



Health and Safety Executive  
Occupational Medicine and  
Hygiene Laboratory

## MDHS 10/2

Methods for the  
Determination of  
Hazardous Substances

June 1994

# Cadmium and inorganic compounds of cadmium in air

Laboratory method using flame atomic absorption  
spectrometry or electrothermal atomic absorption  
spectrometry

## INTRODUCTION

**Note 1:** *This method updates and replaces MDHS 10.1. The principal changes which have been made are (i) to modify the dissolution technique, which was found to be unreliable for certain cadmium compounds,<sup>2</sup> (ii) to specify the use of samplers for inhalable or respirable dust, as appropriate, (iii) to recommend the use of filters that are soluble using the dissolution technique described, and (iv) to describe the use of electrothermal atomic absorption spectrometry for the analysis of sample solutions with a low cadmium concentration.*

### Properties and uses

1 Cadmium is a silver white metal having a melting point of 321°C and a boiling point of 767°C. It has a range of industrial uses that are fully covered in HSE Guidance Note EH1.<sup>3</sup>

### Health effects

2 Health effects of cadmium and cadmium compounds are fully covered in HSE Toxicity Reviews TR 7<sup>4</sup> and TR 24.<sup>5</sup>

### Precautions and first aid

3 HSE leaflet MS(A)<sup>76</sup> summarises the risks involved in working with cadmium and what can be done to control them. Health and safety precautions and first aid are fully covered in HSE Guidance Note EH1.<sup>3</sup>

## Exposure limits

4 Maximum exposure limits (MELs) are published in Guidance Note EH40<sup>7</sup> for cadmium and cadmium compounds (except cadmium oxide fume, cadmium sulphide and cadmium sulphide pigments); cadmium oxide fume; and cadmium sulphide and cadmium sulphide pigments (respirable dust). All have been assigned a long-term exposure limit (8-hour time-weighted average reference period) and cadmium oxide fume has also been assigned a short-term exposure limit (15-minute reference period).<sup>8</sup> See Table 1 for details.

## Analytical methods

5 This is not a 'reference' method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte (eg other methods in the MDHS series<sup>9</sup>). 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.

6 This method has been validated<sup>2</sup> 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 Européenne de Normalisation (CEN) in draft European Standard prEN 482.<sup>10</sup> If an alternative

**Table 1** Maximum exposure limits from 1 April 1994<sup>7</sup>

Substance	Appropriate fraction of airborne particles	Long-term exposure limit (8-hour time-weighted average reference period)	Short-term exposure limit (15 minute reference period)
Cadmium and cadmium compounds (as Cd) (except cadmium oxide fume, cadmium sulphide and cadmium sulphide pigments)	Inhalable	0.025 mg m <sup>-3</sup>	
Cadmium oxide fume (as Cd)	Inhalable	0.025 mg m <sup>-3</sup>	0.05 mg m <sup>-3</sup>
Cadmium sulphide and cadmium sulphide pigments (as Cd)	Respirable	0.04 mg m <sup>-3</sup>	

method is used, it is necessary to demonstrate that it also meets these performance requirements.

## Requirements of the COSHH Regulations

7 The Control of Substances Hazardous to Health (COSHH) Regulations<sup>11</sup> 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.

## SCOPE

### Applicability

8 This MDHS describes a method for determination of the concentration of cadmium and inorganic compounds of cadmium in workplace air using either flame atomic absorption spectrometry or electrothermal atomic absorption spectrometry. It is applicable to the determination of water-soluble cadmium salts and the majority of cadmium-containing materials in industrial use or occurring in workplace air (see paragraph 9). The method is suitable for sampling over periods in the range 15 minutes to 8 hours.

