MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

HSE
Health & Safety Executive

12/2

Chromium and inorganic compounds of chromium in air

Laboratory method using flame atomic absorption spectrometry

April 1996

INTRODUCTION

***Note 1**: This method updates and replaces MDHS 12.[1] The principal changes which have been made are (i) to describe additional dissolution techniques that are effective for chromium-containing dusts that are difficult to take into solution and (ii) to recommend the use of filters that are soluble using the dissolution techniques described.*

Occurrence, properties and uses

1 Occurrence, properties and uses of chromium and its inorganic compounds are fully covered in HSE Guidance Note EH 2.[2]

Effects on health

2 The health effects of chromium and its inorganic compounds are summarised in HSE Guidance Note EH 2[2] and are fully covered in HSE Toxicity Review TR21.[3]

Health and safety precautions

3 HSE leaflet MS(A)16[4] 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.[2]

Exposure limits

4 The Health and Safety Commission has approved three occupational exposure standards for chromium and its inorganic compounds. These long-term exposure limits, 8-hour time-weighted average reference period, are also published in Table 2 of HSE Guidance Note EH40,[6] and are reproduced below:

Chromium	0.5 mg m^{-3}
Chromium (II) inorganic compounds (as Cr)	0.5 mg m^{-3}
Chromium (III) inorganic compounds (as Cr)	0.5 mg m^{-3}

5 Schedule 1 of the Control of Substances Hazardous to Health (COSHH) Regulations[5] specifies a maximum exposure limit (MEL) of 0.05 mg m^{-3}, 8-hour time-weighted average reference period, for chromium (VI) compounds (as Cr). This limit is reproduced in HSE Guidance Note EH 40[6] and the criteria on which it was based are documented in the 1993 edition of HSE Guidance Note EH 64.[7] However, the procedures described in this method are not specific for the determination of chromium (VI) compounds (see paragraph 10).

Analytical methods

6 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.

7 This method has been validated[8] to demonstrate that it complies with the *General requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres* described by the Comité Européen de Normalization (CEN) in European Standard EN 482[9] (see paragraphs A1.6, A2.6, A3.6, A4.6 and A5.6). If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

Requirements of the COSHH Regulations

8 The Control of Substances Hazardous to Health (COSHH) Regulations[5] require that employers make an assessment of the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. The COSHH Regulations also include a requirement that persons who may 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 method. 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.[10]

SCOPE

Applicability

9 This MDHS describes a method for determination of the concentration of chromium and inorganic compounds of chromium in workplace air using flame atomic absorption spectrometry. It is applicable to the determination of chromium compounds and the majority of chromium-containing materials in industrial use or occurring in workplace air. The method is suitable for sampling times in the range 30 minutes to 8 hours.

Note 2: *HSE Guidance Note EH 42[11] advises employers about how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure, and therefore the procedures described in this method are for personal sampling in the breathing zone. The method may be used for background or fixed location sampling, but it should be recognised that, due to aerodynamic effects, samplers designed for personal sampling do not necessarily exhibit the same collection characteristics when used for other purposes.*

10 The procedures described in this method do not give any information about which species of chromium is present. Use MDHS 52/2[12] or MDHS 61[13] when making measurements for comparison with the MEL for chromium (VI) compounds.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedures

11 A number of sample dissolution procedures have been described in this method (see paragraph 62). Their effectiveness has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air, and this is reported in the relevant appendix.

Detection limits

12 The qualitative and quantitative detection limits for chromium, defined as three times and ten times the standard deviation of a blank determination, have been determined[8] separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5).

Overall uncertainty

13 The bias of the analytical method and the component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), have been determined[8] separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5).

14 The overall uncertainty of the method, as defined by CEN,[9] was determined[8] separately for each of the sample dissolution procedures described in this method (see Appendices A1 to A5). In all instances it was within the specification prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

Interferences

15 The analysis is based on atomic absorption spectrometry using a nitrous oxide-acetylene flame at a wavelength of 357.9 nm, where only minimal interferences have been found. Some elements have been reported[14] to interfere with the determination of chromium. These were investigated[8] but found to be insignificant.

PRINCIPLE

16 A measured volume of air is drawn through a filter mounted in an inhalable dust sampler. The sample is then taken into solution according to one of the five methods described in Appendices A1 to A5. The resultant solution is analysed for chromium by aspirating into the nitrous oxide-acetylene flame of an atomic absorption spectrometer. Absorbance measurements are made at 357.9 nm.

REAGENTS

17 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 18).
Do not pipette by mouth.

Water

18 Water complying with the requirements of BS 3978[15] grade 2 water (electrical conductivity less than 0.1 mS m^{-1} and resistivity greater than 0.01 MΩ.m at 25°C).

Nitric acid (HNO_3), concentrated, ρ about 1.42 g ml^{-1}, 69% (m/m) to 71% (m/m)

19 The chromium concentration of the acid shall be less than 0.005 μg ml^{-1}.

WARNING - Concentrated nitric acid is corrosive and oxidising, and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or

safety spectacles etc) should be used when working with concentrated or diluted nitric acid, and sample dissolution with nitric acid should be carried out in a fume cupboard.

