

MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory



16/2

Mercury and its inorganic divalent compounds in air

Laboratory method using Hydrar[®] diffusive badges or pumped sorbent tubes, acid dissolution and analysis by cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry

April 2002

INTRODUCTION

Note 1: This method updates and replaces MDHS 16.¹ The principal changes which have been made are (i) to expand the scope of the method to include the determination of mercury vapour and divalent mercury compounds, rather than mercury vapour only; (ii) to refer to the use of Hydrar as sorbent, since this has now replaced hopcalite; (iii) to describe a diffusive sampling method for mercury vapour, as an alternative to pumped sampling; (iv) to describe the use of flow injection, discrete injection and continuous flow cold vapour systems, rather than the batch cold vapour technique previously described, which has now been largely superseded; and (v) to describe the use of atomic fluorescence spectrometry for analysis of sample solutions, as an alternative to atomic absorption spectrometry.

Note 2: The revised MDHS has been developed in parallel with ISO 17733.²

Requirements of the Control of Substances Hazardous to Health (COSHH) Regulations 1999

General requirements of the COSHH Regulations

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

ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

2 Guidance is given in the Approved Codes of Practice for the Control of Substances Hazardous to Health Regulations (the *General COSHH ACOP*), the Control of Carcinogenic Substances Regulations (the *Carcinogens ACOP*), and the Control of Biological Agents Regulations (the *Biological Agents ACOP*), which are included in a single publication with the COSHH Regulations.⁴

Occurrence, properties and uses

3 Occurrence, properties and uses of mercury and its inorganic compounds are fully covered in HSE Contract Research Report No 76/1995.⁵

4 Mercury occurs as the sulphide in many rocks at low concentration. Mercury is produced by roasting the Cinnabar ore, which contains about 0.5% mercury.

5 Mercury is a silvery-white metal that is liquid at ordinary temperatures and has a boiling point of 356.9°C. Metallic mercury and its compounds have an appreciable vapour pressure at room temperature.

6 The largest industrial use of elemental mercury is as a cathode in the electrolysis of brine solution to produce chlorine gas and sodium hydroxide in the chloralkali process. Because of its unique properties as a metal which is liquid at room temperature, ie its high density, electrical conductivity and coefficient of expansion, it is widely used in the manufacture of temperature and pressure measuring instruments and electrical switchgear. Mercury vapour has special electrical discharge characteristics which are exploited in fluorescent lights, mercury discharge lamps and rectifiers manufactured by the electrical industry. Mercury is combined with a number of metals, notably gold, silver, tin and copper, to

produce amalgams used for tooth fillings in dentistry. Mercury is the starting point for the manufacture of mercury compounds, such as mercuric oxide, which is used in certain cell batteries, and mercuric chloride, which is used in pharmaceutical products and laboratory chemicals. Monovalent mercury compounds exist, but are rarely encountered in industry.

Note 3: *The COSHH Regulations^{3,4} stipulate that, whenever possible, processes using toxic substances should be substituted by processes using less harmful substances. As a result, the use of mercury and mercury compounds is declining in industry. In particular, the large-scale use of mercury in chloralkali processes is declining dramatically. It is anticipated that this use of mercury will have ceased in the United Kingdom by 2010.*

Health effects

7 The health effects of mercury and its inorganic compounds are summarised in HSE Medical Series Guidance Note MS 12⁶ and are fully covered in HSE Contract Research Report No 76/1995.⁵

8 Exposure to mercury can occur via the respiratory tract and skin. Possible symptoms from an acute exposure include severe nausea, vomiting, abdominal pain, bloody diarrhoea, kidney damage and death. These symptoms usually present themselves within ten days of exposure. Potential symptoms from a chronic exposure include inflammation of the mouth and gums, excessive salivation, loosening of the teeth, kidney damage, muscle tremors, jerky gait, spasms of the extremities, personality changes, depression, irritability and nervousness.

9 Mercury and a number of inorganic divalent compounds have been classified and assigned risk phrases in the Approved Supply List⁷ of the Chemicals (Hazard Information and Packaging for Supply) Regulations.⁸ The risk phrases relating to human health are given in paragraphs 10 to 13.

10 Risk phrases relating to mercury are:

| | |
|-----|------------------------------|
| R23 | Toxic by inhalation |
| R33 | Danger of cumulative effects |

11 Risk phrases relating to mercuric fulminate and oxycyanide are:

| | |
|-----------|--|
| R23/24/25 | Toxic by inhalation, in contact with the skin and if swallowed |
| R33 | Danger of cumulative effects |

12 Risk phrases relating to mercuric chloride are:

| | |
|-----------|---|
| R28 | Very toxic if swallowed |
| R34 | Causes burns |
| R48/24/25 | Toxic: danger of serious damage to health by prolonged exposure in contact with the skin and if swallowed |

13 Risk phrases relating to other inorganic compounds of mercury, with the exception of mercuric sulphide, are:

| | |
|-----------|---|
| R26/27/28 | Very toxic by inhalation, in contact with the skin and if swallowed |
| R33 | Danger of cumulative effects |

Health and safety precautions

14 HSE Guidance Note EH 17⁹ summarises the risks involved in working with mercury and divalent mercury compounds and gives advice on prevention and control of exposure, emergency procedures and health surveillance. Health surveillance requirements and procedures are described in detail in HSE Medical Series Guidance Note MS 12.⁶

Exposure

15 Exposure to mercury can occur via the respiratory tract and skin. If ingested, it can also be absorbed in minute amounts by the gastrointestinal tract. Mercury may be inhaled either as mercury vapour and/or as particulate-containing mercury compounds and/or adsorbed mercury vapour and/or adsorbed volatile organomercury compounds. The concentration of mercury vapour in air saturated by contact with liquid mercury is well in excess of exposure limits at normal temperatures and rapidly increases as the temperature increases. At 20°C, 30°C and 40°C the vapour pressure of mercury is equivalent to concentrations of 13.2 mg m⁻³, 29.5 mg m⁻³ and 62.6 mg m⁻³ respectively. The high vapour pressure of mercury, combined with the risk of accumulative health effects, makes it necessary to have good control measures in place to avoid exposure. The propensity for small beads of liquid mercury to roll away and escape into cracks when spillages occur makes contamination of premises likely unless strict clean-up procedures are observed. Divalent mercury compounds can be breathed in as dusts. In addition, some inorganic divalent compounds are unstable and decompose readily to form the free metal, which then acts as a source of mercury vapour. Mercury vapour can also be released in processes that involve the heating of mercury amalgams. It can arise, for instance, in the preparation of mercury amalgam for dental fillings.

Exposure limits

16 The Health and Safety Commission has approved two occupational exposure standards for mercury. These limits are published in Table 2 of HSE Guidance Note EH 40.¹⁰

17 A long-term exposure limit of 0.025 mg m⁻³, 8-hour time-weighted average (TWA) reference period, has been set for *mercury and its inorganic divalent compounds (as Hg)*. The criteria on which this limit is based are documented in HSE Guidance Note EH 65/19¹¹ and are summarised in Guidance Note EH 64 (1995 Supplement).¹²

18 Alkyl mercury compounds are considered to be more toxic than mercury vapour and divalent mercury compounds. Consequently, a lower long-term exposure limit of 0.01 mg m⁻³, 8-hour TWA reference period, has been set for *mercury alkyls (as Hg)*, and a short-term exposure limit of 0.03 mg m⁻³, 15-minute reference period,

also applies. However, measurement of alkyl mercury compounds is not covered by the method described in this MDHS.

Note 4: Regulation 7 of the COSHH Regulations^{3,4} lays down the requirements for using maximum exposure limits (MELs) and occupational exposure standards (OESs) for the purpose of achieving adequate control of worker exposure.

Note 5: No occupational exposure standards have been set for monovalent mercury compounds or aryl mercury compounds. However, the general requirements of the COSHH Regulations apply (see paragraph 1).

Analytical methods

19 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.

20 The diffusive badge and pumped sorbent tube methods described in this MDHS have both been validated^{13,14} to demonstrate that they comply with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.¹⁵ If an alternative method is used, it is necessary to demonstrate that it also meets these performance requirements.