**Note 2:** *The method described is for determination of total cadmium-in-air. It is not practicable to separately determine cadmium oxide or cadmium sulphide in the presence of other cadmium compounds, and therefore if mixed exposure is likely it is recommended that the most stringent exposure limit is applied (see paragraph 4).*

**Note 3:** *HSE Guidance Note EH42<sup>12</sup> 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 the samplers used do not necessarily exhibit the same collection characteristics as when they are used for personal sampling.*

## METHOD PERFORMANCE

### Effectiveness of sample dissolution procedure

9 The sample dissolution procedure has been tested on a range of cadmium-containing materials in industrial use or occurring in workplace air<sup>2</sup> and was found to be effective for cadmium metal, cadmium oxide, cadmium

selenide, cadmium sulphide, cadmium telluride, cadmium sulphide and seleno-sulphide pigments, and glass enamels containing cadmium pigments.

**Note 4:** *The effectiveness of the sample dissolution procedure described previously in MDHS 10<sup>1</sup> was also tested and found to be unreliable for cadmium selenide, cadmium sulphide, cadmium telluride, cadmium sulphide and seleno-sulphide pigments, and glass enamels containing cadmium pigments. However, it is effective for cadmium metal, cadmium oxide and water-soluble cadmium salts.*

### Detection limits

10 The qualitative and quantitative detection limits for cadmium, defined as three times and ten times the standard deviation of a blank determination, have been determined to be 0.0036  $\mu\text{g ml}^{-1}$  and 0.012  $\mu\text{g ml}^{-1}$  for flame atomic absorption spectrometry; and 0.071  $\text{ng ml}^{-1}$  and 0.24  $\text{ng ml}^{-1}$  for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml, this corresponds to cadmium in air concentrations of 1.2  $\mu\text{g m}^{-3}$  and 4  $\mu\text{g m}^{-3}$  for flame atomic absorption spectrometry; and 0.024  $\mu\text{g m}^{-3}$  and 0.08  $\mu\text{g m}^{-3}$  for electrothermal atomic absorption spectrometry.

### Overall uncertainty

11 Laboratory experiments<sup>2</sup> indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for 130 spiked filters in the range 0.15  $\mu\text{g}$  to 96  $\mu\text{g}$  of cadmium was determined to be 100.3% using flame atomic absorption spectrometry; and the mean analytical recovery for 50 spiked filters in the range 0.01  $\mu\text{g}$  to 0.6  $\mu\text{g}$  of cadmium was determined to be 97.9% using electrothermal atomic absorption spectrometry.

12 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), was determined to be less than 10% for samples in the range 0.15  $\mu\text{g}$  to 1  $\mu\text{g}$  and less than 3% for samples in the range 1  $\mu\text{g}$  to 96  $\mu\text{g}$  using flame atomic absorption spectrometry; and less than 5% for samples in the range 0.01  $\mu\text{g}$  to 0.6  $\mu\text{g}$  using electrothermal atomic absorption spectrometry.

13 The overall uncertainty of the method, as defined by CEN,<sup>10</sup> was determined to be less than 25% for samples in the range 0.15  $\mu\text{g}$  to 1  $\mu\text{g}$  and less than 15% for samples in the range 1  $\mu\text{g}$  to 96  $\mu\text{g}$  using flame atomic absorption spectrometry; and less than 17% for samples in the range 0.01  $\mu\text{g}$  to 0.6  $\mu\text{g}$  using electrothermal atomic absorption spectrometry. These figures are within the specification of 30% prescribed by CEN<sup>10</sup> for the overall uncertainty of measurements for comparison with limit values.

### Interferences

14 High concentrations of silicate are reported<sup>13</sup> to interfere with the determination of cadmium by flame

atomic absorption spectrometry. However, using the dissolution procedure described, it is unlikely that significant quantities of silicate will be solubilised. No interferences specific to the determination of cadmium are documented for electrothermal atomic absorption spectrometry.