Nitric acid, diluted 1 + 3

20 Carefully add 250 ml of concentrated nitric acid (paragraph 19) to 600 ml of water (paragraph 18) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Note 3: *1 + 3 nitric acid is required only for the procedure described in Appendix A4.*

Nitric acid, diluted 1 + 9

21 Add approximately 800 ml of water (paragraph 18) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 19) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Hydrochloric acid (HCl), concentrated, ρ about 1.18 g ml^{-1}, 36.5% (m/m) to 38% (m/m)

22 The chromium concentration of the acid shall be less than 0.005 µg ml^{-1}.

WARNING - Concentrated hydrochloric acid is corrosive and hydrochloric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted hydrochloric acid, and sample dissolution with hydrochloric acid should be carried out in a fume cupboard.

Hydrochloric acid, diluted 1 + 1

23 Carefully add 500 ml of concentrated hydrochloric acid (paragraph 22) to 450 ml of water (paragraph 18) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Hydrochloric acid, diluted 1 + 4

24 Carefully add 200 ml of concentrated hydrochloric acid (paragraph 22) to 600 ml of water (paragraph 18) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.
Note 4: *1 + 4 hydrochloric acid is required only for the procedure described in Appendix A5.*

Hydrochloric, diluted 1 + 9

25 Add approximately 800 ml of water (paragraph 18) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated hydrochloric acid (paragraph 22) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Note 5: *1 + 9 hydrochloric acid is required only for the procedure described in Appendix A5.*

Perchloric acid ($HClO_4$), ρ about 1.67 g ml^{-1}, approximately 70% (m/m)

26 The chromium concentration of the acid shall be less than 0.002 µg ml^{-1}.

Note 6: *Perchloric acid is required only for the procedure described in Appendix A2.*

WARNING - Perchloric acid is corrosive and oxidising, and its fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with concentrated or diluted perchloric acid, and sample dissolution with perchloric acid should be carried out in a fume cupboard with a scrubber unit specially designed for use with perchloric acid.

Potassium hydrogen sulphate ($KHSO_4$)

27 The chromium content of the salt shall be less than 0.05 µg g^{-1}.

Note 7: *Potassium hydrogen sulphate is required only for the procedure described in Appendix A4.*

Sodium peroxide (Na_2O_2)

28 The chromium content of the salt shall be less than 20 µg g^{-1}.

Note 8: *Sodium peroxide is required only for the procedure described in Appendix A5.*

Stock standard chromium solution, 1000 µg ml^{-1} of chromium

29 Use a commercially available standard solution at a concentration of 1000 µg ml^{-1} of chromium. Observe the manufacturer's expiry date or recommended shelf life.

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

30 Accurately weigh 1.000 g of chromium metal, 99.9% Cr (m/m), into a 100 ml beaker, add 20 ml of 1 + 1 hydrochloric acid (paragraph 23), cover with a watch glass and heat on a hotplate (paragraph 42) in a fume cupboard until the metal is completely dissolved. Remove the

beaker from the hotplate, allow to cool, quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

Note 9: *Chromium standard solution prepared according to the instructions in paragraph 30 may be stored in a polypropylene bottle (paragraph 38) for a period of one year without deterioration.*

WARNING - Chromium and chromium compounds have

been assigned various risk phrases in the Approved Supply List[16] for the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994[17] (the 'CHIP 2' Regulations). Care should be taken when working with chromium metal and solutions containing chromium.

Laboratory detergent solution

31 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 18) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Samplers for collection of the inhalable fraction of the airborne particles

32 Samplers, with protective covers, for collection of the inhalable fraction of the airborne particles, as defined in European Standard EN 481.[18] Inhalable dust samplers suitable for personal sampling are described in MDHS 14.[19]

Note 10: *In general, the collection characteristics of inhalable samplers can be such that particulate material collected on the filter is the inhalable fraction of the airborne particles, and any deposited on the internal surfaces of the sampler is not of interest. However, some samplers are designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, in which case any particulate material deposited on the internal surfaces of the sampler is part of the sample. Samplers of this type incorporate an internal filter cassette which may be removed from the sampler to enable this material to be easily recovered. Refer to the manufacturer's instructions to ascertain what constitutes the inhalable fraction of the sample.*

Note 11: *Samplers manufactured in non-conducting material have electrostatic properties which may influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.*

Filters

33 Filters, of a diameter suitable for use in the samplers (paragraph 32), with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter. The use of filters that are soluble using the sample preparation procedure described is recommended, and mixed cellulose ester membrane filters of 0.8 µm mean pore diameter are considered to be most suitable.
The chromium content shall be less than 0.001 µg per filter.

Note 12: *Glass fibre or other filters which do not dissolve using the sample preparation procedure described may be used, but extra care needs to be taken to ensure quantitative transfer of sample solutions to volumetric flasks (see Appendices A1 to A5).*

Sampling pumps

34 Sampling pumps, complying with the provisions of draft European Standard prEN 1232,[20] with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the appropriate flow rate (see paragraph 49) to within ±5% of the nominal value throughout the sampling period (see paragraph 50), and capable of being worn by persons without impeding normal work activity. The pumps shall give a pulsation-free flow (if necessary, a pulsation damper shall be incorporated between the sampler and the pump, as near to the pump as possible). Flow-stabilised pumps may be required to maintain the flow rate within the specified limits.

