compounds are skin irritants and can produce an allergic skin response (skin sensitisation) as well as occupational asthma (respiratory sensitisation).

9 Repeated inhalation exposure to soluble hexavalent chromium compounds leads to irritation, inflammation and ulceration of the respiratory tract, with fibrosis and emphysema also reported.

10 In relation to genotoxicity and carcinogenicity, there are no reliable human data. However, the results of animal studies raise concerns for the potential for hexavalent chromium compounds to cause genetic damage and to produce lung cancer following inhalation. From the very limited information available, there does not appear to be any concern for effects on the developing fetus. There is no information in relation to effects on fertility.

11 Chromium (VI) compounds are classified in the Approved Supply List<sup>8</sup> of the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994<sup>9</sup> (the 'CHIP 2' Regulations) as:

Carc. Cat. 2; R49 May cause cancer by inhalation  
R43 May cause sensitisation by skin contact

12 Individually, chromium trioxide is classified in the Approved Supply List<sup>8</sup> of the 'CHIP 2' Regulations<sup>9</sup> as:

Carc. Cat. 1; R49 May cause cancer by inhalation  
R25 Toxic if swallowed  
R35 Causes severe burns  
R43 May cause sensitisation by skin contact

13 Reference should be made to the Approved Supply List<sup>8</sup> of the 'CHIP 2' Regulations<sup>9</sup> for the appropriate classification of other individual chromium (VI) compounds.

## Health and safety precautions

14 HSE leaflet MS(A)16<sup>10</sup> summarises the risks involved in working with chromium and what can be done to control them. Prevention and control of exposure, emergency procedures and health surveillance are described more fully in HSE Guidance Note EH 2.<sup>6</sup>

## Exposure limit

15 Schedule 1 of the *COSHH Regulations*<sup>3</sup> specifies a maximum exposure limit (MEL) of 0.05 mg m<sup>-3</sup>, 8-hour time-weighted average reference period, for chromium (VI) compounds (as Cr). This limit is reproduced in HSE Guidance Note EH 40<sup>11</sup> and the criteria on which it is based are documented in HSE Guidance Note EH 64.<sup>12</sup>

## Analytical methods

16 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. 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 that they have been shown to have the accuracy and reliability appropriate to the application.

17 This method has been validated<sup>13</sup> to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.<sup>14</sup> If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

## SCOPE

18 This MDHS describes a field method for measuring the concentration of hexavalent chromium in workplace air containing chromium plating mist. This method is suitable for making fixed point measurements above or adjacent to chromium plating baths, for the purpose of demonstrating compliance with Regulation 10(2) of the *COSHH Regulations*.<sup>3</sup> Sampling times in the range 15 minutes to 2 hours are recommended<sup>13</sup> for measurements made using a spectrophotometer or colorimeter, but a minimum sampling time of 1 hour should be used when measurements are made using a comparator (see note 3).

19 The method can also be used for measuring personal exposure to hexavalent chromium. However, personal exposures are normally substantially lower than the lower limit of the working range of the method (see paragraph 20) unless control of chromium plating mist emissions is poor. It is therefore recommended that, where possible (see note 2), personal exposure to hexavalent chromium is assessed by measuring total chromium.

**Note 2:** *Measuring procedures for total chromium in air,*

eg MDHS 12/2,<sup>15</sup> 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. 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 measurements.

## METHOD PERFORMANCE

### Lower limit of the working range

20 The qualitative and quantitative detection limits for hexavalent chromium, defined as three times and ten times the standard deviation of a blank determination, have been determined<sup>13</sup> to be 0.04 µg and 0.14 µg. For the minimum air sample volume of 30 litres this corresponds to hexavalent chromium-in-air concentrations of 0.0015 mg m<sup>-3</sup> and 0.005 mg m<sup>-3</sup>, respectively. However, field trials<sup>16</sup> have shown that recovery of hexavalent chromium is affected by the presence of dust or reducing agents in the sampled air (see paragraph 36). In such circumstances the lower limit of the working range of the method can increase from 0.005 mg m<sup>-3</sup> to as much as 0.05 mg m<sup>-3</sup> (see paragraph 38). Nevertheless, a more usual value for the lower limit of the working range, which will apply under most circumstances, is 0.025 mg m<sup>-3</sup>. This is adequate for making fixed point measurements above or adjacent to chromium plating baths, for the purpose of demonstrating compliance with Regulation 10(2) of the COSHH Regulations,<sup>3</sup> but the method is clearly of limited use for making personal exposure measurements.

### Bias

#### Sampler bias

21 The bias of inhalable samplers has been shown<sup>17</sup> to vary considerably. However, a bias of less than ±5% is typical for the samplers recommended in MDHS 14/2.<sup>18</sup> This value was therefore used when estimating the bias of the measuring procedure as a whole using Equation 1.

#### Analytical bias

22 The mean analytical recovery for 90 filters spiked with between 0.3 µg and 24.0 µg of Cr(VI) has been determined<sup>13</sup> to be 98.4 ± 4.4%.

23 Laboratory experiments<sup>13</sup> therefore indicate that the analytical method does not exhibit significant bias. An analytical bias of zero was therefore substituted in Equation 1 when estimating the bias of the measuring procedure as a whole.

#### Combination of sampling and analytical bias

24 The bias of the measuring procedure as a whole is given by:

$$(1 + bias) = (1 + bias_{\text{sampler}}) \times (1 + bias_{\text{analysis}}) \quad \text{Equation 1}$$

## Precision

### Imprecision of the aerosol sampling process

25 The imprecision of the aerosol sampling process usually depends strongly on the size distribution of the airborne particles sampled, and it can depend on other factors, such as windspeed. Draft European Standard EN (00137009)<sup>19</sup> suggests calculating approximate values of the imprecision of the sampling process relevant to the workplace atmosphere to be sampled, using information given in the sampler test report.

26 However, this approach is not practicable for assessing the performance of a measuring procedure intended for general application. The results of a study to evaluate the performance of inhalable samplers<sup>17</sup> suggest that the relative standard deviation of the aerosol sampling process is normally less than 5% for inhalable samplers that meet the requirements of draft European Standard EN (00137009).<sup>19</sup> The relative standard deviation of the aerosol sampling process,  $RSD_{\text{sampler}}$ , was therefore taken to be 5% when estimating the imprecision of the measuring procedure as a whole using Equation 2. Imprecision arising from flow rate variability

27 In the case of aerosol samplers where there is no interaction between particle size selection characteristics and volumetric flow rate, at least for small changes in flow rate, the imprecision arising from flow rate variability can be estimated simply. BS EN 1232 *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods*<sup>20</sup> prescribes a maximum allowable error in the volumetric flow rate of ±5%. Assuming that this is met on 99% of all occasions, the flow-related relative standard deviation,  $RSD_{\text{flow}}$ , is equal to 0.05/3. This value was therefore used when estimating the imprecision of the measuring procedure as a whole using Equation 2.

### Imprecision arising from analytical variability

28 The relative standard deviation of the analytical method,  $RSD_{\text{analysis}}$ , has been determined<sup>13</sup> to be less than 4% for samples in the range 0.15 µg to 24.0 µg, for measurements made with a spectrophotometer. The determined relative standard deviations were substituted in Equation 2 to estimate the imprecision of the measuring procedure as a whole for each mass of hexavalent chromium.