## PRINCIPLE

15 A measured volume of air is drawn through a filter mounted in an inhalable or respirable dust sampler, as appropriate (see paragraph 4). The filter and collected sample are then treated with 5 ml of 1 + 1 nitric acid and heated on a hot plate until about 1 ml of concentrated nitric acid solution remains. This is diluted to 10 ml with water and the resultant solution is analysed for cadmium by aspirating into the oxidising air-acetylene flame of an atomic absorption spectrometer. Absorbance measurements are made at 228.8 nm. For accurate determination when the concentration of cadmium in the solution is low, the analysis may be repeated using electrothermal atomic absorption spectrometry. Aliquots of the sample solution and a matrix modifier solution are injected onto a solid, pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube, and after drying and ashing stages the sample is atomised electrothermally. Absorbance measurements are made at 228.8 nm with background correction.

## REAGENTS

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

### Water

17 Water complying with the requirements of BS 3978<sup>14</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).

**Nitric acid (HNO<sub>3</sub>), concentrated, ρ about 1.42 g ml<sup>-1</sup>, 69% (m/m) to 71% (m/m)**

18 The cadmium concentration of the acid should be less than 0.005 µg ml<sup>-1</sup>.

**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 + 1**

19 Carefully add 500 ml of concentrated nitric acid (paragraph 18) to 450 ml of water (paragraph 17) 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.

**Nitric acid, diluted 1 + 9**

20 Add approximately 800 ml of water (paragraph 17) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 18) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

**Stock standard cadmium solution, 1000 µg ml<sup>-1</sup> of cadmium**

21 Use a commercially available standard solution at a concentration of 1000 µg ml<sup>-1</sup> of cadmium. Observe the manufacturer's expiry date or recommended shelf life. Alternatively prepare a stock cadmium standard solution by the following procedure.

22 Accurately weigh 1.000 g of cadmium metal, 99.9% Cd (m/m), into a 100 ml beaker, add 20 ml of 1 + 1 nitric acid (paragraph 19), cover with a watch glass and heat on a hot plate (paragraph 35) in a fume cupboard until the metal is completely dissolved. Remove the beaker from the hot plate, allow to cool, quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water (paragraph 17), stopper and mix thoroughly.

**Note 5:** Cadmium standard solution prepared according to the instructions in paragraph 22 may be stored in a polypropylene bottle (paragraph 34) for a period of one year without deterioration.

**Working standard cadmium solution A, 100 µg ml<sup>-1</sup> of cadmium**

23 Accurately pipette 10.0 ml of stock cadmium standard solution (paragraphs 21 or 22) into a 100 ml volumetric flask. Add 1 ml of concentrated nitric acid (paragraph 18), dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare this solution fresh weekly.

**Working standard cadmium solution B, 1.00 µg ml<sup>-1</sup> of cadmium**

24 Accurately pipette 100 µl of stock cadmium standard solution (paragraphs 21 or 22) into a 100 ml volumetric flask. Add 1 ml of concentrated nitric acid (paragraph 18), dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare this solution fresh daily.

**Matrix modifier solution, 0.1% (m/v) Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 2.0% (m/v) NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>**

25 Weigh 0.100 g of magnesium nitrate, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and 2.00 g of ammonium di-hydrogen phosphate, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, into a 250 ml beaker. Add 50 ml water (paragraph 17) and swirl to dissolve. Add 10 ml of concentrated nitric acid (paragraph 18), swirl to mix, and

quantitatively transfer the solution into a 100 ml volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

### Laboratory detergent solution

26 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 17) according to the manufacturer's instructions.

## SAMPLING EQUIPMENT

### Samplers for collection of the inhalable fraction of airborne particles

27 Samplers, with protective covers, for collection of the inhalable fraction of airborne particles, as defined in European Standard EN 481.<sup>15</sup> The seven-hole sampling head described in MDHS 14<sup>16</sup> and the IOM (Institute of Occupational Medicine) inhalable dust sampler are suitable for personal sampling. Samplers manufactured in non-conducting plastic should not be used as these have electrostatic properties which may influence representative sampling.