PRINCIPLE

21 This method describes the collection of airborne mercury, both in its elemental state as a vapour and in its divalent state as a particulate, and its subsequent analysis using cold vapour atomic absorption spectrometry (CVAAS) or cold vapour atomic fluorescence spectrometry (CVAFS).

22 Mercury vapour is collected either passively or actively. Passive sampling relies upon the principle of controlled diffusion into a badge, whereas active sampling involves drawing a known volume of air through a sorbent tube using a pump. In both the diffusive badge and pumped sorbent tube methods, mercury vapour entering the sampling device is collected on a proprietary sorbent that is widely known as Hydrar (see note 6).

Note 6: Hydrar is a name previously given by SKC Inc to the sorbent used in the diffusive badges and pumped sorbent tubes it manufactures for sampling mercury vapour. Hydrar is a granular preparation of hopcalite (a mixture of copper and manganese oxides) deposited on a ceramic substrate. Hopcalite has been shown to have an irreversible affinity for mercury and be a suitable sorbent for sampling mercury vapour.^{16,17} Hydrar is manufactured by Carus under the trade name Carulite 300, primarily for

use as an industrial catalyst. SKC uses Carulite 300 in its diffusive badges and pumped sorbent tubes, after grinding to a suitable mesh size, and it now refers to this sorbent as Anasorb C 300.

23 If it is known that no particulate inorganic mercury compounds are present in the test atmosphere, mercury vapour is collected using a diffusive badge or by drawing a known volume of air through a sorbent tube using a pump.

24 If it is known that no mercury vapour is present in the test atmosphere, particulate inorganic mercury compounds are collected by drawing a known volume of air through a quartz fibre filter mounted in a sampler designed to collect the inhalable fraction of airborne particles, as defined in BS EN 481,¹⁸ using a pump.

25 A pumped sorbent tube is also used for sampling air that contains both mercury vapour and particulate inorganic mercury compounds. The sorbent tube, which collects mercury vapour, is preceded by a quartz fibre filter to collect particulate inorganic mercury compounds, unless these do not make up a significant proportion (>10%) of the total inorganic mercury (mercury vapour and particulate inorganic mercury compounds) present in the test atmosphere (see note 41).

26 After sample collection, the sorbent and/or filter are treated with 2 ml of concentrated nitric acid and 2 ml of hydrochloric acid and heated in a thermostatically-controlled water bath at 50°C for 1 h to dissolve the collected mercury.

27 Sample solutions are mixed with tin (II) chloride solution in a continuous flow, flow injection, or discrete injection cold vapour generation system. Mercury vapour is formed by reduction of divalent mercury ions, and this is flushed by a stream of inert gas into the measurement cell of an atomic absorption spectrometer or an atomic fluorescence spectrometer equipped with a mercury hollow cathode lamp or electrodeless discharge lamp. Absorbance or fluorescence measurements are made at 253.7 nm and analytical results are obtained by the analytical curve technique.

SCOPE

28 This MDHS describes diffusive badge and pumped sorbent tube methods for determination of time-weighted average concentrations of mercury and divalent mercury compounds in workplace air.

Note 7: HSG173¹⁹ 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 methods described in this measuring procedure are for personal sampling in the breathing zone. However, the methods may also be used for fixed place or static 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. In particular, the collection efficiency of static sampling using diffusive badges in still air conditions is low²⁰ (see paragraph B4).

29 The diffusive badge and pumped sorbent tube methods described are both suitable for the determination of the concentration of mercury vapour for assessment of exposure against the long-term exposure limit for mercury. The diffusive badge method is suitable for sampling times in excess of 6 h. The pumped sorbent tube method is suitable for sampling times in the range 1 h to 8 h when sampling at a flow rate of 200 ml min⁻¹ using a 200 mg tube.

30 There is no short-term exposure limit for mercury. However, it might sometimes be necessary to sample for short times to evaluate the risk from a process which takes place over a short duration. Sampling can be carried out over time periods as short as 15 min using a large capacity pumped sorbent tube containing 500 mg of Hydrar at a flow rate of 2 l min⁻¹. However, hand-held instruments are available that give an instantaneous reading of the concentration of mercury in air, and these are generally more convenient for short-term sampling and rapid surveying purposes.

31 The pumped sorbent tube method is also suitable for measuring mercury vapour and particulate divalent mercury compounds when both are present in the test atmosphere. In this case, mercury vapour is collected on the sorbent and particulate mercury is collected on the glass wool plugs that retain the sorbent. The efficiency of capture of particulate by the sorbent tube method has not been assessed, but it is reasonable to assume that it is high. Consequently, it is acceptable to analyse for total mercury collected on the sorbent and glass fibre plugs in order to estimate total mercury-in-air concentrations when it is known that the majority of the mercury sampled is in the vapour state. In situations where high levels of particulate are present, it is necessary to precede the sorbent tube with a quartz fibre filter to prevent blockage of the glass fibre plugs. The filter is then analysed together with the contents of the sorbent tube. When it is known that mercury is only present in the atmosphere in the particulate state, sampling using a quartz fibre filter alone is adequate.

32 The diffusive badge method is not applicable to the measurement of particulate mercury.

33 The diffusive badge and pumped sorbent tube methods are both suitable for measurement of airborne mercury in the concentration range 0.0025 mg m⁻³ to 0.050 mg m⁻³. Higher concentrations can be measured by dilution of the sample solution (see paragraph 204). The maximum concentration measurable is eventually limited by the sorptive capacity of the Hydrar used (see paragraph 58 for information on the maximum uptake of diffusive badges and paragraph 59 for information on breakthrough volumes of sorbent tubes).

34 Very low concentrations of mercury can be measured by sampling at a flow rate of 2 l min⁻¹ with sorbent tubes containing 500 mg of Hydrar. However, the lowest concentration of mercury that can be measured is limited by the rather high blank, which is due to traces of mercury in the sorbent. If low concentrations of mercury are to be measured, consideration should be given to using a technique which has a lower mercury blank. For instance, the use of gold sorbent tubes and thermal desorption atomic fluorescence spectrometry is the accepted analytical procedure for measuring mercury at environmental levels.²²

METHOD PERFORMANCE

Note 8: The method performance data presented in this MDHS are derived primarily from work carried out at the Health and Safety Laboratory (HSL).¹⁴ This supplements data obtained by the US Occupational Safety and Health Administration (OSHA), which are documented in the back-up report of OSHA method ID-140.²⁰ Further laboratory and field evaluations of the performance of Hydrar diffusive badges and pumped sorbent tubes have been made in a joint exercise carried out by OSHA and the US National Institute for Occupational Safety and Health (NIOSH).²¹

Detection limits

35 Using flow injection CVAAS, the qualitative and quantitative detection limits for mercury, defined as three times and ten times the standard deviation of a blank determination, have been determined¹⁴ to be 0.009 µg and 0.030 µg for samples of mercury vapour collected on 200 mg Carulite (Hydrar) sorbent tubes; 0.010 µg and 0.033 µg for samples of mercury collected on 200 mg Carulite (Hydrar) sorbent tubes with quartz fibre prefilters; 0.012 µg and 0.040 µg for samples of mercury collected on Carulite (Hydrar) diffusive samplers; and 0.003 µg and 0.009 µg for samples of mercury in particulate collected on quartz fibre filters. For the minimum air sample volume of 12 litres using 200 mg Carulite (Hydrar) sorbent tubes, this corresponds to mercury-in-air concentrations of 0.001 mg m⁻³ and 0.003 mg m⁻³, respectively; or 0.001 mg m⁻³ and 0.003 mg m⁻³, respectively, for 200 mg Carulite (Hydrar) sorbent tubes with quartz fibre prefilters. For the minimum exposure time of 6 h using Carulite (Hydrar) diffusive samplers (equivalent to an air uptake volume of 7.2 litres), it corresponds to mercury-in-air concentrations of 0.002 mg m⁻³ and 0.006 mg m⁻³, respectively. For the minimum air volume of 30 litres sampled using quartz fibre filters, it corresponds to mercury-in-air concentrations of 0.0001 mg m⁻³ and 0.0003 mg m⁻³, respectively.