**Note 3:** *The precision of measurements made with a comparator has not been determined, but comparator measurements are less precise than measurements made with a spectrophotometer or colorimeter. The recommended minimum sampling time is therefore increased from 15 minutes to 1 hour when analysis is carried out using a comparator (see paragraph 73).*

### Combination of sampling and analytical precision

29 The imprecision of the measuring procedure as a whole is given by:

$$RSD^2 = RSD_{\text{sampler}}^2 + RSD_{\text{flow}}^2 + RSD_{\text{analysis}}^2 \quad \text{Equation 2}$$

### Overall uncertainty

30 The overall uncertainty for a measuring procedure is defined in BS EN 482<sup>14</sup> as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is expressed in percentage terms, by a combination of bias and precision according to the following equation:

$$OU = \frac{|\bar{x} - x_{\text{ref}}| + 2\sigma_{(n-1)}}{x_{\text{ref}}} \times 100\% \quad \text{Equation 3}$$

where: *OU* is the overall uncertainty of the procedure;

$\bar{x}$  is the mean value of results of *n* repeated measurements;

$x_{\text{ref}}$  is the true or accepted reference value; and

$\sigma_{(n-1)}$  is the standard deviation of *n* repeated measurements.

31 Equation 3 can be rewritten as:

$$OU = [|\textit{bias}| + (2 \times RSD)] \times 100\% \quad \text{Equation 4}$$

where: *bias* is the difference between the mean measured concentration and the true or reference concentration, divided by the true or reference concentration, ie  $\frac{(\bar{x} - x_{\text{ref}})}{x_{\text{ref}}}$ ; and

*RSD* is the relative standard deviation of *n* repeated measurements defined as  $\frac{\sigma_{(n-1)}}{x_{\text{ref}}}$ .

32 The overall uncertainty can then be estimated by substituting in Equation 4 the values for bias and relative standard deviation calculated using Equations 1 and 2. In this manner, the overall uncertainty for measurements made with a spectrophotometer has been estimated<sup>13</sup> 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.

33 BS EN 482<sup>14</sup> prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be <50% for measurements in the range 0.1 to 0.5 times the limit value, and <30% for measurements in the range 0.5 to 2.0 times the limit value.

34 The spectrophotometer or colorimeter method therefore complies with the overall uncertainty requirements of BS EN 482<sup>14</sup> when measuring hexavalent chromium in air concentrations between 0.1 and 2 times the maximum exposure limit (see paragraph 15) using

sampling times between 15 minutes and 2 hours and a volumetric flow rate of 2 l min<sup>-1</sup>.

35 The performance of the comparator method has not been fully characterised. However, by analogy with the spectrophotometer method, it is expected that the comparator method will comply with the overall uncertainty requirements of BS EN 482<sup>14</sup> provided that a minimum sampling time of 1 hour is used.

### Interferences

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

37 Field trials<sup>16</sup> indicate that the maximum negative bias observed is typically around 0.005 mg m<sup>-3</sup> of hexavalent chromium. However, dust generated by grinding metal components in preparation for plating has been found<sup>16</sup> to lead to serious underestimates of hexavalent chromium-in-air concentrations.

38 It has been estimated<sup>13</sup> that, in order for this method to comply with the CEN requirements for overall uncertainty, as prescribed in BS EN 482,<sup>14</sup> the bias of the analytical method should be no greater than 10%. On this basis, potential interference by reducing agents and dust (see paragraph 37) can increase the lower limit of the working range from 0.005 mg m<sup>-3</sup> to 0.05 mg m<sup>-3</sup> of hexavalent chromium.

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

### PRINCIPLE

40 The method described is based upon the spectrophotometric determination of the magenta chromagen ( $\lambda_{\text{max}} = 540 \text{ nm}$ ) formed when 1,5-diphenylcarbazide reacts with hexavalent chromium in sulphuric acid solution.

41 A sample of chromium plating mist is collected by drawing a measured volume of air through a sodium hydroxide-treated membrane filter mounted in an inhalable sampler.

42 The filter is leached with dilute sulphuric acid to dissolve any soluble hexavalent chromium compounds present, the colorimetric reagent (1,5-diphenylcarbazide solution) is mixed with the sample solution, and the colour developed is measured after a ten minute delay using a spectrophotometer, colorimeter or comparator.

43 If a spectrophotometer or colorimeter is used to measure the colour developed, hexavalent chromium-in-air concentrations are determined by a calibration curve technique. If a comparator is used, hexavalent chromium-in-air concentrations are estimated by visual comparison of the colour developed with standard colour discs. The

comparator method has the advantage of simplicity, since no calibration standards need to be prepared, and no calibration of instrumentation is necessary. However, by its very nature, the comparator method yields less precise results.

## REAGENTS

44 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 45). Do not pipette by mouth.

### Water

45 Water complying with the requirements of BS 3978<sup>21</sup> grade 2 water (electrical conductivity less than 0.1 mS m<sup>-1</sup> and resistivity greater than 0.01 MΩ.m at 25°C).

### Sodium hydroxide pellets

46 The concentration of hexavalent chromium shall be less than 10 µg kg<sup>-1</sup>.

### Sodium hydroxide solution, 1 M

47 Dissolve 4 g of sodium hydroxide pellets (paragraph 46) in 50 ml of water (paragraph 45). Allow to cool and quantitatively transfer to a 100 ml volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

### Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), concentrated, ρ about 1.84 g ml<sup>-1</sup>, about 98% (m/m)

48 The concentration of hexavalent chromium shall be less than 0.1 µg ml<sup>-1</sup>.

**WARNING** - Concentrated sulphuric acid is corrosive and causes burns. Avoid exposure by contact with the skin or eyes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with the concentrated or diluted sulphuric. Fumes produced by heating concentrated sulphuric acid are irritant, and this operation should therefore be carried out in a fume hood. Caution should be exercised if adding water to sulphuric acid, since this reacts violently with water (preferably prepare acid/water mixtures by adding acid to water).

### Sulphuric acid, 0.25 M

49 Add approximately 500 ml of water (paragraph 45) to a 1 litre volumetric flask. Carefully add 14 ml of concentrated sulphuric acid (paragraph 48) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

### 1,5-diphenylcarbazide solution, 0.25% (m/v) in 50% (v/v) acetone

50 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 (paragraph 45), stopper and mix thoroughly.

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

### Stock standard hexavalent chromium solution, 1000 µg ml<sup>-1</sup> of Cr(VI)

52 Use a commercially available standard hexavalent chromium solution at a concentration of 1000 µg ml<sup>-1</sup>. Observe the manufacturer's expiry date or recommended shelf life.

Alternatively prepare a standard hexavalent chromium solution by the following procedure:

53 Accurately weigh 2.828 g ± 0.001 g of dried potassium dichromate, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, into a 100 ml beaker, add 25 ml of water (paragraph 45) and swirl to dissolve. Quantitatively transfer to a 1 litre volumetric flask, dilute to the mark with water and mix thoroughly.

**Note 4:** Hexavalent chromium standard solution prepared according to the instructions in paragraph 53 may be stored in a polypropylene bottle (paragraph 65) for a period of one year without deterioration.

**WARNING** - Hexavalent chromium compounds have been assigned various risk phrases in the Approved Supply List<sup>8</sup> of the 'CHIP 2' Regulations<sup>9</sup> (see paragraphs 11-13). Great care should be taken when working with potassium dichromate and solutions containing hexavalent chromium to avoid skin contamination.