**Note 6:** *In general, the collection characteristics of inhalable samplers (eg the seven-hole sampling head) are such that particulate material collected on the filter is the inhalable fraction of 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. Certain samplers of this type (eg the IOM inhalable dust sampler) incorporate an internal filter cassette which may be removed from the sampler to enable this material to be easily recovered.*

### Samplers for collection of the respirable fraction of airborne particles

28 Cyclone samplers for collection of the respirable fraction of airborne particles, as defined in European Standard EN 481.<sup>15</sup> A diagrammatic illustration of a cyclone sampler is given in MDHS 14.<sup>16</sup>

### Filters

29 Filters, of a diameter suitable for use in the selected sampler (paragraph 27 or 28), with a retentivity of not less than 99% for 0.3 µm mass median aerodynamic diameter particles. 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 cadmium content should be less than 0.001 µg per filter.

**Note 7:** *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 (paragraph 61).*

### Sampling pumps

30 Sampling pumps, with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the appropriate flow rate (see paragraph 41) to within ±5% of the nominal value throughout the sampling period (see paragraph 42), and capable of being worn by persons without impeding normal work activity. The pumps should give a pulsation-free flow (if necessary, a pulsation damper should be incorporated between the sampling head 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

31 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 41) to within ±5%, and calibrated against a primary standard.

**Note 8:** *The flowmeter incorporated in the pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded sampler in line, and that it is read in a vertical orientation if it is of the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampling head and the flowmeter, since in this event a flowmeter in the pump or elsewhere in line will give an erroneous flow rate.*

**Note 9:** *A soap bubble flowmeter may be used as a primary standard, provided its accuracy is traceable to national standards (see Appendix 1).*

### Ancillary equipment

32 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 50), to transport samples to the laboratory.

## LABORATORY APPARATUS

### Glassware, made of borosilicate glass

33 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS 1792.<sup>17</sup>

**Note 10:** *It is recommended that a set of glassware is reserved for the analysis of cadmium by this method.*

### Polypropylene bottle

34 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 22), cleaned before use by soaking in 1 + 9 nitric acid (paragraph 20) for at least 24 hours and then rinsing thoroughly with water (paragraph 17). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

### Hot plate

35 A thermostatically controlled hot plate, capable of maintaining the required surface temperature.

### Disposable gloves

36 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

37 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,<sup>18-21</sup> for the preparation of standards for calibration of the atomic absorption spectrometer (paragraphs 62 and 71) and dilution of samples (paragraphs 68 and 78). 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.

### Atomic absorption spectrometer

38 An atomic absorption spectrometer, fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with either a cadmium hollow cathode lamp or electrodeless discharge lamp. If electrothermal atomic absorption spectrometry is to be carried out, the atomic absorption spectrometer should be capable of carrying out simultaneous background correction at 228.8 nm, either by using a continuum source such as a deuterium lamp to measure non-specific attenuation, or by using Zeeman or Smith-Hieftje background correction systems.

### Electrothermal atomiser

39 An electrothermal atomiser, fitted with a solid, pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube, supplied with argon as a purge gas, and equipped with an autosampler capable of injecting microlitre volumes onto the platform.

**Note 11:** *Some manufacturers of atomic absorption spectrometers use an alternative design of electrothermal atomiser to achieve a constant temperature environment during atomisation, and some use aerosol deposition as a means of sample introduction. The use of such accessories is acceptable, but the method performance may be different from that described in paragraphs 10 to 13.*

### Disposable autosampler cups

40 Disposable polystyrene autosampler cups for use in the autosampler used with the electrothermal atomiser. Soak in 1 + 9 nitric acid (paragraph 20) before use.

**Note 12:** *Disposable polystyrene autosampler cups are also useful for containing solutions to be pipetted in microlitre quantities.*

## SAMPLING

### Sampling procedure

41 Select a sampler to collect the appropriate fraction of airborne particles (see paragraph 4) and use at the flow rate at which the sampler (paragraphs 27 or 28) exhibits the required collection characteristics. Refer to MDHS 14<sup>16</sup> for the flow rate to be used when sampling with a seven-hole sampling head, IOM inhalable dust sampler or cyclone sampler.