36 Similarly, using discrete injection CVAAS, the qualitative and quantitative detection limits for mercury have been determined¹⁴ to be 0.002 µg and 0.008 µg for samples of mercury vapour collected on 200 mg Carulite (Hydrar) sorbent tubes. For the minimum air sample volume of 12 litres, this corresponds to mercury-in-air concentrations of 0.0002 mg m⁻³ and 0.0007 mg m⁻³, respectively.

Upper limits of the analytical range

37 The upper limit of the useful analytical range is limited by the linear dynamic range of the spectrometer.

38 Using a flow injection CVAAS system with a 0.5 ml sample injection volume, the calibration obtained¹⁴ was significantly curved at mercury concentrations above $0.1 \mu\text{g ml}^{-1}$. This is equivalent to 2.5 μg of mercury for the 25 ml sample solution volume used for diffusive badges or 5 μg of mercury for the 50 ml sample solution volume used for pumped samplers. If greater amounts of mercury are collected, dilution of sample solutions or the use of a smaller sample loop is required.

39 Using discrete injection CVAFS, the calibration obtained was close to linear over a much greater concentration range, and mercury concentrations up to at least $10 \mu\text{g ml}^{-1}$ could be measured without dilution of the sample. This is equivalent to 250 μg of mercury for the 25 ml sample solution volume used for diffusive badges, or 500 μg of mercury for the 50 ml sample solution volume used for pumped samplers.

Blank mercury values

40 Hydrar used in diffusive badge sorbent capsules and sorbent tubes contains trace amounts of mercury. Laboratory experiments¹⁴ have established that the 800 mg of Hydrar used in sorbent capsules typically has a mercury blank of 0.08 μg , while the 200 mg of Hydrar used in standard sorbent tubes typically contains 0.02 μg of mercury.

Note 9: *The blank due to mercury impurities in the Hydrar has much more influence on the accuracy of analysis of diffusive badges than that of pumped sorbent tubes. This is because the quantity of Hydrar is four times greater and because the sampling rate is 10 times lower. The net effect is to make the blank 40 times greater compared with the mass of mercury vapour sampled. Technically, both methods do not meet the BS EN 838 and BS EN 1076 requirement that the blank value should not exceed one third of the analyte collected at one tenth of the limit value for the minimum sampling time. However, the consistency of the mercury blanks within batches of Carulite (Hydrar) is such that conformity with the overall criteria of the standards is nevertheless achieved using both sampling methods.*

Analytical bias

41 Laboratory experiments have shown that the analytical method does not exhibit significant bias. The mean analytical recovery has been determined¹⁴ to be 97.4% for 200 mg Carulite (Hydrar) sorbent tubes dosed in the range 0.15 μg to 4.8 μg of mercury, 96.2% for 200 mg Carulite (Hydrar) sorbent tubes with quartz fibre prefilters dosed with 2.4 μg of mercury, and 93.3% for quartz fibre filters dosed with 2.4 μg of mercury.

Analytical precision

42 The component of the coefficient of variation of the

method that arises from analytical variability, CV(analysis), is dependent on a number of factors, including the analytical instrumentation used, and it is at a minimum when the concentration of mercury in the test solution is in the mid-range of the calibration. Laboratory experiments have been carried out to obtain figures of merit for CV(analysis). Using flow injection CVAAS, CV(analysis) has been determined¹⁴ to be 0.7% for 200 mg Carulite (Hydrar) sorbent tubes dosed with 2.4 μg of mercury, 3.9% for 200 mg Carulite (Hydrar) sorbent tubes with quartz fibre prefilters dosed with 2.4 μg of mercury, and 2.2% for quartz fibre filters dosed with 2.4 μg of mercury. Using discrete injection CVAFS, CV(analysis) has been determined¹⁴ to be 4.1% for 200 mg Carulite (Hydrar) sorbent tubes dosed with 2.4 μg of mercury.

Note 10: *See Appendix A for details of the instrumentation used.*

Overall bias of sampling and analytical methods

43 Laboratory experiments have been performed¹⁴ to determine the overall bias of the combined sampling and analysis methods. These experiments were carried out by sampling mercury vapour generated at concentrations between 0.0025 mg m^{-3} and 0.05 mg m^{-3} at a temperature of 20°C and a relative humidity of 50% and comparing results with an independently calibrated method. An average recovery of 91.8% was obtained for 200 mg Carulite (Hydrar) sorbent tubes, referenced against direct analysis using gold trapping thermal desorption atomic fluorescence spectrometry. The two methods agreed to better than $\pm 10\%$, and it was therefore concluded that the sorbent tube method exhibits no significant bias. An average recovery of 92.4% was obtained for diffusive badges when compared with measurements made using 200 mg Carulite (Hydrar) sorbent tubes. This result is consistent with a systematic bias of -7% reported by OSHA,²⁰ and it can be attributed to a small error in the nominal uptake rate of the diffusive badges given by the manufacturer.²³

Overall precision of sampling and analytical methods

44 Laboratory experiments have been performed¹⁴ to determine the overall coefficient of variation, CV(overall), of the combined sampling and analysis methods. These experiments were carried out by sampling mercury vapour generated at concentrations between 0.0025 mg m^{-3} and 0.05 mg m^{-3} at a temperature of 20°C and a relative humidity of 50%. The average CV(overall) determined using flow injection CVAAS was 3.7% for samples collected on 200 mg Carulite (Hydrar) sorbent tubes at 200 ml min^{-1} for sampling periods ranging from 1 h to 8 h, and 6.3% for samples collected on diffusive badges for sampling periods ranging from 2 h to 8 h.

Overall uncertainty

45 The sampling and analytical methods described for measuring mercury vapour using either diffusive badges or pumped sorbent tubes, and for measuring divalent mercury in air using pumped quartz fibre filters, have been evaluated to demonstrate compliance with BS EN 482

*Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents.*¹⁵ This European Standard prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be <50% for measurements in the range 0.1 to 0.5 times the limit value (LV) of 0.025 mg m⁻³ of mercury in air, and <30% for measurements in the range 0.5 LV to 2.0 LV.

46 The overall uncertainty for a measuring procedure is defined in BS EN 482¹⁵ as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is expressed in percentage terms, by a combination of bias and precision according to the following equation:

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

where: OU is the overall uncertainty of the procedure;

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

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

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

47 Equation 1 can be rewritten as:

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

where: $bias$ is the difference between the mean measured concentration and the true or reference concentration, divided by the true or reference concentration, ie:

$$\frac{(\bar{x} - x_{ref})}{x_{ref}}$$

and: RSD is the relative standard deviation of n repeat measurements defined as:

$$\frac{\sigma_{(n-1)}}{x_{ref}}$$

48 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 838²⁴ to assess whether the diffusive badge method for measurement of mercury vapour meets the general performance requirements specified in BS EN 482¹⁵ for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with the limit value of 0.025 mg m⁻³, the method meets the overall uncertainty requirements for sampling times close to 8 h, but not for sampling times as short as 4 h.

49 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 1076²⁵ to assess whether the pumped sorbent tube method for

measurement of mercury vapour meets the general performance requirements specified in BS EN 482¹⁵ for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with the limit value of 0.025 mg m⁻³ using a 200 mg Carulite (Hydrar) sorbent tube at a sampling rate of 200 ml min⁻¹, the method meets the overall uncertainty requirements for sampling times in the range 1 h to 8 h.

Note 11: 500 mg Carulite (Hydrar) sorbent tubes may be used to sample lower concentrations of mercury vapour or for shorter sampling times. However, no validation data are available for this method.