Flowmeter

35 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 49) to within ±1%, and calibrated against a primary standard.

Note 13: *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 paragraph 54), provided they have adequate sensitivity.*

Ancillary equipment

36 Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sampler to the sampling pump; belts or harnesses to which the sampling 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 58), to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

37 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and one-mark volumetric flasks, class A, complying with the requirements of BS 1792.[21]

Note 14: *It is recommended that a set of glassware is reserved for the analysis of chromium by this method (see paragraph 66).*

Polypropylene bottle

38 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 30), cleaned before use by soaking in 1 + 9 nitric acid (paragraph 21) for at least 24 hours and then rinsing thoroughly with water (paragraph 18). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

Disposable gloves

39 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

Piston operated volumetric apparatus

40 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,[22-25] for the preparation of calibration solutions (paragraphs A1.12, A2.12, A3.14, A4.16 and A5.14), and dilution of sample solutions (paragraph 74). A suitable set might include micropipettes covering the ranges 10 µl to 100 µl, 100 µl to 1000 µl and 1000 µl to 5000 µl. Dispensers for dispensing acid.

Filter paper

41 A hardened, ashless, cellulose (paper) filter of medium filtering speed and retentivity.

Hotplate

42 A thermostatically controlled hotplate, capable of maintaining the required surface temperature.

Microwave digestion system

43 A commercial, closed vessel microwave digestion system, designed for laboratory use, with power output regulation, equipped with a turntable of sample vessels able to withstand pressures in excess of 100 psi, and fitted with a pressure control system.

Note 15: *The microwave digestion system and vessels are only required for the procedure described in Appendix A3.*

Porcelain crucibles

44 Fused porcelain crucibles, low form, 30 ml capacity, with matching lids.

Note 16: *Porcelain crucibles are only required for the procedure described in Appendix A4.*

Zirconium crucibles

45 Zirconium crucibles, straight wall, 20 ml capacity.

Note 17: *Zirconium crucibles are only required for the procedure described in Appendix A5.*

Meker burner

46 Natural gas burner, Meker pattern, Amal major.

Muffle furnace

47 Electric muffle furnace, capable of maintaining a temperature of 650°C.

Atomic absorption spectrometer

48 An atomic absorption spectrometer, fitted with a nitrous oxide-acetylene burner, supplied with nitrous oxide and acetylene, and equipped with a chromium hollow cathode lamp.

SAMPLING

Sampling procedure

49 Use the samplers (paragraph 32) at the design flow rate, so that they exhibit the required collection characteristics. Refer to the manufacturer's instructions.

50 Select a suitable sampling time, such that the filter does not become overloaded with aerosol. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in Guidance Note EH 42.[11])

Preparation of sampling equipment

Perform the following in an area where chromium contamination is known to be low.

51 Clean the samplers (paragraph 32) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 31), rinse thoroughly with water (paragraph 18), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

52 Load the filters (paragraph 33) into clean, dry samplers (see paragraph 51) using clean, flat-tipped tweezers (paragraph 36). Connect each loaded sampler to a sampling pump (paragraph 34) using plastic tubing (paragraph 36), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 35) to the sampler so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate (see paragraph 49) with an accuracy of ±5%. Switch off the pump and seal the sampler with its protective cover to prevent contamination with chromium during transport to the sampling position.

Note 18*: It might be necessary to allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (refer to the manufacturer's recommendations). If this is the case, discard the used filter after the warm-up period and load a new one into the sampler for collection of the sample. Then attach the calibrated flowmeter again and readjust the flow rate to the appropriate value (see paragraph 49) with an accuracy of ±5%.*

Collection of samples

53 Fix the sampler to the lapel of the worker, in the breathing zone and as close to the mouth and nose as practicable. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 36) around the waist. When ready to begin sampling, remove the protective cover from the sampler and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, set this to zero.

54 Since it is possible for a filter to become clogged, monitor the performance of the sampler frequently, a minimum of once per hour. Measure the flow rate with an accuracy of ±5% using the calibrated flowmeter (paragraph 35) and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within ±5% of the nominal value throughout the sampling period.

Note 19: *Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised sampling pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside ±5% of the nominal value.*

55 At the end of the sampling period (see paragraph 50), measure the flow rate with an accuracy of ±5% using the calibrated flowmeter (paragraph 35), switch off the sampling pump, and record the flow rate and the time. Also observe the reading on the elapsed time indicator, if fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within ±5%, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

56 Carefully record the sample identity and all relevant sampling data (see Appendix B). Calculate the mean flow rate by averaging the flow rate measurements taken throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in litres per minute by the sampling time, in minutes.

57 With each batch of ten samples, submit for analysis two unused filters from the same lot of filters used for sample collection. Subject these blank filters to exactly the same handling procedure as the samples, but draw no air through them.

Transportation

Perform the following in an area where chromium contamination is known to be low.