### 'Working' standard hexavalent chromium solution, 100 µg ml<sup>-1</sup> of Cr(VI)

54 Accurately pipette 10.0 ml of stock standard hexavalent chromium solution (paragraph 52 or 53) into a 100 ml volumetric flask, and dilute to the mark with water (paragraph 45), stopper and mix thoroughly.

55 This solution should be stable for up to one year.

### Laboratory detergent solution

56 A laboratory grade detergent suitable for cleaning of samplers and laboratory glassware, diluted with water (paragraph 45) according to the manufacturer's instructions.

## SAMPLING EQUIPMENT

### Inhalable samplers

57 Samplers, with protective covers, designed to collect the inhalable fraction of airborne particles, as defined in BS EN 481,<sup>22</sup> and complying with the provisions of draft European Standard EN (00137009).<sup>19</sup> Inhalable samplers suitable for personal sampling are described in MDHS 14/2.<sup>18</sup>

**Note 5:** In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling. However, they are suitable for use when

making fixed point measurements above or adjacent to chromium plating baths for the purpose of demonstrating compliance with Regulation 10(2) Schedule 4 of the COSHH Regulations.<sup>3</sup>

**Note 6:** Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge which can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample. It is advisable to avoid using such samplers, since otherwise it will be necessary to rinse the internal surfaces with 0.25 M sulphuric acid in the analytical step (see paragraph 96).

**Note 7:** Samplers manufactured in non-conducting material have electrostatic properties which can influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.

#### Filters

58 Filters, of a diameter suitable for use in the samplers (paragraph 57), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter, and suitable for collection of hexavalent chromium in chromium plating mists. Sodium hydroxide-treated hydrophilic Durapore<sup>®</sup> modified polyvinylidene fluoride membrane filters, 5 µm pore size, manufactured by Millipore, or sodium hydroxide-treated DM Metrice<sup>®</sup> 800 vinyl/acrylic co-polymer membrane filters, 0.8 µm pore size, manufactured by Gelman, are recommended. Prepare these by soaking the filters overnight in 1 M sodium hydroxide solution (paragraph 47), and allowing them to dry in a chromium-free environment.

**Note 8:** Sodium hydroxide-treated Durapore<sup>®</sup> filters and sodium hydroxide-treated DM 800 filters are chromium-free (ie contain less than 0.01 µg of chromium, extractable under the conditions of the test).

**Note 9:** Details of other filters which may be used are given in Appendix C.

#### Sampling pumps

59 Sampling pumps, complying with the provisions of BS EN 1232,<sup>20</sup> and compatible with the samplers used (paragraph 57).

**Note 10:** Existing users may continue to use sampling pumps that do not fully comply with the provisions of BS EN 1232,<sup>20</sup> provided that they take steps to ensure that the required volumetric flow rate (see paragraph 72) is maintained to within ±5% of the nominal value throughout the sampling period.

60 BS EN 1232<sup>20</sup> requires that sampling pumps have, as a minimum, the following features:

- an automatic control which keeps the volumetric flow rate constant in the case of changing back pressure;
- either a malfunction indicator, which, following completion of sampling, indicates that the air flow has been reduced or interrupted during sampling; or an automatic cut-out, which stops the pump if the flow rate is reduced or interrupted; and
- a facility for the adjustment of flow rate, such that it can only be actuated with the aid of a tool (eg screw driver) or requires special knowledge for operation (eg via software), so as to preclude inadvertent readjustment of the flow rate during use.

**Note 11:** An integral timer is a highly desirable additional feature.

61 BS EN 1232<sup>20</sup> requires that the performance of the pumps is such that:

- the pulsation of the flow rate does not exceed 10%;
- a flow rate set within the nominal range does not deviate by more than ±5% from the initial value under increasing back pressure;
- within the range of ambient temperatures from 5°C to 40°C, the flow rate measured under operating conditions does not deviate by more than ±5% from the flow rate at 20°C;
- the operating time is at least 2 h, and preferably 8 h; and
- the flow rate does not deviate by more than ±5% from the initial value during the operating time.

#### Flowmeter

62 Flowmeter, portable, capable of measuring the required volumetric flow rate (see paragraph 72) to within ±1%, and calibrated against a primary standard, ie a flowmeter whose accuracy is traceable to national standards.

**Note 12:** Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers (see note 20), provided they have adequate sensitivity.

#### Ancillary equipment

63 Flexible tubing, of a diameter suitable for ensuring a leakproof fit, to connect the sampler to the pump; a belt to which the pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport

cassettes, or similar, if required (see paragraph 87), in which 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 (see paragraph 80).

## LABORATORY APPARATUS

### Glassware, made of borosilicate glass

64 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS 1792.<sup>23</sup>

**Note 13:** *Chromic acid shall not be used for cleaning any glassware used in this method.*

**Note 14:** *It is recommended that a set of glassware is reserved for the analysis of hexavalent chromium by this method (see paragraph 94).*

### Polypropylene bottle

65 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraphs 52 and 53) cleaned before use by soaking in 0.25 M sulphuric acid (paragraph 49) for at least 24 hours and then rinsing thoroughly with water (paragraph 45). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

### Disposable gloves

66 Disposable gloves, impermeable, to protect the hands from contact with toxic and corrosive substances. PVC gloves are suitable.

### Disposable labware

67 Disposable plastic beakers are a useful alternative to 50 ml glass beakers, and are suitable for use in various stages of the analytical procedure described. These should be chromium-free (ie contain less than 0.01 µg of chromium, extractable under the conditions of the test).

### Piston operated volumetric apparatus (POVA)

68 An adjustable micropipette covering the range 20 µl to 200 µl is recommended for preparation of calibration solutions. Additional micropipettes, multi-dispensing pipettes, or bottletop dispensers are recommended for reagent addition and for dilution of the sample solution. POVA used shall comply with the requirements of BS 7653-1 to BS 7653-4.<sup>24-27</sup>

**Note 15:** *POVA should be of the positive displacement type when handling solutions with a volatile component, eg 1,5-diphenylcarbazine solution (paragraph 50).*

**Note 16:** *If the comparator technique is used, less accurate apparatus (eg measuring cylinders) may be*

*used for dispensing 0.25 M sulphuric acid and 1,5-diphenylcarbazine solution, since the precision of the analytical measurement is such that use of POVA is unwarranted.*

### Spectrophotometer, colorimeter or comparator

*Either*

69 A spectrophotometer or colorimeter capable of measuring in the region of 540 nm, together with appropriate flow-through cell, matched cells or measuring tubes (10 mm path length), is required if the procedure described in paragraphs 104-109 is to be followed.

*or*

70 A Lovibond comparator, 'Chromium (VI)' comparator disc 6/62, and comparator tubes are required if the procedure described in paragraphs 110-113 is to be followed. 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<sup>-3</sup> of hexavalent chromium for the recommended minimum sample volume of 120 litres of air. (This apparatus is available from The Tintometer Ltd, The Colour Laboratory, Waterloo Road, Salisbury, SP1 2JY.)

## SAMPLING

### Preliminary considerations

#### *Suitability of the measuring procedure*

71 Give consideration to whether there could be a significant amount of reducing agents or dust present in the workplace air, since their presence can lead to low results (see paragraphs 36-38). If it is believed that there could be significant interference, follow the procedure given in Appendix D to assess whether the method is suitable for use under the test conditions.

#### *Use of samplers*

72 Use the samplers (paragraph 57) at their design flow rate, and in accordance with the instructions provided by the manufacturer, so that they collect the intended fraction of airborne particles.