50 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 13890²⁶ to assess whether the pumped sampling methods for measurement of particulate inorganic mercury compounds meet the general performance requirements specified in BS EN 482¹⁵ for the overall uncertainty of measurements made for comparison with limit values. The results demonstrated that, for measurements made for comparison with the limit value of 0.025 mg m⁻³ using a 200 mg Carulite (Hydrar) sorbent tube with a quartz fibre prefilter at a sampling rate of 200 ml min⁻¹, the method meets the overall uncertainty requirements for sampling times in the range 1 h to 8 h. For measurements made for comparison with the limit value of 0.025 mg m⁻³ using a quartz fibre filter mounted in an inhalable sampler used at a typical sampling rate of 2 l min⁻¹, the method meets the overall uncertainty requirements for sampling times as short as 15 min.

51 Flow injection CVAAS was used for measuring mercury in all the experiments referred to in paragraphs 48 to 50. However, it was demonstrated¹⁴ that equally good performance could be obtained using discrete injection CVAAS.

The effects of exposure concentration and time on sampler performance

52 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 838²⁴ to determine the effect of exposure concentration and time on the performance of the diffusive badges. These experiments were carried out by sampling mercury vapour generated at concentrations between 0.1 LV (0.0025 mg m⁻³) and 2 LV (0.05 mg m⁻³) at a temperature of 20°C and a relative humidity of 50%. Results demonstrated that the effect of exposure concentration is negligible for sampling periods close to 8 h.

53 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 1076²⁵ to determine the effect of exposure concentration and time on the performance of 200 mg Carulite (Hydrar) sorbent tubes. These experiments were carried out by sampling mercury vapour generated at concentrations between 0.1 LV (0.0025 mg m⁻³) and 2 LV (0.05 mg m⁻³) at a temperature of 20°C and a relative humidity of 50%. Results demonstrated that the effect of exposure concentration and time is negligible for sampling periods up to 8 h.

The effects of temperature and humidity on sampler performance

54 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 838²⁴ to determine the effect of atmospheric temperature and humidity on the performance of the diffusive badges. These experiments were carried out by sampling mercury vapour at 2 LV (0.05 mg m⁻³) at temperature extremes of 5°C and 40°C and relative humidity extremes of 20% and 70%. Results showed that the method complies with the performance requirements of BS EN 482¹⁵ within these extremes of temperature and humidity. However, they also indicated that the use of a temperature-corrected uptake rate could significantly improve accuracy at the extremes of the temperature range tested (see paragraph 111).

55 Laboratory experiments have been performed¹⁴ in accordance with the procedures given in BS EN 1076²⁵ to determine the effect of atmospheric temperature and humidity on the performance of 200 mg Carulite (Hydrar) sorbent tubes. These experiments were carried out by sampling mercury vapour at 2 LV (0.05 mg m⁻³) at temperature extremes of 5°C and 40°C and relative humidity extremes of 20% and 70%. Results demonstrated that the effect of temperature and humidity is negligible within these extremes.

Note 12: Procedures for temperature and pressure correction of results are given in paragraph 207.

Effect of air velocity on performance of diffusive badges

56 The manufacturer's literature²³ states that the uptake rate of the diffusive badge remains more or less constant for wind speeds in the range 7.5 m min⁻¹ to 230 m min⁻¹. However, in still air conditions (below about 7.5 m min⁻¹) the uptake rate can drop by up to 30%, and in very high wind speeds (in excess of about 230 m min⁻¹) erratic increases in sampling rate can occur. Similar data have been obtained in laboratory experiments carried out by OSHA.²⁰ The observed face velocity effects have implications for the field of application of diffusive badges (see paragraph B4).

Sample uptake rate and sampling capacity of diffusive badges

57 The sample uptake rate of the diffusive badge given by the manufacturer²³ is 20.0 ml min⁻¹ at 20°C and a pressure of 101.3 kPa. This compares with an uptake rate of 18.5 ml min⁻¹ determined by OSHA²⁰ and an uptake rate of 18.6 ml min⁻¹ determined by HSL¹⁴ in laboratory experiments carried out in accordance with the procedures given in BS EN 838²⁴ at a temperature of 20°C and a relative humidity of 50%. Despite the close agreement between these two sets of data, it is recommended that the 20.0 ml min⁻¹ nominal uptake rate by the manufacturer is used to calculate the concentration of mercury in air. Although this appears to introduce a sampling bias of -7%, the overall uncertainty requirements of BS EN 482¹⁵ were nevertheless found to be met (see paragraph 48).

58 Laboratory experiments carried out by OSHA with diffusive badges have shown²⁰ that mercury vapour concentrations of 0.21 mg m⁻³ can be sampled for up to 120 h without decrease in uptake rate. This indicates that the sampling capacity of the 800 mg of Hydrar contained in the diffusive badges is at least 30 µg of mercury vapour.

Collection efficiency, breakthrough volume and sampling capacity of sorbent tubes

59 Laboratory experiments have shown¹⁴ that the collection efficiency of sorbent tubes is close to 100%. Breakthrough was found to be less than 0.5% when sampling mercury vapour at 2 LV (0.05 mg m⁻³) for 24 h using an elevated flow rate of 500 ml min⁻¹ at a temperature of 20°C and a relative humidity of 50%. The breakthrough volume is therefore greater than 720 litres for mercury vapour at a concentration of 0.05 mg m⁻³. This corresponds to a sampling capacity of at least 36 µg of mercury vapour.

Storage stability

60 Laboratory experiments carried out by OSHA have shown²⁰ that samples of mercury vapour collected using diffusive badges are stable for at least one month when the sorbent capsules are sealed in the plastic pouches in which they were supplied, and that samples of mercury vapour collected using pumped sorbent tubes are stable for at least one month when the tubes are sealed with their plastic caps.

Mechanical strength

61 Mechanical strength tests for diffusive samplers specified in BS EN 838²⁴ were not carried out since the test equipment was not available. However, it was noted that Carulite (Hydrar) granules can be pulverised to a degree when a sorbent capsule is loaded into a diffusive badge and rapped repeatedly. As a consequence, Carulite (Hydrar) can escape from the capsule and contaminate the gauze discs used in the sampler. It has been shown that a significant proportion of the sampled mercury can be trapped on contaminated gauze and therefore not enter the capsule. It is therefore considered likely that the diffusive badge would not have passed the mechanical strength test. The diffusive badge should consequently be regarded as unsuitable for personal sampling to monitor the exposure of those engaged in vigorous occupations when it is inevitable that the badges will be repeatedly knocked.

Interferences

62 In the chloralkali process, mercury vapour commonly co-exists in the atmosphere with chlorine. Chlorine can react with mercury vapour in the air to form particulate mercuric chloride,²⁷ and therefore diffusive badges are unsuitable for making measurements of mercury-in-air in chloralkali works. However, chlorine does not interfere with the sampling process using sorbent tubes. This is because the particulate mercuric chloride formed is trapped on the glass wool retaining plugs or on the prefilter, if used, and it is subsequently analysed together with mercury vapour collected on the sorbent.

63 Any compound with the same absorption wavelength as mercury (253.7 nm) can cause interference in CVAAS. Some volatile organic compounds (eg benzene, toluene, acetone, carbon tetrachloride) absorb at this wavelength, and are considered analytical interferences. These compounds are not expected to be retained on Hydrar during sample collection, but they can occur as contaminants in the reagents used during sample preparation. However, such analytical interferences are rendered insignificant by using organic-free deionised water and reagent grade chemicals or by blank subtraction. CVAFS does not suffer from interference by volatile organic compounds that absorb at 253.7 nm since they do not re-emit at this wavelength.²⁸

64 No data are available concerning whether gaseous organo-mercury compounds are collected by Hydrar, and neither the diffusive badge method nor the pumped sorbent tube method has been assessed to establish whether it collects and measures organo-mercury compounds. If present, they could therefore cause a positive interference.

65 If organo-mercury compounds contained in or absorbed onto airborne particles are present in the test atmosphere, they will be collected on filters. The effectiveness of the sample dissolution method described has not been assessed for such compounds. If present, they could therefore cause a positive interference.

REAGENTS

66 During the analysis, use only reagents of recognised analytical grade, and only water as specified in paragraph 67.

Water

67 Water complying with the requirements of BS 3978²⁹ 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 (HNO₃), concentrated, ρ about 1.42 g ml⁻¹, 69% (m/m) to 71% (m/m)

68 The concentration of mercury shall be less than 0.01 µg ml⁻¹.

WARNING - Concentrated acid is corrosive and oxidising, and 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 the concentrated or diluted acid, and concentrated acid should be used in a fume hood.