58 For samplers which collect the inhalable fraction of airborne particles on the filter (see note 10), remove the filter from each sampler using clean flat-tipped tweezers (paragraph 36), place in a labelled filter transport cassette (paragraph 36) and close with a lid.

59 For samplers which have an internal filter cassette (see note 10), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

60 For samplers designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction but which do not have an internal filter cassette (see note 10), and for samplers of the disposable cassette type, transport the samples to the laboratory in the samplers in which they were collected.

61 Transport the filter transport cassettes (see paragraph 58), sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) to the laboratory in a container which has been designed to prevent damage to samples in transit and which has been labelled to assure proper handling.

ANALYSIS

Wear disposable gloves (paragraph 39) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.

Selection of sample dissolution procedure

62 Select a suitable sample dissolution procedure from those described in Appendices A1 to A5. Take into consideration the nature of the chromium-containing material present in the test atmosphere and the availability of laboratory apparatus. In many instances the nature of the matrix will be such that chromium is readily soluble in acid, in which case use the hydrochloric/nitric acid dissolution procedure described in Appendix A1. However, if chromium is in a more difficult matrix, eg refractory dusts or stainless steel welding fume, use one of the more vigorous dissolution procedures described in Appendices A2 to A5.

Cleaning of glassware

63 Before use, clean all glassware (paragraph 37) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 31) and then rinse thoroughly with water (paragraph 18). Alternatively, use a laboratory washing machine.

64 After initial cleaning (paragraph 63), clean all beakers used in the sample dissolution procedures (see paragraphs A1.8 to A1.11, A2.8 to A2.11 and A5.12) with hot nitric acid. Fill to one third capacity with concentrated nitric acid (paragraph 19), cover with a watch glass, heat to approximately 150°C on the hotplate (paragraph 42) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 18).

65 After initial cleaning (paragraph 63), clean all glassware other than beakers used in the sample dissolution procedure by soaking in 1 + 9 nitric acid (paragraph 21) for at least 24 hours and then rinsing thoroughly with water (paragraph 18).

Concentration of chromium in air

80 Calculate the concentration of chromium in air, $\rho(Cr)$ in milligrams per cubic metre (mg m^{-3}), using the equation:

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

66 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 63 to 65, and which has been reserved for determination of chromium by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 21) and then with water (paragraph 18).

Preparation of sample and blank solutions

67 Refer to the relevant appendix and prepare the sample and blank solutions using the selected sample dissolution procedure (paragraph 62).

ANALYSIS BY FLAME ATOMIC ABSORPTION SPECTROMETRY

Preparation of calibration solutions

68 Prepare matrix-matched calibration solutions. Refer to the appendix relevant to the selected sample dissolution procedure (see paragraph 62).

Atomic absorption measurements

69 Set up the atomic absorption spectrometer (paragraph 48) to determine chromium at a wavelength of 357.9 nm using a nitrous oxide-acetylene flame. Follow the manufacturer's recommendations for specific operating parameters, and use background correction. The sensitivity, defined as the concentration required to produce a signal of 1% absorbance or 0.0044 absorbance units, is about 0.30 µg ml^{-1} of chromium.

70 Adjust the spectrometer zero while aspirating the 0 µg ml^{-1} calibration solution (paragraph 68). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

71 Aspirate the calibration solutions (paragraph 68) into the flame in order of increasing concentration and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, generate a calibration for chromium by carrying out a linear regression. For instruments without this capability, prepare a calibration graph by plotting the absorbance of the calibration solutions versus the chromium concentration.

72 Aspirate the sample and blank solutions (paragraph 67) into the flame and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, use the calibration function to determine the concentration of chromium in the sample and blank solutions and obtain a direct read-out of the results in µg ml^{-1} of chromium. For instruments without this capability, determine the concentration of chromium in µg ml^{-1} from the calibration graph (paragraph 71).

73 Aspirate a mid-range calibration solution into the flame after each five to ten sample solutions and make an absorption measurement. If this indicates that the sensitivity has changed by more than ±5%, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis and recalibrate the spectrometer as described in paragraph 71; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

74 If high concentrations of chromium are found, dilute the sample solutions to bring the concentration within the calibration range, and repeat the analysis. Make all dilutions so that the final matrix is consistent with the dissolution procedure used. Record the dilution factor.

75 Calculate the mean chromium concentration of the blank solutions.

QUALITY CONTROL MEASURES

76 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.[26]

77 If chromium analysis is performed frequently it is recommended that internal quality control is performed. In such instances, prepare quality control filters by spiking a large batch of filters with microlitre volumes of a solution of known chromium concentration. Analyse a random selection of at least 20 filters, each along with a different analytical batch, and calculate the mean value and standard deviation of the readings. Assuming that the distribution of these values is Gaussian, construct a Shewhart chart with warning and action limits at ±2SD and ±3SD respectively. Subsequently, analyse a quality control filter with each analytical batch and plot the result on the Shewhart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.[26] Take care to ensure that the quality control filters are stored under conditions which ensure maximum stability.