#### *Sampling period*

73 Select an appropriate sampling period, taking into account the purpose of the measurement. A minimum sampling time of 15 minutes is recommended when analysis is carried out using a spectrophotometer or colorimeter, or 1 hour when analysis is carried out using a comparator. Advice on monitoring strategies for toxic substances is given in Health and Safety Guidance Booklet HS(G) 173.<sup>28</sup> For measurements made above or adjacent to chromium plating baths, for the purpose of demonstrating compliance with Regulation 10(2) of the COSHH Regulations,<sup>3</sup> sampling shall be carried out while the current is being passed

through the chromic acid solution under normal operating conditions.

### **Handling of filters**

74 To minimise the risk of damage or contamination, only handle filters using flat-tipped tweezers (paragraph 63), in a clean area. Wear disposable gloves (paragraph 66) to prevent the possibility of contamination.

### **Preparation for sampling**

#### **Cleaning of samplers**

75 Clean the samplers (paragraph 57) before use. Disassemble the samplers, soak in laboratory detergent solution, rinse thoroughly with water (paragraph 45), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

#### **Loading the samplers with filters**

76 Load clean samplers (see paragraph 75) with filters (paragraph 58), label each sampler so that it can be uniquely identified, and seal with its protective cover to prevent contamination.

#### **Setting the volumetric flow rate**

*Perform the following in a clean area, where the concentration of airborne particles is low:*

77 Connect each loaded sampler (paragraph 76) to a sampling pump (paragraph 59) using flexible tubing (paragraph 63), ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the sampling pump, attach the calibrated flowmeter (paragraph 62) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate (see paragraph 72). Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

**Note 17:** *If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).*

#### **Blanks**

78 Retain as blanks, one unused loaded sampler from each batch of ten prepared, subject to a minimum of three. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through the filters.

### **Sampling position**

#### **Static sampling for testing compliance with Regulation 10(2) of the COSHH Regulations**

##### *General*

79 Place the sampler (paragraph 77) in a suitable position above or adjacent to the chromium plating bath,

where it will collect any uncontrolled emission of chromium acid mist. The exact position will depend on the process, the type of plant used and the degree of enclosure. In particular, it is necessary to avoid placing the sampler in a position where it will impede the process, or where it is likely to be contaminated by electrolyte splashes when jigs are placed or removed. Observe the guidelines given in paragraphs 80-84 when selecting the sampling position, and always sample at the same position when making repeat measurements.

##### *Manual baths*

80 Position the sampler (paragraph 77) 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 suppressant is used without extraction ventilation, position the sampler 300 mm above the surface of the electrolyte, with the filter in the vertical position.

**Note 18:** *As an alternative to sampling during normal working, sampling may be carried out while using a dummy cathode of similar surface area to the average batch process, operated at the same current density. This procedure is preferred as it will eliminate the various problems likely to be encountered while sampling for one hour during manual decorative chrome plating, such as impeding transfer of jigs and risks of splashing the sampler.*

##### *Automatic and semi-automatic processes*

81 Placing the sampler over the bath is impracticable on grounds of safety. 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 (paragraph 77) at the sampling point, with its inlet orientated toward the centre of the bath and with the filter in the vertical position.

##### *Enclosed processes*

82 Enclosed systems are usually provided with access points to the chromium plating bath for purposes of process control. 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 (paragraph 77) at the sampling point, with its inlet orientated toward the centre of the bath and with the filter in the vertical position.

#### **Personal sampling**

83 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 63) around the waist, or place it in a convenient pocket.

## Collection of samples

84 When ready to begin sampling, remove the protective cover from the sampler and switch on the sampling pump. Record the time and volumetric flow rate at the start of the sampling period, and if the sampling pump is fitted with an integral timer, check that this is reset to zero.

**Note 19:** *If the temperature or pressure at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 77), the volumetric flow rate could change and it might need to be re-adjusted before sampling.*

**Note 20:** *If the sampling pump used does not comply with BS EN 1232<sup>20</sup> (see note 10), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 62) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within  $\pm 5\%$  of the nominal value throughout the sampling period.*

85 At the end of the sampling period (see paragraph 73), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the calibrated flowmeter (paragraph 62), and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

86 Carefully record the sample identity and all relevant sampling data (see Appendix A).

## Transportation

87 For samplers which collect airborne particles on the filter (see note 6), remove the filter from each sampler, place in a labelled filter transport cassette (paragraph 63) and close with a lid. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

88 For samplers which have an internal filter cassette (see note 6), remove the filter cassette from each sampler and fasten with its lid or transport clip.

89 For samplers designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, but which do not have an internal filter cassette (see note 6), transport the samples to the laboratory in the samplers in which they were collected.

90 Transport the samples (paragraphs 87-89) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

91 Proceed with the analysis immediately after sampling. If this is impracticable, store the sample in a cool dark location until analysis is possible. Analysis can be carried out for up to four weeks after sampling provided

the samples were taken on sodium hydroxide-treated filters and are sealed in air-tight containers.

**Note 21:** *Hexavalent chromium can be reduced by plasticisers released into the air from plastic. For this reason, sample filters should not be stored in plastic bags or plastic containers made from polymers containing plasticisers.*

## ANALYSIS

*Wear disposable gloves (paragraph 66) during analysis to protect the hands from toxic, corrosive and oxidising reagents.*

### Cleaning of glassware

92 Before use, clean all glassware (paragraph 64) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 56) and then rinse thoroughly with water (paragraph 45). Alternatively, use a laboratory washing machine.

93 After initial cleaning (paragraph 92), clean all glassware by soaking in 0.25 M sulphuric acid (paragraph 49) for at least 24 hours and then rinsing thoroughly with water (paragraph 45).

94 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 92 and 93, and which has been reserved for determination of hexavalent chromium by this method, can be adequately cleaned by rinsing thoroughly with 0.25 M sulphuric acid (paragraph 49) and then with water (paragraph 45).

### Preparation of sample and blank solutions

95 Open the filter transport cassettes (see paragraph 87), sampler filter cassettes (see paragraph 88) or samplers (see paragraphs 87 and 89) and transfer each filter into an individual, labelled, disposable plastic beaker (paragraph 67) or 50 ml glass beaker (paragraph 64) using clean flat-tipped tweezers (paragraph 63). Follow the same procedure for the blanks (paragraph 78).

96 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler form part of the sample (see note 6), wash any particulate material adhering to the internal surfaces into the beaker using an aliquot of the 8 ml of 0.25 M sulphuric acid used to leach the sample filters (see paragraph 97).

97 Accurately add 8 ml of 0.25 M sulphuric acid (paragraph 49) to each beaker. Wait twenty minutes for dissolution of the sample to take place, swirling the solution occasionally, and proceed as in paragraph 99.

### Preparation of solutions for calibration of the spectrophotometer or colorimeter

98 Accurately dispense 0, 20, 40, 60, 80 and 100  $\mu\text{l}$  of the working standard hexavalent chromium solution (paragraph 54) into separate disposable plastic beakers (paragraph 67) or 50 ml glass beakers (paragraph 64).

Accurately add 8 ml of 0.25 M sulphuric acid (paragraph 49), and proceed as in paragraph 99.

### Colour development

99 Accurately add 2 ml of 1,5-diphenylcarbazide solution (paragraph 50) to the calibration solution (paragraph 98) or sample solution (paragraph 97), and swirl to mix. Wait ten minutes, swirling the solution occasionally, then transfer the solution to the cell or measuring tube of the spectrophotometer/colorimeter/comparator, following the instructions in paragraphs 100 and 101, and make measurements as prescribed in paragraph 102 or 103.