Nitric acid, diluted 1 + 9 with water

69 Add approximately 700 ml of water (paragraph 67) to a 1 litre one-mark volumetric flask (paragraph 92). Carefully add 100 ml of concentrated nitric acid (paragraph 68) 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, 35% (m/m) to 36% (m/m)

70 The concentration of mercury shall be less than 0.01 µg ml⁻¹.

WARNING - Concentrated hydrochloric acid is corrosive, and hydrochloric acid vapour is irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapour. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with the concentrated or diluted hydrochloric acid, and concentrated hydrochloric acid should be used in a fume hood. The vapour pressure of hydrochloric acid is high, so beware of pressure build-up in stoppered flasks when preparing acid/water mixtures.

Nitric acid and hydrochloric acid, diluted 1 + 1 + 23 with water

71 Add approximately 700 ml of water (paragraph 67) to a 1 litre one-mark volumetric flask (paragraph 92). Carefully add 40 ml of concentrated nitric acid (paragraph 68) and 40 ml of concentrated hydrochloric acid (paragraph 70) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Note 13: This reagent is only required for analysis of sorbent tube samples.

Nitric acid and hydrochloric acid, diluted 2 + 2 + 21 with water

72 Add approximately 700 ml of water (paragraph 67) to a 1 litre one-mark volumetric flask (paragraph 92). Carefully add 80 ml of concentrated nitric acid (paragraph 68) and 80 ml of concentrated hydrochloric acid (paragraph 70) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Note 14: This reagent is only required for analysis of diffusive badge samples.

Tin (II) chloride, hydrated (SnCl₂·2H₂O)

73 The concentration of mercury shall be less than 10 µg kg⁻¹.

Tin (II) chloride, 1% (m/v) solution

74 Weigh 10 g of tin (II) chloride (paragraph 73) into a 500 ml beaker, add 30 ml of hydrochloric acid (paragraph 70), cover with a watchglass and leave for approximately 15 min until dissolved. Transfer to a 1000 ml volumetric flask (paragraph 92), dilute to the mark with water (paragraph 67), stopper and mix thoroughly. Prepare this solution fresh on the day of use.

Stock mercury standard solution, 1000 mg l⁻¹ of mercury

75 Use a commercial standard solution with a certified mercury concentration traceable to national standards. Observe the manufacturer's expiration date or recommended shelf life.

WARNING - Mercury compounds are toxic by skin absorption. Great care should be taken when working with solutions containing mercury to avoid skin contamination

Working mercury standard solution A, 10 mg l⁻¹ of mercury

76 Accurately pipette 0.5 ml of stock mercury standard solution (paragraph 75) into a 50 ml volumetric flask (paragraph 92). Add 1 ml of concentrated nitric acid (paragraph 68), dilute to the mark with water (paragraph 67), stopper and mix thoroughly. Prepare this solution fresh weekly.

Working mercury standard solution B, 1 mg l⁻¹ of mercury

77 Accurately pipette 5 ml of stock mercury standard solution (paragraph 75) into a 50 ml volumetric flask (paragraph 92). Add 1 ml of concentrated nitric acid (paragraph 68), dilute to the mark with water (paragraph 67), stopper and mix thoroughly. Prepare this solution fresh weekly.

Laboratory detergent solution

78 A laboratory grade detergent, suitable for cleaning of samplers and labware, diluted with water (paragraph 67) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Sampling equipment for diffusive sampling

Diffusive badges for mercury

79 Diffusive badges for mercury, manufactured by SKC, catalogue number 520-03. These are lightweight, reusable personal samplers designed to be worn in the breathing zone of individuals who are potentially exposed to mercury vapour. They are designed to sample mercury vapour at an uptake rate equivalent to 0.02 l min⁻¹ at 20°C and 101.3 kPa. The function of the badge is described in SKC Operating Instructions Form No 3758.²³ The badge is illustrated as an exploded diagram in Figure 1.

Sorbent capsules

80 Sorbent capsules, containing 800 mg of Anasorb C 300 (Hydrar), manufactured by SKC, catalogue number 520-02A, designed to be used in SKC diffusive badges, (paragraph 79). The capsules are distributed sealed in plastic pouches, in which they are resealed after sampling in order to prevent contamination during transport and storage.

Note 15: Mercury vapour enters the diffusive badges by positive controlled diffusion. It is then irreversibly absorbed by Hydrar contained in the sorbent capsule. No sampling pump is required. Samplers can be cleaned and reused with new sorbent capsules.

Note 16: Similar diffusive badges and sorbent capsules packed with Hydrar may be used if it can be demonstrated that they give equivalent performance. Sorbent capsules packed with hopcalite might also be suitable.

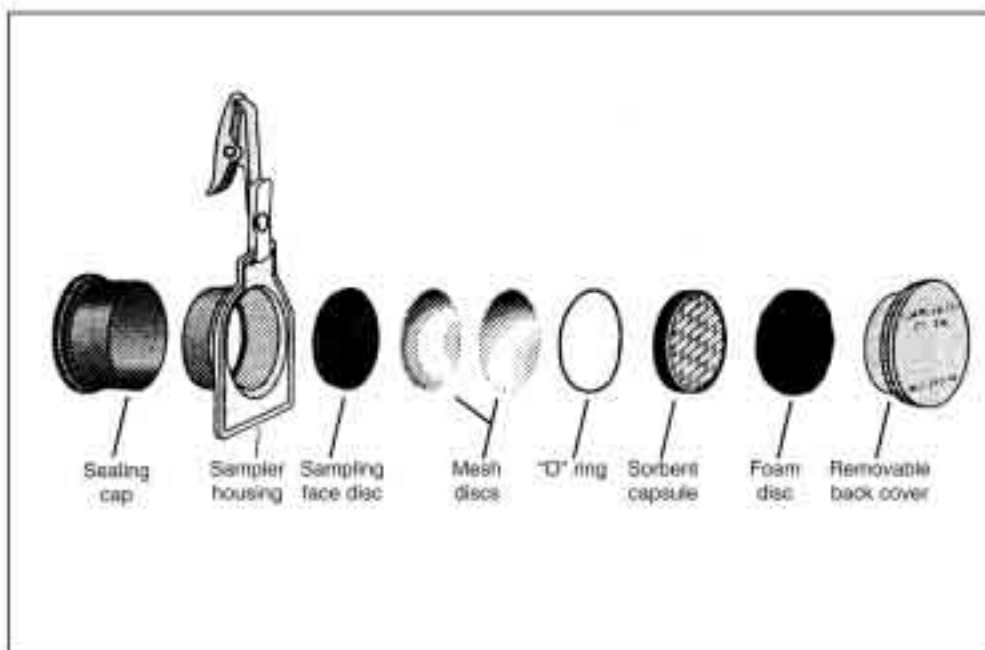


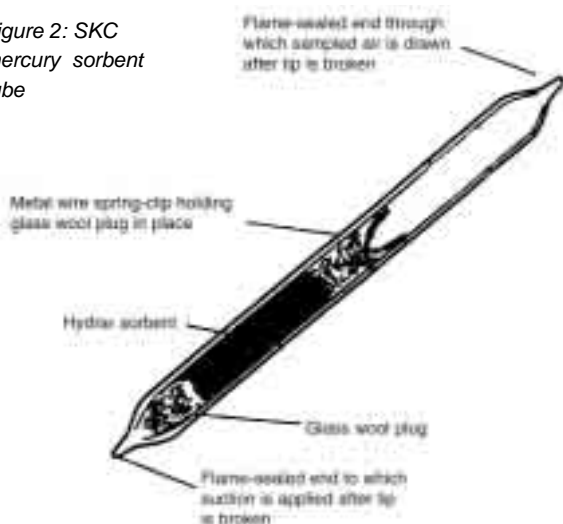
Figure 1: SKC 520 series diffusive sampler badge for mercury vapour

Sampling equipment for pumped sampling

Sorbent tubes

81 Sorbent tubes, glass, containing 200 mg or 500 mg of Hydrar, flame sealed at each end, with plastic end caps. The construction of a sorbent tube is illustrated in Figure 2.