78 It is strongly recommended that all laboratories undertaking the determination of toxic elements in workplace air 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.[26]

CALCULATION

Volume of air sample

79 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.

where $\rho(Cr)_0$ is the mean concentration, in µg ml^{-1}, of chromium in the blank solutions (paragraph 72);

$\rho(Cr)_1$ is the concentration, in µg ml^{-1}, of chromium in the sample solution (paragraph 72);

V is the volume, in litres, of the air sample (see paragraph 79);

V_0 is the volume, in ml, of the blank solutions, ie 10 ml, 25 ml or 50 ml (see paragraph 67);

V_1 is the volume, in ml, of the sample solution, ie 10 m, 25 ml or 50 ml (see paragraph 67);

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

DF_1 is the dilution factor for the sample solutions (paragraph 74).

TEST REPORT

81 Appendix B gives recommendations for information to be included in the test report.

APPENDIX A1 Hydrochloric acid/nitric acid sample dissolution procedure

SCOPE

A1.1 This appendix describes a dissolution procedure using hydrochloric acid and nitric acid on a hotplate. It is applicable when chromium compounds present in the sample are readily soluble in acid.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A1.2 This sample dissolution procedure has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air and has been found to be effective for chromium metal, lead chromate and chromium borides.

Detection limits

A1.3 The qualitative and quantitative detection limits as determined[8] for this procedure were 0.03 µg ml^{-1} and 0.10 µg ml^{-1} respectively. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to chromium in air concentrations of 10 µg m^{-3} and 33 µg m^{-3} respectively.

Overall uncertainty

A1.4 Laboratory experiments[8] indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 100 spiked filters in the range 3 µg to 960 µg of chromium was determined to be 103.4 ± 3.5%.

A1.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined[8] to be less than 5% for samples in the range 3 µg to 960 µg.

A1.6 The overall uncertainty of the method, as defined by CEN,[9] was estimated[8] to be less than 30% for samples in the range 3 µg to 960 µg. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

PRINCIPLE

A1.7 The filter and collected sample are treated with 1 ml of concentrated hydrochloric acid. 5 ml of concentrated nitric acid is then added and the sample solution is heated on a hotplate until about 1 ml of concentrated nitric acid solution remains. (Hydrochloric acid is added before nitric acid to prevent passivation of chromium metal, if present.) This is diluted to 10 ml for subsequent analysis for chromium by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A1.8 Open the filter transport cassettes (see paragraph 58), sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 36). Follow the same procedure for the blank filters (paragraph 57).

A1.9 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 10), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 18).

A1.10 Add 1 ml of concentrated hydrochloric acid (paragraph 22) to each beaker, partially cover with a watch glass, and heat to approximately 100°C on a hotplate (paragraph 42) in a fume cupboard until the deposit on the filter has dissolved. Add 5 ml of concentrated nitric acid (paragraph 19) and heat to approximately 150°C on a hotplate (paragraph 42) in a fume cupboard until the filter has dissolved and the solution has been reduced to approximately 1 ml. Remove each beaker from the hotplate and allow to cool.

A1.11 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 18) and quantitatively transfer each solution to an individual, labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 41) which has been pre-washed with 1 + 9 nitric acid (paragraph 21) and then with water. Finally, dilute to the mark with water, stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

A1.12 Prepare at least six calibration solutions to cover the range 0 µg ml^{-1} to 5 µg ml^{-1} of chromium. Add 50 ml of water (paragraph 18) and 10 ml of concentrated nitric acid (paragraph 19) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard chromium solution (paragraph 29 or 30) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

A1.13 Proceed with the analysis as described in paragraphs 69 to 75.

APPENDIX A2 Nitric acid/perchloric acid sample dissolution procedure

SCOPE

A2.1 This appendix describes a dissolution procedure using nitric acid and perchloric acid on a hotplate. It is useful in instances when chromium compounds present in the sample are not readily soluble in acid, and the hydrochloric acid and nitric acid procedure described in Appendix A1 could be ineffective.

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A2.2 This sample dissolution procedure has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes and dust from the operation of an electric furnace.

Detection limits

A2.3 The qualitative and quantitative detection limits as determined[8] for this procedure were 0.03 µg ml^{-1} and 0.10 µg ml^{-1} respectively. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to chromium in air concentrations of 10 µg m^{-3} and 33 µg m^{-3} respectively.

Overall uncertainty

A2.4 Laboratory experiments[8] indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 100 spiked filters in the range 3 µg to 960 µg of chromium was determined to be 102.8 ± 3.5%.

A2.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined[8] to be less than 6% for samples in the range 3 µg to 960 µg.

A2.6 The overall uncertainty of the method, as defined by CEN,[9] was estimated[8] to be less than 25% for samples in the range 3 µg to 960 µg. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

PRINCIPLE

A2.7 The filter and collected sample are treated with 5 ml of nitric acid and 1 ml of perchloric acid and heated on a hotplate until about 1 ml of acid solution remains. This is diluted to 10 ml for subsequent analysis for chromium by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A2.8 Open the filter transport cassettes (see paragraph 58), sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 36). Follow the same procedure for the blank filters (paragraph 57).

A2.9 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 10), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 18).

A2.10 Add 5 ml of concentrated nitric acid (paragraph 19), cover the beaker and digest on a hotplate until the filter dissolves. Slide back the watch glasses so that the beakers are only partially covered, add 1 ml of perchloric acid (paragraph 26), and continue to heat until dense, white fumes of perchloric acid are evolved and until approximately 1 ml of acid remains. Remove each beaker from the hotplate and allow to cool.