**Note 22:** *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.*

### Filling the cell or measuring tube

100 Rinse the cell or measuring tube with water (paragraph 45) between each blank, sample, or calibration solution.

101 Transfer each blank, sample, or calibration solution (paragraph 99) to the cell or measuring tube, by firstly rinsing out with the blank, sample, or calibration solution concerned and then re-filling for measurement purposes. Follow this procedure in order to ensure that there is no dilution with traces of water remaining in the cell or measuring tube following rinse out of the previous blank, sample, or calibration solution (see paragraph 100).

### Measurement

#### Either

102 Measure the absorbance using a spectrophotometer or colorimeter, as described in paragraphs 104-109.

or

103 Determine the hexavalent chromium-in-air concentration directly using a comparator, by visual comparison of colour intensity with standard colour discs, as described in paragraphs 110-113.

### Absorbance measurement using a spectrophotometer or colorimeter

104 Set up the spectrophotometer or colorimeter (paragraph 69) to make measurements at a wavelength of 540 nm, the maximum absorbance of the magenta chromogen, as recommended in the manufacturer's handbook. At this wavelength the sensitivity for hexavalent chromium (concentration giving an absorbance measurement of 0.0044 units) is about 0.0055  $\mu\text{g ml}^{-1}$  using a 10 mm path-length cell or measuring tube. A linear calibration graph is obtained for calibration standards from 0 to 1  $\mu\text{g ml}^{-1}$  of hexavalent chromium.

105 Adjust the spectrophotometer or colorimeter zero with water (paragraph 45) in the cell or measuring tube, and then determine the absorbances of the calibration solutions in increasing order of concentration. Plot a calibration graph of absorbance against concentration.

**Note 23:** *The calibration solutions prepared in paragraphs 98 and 99 nominally contain 0, 0.2, 0.4, 0.6, 0.8, and 1.0  $\mu\text{g ml}^{-1}$  of hexavalent chromium (see Appendix B).*

106 Measure the absorbances of the blank and sample solutions, and obtain the concentration of hexavalent chromium in these solutions from the calibration graph. Then use Equation 6 (see paragraph 115) to calculate hexavalent chromium-in-air concentrations.

107 Check the spectrophotometer or colorimeter zero regularly throughout the measurement period with water (paragraph 45) in the cell or measuring tube. Re-adjust as necessary.

108 If the hexavalent chromium concentration of a sample solution is found to be over-range, ie greater than 1  $\mu\text{g ml}^{-1}$ , dilute the sample solution by a suitable factor with 0.25 M sulphuric acid (paragraph 49) and 1,5-diphenylcarbazide solution (paragraph 50) that have been pre-mixed in the ratio 4:1. Do this without delay, and immediately carry out measurement on the diluted solution. Record the dilution factor. Then use Equation 5 (see paragraph 116) to calculate hexavalent chromium-in-air concentrations.

109 Calculate the mean hexavalent chromium concentration of the blank solutions.

### Determination of hexavalent chromium-in-air concentrations using a comparator

110 Place the cell containing the sample solution in the right-hand side of the Lovibond comparator (paragraph 70), and a cell containing water (paragraph 45) in the left-hand reference side. Match the colour against the standard 'Chromium (VI)' comparator disc, and read from the disc the apparent concentration of hexavalent chromium-in-air. Measure the blank solutions in an identical manner to the sample solutions, and calculate the mean apparent concentration of hexavalent chromium in air of the blank solution measurements.

111 The apparent concentration of hexavalent chromium-in-air read off the comparator disc is based upon a sample volume of 120 litres of air. If the volume of air sampled was 120 litres ( $\pm 10\%$ ), and if the blank solutions do not produce a measurable apparent hexavalent chromium-in-air concentration, then the apparent concentration of hexavalent chromium-in-air read off the comparator disc may be taken to be the actual concentration of hexavalent chromium-in-air.

112 If the volume of air sampled was other than 120 litres ( $\pm 10\%$ ), or if the blank solutions produce a measurable apparent hexavalent chromium-in-air concentration, then calculate the actual concentration of hexavalent chromium-in-air using Equation 8 (see paragraph 118).

113 If the hexavalent chromium concentration of a sample solution is found to be over-range, ie greater than 0.1 mg m<sup>-3</sup> of hexavalent chromium-in-air, dilute the sample solution by a suitable factor with 0.25 M sulphuric acid (paragraph 49) and 1,5-diphenylcarbazine solution (paragraph 50) that have been pre-mixed in the ratio 4:1. Do this without delay, and immediately carry out measurement on the diluted solution. Record the dilution factor. Then calculate the actual concentration of hexavalent chromium-in-air using Equation 7 (see paragraph 117).

## CALCULATIONS

### Volume of air sample

114 Calculate the mean flow rate during the sampling period by averaging the flow rate measurements taken at the start and end of the sampling period. Then calculate the volume, in litres, of the air sample by multiplying the mean flow rate, in litres per minute, by the sampling time, in minutes.

### Concentration of hexavalent chromium in air

#### Calculation when using a spectrophotometer or colorimeter

115 Calculate the concentration of hexavalent chromium in air,  $\rho(\text{CrVI})$ , in milligrams per cubic metre (mg m<sup>-3</sup>), using the equation:

$$\rho(\text{CrVI}) = \frac{[\rho(\text{CrVI})_1 \times V_1 \times DF_1] - [\rho(\text{CrVI})_0 \times V_0 \times DF_0]}{V} \quad \text{Equation 5}$$

where

$\rho(\text{CrVI})_1$  is the concentration, in  $\mu\text{g ml}^{-1}$ , of hexavalent chromium in the sample solution (see paragraph 106 or 108);

$\rho(\text{CrVI})_0$  is the mean concentration, in  $\mu\text{g ml}^{-1}$ , of hexavalent chromium in the blank solutions (see paragraph 109);

$V_1$  is the volume, in ml, of the sample solution, ie 10 ml (see Appendix B)

$V_0$  is the volume, in ml, of the blank solutions, ie 10 ml (see Appendix B);

$DF_1$  is the dilution factor for the sample solution (see paragraph 108);

$DF_0$  is the dilution factor for the blank solutions, ie 1; and

$V$  is the volume, in litres, of the air sample (see paragraph 114).

116 For normal use the volume of sample and blank solutions is 10 and the dilution factor for sample and blank measurements is 1, so Equation 5 reduces to:

$$\rho(\text{CrVI}) = \frac{[\rho(\text{CrVI})_1 - \rho(\text{CrVI})_0] \times 10}{V} \quad \text{Equation 6}$$

### Calculation when using a comparator

117 Calculate the concentration of hexavalent chromium in air,  $\rho(\text{CrVI})$ , in milligrams per cubic metre (mg m<sup>-3</sup>), using the equation:

$$\rho(\text{CrVI}) = [\rho(\text{CrVI})_1 \times DF_1 - \rho(\text{CrVI})_0 \times DF_0] \times \frac{120}{V} \quad \text{Equation 7}$$

where

$\rho(\text{CrVI})_1$  is the apparent concentration, in mg m<sup>-3</sup>, of hexavalent chromium in air from the sample solution measurement (see paragraph 110 or 113);

$\rho(\text{CrVI})_0$  is the mean apparent concentration, in mg m<sup>-3</sup>, of hexavalent chromium in air of the blank solution measurements (see paragraph 110);

$DF_1$  is the dilution factor for the sample solution (see paragraph 113);

$DF_0$  is the dilution factor for the blank solutions, ie 1;

120 is the volume of air, in litres, for which the comparator disc readings apply; and

$V$  is the volume, in litres, of the air sample (see paragraph 114).