Figure 2: SKC mercury sorbent tube



Note 17: Two sorbent tubes packed with Anasorb C 300 (Hydrar) are commercially available from SKC. The smaller, standard tube is 70 mm long, with a 6 mm OD and a 4 mm ID, and contains 200 mg of Anasorb C 300 (Hydrar) retained by small glass wool plugs. The larger tube is 110 mm long, with an 8 mm OD and a 6 mm ID. It contains 500 mg of Anasorb C 300 (Hydrar) and is intended for sampling at higher air flow rates, in order to measure low concentrations of mercury, or for shorter sampling periods (<1 h). The catalogue numbers of the standard and large SKC sorbent tubes are 226-17-1A and 226-17-3A, respectively. Similar sorbent tubes packed with Hydrar can be used if it can be demonstrated that they give equivalent performance. Sorbent tubes packed with hopcalite might also be suitable.

Note 18: Sorbent tubes containing Hydrar have a lower mercury blank than sorbent tubes containing hopcalite, which reduces the minimum air sample volume which can be used. On the other hand, Hydrar has the disadvantage that it is more friable than hopcalite. This means that it is liable to be pulverised if handled roughly, and poor grades of Hydrar have a high proportion of 'fines'. These can cause problems by clogging the glass wool plugs of the sorbent tubes, reducing the achievable air sampling rates.

Note 19: Hopcalite is completely dissolved during sample preparation, yielding a clear blue/green solution. However, an insoluble residue remains after treatment of Hydrar with acid, resulting in a milky suspension. This has to be removed before analysis by centrifugation or filtration.

Sorbent tube holders

82 Sorbent tube holders, designed for use with the sorbent tubes (paragraph 81) and with minimal contact of sampled air with the internal surfaces of the tube holder, so as to reduce the risk of loss of mercury vapour by surface adsorption. When assembled, the tube and holder shall not allow any leakage of sampled air.

Prefilter assembly

83 A prefilter assembly consisting of a quartz fibre filter (paragraph 86) mounted in a plastic filter cassette or inhalable sampler (paragraph 85), and connected to the intake of the sorbent tube with a minimum length of inert plastic tubing, eg Tygon® or polytetrafluoroethylene (PTFE) tubing.

Note 20: A prefilter assembly is only required if the concentration of airborne particles is sufficiently high that there is a risk of blockage of the glass wool plugs which retain the Hydrar sorbent in the tubes, or if the concentration of mercury vapour is to be determined separately from particulate divalent mercury.

Sampling cassettes

84 Sampling cassettes, plastic, disposable, for mounting quartz fibre filters (paragraph 86) to form a prefilter assembly (paragraph 83), if required (see paragraph 131).

Inhalable samplers

85 Samplers, with protective covers, designed to collect the inhalable fraction of airborne particles, as defined in BS EN 481,¹⁸ and complying with the provisions of BS EN 13205.³⁰ Inhalable samplers suitable for personal sampling are described in MDHS 14/3.³¹

Note 21: In general, personal samplers for collection of the inhalable fraction of airborne particles do not exhibit the same size-selective characteristics if used for static sampling.

Note 22: Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge, which can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample. It is advisable to avoid using such samplers, since otherwise it will be necessary to include dust collected on the internal surfaces in the analytical step (see note 58).

Note 23: Samplers manufactured in non-conducting material have electrostatic properties, which can influence representative sampling. Electrostatic influences should be reduced, where possible, by using samplers manufactured from conducting material.

Filters

86 Quartz fibre filters, of a diameter suitable for use in the plastic filter cassettes or inhalable samplers (paragraph 83 or 85), and with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter. The mercury released from the filters during sample dissolution shall not exceed 0.1 µg.

Note 24: Whatman QMA filters have been demonstrated¹⁴ to have low mercury blanks and do not absorb mercury vapour from the sampled air or mercury from the sample solutions. They are therefore suitable for collecting samples of particulate inorganic mercury compounds. Other quartz fibre filters or glass fibre filters may be used if it can be demonstrated that they similarly do not affect the analytical results obtained. Mixed cellulose ester filters have been used successfully as prefilters, but it is necessary to use a different analytical procedure³² for their subsequent analysis. It has been reported⁶⁷ that there can be significant loss of mercury vapour if mixed cellulose filters are used as prefilters. However, these results were not duplicated in a subsequent series of experiments.²¹

Sampling pumps

87 Sampling pumps, complying with the provisions of BS EN 1232,³³ compatible with the samplers used (paragraphs 83 and 85), and capable of running continuously for 8 h at the recommended flow rate of 0.2 l min⁻¹ for 200 mg sorbent tubes, 2 l min⁻¹ for 500 mg sorbent tubes or 2 l min⁻¹ for inhalable samplers.

Note 25: Existing users may continue to use sampling pumps that do not fully comply with the provisions of BS EN 1232,³³ provided that they take steps to ensure that the required volumetric flow rate (see note 47) is maintained to within ±5% of the nominal value throughout the sampling period.

88 BS EN 1232³³ requires that sampling pumps have, as a minimum, the following features:

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

Note 26: An integral timer is a highly desirable additional feature.

89 BS EN 1232³³ requires that the performance of the pumps is such that:

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

Flowmeter

90 Flowmeter, portable, with an accuracy that is sufficient to enable the volumetric flow rate (see paragraphs 131 to 133) to be measured to within ±5%. The calibration of the flowmeter shall be checked against a primary standard, ie a flowmeter whose accuracy is traceable to national standards.

Note 27: It is recommended that the flowmeter used should be capable of measuring the volumetric flow rate to within ±2% or better.

Note 28: Flowmeters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers (see note 47), provided they have adequate sensitivity.

Ancillary equipment

91 Flexible tubing, of a diameter and length suitable for making a leak-proof connection between the sampling pumps and the sorbent tubes and/or the samplers; a belt to which the pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes, or similar, if required (see paragraph 152), in which to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

92 A selection of laboratory glassware, including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS EN ISO 1042.³⁴

Note 29: It is recommended that a set of glassware is reserved for the analysis of mercury by this method.

Piston operated volumetric instruments

93 Pipettors and dispensers, complying with the requirements of BS EN ISO 8655-1,³⁵ and tested in

accordance with BS EN ISO 8655-4:³⁸ pipettors, complying with the requirements of BS EN ISO 8655-2,³⁶ as an alternative to one-mark pipettes, for the preparation of standard solutions, calibration solutions and dilution of samples; and dispensers, complying with the requirements of BS EN ISO 8655-5,³⁷ for dispensing acids.

Plastic centrifuge tubes

94 Centrifuge tubes, disposable, with screw caps or push-fit closures, suitable for performing the sample dissolutions described in paragraphs 163 and 173, with graduations at 25 ml if sorbent capsule samples are to be analysed or at 50 ml if sorbent tube samples are to be analysed. The graduation marks shall be accurate to $\pm 5\%$. The tubes shall be free of mercury contamination. The plastic shall be demonstrated to resist the acid digestion process, and not to affect the recovery of mercury from spiked sorbent tubes.

Note 30: *Sarstedt graduated plastic centrifuge tubes, Catalogue No 62.548.004, have been found suitable in tests at the Health and Safety Laboratory.*

Glass cutting equipment for opening sorbent tubes

95 A special tool (commercially available) for breaking the sealed ends of the sorbent tubes and retaining the broken glass shards produced. Alternatively, a glass cutting knife may be used.

96 Glass cutting wheel, designed for scoring glass tubing, for breaking open sorbent tubes. Alternatively, a glass cutting knife may be used. Rubber grips designed for safely breaking glass tubing are also advisable.

Water bath

97 Water bath, thermostatically controlled, capable of maintaining a temperature of approximately 50°C (see paragraphs 163 and 173).