42 Select a sampling period of an appropriate duration, such that the filter does not become overloaded with particulate material. (An eight-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in Guidance Note EH42.<sup>12</sup>)

### Preparation of sampling equipment

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

43 Clean the samplers (paragraphs 27 or 28) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 26), rinse thoroughly with water (paragraph 17), wipe with absorptive tissue and allow to dry thoroughly before reassembly.

44 Load the filters (paragraph 29) into clean, dry samplers (see paragraph 43) using clean, flat-tipped tweezers (paragraph 32). Connect each loaded sampler to a sampling pump (paragraph 30) using plastic tubing (paragraph 32), ensuring that no leaks can occur. Switch on the pump, attach the calibrated flowmeter (paragraph 31) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the appropriate flow rate (see paragraph 41) with an accuracy of ±5%. Remove the flowmeter and allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (follow the manufacturer's recommendations). Then discard the used filter and load a new one into the sampler for collection of the sample. Finally, attach the calibrated flowmeter again, readjust the flow rate to the appropriate value with an accuracy of ±5%, switch off the pump and seal the sampler with its protective cover to prevent contamination with cadmium during transport to the sampling position.

## Collection of samples

45 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 around the waist (paragraph 32). When ready to begin sampling, remove the protective cover from the sampling head 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.

46 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  $\pm 5\%$  using the calibrated flowmeter (paragraph 31) 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.

**Note 13:** *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  $\pm 5\%$  of the nominal value.*

47 At the end of the sampling period (see paragraph 42), measure the flow rate with an accuracy of  $\pm 5\%$  using the calibrated flowmeter (paragraph 31), 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  $\pm 5\%$ , 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.

48 Carefully record the sample identity and all relevant sampling data (see Appendix 3). 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.

49 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 cadmium contamination is known to be low.*

50 For samplers which collect the appropriate fraction of airborne particles on the filter (eg the seven-hole sampling head and cyclone samplers), remove the filter

from each sampler using clean flat-tipped tweezers (paragraph 32), place in a labelled filter transport cassette (paragraph 32) and close with a lid.

51 For samplers which have an internal filter cassette (eg the IOM sampler), remove the filter cassette from each sampler, fasten with the transport clip supplied by the manufacturer, and label appropriately.

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

53 Transport the filter transport cassettes (paragraph 50), sampler filter cassettes (paragraph 51) or samplers (paragraph 52) 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 36) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.*

### Cleaning of glassware

54 Before use, clean all glassware (paragraph 33) to remove any residual grease or chemicals. First soak overnight in laboratory detergent solution (paragraph 26) and then rinse thoroughly with water (paragraph 17).

55 After initial cleaning (paragraph 54), clean all beakers used in the sample dissolution procedure (paragraph 60) with hot nitric acid. Fill to one-third capacity with concentrated nitric acid (paragraph 18), cover with a watch glass, heat to approximately  $150^{\circ}\text{C}$  on the hot plate (paragraph 35) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 17).

56 After initial cleaning (paragraph 54), clean all glassware other than beakers used in the sample dissolution procedure (paragraph 60) by soaking in 1 + 9 nitric acid (paragraph 20) for at least 24 hours and then rinsing thoroughly with water (paragraph 17).

57 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 54 to 56, and which has been reserved for determination of cadmium by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 20) and then with water (paragraph 17).

### Preparation of sample and blank solutions

58 Open the filter transport cassettes (paragraph 50), sampler filter cassettes (paragraph 51) or samplers (paragraph 52) and transfer each filter into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 32).

59 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 a minimum volume of water (paragraph 17). Follow the same procedure for the blank filters (paragraph 49).