118 For normal use the dilution factor for sample and blank measurements is 1, and there will be no measurable blank, so Equation 7 reduces to

$$\rho(\text{CrVI}) = \rho(\text{CrVI})_1 \times \frac{120}{V} \quad \text{Equation 8}$$

## TEST REPORT

119 Appendix A gives recommendations for information to be included in the test report.

## RECORD KEEPING

120 Maintain a suitable record for each chromium plating bath above or adjacent to which measurements are made. Maintain records in a form that will enable long-term trends in measurement results to be determined by comparing results averaged over consecutive six-month periods. Keep monitoring results for at least five years, as required by Regulation 10(2) of the COSHH Regulations.<sup>3</sup>

## ACTION REQUIRED WHEN HIGH RESULTS ARE OBTAINED

121 If the result of any measurement made above or adjacent to a chromium plating bath is significantly higher than normal or average for that bath, investigate the circumstances to determine the reason for the excursion.

Check the operating conditions and, if applicable, the efficiency of the engineering control measures. If spray suppressants are in use, check whether the appropriate additions have been made.

## QUALITY CONTROL MEASURES

122 Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.<sup>29</sup>

123 If hexavalent chromium analysis is performed frequently it is recommended that internal quality control is performed. In such instances, prepare low and high quality control solutions at 10% and 90% of the calibration range. Analyse these a suitable number of times (eg twenty) on separate occasions, and calculate the mean and standard deviation of the measured hexavalent chromium concentration for each quality control solution. Assuming that the distribution of these values is Gaussian, construct a Shewhart chart for each quality control solution with warning and action limits at  $\pm 2$  SD and  $\pm 3$  SD respectively. Subsequently, analyse the quality control solutions with each analytical batch and plot the result on the Shewhart charts. Compare the internal quality control results with the target values and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.<sup>29</sup> Take care to ensure that the quality control solutions are stored under conditions which ensure maximum stability.

124 It is recommended that all laboratories undertaking the determination of hexavalent chromium in chromium plating mists should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are given in MDHS 71.<sup>29</sup> However, at present the WASP scheme does not encompass hexavalent chromium.

## ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield, S3 7HQ (telephone 0114 289 2000).

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.

## APPENDIX A: Recommendations for the test report

*It is recommended that the test report should include the following information:*

- (a) a complete identification of the air sample, including the date of sampling, the place of sampling, the chromium plating bath for which the fixed point measurement was made, or the identity of the individual whose breathing zone was sampled (see note 24);
- (b) a reference to this MDHS, including information about which analytical technique was used, and a description of any deviation from the procedures described;
- (c) the type, diameter and pre-treatment of filter used;
- (d) the type of sampler used;
- (e) the type of sampling pump used;
- (f) the type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
- (g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- (h) the volume of air sampled, in litres;
- (i) the name of the person who collected the sample;
- (j) the time-weighted average mass concentration of hexavalent chromium found in the air sample, in milligrams per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

**Note 24:** *The precise location of sampling positions above or adjacent to chromium plating baths should be clearly identified for record keeping purposes.*

## APPENDIX B: Notes on preparation of calibration solutions

B1 The calibration solution concentrations given in note 20 are technically not exactly correct, since the final volume obtained on mixing 2 ml of an aqueous solution with 8 ml of a 50% (v/v) acetone solution is not exactly 10 ml. However, for the purposes of this method the calibration solution concentrations are defined as in note 23, and the final volume is defined as 10 ml. In this manner no error is introduced.

B2 The addition of microlitre quantities of working standard hexavalent chromium solution introduces uncompensated error in the final volume of the calibration solutions prepared in paragraphs 98 and 99. However, the maximum error is about 1% (in the case of the high calibration solution), and the overall error in the calibration line is less than this. The error introduced is therefore not significant in the context of the overall uncertainty of the method (paragraph 32).

## APPENDIX C: Notes on the choice of sample filter

C1 Hexavalent chromium in acid solution is a powerful oxidising agent. It reacts with many organic and polymeric materials, and in the process is reduced to the trivalent state. Consequently, the selection of the filter material used for collecting hexavalent chromium plating mists is of paramount importance.

C2 The material from which the filter is made should be chemically inert, and there is an advantage if the oxidising potential of chromic acid mist collected on the filter is counteracted by treating the filter with an alkali. This lessens the tendency of hexavalent chromium to react with organic compounds in the filter material or reducing agents and dust present in the sampled air, and it improves sample stability.

C3 Inert filter materials, such as PVC and PTFE, are inert, but they are also hydrophobic and therefore unsuitable for treatment with alkali since they are not easily wetted. Only two filters have been found which are both inert and sufficiently hydrophilic to be wettable. These are hydrophilic Durapore<sup>®</sup> modified polyvinylidene fluoride membrane filters, manufactured by Millipore, and DM Metrice<sup>®</sup> 800 vinyl/acrylic co-polymer membrane filters, manufactured by Gelman. Hence these filters, treated with sodium hydroxide as described in paragraph 58, are specified in the method as the filters of choice.

C4 Other filters which have been recommended in other countries for sampling hexavalent chromium plating mists include quartz fibre filters and PVC filters (notably Gelman GLA 5000 filters). In field trials,<sup>30,31</sup> both of these filters compared reasonably well with sodium hydroxide-treated Durapore<sup>®</sup> filters, but both had some disadvantages. Nevertheless, the fact that they can be used straight from the packet makes them an attractive alternative to membrane filters which require treatment with sodium hydroxide.

C5 Quartz fibre filters or PVC filters may be used instead of the sodium hydroxide-treated membrane filters specified in the method if it is known that reducing agents and dust are unlikely to be present in significant concentrations in the workplace air, and provided that analysis is carried out on the same day as sampling.

**Note 25:** *If quartz fibre filters or untreated PVC filters are to be used it is recommended that the procedure described in Appendix D is followed to assess whether reducing agents and dust could cause significant interference.*

C6 Quartz fibre filters suffer from the disadvantage that it is necessary to centrifuge sample solutions prior to colorimetric measurement. (This is to remove fibres from suspension which would otherwise give false-positive results due to their light-scattering properties.)

C7 GLA 5000 filters are not easily wetted, and therefore greater care is necessary to ensure that all chromium is washed from the filter during the acid leaching stage of the method. The filters are also more prone to pick up static, making them difficult to handle, and hexavalent chromium collected on the filters is more vulnerable to reduction than on sodium hydroxide-treated membrane filters.

## APPENDIX D: Procedure for assessing whether reducing agents and dust could cause significant interference

D1 Hexavalent chromium plating baths are sometimes sited close to operations that release reducing agents into the air, or in areas with high levels of air pollution. In such cases, hexavalent chromium-in-air concentrations could be underestimated (see paragraphs 36-38). The following procedure may be used to estimate whether extraneous material collected on the filters has the capacity to reduce hexavalent chromium.

D2 Collect a sample of background air in the workplace in which hexavalent chromium-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 filter that will be used in the test method.

D3 Place the sample filter and an unused filter into separate disposable plastic beakers (paragraph 67) or 50 ml glass beakers (paragraph 64). Dispense 60 µl of working standard hexavalent chromium solution (paragraph 54) into each beaker, taking care that the solution does not come in contact with the filters to be analysed.