Note 20: *It has been reported that there is a possibility of chromium being lost as volatile chromyl chloride when fuming samples with perchloric acid for times in excess of ten minutes.[27] However, no loss has been found[8] in the work carried out to validate this method.*

A2.11 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 18) and quantitatively transfer each solution to an individual, labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 41) which has been pre-washed with 1 + 9 nitric acid (paragraph 21) and then with water. Finally, dilute to the mark with water, stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

A2.12 Prepare at least six calibration solutions to cover the range 0 μg ml^{-1} to 5 μg ml^{-1} of chromium. Add 50 ml of water (paragraph 18) and 10 ml of perchloric acid (paragraph 26) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard chromium solution (paragraph 29 or 30) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

A2.13 Proceed with the analysis as described in paragraphs 69 to 75.

APPENDIX A3 Microwave-assisted sample dissolution procedure

SCOPE

A3.1 This appendix describes a microwave-assisted dissolution procedure using nitric acid. It is particularly useful in instances when chromium compounds present in the sample are not readily soluble in acid, and the hydrochloric acid and nitric acid procedure described in Appendix A1 could be ineffective.

Note 21: *This procedure is only suitable for dissolution of samples collected over sampling times in the range 2 to 8 hours. For shorter sampling times, the overall uncertainty does not meet the specification prescribed by CEN[9] for measurements in the range 0.1 to 0.5 times the limit value, ie <50%.*

Note 22: *The procedure described is for use with lined sample vessels designed for carrying out microwave digestions at pressures up to 200 psi. These vessels consist of a chemically resistant inner liner and cover (usually made of Teflon) which contains and isolates the sample solution from a higher strength outer pressure vessel structure. Other types of sample vessel designed to operate at equivalent or higher pressures may be used.*

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A3.2 This sample dissolution procedure has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes and dust from the operation of an electric furnace.

Detection limits

A3.3 The qualitative and quantitative detection limits as determined[8] for this procedure were 0.03 μg ml^{-1} and 0.10 μg ml^{-1} respectively. For an air sample volume of 240 litres and a sample solution volume of 50 ml this corresponds to chromium in air concentrations of 6.3 μg m^{-3} and 20.8 μg m^{-3} respectively.

Overall uncertainty

A3.4 Laboratory experiments[8] indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 42 spiked filters in the range 12 μg to 960 μg of chromium was determined to be 102.8 ± 3.2%.

A3.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined[8] to be less than 6.2% for samples in the range 12 μg to 960 μg.

A3.6 The overall uncertainty of the method, as defined by CEN,[9] was estimated[8] to be less than 24.3% for samples

in the range 12 µg to 960 µg. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

PRINCIPLE

A3.7 The filter and collected sample are treated with 5 ml of concentrated nitric acid and digested in a sealed microwave digestion vessel. The resultant solution is diluted to 50 ml for subsequent analysis for chromium by flame atomic absorption spectrometry.

CLEANING OF TEFLON LINERS

A3.8 Clean the teflon liners of the sample vessels with concentrated nitric acid before use. Follow the procedure described in paragraphs A3.11 and A3.12 and then rinse the liners thoroughly with water (paragraph 18).

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A3.9 Open the filter transport cassettes (see paragraph 58), sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) and transfer each filter into the teflon liner of a labelled sample vessel using clean flat-tipped tweezers (paragraph 36). Follow the same procedure for the blank filters (paragraph 57).

A3.10 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 10), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 18)**.**

A3.11 Add 5 ml of concentrated nitric acid (paragraph 19) to each liner and cover with its lid. Then seal the sample vessels with their screw caps and place them, evenly distributed, in the turntable of the microwave digestion system (paragraph 43).

A3.12 Program microwave digestion system to operate for 30 minutes at full power, using the pressure control system to prevent the pressure in the control vessel exceeding 100 psi. When the program has run, allow the vessels to cool and the pressure to return to <10 psi.

A3.13 Remove the turntable from the microwave digestion system and place in a fume cupboard. Carefully open each sample vessel, rinse the lid and sides of the liner with water (paragraph 18), and quantitatively transfer the solution to an individual, labelled 50 ml volumetric flask. If necessary, remove any undissolved particulate matter by filtering through a cellulose (paper) filter (paragraph 41) which has been pre-washed with 1 + 9 nitric acid (paragraph 21) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

Note 23: *The procedure described is for a microwave digestion system with a nominal output power of 700 W with pressure control. If the system also has temperature control, this can also be utilised to control the sample dissolution conditions, but the method performance could be different from that given above.*

PREPARATION OF CALIBRATION SOLUTIONS

A3.14 Prepare at least six calibration solutions to cover the range 0 µg ml^{-1} to 5 µg ml^{-1} of chromium. Add 50 ml of water (paragraph 18) and 10 ml of concentrated nitric acid (paragraph 19) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of stock standard chromium solution (paragraph 29 or 30) into each flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

A3.15 Proceed with the analysis as described in paragraphs 69 to 75.