60 Add 5 ml of 1 + 1 nitric acid (paragraph 19) to each beaker, partially cover with a watch glass, and heat to approximately 150°C on a hot plate (paragraph 35) in a fume cupboard until the filter has dissolved and the solution has been reduced to approximately 1 ml. Remove each beaker from the hot plate and allow to cool.

61 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 17), and transfer each solution quantitatively to a labelled 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter which has been pre-washed with 1 + 9 nitric acid (paragraph 20) and then with water. Finally, dilute to the mark with water, stopper and mix thoroughly.

#### **Analysis by flame atomic absorption spectrometry**

**Note 14:** *Laboratory experiments<sup>2</sup> have shown that flame atomic absorption measurements of cadmium are not affected significantly by variation in the nitric acid concentration within the range 5% to 25% (v/v). However, it is good laboratory practice to match sample and standard matrices as far as is reasonably practicable.*

#### **Preparation of calibration solutions**

62 Prepare at least six calibration solutions to cover the range 0 µg ml<sup>-1</sup> to 1 µg ml<sup>-1</sup> of cadmium. Add 20 ml of 1 + 1 nitric acid (paragraph 19) to separate, labelled 100 ml volumetric flasks. Accurately pipette the appropriate volume of working standard cadmium solution A (paragraph 23) into each flask, dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare these solutions fresh daily.

#### **Atomic absorption measurements**

63 Set up the atomic absorption spectrometer (paragraph 38) to determine cadmium at a wavelength of 228.8 nm using an oxidising air-acetylene flame. Follow the manufacturer's recommendations for specific operating parameters, and use background correction if appropriate. The sensitivity, defined as the concentration required to produce a signal of 1% absorbance or 0.0044 absorbance units, is about 0.016 µg ml<sup>-1</sup> of cadmium.

64 Adjust the spectrometer zero while aspirating the blank calibration solution (paragraph 62). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

65 Aspirate the calibration solutions (paragraph 62) 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 cadmium 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 cadmium concentration.

66 Aspirate the sample and blank solutions (paragraph 61) 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 cadmium in the sample and blank solutions and obtain a direct readout of the results in µg ml<sup>-1</sup> of cadmium. For instruments without this capability, determine the concentration of cadmium in µg ml<sup>-1</sup> from the calibration graph (paragraph 65).

67 Aspirate a mid-range standard 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, recalibrate the spectrometer as described in paragraph 65; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

68 If high concentrations of cadmium 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 nitric acid concentration is 1 + 9. Record the dilution factor.

69 Calculate the mean cadmium concentration of the blank solutions.

70 If the concentration of cadmium in the sample solutions is less than 0.05 µg ml<sup>-1</sup>, consider repeating the analysis using electrothermal atomic absorption spectrometry (see paragraphs 71 to 79) since this technique gives more precise measurements at low concentrations.

#### **Analysis by electrothermal atomic absorption spectrometry**

**Note 15:** *Cadmium is present at a low level in the environment and it is essential that strict standards of cleanliness are observed to avoid contamination of labware. This is particularly important when carrying out electrothermal atomic absorption spectrometry since the technique exhibits a very low detection limit. Ensure that all glassware is cleaned thoroughly before use in accordance with paragraphs 54 to 57, and that autosampler cups (paragraph 40) are stored in 1 + 9 nitric acid (paragraph 20) until required.*

## Preparation of working calibration solutions

71 Prepare a working calibration solution at a concentration of 2.5 ng ml<sup>-1</sup> of cadmium. Accurately pipette 250 µl of working standard cadmium solution B (paragraph 24) into a 100 ml volumetric flask. Add about 50 ml of water (paragraph 17) and 20 ml of 1 + 1 nitric acid (paragraph 19) and swirl to mix. Dilute to the mark with water (paragraph 17), stopper and mix thoroughly. Prepare this solution fresh daily.

72 Prepare a working calibration blank solution following the procedure in paragraph 71, but omitting the 250 µl of working standard cadmium solution B (paragraph 24).