Centrifuge

98 A laboratory centrifuge, equipped with rotor-buckets suitable for use with the centrifuge tubes (paragraph 94).

Analytical balance

99 An analytical balance, capable of weighing to $\pm 0.1 \mu\text{g}$.

Disposable gloves

100 Disposable gloves, impermeable, for prevention of contamination and to protect the hands from contact with toxic and corrosive substances. PVC gloves are suitable.

Ancillary equipment

101 Tweezers, pointed, and/or a needle or short length of wire, or other suitable tools, for removing glass wool plugs from sorbent tubes and screens from sorbent capsules.

Filter funnels, polypropylene

102 Filter funnels, polypropylene, of a size suitable for use in transferring washings from the internal surfaces of an inhalable sampler (paragraph 85) into a centrifuge tube (paragraph 94), if required (see note 58).

ANALYTICAL INSTRUMENTATION

Atomic absorption spectrometer or atomic fluorescence spectrometer

Either

103 An atomic absorption spectrometer equipped with a mercury hollow cathode lamp or electrodeless discharge lamp.

or

104 An atomic fluorescence spectrometer, designed for mercury analysis.

Note 31: *Atomic fluorescence spectrometers used for mercury analysis are usually part of dedicated systems designed solely for mercury analysis or dual purpose systems designed for analysis of mercury and hydride-forming elements such as arsenic, antimony, selenium etc.*

Mercury cold vapour generation system

Either

105 A flow injection analysis system, set up for mercury cold vapour generation and operated according to the manufacturer's instructions, incorporating (i) reservoirs for tin (II) chloride solution and acid blank, (ii) multi-channel peristaltic pumps, fitted with appropriate acid-resistant pump tubing, (iii) an autosampler for presentation of the test solution, (iv) an inert injection valve, either solenoid or pneumatically actuated, to inject a reproducible volume of test solution into the acid blank stream, (v) a chemically inert mixing piece(s) to facilitate mixing of acid blank or test solution, tin (II) chloride solution and inert purge gas streams, (vi) a reaction coil (optional), and (vii) a gas/liquid separator, with inlet for the reaction liquid stream and outlets for waste liquid and the purge gas plus gaseous products. A schematic diagram of a typical system is given in Figure 3a.

or

106 A continuous flow or discrete injection mercury cold vapour generation system, set up and operated according to the manufacturer's instructions, incorporating (i) reservoirs for tin (II) chloride solution and acid blank, (ii) an autosampler for presentation of the test solution (optional), (iii) an inert switching valve(s), solenoid or pneumatically actuated, to facilitate switching between sample and acid blank streams (optional), (iv) peristaltic pumps or a multi-channel peristaltic pump, fitted with appropriate acid-resistant pump tubing, (v) a chemically inert mixing piece(s) to facilitate mixing of acid blank or

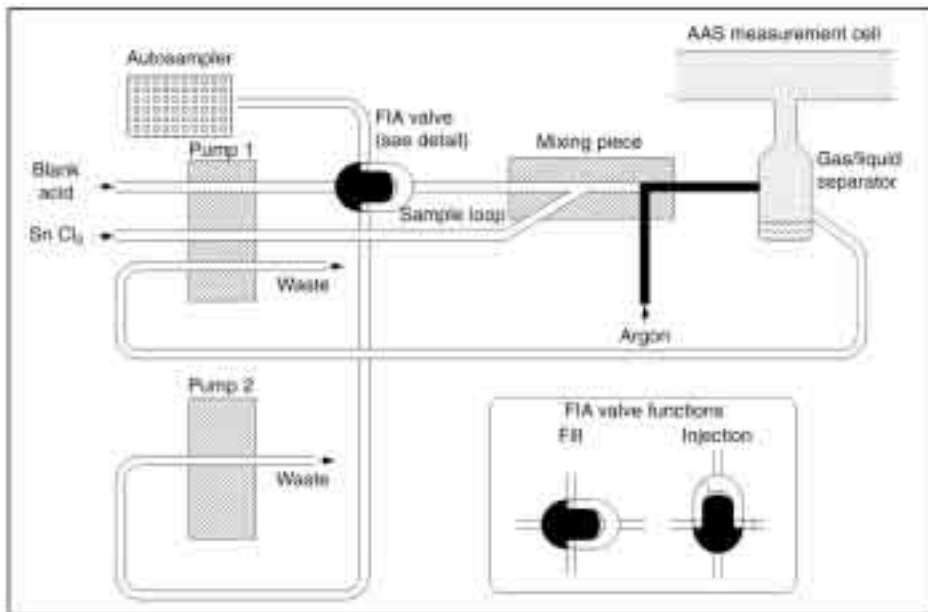


Figure 3a: Schematic diagram of a typical FI-CVAAS system

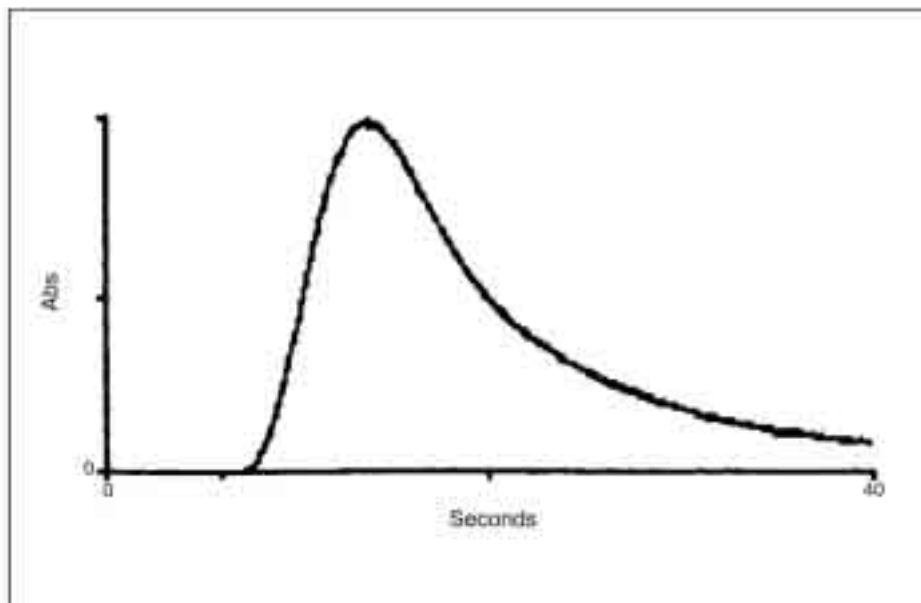


Figure 3b: Typical output of a FI-CVAAS system

test solution, tin (II) chloride solution and inert gas streams, (vi) a reaction coil (optional), and (vii) a gas/liquid separator, with appropriate inlets for the reaction liquid stream and inert purge gas, and outlets for waste liquid and the purge gas plus gaseous products. Schematic diagrams of typical systems are given in Figures 4a and 5a.

Note 32: In both flow injection and discrete injection systems, a volume of sample is introduced into the blank acid stream resulting in a peak atomic spectrometer output (see Figures 3b and 4b). In flow injection systems, the sample volume introduced is determined by the volume of a sample loop. In discrete injection systems, the sample volume introduced is controlled by the length of time for which the sample valve is switched.

Note 33: Continuous flow mercury cold vapour generation systems all work on the same principle, but the plumbing of the various systems is different. In particular, the configuration of some continuous flow hydride generation systems is such that there is no switching valve(s), and both acid and test solution are continuously pumped to an additional mixing piece situated upstream of the mixing piece where the tin (II) chloride solution is introduced. In either case, the effect is a step change in the atomic spectrometer output (see Figure 5b).