**Note 26:** *60 µl of working standard hexavalent chromium contains 6.0 µg of hexavalent chromium, which is equivalent to a sample collected at the lower limit of the working range (see paragraph 20) for a sampling time of two hours.*

D4 Analyse the spiked sample and blank filters for hexavalent chromium, as described in paragraphs 95-113.

D5 Compare the hexavalent chromium result obtained for the spiked sample filter with that obtained for the spiked blank filter. 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, the implication is that the method will not comply with the overall uncertainty requirements of BS EN 482.<sup>14</sup>

D6 Under such circumstances, it is recommended that, where possible (see note 2), personal exposure to hexavalent chromium is assessed by measuring total chromium. A suitable measuring procedure for total chromium in air is given in MDHS 12/2.<sup>15</sup>

## REFERENCES

- 1 Health and Safety Executive Methods for the Determination of Hazardous Substances *Hexavalent chromium in chromium plating mists: colorimetric field method using 1,5-diphenylcarbazide* MDHS 52/2 HSE Books 1990 ISBN 0 7176 0346 6
- 2 Health and Safety Executive Environmental Hygiene Series Guidance Note *Chromic acid concentrations in air* EH 6 (revised) HSE Books 1991 ISBN 0 11 885573 5 (withdrawn)
- 3 *Control of Substances Hazardous to Health Regulations 1994* SI 1994/3246 HMSO 1994 ISBN 0 11 043721 7, as amended by the *Control of Substances Hazardous to Health (Amendment) Regulations 1996* SI 1996/3138 HMSO 1996 ISBN 0 11 063430 6, and the *Control of Substances Hazardous to Health (Amendment) Regulations 1997* SI 1997/11 TSO 1997 ISBN 0 11 063577 9
- 4 Health and Safety Commission *General COSHH ACOP (Control of Substances Hazardous to Health) and Carcinogens ACOP (Control of Carcinogens) and Biological Agents ACOP (Control of Biological Agents): Control of Substances Hazardous to Health Regulations 1994 Approved Codes of Practice* L5 HSE Books 1997 ISBN 0 7176 1308 9
- 5 Health and Safety Executive Engineering Information Sheet *Monitoring requirements in the electroplating industry* Engineering Information Sheet 3 HSE Books 1998
- 6 Health and Safety Executive Environmental Hygiene Series Guidance Note *Chromium and its inorganic compounds: health hazards and precautionary measures* EH 2 HSE Books 1998 ISBN 0 7176 1502 2
- 7 Health and Safety Executive Toxicity Review *The toxicity of chromium and inorganic chromium compounds* TR 21 HSE Books 1989 ISBN 0 11 885521 2
- 8 Health and Safety Commission *Approved supply list (supplement to the third edition): information approved for the classification and labelling of substances and preparations dangerous for supply* L76 (suppl) HSE Books 1997 ISBN 0 7176 1378 X
- 9 *Chemicals (Hazard Information and Packaging for Supply) Regulations 1994* SI 1994/3247 HMSO 1994 ISBN 0 11 043877 9, as amended by the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 1996* SI 1996/1092 HMSO 1996 ISBN 0 11 054570 2
- 10 Health and Safety Executive *Chromium and you* leaflet MS(A) 16 HSE Books 1991
- 11 Health and Safety Executive Environmental Hygiene Series Guidance Note *Occupational exposure limits* EH40/98 (updated annually) HSE Books 1998 ISBN 0 7176 1474 3
- 12 Health and Safety Executive Environmental Hygiene Series Guidance Note *Summary criteria for occupational exposure limits* EH 64 1996 HSE Books ISBN 0 7176 1085 3
- 13 Foster R D, Usher J M and Howe A M *Hexavalent chromium in chromium plating mists: colorimetric field method using 1,5-diphenylcarbazide: backup data report for MDHS 52/3* HSL Internal Report IS/97/05 1997
- 14 British Standards Institution *Workplace atmospheres: general requirements for the performance of procedures for the measurement of chemical agents* BS EN 482 BSI 1994 ISBN 0 580 23644 7
- 15 Health and Safety Executive Methods for the Determination of Hazardous Substances *Chromium and inorganic compounds of chromium in air* MDHS 12/2 HSE Books 1996 ISBN 0 7176 1181 7
- 16 Foster R D, Howe A M, Cottrell S J and Northage C *An investigation of the exposure of workers to hexavalent chromium in the air of chrome plating works* HSL Internal Report IR/L/IS/95/15 1996
- 17 Kenny et al A collaborative European study of personal inhalable aerosol sampler performance *Ann Occup Hyg* 1997 **41** 135-153
- 18 Health and Safety Executive Methods for the Determination of Hazardous Substances *General methods for sampling and gravimetric analysis of respirable and total inhalable dust* MDHS 14/2 HSE Books 1997 ISBN 0 7176 1295 3
- 19 Comité Européen de Normalization (CEN)/ Technical Committee 137/Working Group 3 (CEN/TC137/WG3) *Assessment of performance of instruments for measurement of airborne particles* EN (00137009) CEN 1997 CEN/TC137/WG3 document N192
- 20 British Standards Institution *Workplace atmospheres: pumps for personal sampling of chemical agents: requirements and test methods* BS EN 1232 BSI 1997 ISBN 0 580 28328 3
- 21 British Standards Institution *Specification for water for laboratory use* BS 3978 BSI 1993 ISBN 0 580 16312 1
- 22 British Standards Institution *Workplace atmospheres: size fraction definitions for measurement of airborne particles* BS EN 481 BSI 1993 ISBN 0 580 22140 7
- 23 British Standards Institution *Specification for one-mark volumetric flasks* BS 1792 BSI 1993 ISBN 0 580 12754 0
- 24 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 1: Glossary of terms* BS 7653-1 BSI 1993 ISBN 0 580 22114 8

25 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 2: Methods of operation* BS 7653-2 BSI 1993 ISBN 0 580 22123 7

26 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 3: Methods of test* BS 7653-3 BSI 1993 ISBN 0 580 22125 3

27 British Standards Institution *Piston and/or plunger operated volumetric apparatus (POVA) Part 4: Specification for conditions of test, safety and supply* BS 7653-4 BSI 1993 ISBN 0 580 22124 5

28 Health and Safety Executive Health and Safety Guidance Booklet *Monitoring strategies for toxic substances* HSG173 HSE Books 1997 ISBN 0 7176 1411 5

29 Health and Safety Executive Methods for the Determination of Hazardous Substances *Analytical quality in workplace air monitoring* MDHS 71 HSE Books 1991 ISBN 0 11 885976 5

30 Foster R D and Howe A M *Investigation of the performance of filters for sampling chromic acid mist generated by a hard chrome plating process using a 'Sputnik' multiport sampler* HSL Internal Report IR/L/IS/95/04 1995

31 Foster R D and Howe A M *Further investigations of the MDHS 52 method using a 'Sputnik' multiport sampler* HSL Internal Report IR/L/IS/96/01 1996