APPENDIX A4 Potassium hydrogen sulphate fusion procedure

SCOPE

A4.1 This appendix describes a fusion procedure using potassium hydrogen sulphate. It is particularly useful in instances when chromium compounds present in the sample are not soluble in acid, and the dissolution procedures described in Appendices A1, A2 and A3 could be ineffective.

Note 24: *This procedure is only suitable for dissolution of samples collected over a sampling time of 8 hours. For shorter sampling times, the overall uncertainty does not meet the specification prescribed by CEN[9] for measurements in the range 0.1 to 0.5 times the limit value, ie <50%.*

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A4.2 This sample dissolution procedure has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes, dusts from nickel smelting and other industrial activities.

Detection limits

A4.3 The qualitative and quantitative detection limits as determined[8] for this procedure were 0.05 µg ml^{-1} and 0.18 µg ml^{-1} respectively. For an air sample volume of 960 litres and a sample dilution volume of 250 ml this corresponds to chromium in air concentrations of 13 µg m^{-3} and 47 mg m^{-3} respectively.

Overall uncertainty

A4.4 Laboratory experiments[8] indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 36 spiked filters in the range 48 µg to 960 µg of chromium was determined to be 98.0 ± 2.6%.

A4.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined[8] to be less than 9.2% for samples in the range 48 µg to 960 µg.

A4.6 The overall uncertainty of the method, as defined by CEN,[9] was estimated[8] to be less than 25.4% for samples in the range 48 µg to 960 µg. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

PRINCIPLE

A4.7 The filter and collected sample are placed in a fused porcelain crucible and wet-ashed with 0.5 ml of concentrated nitric acid. 2.5 g of molten potassium hydrogen sulphate is then poured over the sample, which is then covered with the crucible lid and placed in a muffle furnace at 650°C for 1 hour. The fused bead is dissolved in 10 ml of 1 + 3 nitric acid, made to 25 ml with water, and further diluted by a factor of ten for subsequent analysis for chromium by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A4.8 Open the filter transport cassettes (see paragraph 58), sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) and transfer each filter into an individual, labelled 30 ml fused porcelain crucible (paragraph 44) using clean flat-tipped tweezers (paragraph 36). Follow the same procedure for the blank filters (paragraph 57).

A4.9 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 10), wash any particulate material adhering to the internal surfaces into the crucible using a minimum volume of water (paragraph 18).

A4.10 Add 0.5 ml of concentrated nitric acid (paragraph 19) to each crucible and wet-ash the filter by gently heating over a Meker burner (paragraph 46) and slowly boiling off the nitric acid (care should be taken to avoid loss of sample during heating as the acid will spit if heated strongly).

A4.11 Weigh 2.5 g portions of potassium hydrogen sulphate (paragraph 27) into separate porcelain crucibles (paragraph 44) and heat over a Meker burner (paragraph 46) until molten. Then pour a portion of molten flux over each ashed sample (paragraph A4.10) and cover with a crucible lid.

A4.12 Place the covered crucibles in a muffle furnace (paragraph 47) at a temperature of 650°C. Remove the crucibles after 1 hour and place on a heat-proof surface and allow to cool.

A4.13 Remove the crucible lids and gently tap each fused bead into an individual, labelled 50 ml beaker. Rinse each crucible with two 5 ml aliquots of 1 + 3 nitric acid (paragraph 20) and add the washings to the beaker. Cover the beakers with watch glasses and heat on a hotplate to dissolve the fused beads.

A4.14 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 18) and quantitatively transfer each solution to an individual, labelled 25 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 41) which has been pre-washed with 1 + 9 nitric acid (paragraph 21) and then with water. Finally dilute to the mark with water, stopper and mix thoroughly.

A4.15 Further dilute the sample solutions for analysis. Accurately pipette 1 ml of each sample solution (paragraph A4.14) into an individual, labelled 10 ml volumetric flask, dilute to the mark with water (paragraph 18), stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

A4.16 Prepare at least six calibration solutions to cover the range 0 µg ml^{-1} to 5 µg ml^{-1} of chromium. Add 50 ml of water (paragraph 18) and 10 ml of 1 + 9 nitric acid (paragraph 21) to separate, labelled 100 ml volumetric flasks. Weigh out an appropriate number of 1 g portions of potassium hydrogen sulphate (paragraph 27), transfer a portion to each flask and swirl to dissolve. Accurately pipette the appropriate volume of stock standard chromium solution (paragraph 29 or 30) into each flask, dilute to the mark with water (paragraph 18), stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

A4.17 Proceed with the analysis as described in paragraphs 69 to 75.

APPENDIX A5 Sodium peroxide fusion procedure

SCOPE

A5.1 This appendix describes a fusion procedure using sodium peroxide. It is particularly useful in instances when chromium compounds present in the sample are not soluble in acid, and the dissolution procedures described in Appendices A1, A2 and A3 could be ineffective.

Note 25: *This procedure is only suitable for dissolution of samples collected over sampling times in the range 2 to 8 hours. For shorter sampling times, the overall uncertainty does not meet the specification prescribed by CEN.*[9]

METHOD PERFORMANCE

Effectiveness of sample dissolution procedure

A5.2 This sample dissolution procedure has been tested[8] on a range of chromium-containing materials in industrial use or occurring in workplace air and has been found to be effective for welding fumes, dusts from nickel smelting and other industrial activities.