## Atomic absorption measurements

73 Set up the atomic absorption spectrometer (paragraph 38) and electrothermal atomiser (paragraph 39) to determine cadmium at a wavelength of 228.8 nm using background correction. Follow the manufacturer's recommendations for specific operating parameters.

**Note 16:** *The operating parameters for electrothermal atomic absorption spectrometry vary considerably between different instruments, much more so than for flame atomic absorption spectrometry. A Perkin-Elmer 5100PC atomic absorption spectrometer with Zeeman HGA-600 graphite furnace module and AS-60 autosampler was used in the validation of this method,<sup>2</sup> and the operating parameters used are given in Appendix 2. The characteristic mass for cadmium, defined as the number of picograms required to give 0.0044 absorbance-seconds, was determined to be 0.8 pg for this analytical system. This is equivalent to a sample solution concentration of 0.04 ng ml<sup>-1</sup> of cadmium for a 20 µl sample solution injection volume.*

74 Programme the autosampler to prepare matrix-modified calibration, sample solutions and blank solutions in situ on a pyrolytic graphite platform mounted in the pyrolytically-coated graphite tube of the electrothermal atomiser. Prepare at least six matrix-modified calibration solutions to cover the range 0 ng ml<sup>-1</sup> to 2.5 ng ml<sup>-1</sup> using the working calibration solution (paragraph 71), the working calibration blank solution (paragraph 72) and the matrix modifier solution (paragraph 25). Prepare matrix-modified sample and blank solutions using the sample and blank solutions (paragraph 61) and the matrix modifier solution (paragraph 25). See Table 3 for typical autosampler injection volumes.

**Note 17:** *The procedure described above may be varied to accommodate the use of electrothermal atomisers of alternative design (see note 11).*

**Note 18:** *Matrix-modified calibration and test solutions may be prepared in volumetric flasks as an alternative to preparation in situ using the autosampler.*

**Note 19:** *Sample test solutions should be diluted (see paragraph 78) before analysis by electrothermal atomic*

*absorption spectrometry (see paragraph 70) if results obtained by flame atomic absorption spectrometry indicate that the cadmium concentration is above the upper limit of the calibration range for electrothermal atomic absorption spectrometry (see paragraph 74).*

75 Set up the analytical sequence in the microprocessor or personal computer. Specify an appropriate number of replicate analyses for each solution, and insert a calibration blank solution and a mid-range calibration solution after each five to ten sample solutions to monitor for baseline drift and sensitivity change respectively.

76 Place the working calibration solution (paragraph 71), the working calibration blank solution (paragraph 72), the matrix modifier solution (paragraph 25), and the sample and blank solutions (paragraph 61) in separate acid-washed autosampler cups (paragraph 40) and position as appropriate in the autosampler carousel. Analyse the matrix-modified calibration, sample and blank solutions, using the microprocessor or personal computer software to generate a calibration and obtain a direct readout of sample and blank results in ng ml<sup>-1</sup> of cadmium.

77 If significant baseline drift is observed during the course of the analysis, or if the sensitivity changes 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 76. In either case, reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

78 If concentrations of cadmium above the upper limit of the calibration range are found, dilute the sample solutions to bring them within the calibration range, and repeat the analysis. Make all dilutions so that the final nitric acid concentration is 1 + 9. Record the dilution factor.

79 Calculate the mean cadmium concentration of the blank solutions.

## QUALITY CONTROL MEASURES

80 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>22</sup>

81 If cadmium 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 cadmium 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  $\pm 2SD$  and  $\pm 3SD$  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.<sup>22</sup> Take care to ensure that the quality control filters are stored under conditions which ensure maximum stability.