## TITLES IN THE MDHS SERIES

- |      |                                                                                                      |      |                                                                                                            |
|------|------------------------------------------------------------------------------------------------------|------|------------------------------------------------------------------------------------------------------------|
| 1    | Acrylonitrile charcoal tube/gas chromatography (GC)                                                  | 51/2 | Quartz in respirable dusts <i>X-ray diffraction (direct method)</i>                                        |
| 2    | Acrylonitrile pumped thermal desorption/GC                                                           | 52/3 | Hexavalent chromium in chromium plating mists<br><i>colorimetric (1,5-diphenylcarbazine)</i>               |
| 3    | Standard atmospheres syringe injection                                                               | 53   | 1,3 Butadiene <i>thermal desorption/GC</i>                                                                 |
| 4    | Standard atmospheres permeation tube                                                                 | 54   | Protocol for assessing the performance of a pumped<br>sampler for gases and vapours                        |
| 5    | On-site validation of methods                                                                        | 55   | Acrylonitrile <i>diffusive/thermal desorption/GC</i>                                                       |
| 6/3  | Lead atomic absorption (AA)                                                                          | 56/2 | Hydrogen cyanide <i>ion-selective electrode</i>                                                            |
| 7    | Lead <i>X-ray fluorescence (XRF)</i>                                                                 | 57   | Acrylamide <i>liquid chromatography</i>                                                                    |
| 10/2 | Cadmium AA                                                                                           | 59   | Manmade mineral fibres                                                                                     |
| 12/2 | Chromium AA                                                                                          | 60   | Mixed hydrocarbons                                                                                         |
| 14   | Total inhalable and respirable dust <i>gravimetric</i>                                               | 61   | Total hexavalent chromium compounds in air <i>colorimetric</i>                                             |
| 15   | Carbon disulphide charcoal tube/GC                                                                   | 62   | Aromatic carboxylic acid anhydrides                                                                        |
| 16   | Mercury adsorbent tube (Hydrar) AA                                                                   | 63   | Butadiene <i>diffusive/thermal desorption/GC</i>                                                           |
| 17   | Benzene charcoal tube/GC                                                                             | 64   | Toluene charcoal <i>diffusive/solvent desorption/GC</i>                                                    |
| 18   | Tetra alkyl lead <i>continuous monitoring</i>                                                        | 65   | Mine road dust: determination of incombustible matter                                                      |
| 19   | Formaldehyde <i>colorimetric (Chromotropic acid)</i>                                                 | 66   | Mixed hydrocarbons (C <sub>5</sub> to C <sub>10</sub> ) in air <i>diffusive/<br/>thermal desorption/GC</i> |
| 20   | Styrene pumped charcoal tube/GC                                                                      | 67   | Total (and speciated) chromium in chromium plating mists<br><i>colorimetric (1,5-diphenylcarbazine)</i>    |
| 21   | Glycol ethers charcoal tube/GC                                                                       | 68   | Coal tar pitch volatiles                                                                                   |
| 22   | Benzene thermal desorption/GC                                                                        | 69   | Toluene <i>diffusive/solvent desorption/GC</i>                                                             |
| 23   | Glycol ethers thermal desorption/GC                                                                  | 70   | General methods for sampling airborne gases and vapours                                                    |
| 24   | Vinyl chloride charcoal tube/GC                                                                      | 71   | Analytical quality in workplace air monitoring                                                             |
| 25/2 | Organic isocyanates reagent bubbler/HPLC                                                             | 72   | Volatile organic compounds in air                                                                          |
| 26   | Ethylene oxide charcoal tube/GC                                                                      | 73   | Measurement of air change in factories and offices                                                         |
| 27   | Diffusive sampler evaluation protocol                                                                | 74   | n-Hexane in air <i>diffusive/solvent desorption/GC</i>                                                     |
| 28   | Chlorinated hydrocarbons charcoal tube/GC                                                            | 75   | Aromatic amines <i>solid sorbent/thermal desorption/GC</i>                                                 |
| 29/2 | Beryllium AA                                                                                         | 76   | Cristobalite in respirable dusts <i>X-ray diffraction<br/>(direct method)</i>                              |
| 30/2 | Cobalt AA                                                                                            | 77   | Asbestos in bulk materials                                                                                 |
| 31   | Styrene pumped thermal desorption/GC                                                                 | 78   | Formaldehyde <i>diffusive/solvent desorption/liquid<br/>chromatography</i>                                 |
| 32   | Phthalate esters solvent desorption/GC                                                               | 79   | Peroxodisulphate salts <i>mobile phase ion chromatography</i>                                              |
| 33   | Adsorbent tube standards                                                                             | 80   | Volatile organic compounds <i>diffusive/thermal desorption/GC</i>                                          |
| 34   | Arsine <i>colorimetric (diethyldithiocarbamate)</i>                                                  | 81   | Dustiness of powders and materials                                                                         |
| 35/2 | HF and fluorides <i>ion-selective electrode</i>                                                      | 82   | The dust lamp                                                                                              |
| 36   | Toluene charcoal tube/GC                                                                             | 83   | Resin acids GC                                                                                             |
| 37   | Quartz in respirable airborne dust <i>direct infra-red</i>                                           | 84   | Oil mist from mineral oil-based metalworking fluids                                                        |
| 38   | Quartz in respirable airborne dust <i>KBr disc technique</i>                                         | 85   | Triglycidyl isocyanurate in air <i>pumped filter/<br/>desorption/liquid chromatography</i>                 |
| 39/4 | Asbestos fibres <i>light microscopy (European reference<br/>version)</i>                             | 86   | Hydrazine in air                                                                                           |
| 40   | Toluene thermal desorption/GC                                                                        | 87   | Fibres in air                                                                                              |
| 41/2 | Arsenic AA                                                                                           | 88   | Volatile organic compounds in air <i>diffusive/solvent<br/>desorption/GC</i>                               |
| 42/2 | Nickel AA                                                                                            | 89   | Dimethyl sulphate and diethyl sulphate <i>thermal<br/>desorption/GC-mass spectrometry</i>                  |
| 43   | Styrene <i>diffusive/thermal desorption/GC</i>                                                       |      |                                                                                                            |
| 44   | Styrene <i>diffusive/solvent desorption/GC</i>                                                       |      |                                                                                                            |
| 45   | Ethylene dibromide solvent desorption/GC                                                             |      |                                                                                                            |
| 46/2 | Platinum AA                                                                                          |      |                                                                                                            |
| 47   | Rubber fume in air measured as total particulates<br>and cyclohexane soluble material                |      |                                                                                                            |
| 48   | Newspaper print rooms: measurements of total<br>particulates and cyclohexane soluble material in air |      |                                                                                                            |
| 49   | Aromatic isocyanates <i>acid hydrolysis/ diazotisation</i>                                           |      |                                                                                                            |
| 50   | Benzene <i>diffusive/thermal desorption/GC</i>                                                       |      |                                                                                                            |

©Crown copyright 1998

Applications for reproduction should be made in writing to: Copyright Unit,  
Her Majesty's Stationery Office, St Clements House, 2-16 Colegate, Norwich NR3 1BQ

All rights reserved. No part of this publication may be reproduced, stored in a retrieval  
system, or transmitted in any form or by any means (electronic, mechanical, photocopying,  
recording or otherwise) without the prior written permission of the copyright owner.



**MAIL ORDER** HSE priced and free publications are available from:  
HSE Books, PO Box 1999, Sudbury, Suffolk CO10 6FS Tel: 01787 881165  
Fax: 01787 313995

**RETAIL** HSE priced publications are available from good booksellers

**HEALTH AND SAFETY ENQUIRIES** HSE InfoLine Tel: 0541 545500 or  
write to: HSE Information Centre, Broad Lane, Sheffield S3 7HQ

HSE home page on the World Wide Web:  
<http://www.open.gov.uk/hse/hsehome.htm>

First published 1986  
Second edition 1990  
Third edition 1998

**£12.00 net**

ISBN 0-7176-1520-0



9 780717 615209