Detection limits

A5.3 The qualitative and quantitative detection limits as determined[8] for this procedure were 0.06 µg ml^{-1} and 0.20 µg ml^{-1} respectively. For an air sample volume of 240 litres and a sample dilution volume of 100 ml this corresponds to chromium in air concentrations of 25 µg m^{-3} and 83 µg m^{-3} respectively.

Overall uncertainty

A5.4 Laboratory experiments[8] indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 48 spiked filters in the range 12 µg to 960 µg of chromium was determined to be 102.6 ± 3.7%.

A5.5 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined[8] to be less than 7.5% for samples in the range 12 µg to 960 µg.

A5.6 The overall uncertainty of the method, as defined by CEN,[9] was estimated[8] to be less than 25% for samples in the range 12 µg to 960 µg. This assumes that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV (inter), is negligible and that the coefficient of variation of the method that arises from pump flow rate variability, CV (flow), is limited to 5%. The overall uncertainty is therefore within the specifications prescribed by CEN[9] for measurements for comparison with limit values, ie <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.

PRINCIPLE

A5.7 The filter and collected sample are placed in a zirconium crucible and wet-ashed with 0.5 ml ofconcentrated nitric acid. 1.0 g of sodium peroxide is added to the sample, which is then fused over the reducing flame of a Meker burner. The fused bead is dissolved in 50 ml of 1 + 4 hydrochloric acid, and made to 100 ml with water for subsequent analysis for chromium by flame atomic absorption spectrometry.

PREPARATION OF SAMPLE AND BLANK SOLUTIONS

A5.8 Open the filter transport cassettes (see paragraph 58) or sampler filter cassettes (see paragraph 59) or samplers (see paragraph 60) and transfer each filter into an individual, labelled 20 ml zirconium crucible (paragraph 45) using clean flat-tipped tweezers (paragraph 36). Follow the same procedure for the blank filters (paragraph 57).

A5.9 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 10), wash any particulate material adhering to the internal surfaces into the crucible using a minimum volume of water (paragraph 18).

A5.10 Add 0.5 ml of concentrated nitric acid (paragraph 19) to each crucible and wet-ash the filter by gently heating over a Meker burner (paragraph 46) and slowly boiling off the nitric acid (care should be taken to avoid loss of sample during heating as the acid will spit if heated strongly).

A5.11 Weigh 1.0 g of sodium peroxide (paragraph 28) into each sample crucible (paragraph A5.10) and heat over the reducing flame of a Meker burner until the flux is molten. Maintain the heat for ten minutes at the temperature of liquefaction, periodically swirling the crucibles to aid sample dissolution. Then remove from the flame, place the crucibles on a heat-proof surface and allow to cool.

A5.12 Place each crucible on its side in an individual, labelled 100 ml beaker. Add 50 ml 1 + 4 hydrochloric acid (paragraph 24) to each beaker, cover with a watch glass and heat on a hotplate (paragraph 42) to dissolve the fused bead. Carefully rinse the watch glass and the sides of each beaker with water (paragraph 18). Remove the crucibles using clean plastic tweezers (paragraph 36) and carefully wash the crucibles into their respective beakers with a jet of water (paragraph 18) from a wash bottle.

A5.13 Transfer each solution quantitatively to a labelled 100 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter (paragraph 41) which has been pre-washed with 1 + 9 hydrochloric acid (paragraph 25) and then with water (paragraph 18). Wash the beaker and filter with further portions of water, allowing the filter to completely drain before subsequent washings. Finally dilute to the mark with water, stopper and mix thoroughly.

PREPARATION OF CALIBRATION SOLUTIONS

Flame atomic absorption spectrometry

A5.14 Prepare at least six calibration solutions to cover the range 0 μg ml^{-1} to 5 μg ml^{-1} of chromium. Weigh out an appropriate number of 1 g portions of sodium peroxide (paragraph 28) and transfer to separate, labelled 100 ml beakers. Add 50 ml of water (paragraph 18) and 10 ml of concentrated hydrochloric acid (paragraph 22) to each beaker and bring to the boil on a hotplate (paragraph 42). Continue heating for 30 minutes to destroy the peroxide. Then remove the beakers from the hotplate and allow to cool on a heat-proof surface. Quantitatively transfer the contents of each beaker into an individual, labelled 100 ml volumetric flask and accurately pipette the appropriate volume of stock standard chromium solution (paragraph 29 or 30) into each flask. Finally dilute to the mark with water (paragraph 18), stopper and mix thoroughly. Prepare these solutions fresh weekly.

ANALYSIS

A5.15 Proceed with the analysis as described in paragraphs 69 to 75.

APPENDIX B 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, and the identity of the individual whose breathing zone was sampled;

(b) a reference to this MDHS and a description of any deviation from the procedures described;

(c) the type and diameter 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 chromium found in the air sample, in milligrams per cubic metre;

(k) the name of the analyst;

(l) the date of the analysis.

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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.