82 It is strongly recommended that all laboratories undertaking the determination of cadmium 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.<sup>22</sup>

## CALCULATIONS

### Volume of air sample

83 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 cadmium in air

84 Calculate the concentration of cadmium in air,  $\rho(\text{Cd})$ , in milligrams per cubic metre ( $\text{mg m}^{-3}$ ), using the equation:

$$\rho(\text{Cd}) = \frac{[\rho(\text{Cd})_1 \cdot V_1 \cdot \text{DF}_1 - \rho(\text{Cd})_0 \cdot V_0 \cdot \text{DF}_0]}{V}$$

where

$\rho(\text{Cd})_0$	is the mean concentration, in $\mu\text{g ml}^{-1}$ , of cadmium in the blank solutions (see paragraphs 69 and 79);
$\rho(\text{Cd})_1$	is the concentration, in $\mu\text{g ml}^{-1}$ , of cadmium in the sample solution (see paragraphs 66 and 76);
$V$	is the volume, in litres, of the air sample (see paragraph 83);
$V_0$	is the volume, in ml, of the blank solutions, ie 10 ml (see paragraph 61);
$V_1$	is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 61);
$\text{DF}_0$	is the dilution factor for the blank solutions, ie 1;
$\text{DF}_1$	is the dilution factor for the sample solutions (see paragraphs 68 and 78).

**Note 20:** For low concentrations of cadmium in air determined by electrothermal atomic absorption spectrometry, calculate results in micrograms per cubic metre by using solution concentrations in  $\text{ng ml}^{-1}$  in the above equation.

## TEST REPORT

85 Appendix 3 gives recommendations for information to be included in the test report.

### APPENDIX 1 Primary standard for calibration of portable flowmeter

The primary standard should preferably be a flowmeter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flowmeter may be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A one litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with water (paragraph 17), allowing temperatures to stabilise, drawing off a known volume and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol and four parts water. The burette must be thoroughly wetted with the solution and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. (Traceability of the calibration will require checking of the clocks and use of certificated weights.)

## APPENDIX 2 Typical operating parameters for determination of cadmium by electrothermal atomic absorption spectrometry

Mode: Peak area  
 Integration time: 5 seconds  
 Background correction: Zeeman  
 Injection volumes: 20  $\mu\text{l}$  of calibration, sample or blank solution and 10  $\mu\text{l}$  of matrix modifier solution

**Table 2** Typical temperature profile for determination of cadmium using electrothermal atomic absorption spectrometry

Step	Ramp time (sec)	Hold time (sec)	Furnace temp °C	Argon flow ml min <sup>-1</sup>	Read
1 Dry	40	30	120	300	
2 Ash	10	20	850	300	
3 Cool down	1	15	20	300	
4 Atomise	0	5	1650	0	*
5 Clean	1	5	2600	300	

**Table 3** Typical autosampler injection volumes for the in-situ preparation of matrix-modified calibration, sample and blank solutions

Matrix-modified solution	Volume of working calibration solution ( $\mu\text{l}$ )	Volume of working calibration blank solution ( $\mu\text{l}$ )	Volume of matrix modifier solution ( $\mu\text{l}$ )	Volume of sample or blank solution ( $\mu\text{l}$ )
0 ng ml <sup>-1</sup> calibration solution	-	20	10	-
0.5 ng ml <sup>-1</sup> calibration solution	4	16	10	-
1.0 ng ml <sup>-1</sup> calibration solution	8	12	10	-
1.5 ng ml <sup>-1</sup> calibration solution	12	8	10	-
2.0 ng ml <sup>-1</sup> calibration solution	16	4	10	-
2.5 ng ml <sup>-1</sup> calibration solution	20	-	10	-
Sample or blank solution	-	-	10	20
Sample solution dilution	-	(20 - x)	10	x

The cadmium concentrations in the matrix-modified calibration solutions are notional, in that they relate to the 20  $\mu\text{l}$  volume of sample or blank solution (ie the 10  $\mu\text{l}$  volume of matrix-modifier solution is ignored).

### APPENDIX 3 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 duration of the sampling period 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 cadmium found in the air sample, in milligrams per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

### ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, Broad Lane, Sheffield, S3 7HQ (telephone 0742 892000).

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

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