Note 34: Flow injection and discrete injection systems require a smaller volume of sample solution than continuous flow systems. They are consequently preferable in this application since the volume of sample solution is limited and because mercury readings from

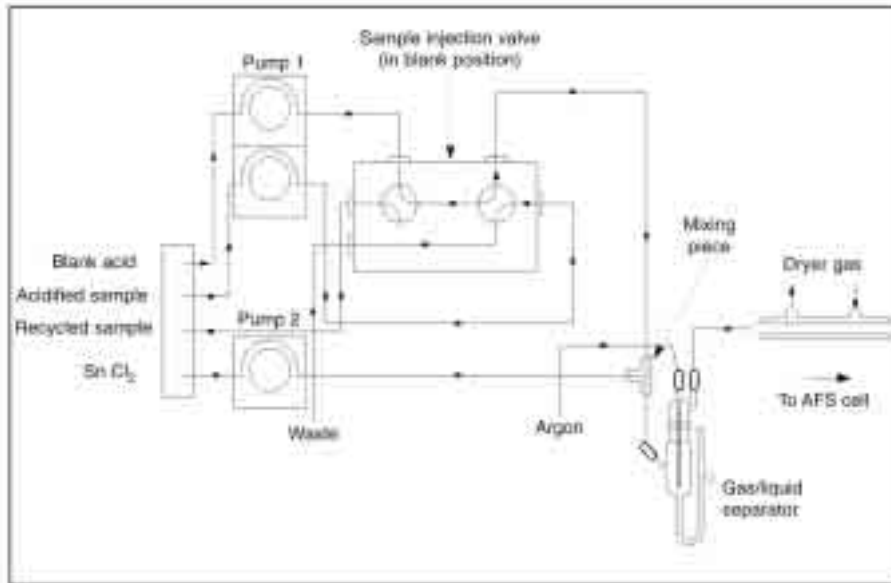


Figure 4a: Schematic diagram of a typical DI-CVAFS system

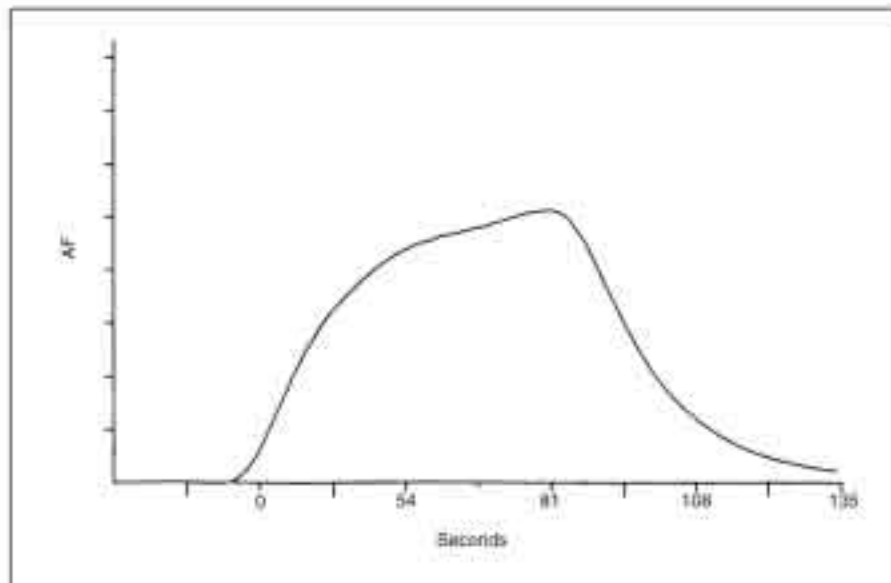


Figure 4b: Typical output from DI-CVAFS system

continuous flow CVAAS and CVAFS systems can be slow to stabilise.

Note 35: Mercury cold vapour generation systems commonly do double duty as hydride generation systems for the determination of such elements as arsenic and antimony. For this other purpose, the reductant used is usually sodium tetrahydroborate rather than tin (II) chloride. Even small residues of sodium borohydride are detrimental to the performance of mercury cold vapour systems using tin (II) chloride. Similarly, traces of iodide from potassium iodide used as a pre-reductant to reduce arsenate to arsenite will complex with mercury to form HgI_4^{2-} , and this does not react with acidic tin (II) chloride.

It is therefore recommended that different gas/liquid separators and reductant tubing are used for the two reductants.

WARNING - Mercury vapour is generated when solutions containing mercury are reacted with tin (II) chloride. This vapour is very toxic, but it will normally be produced only in very small quantities. However, in order to eliminate the possibility of exposure to mercury vapour it is essential that the liquid waste container used is equipped with efficient local exhaust ventilation to prevent any gases emanating from the liquid waste entering the general laboratory environment.

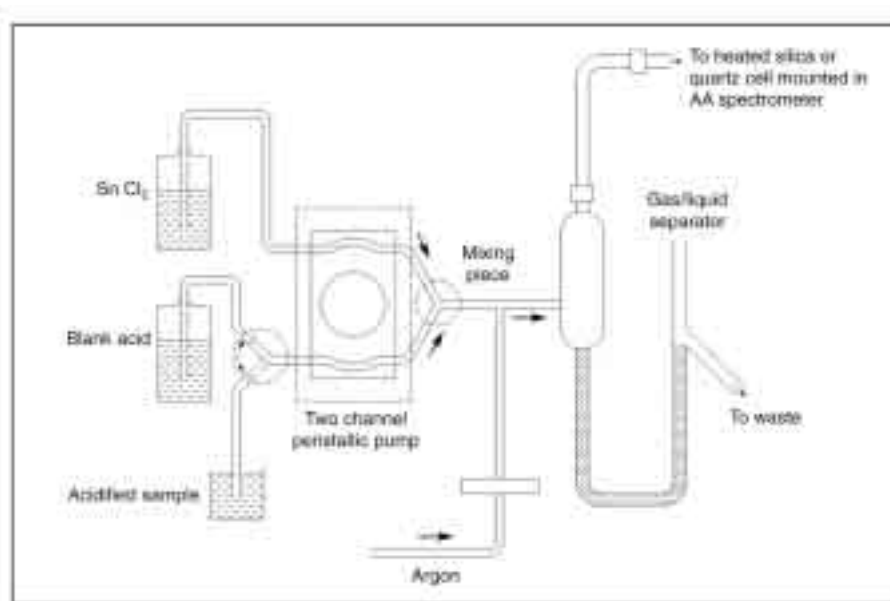


Figure 5a: Schematic diagram of a typical CF-CVAAS system

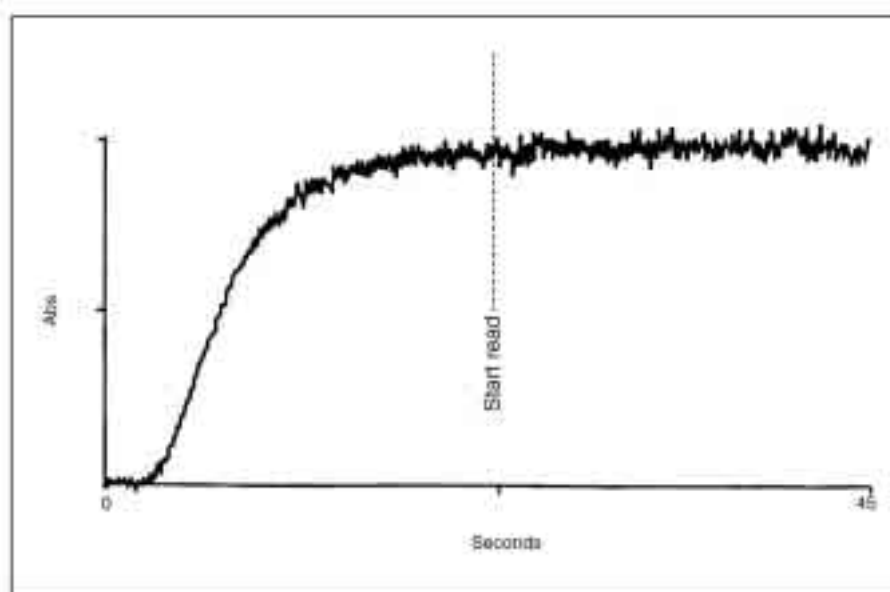


Figure 5b: Typical output of a CF-CVAAS system

107 Spectrometer measurement cell, made of silica or quartz, heated electrically to 100°C to prevent condensation of water vapour on the windows, mounted in the optical path of the atomic absorption spectrometer or the atomic fluorescence spectrometer.

Note 36: Measurement cells are usually an integral part of the atomic fluorescence spectrometry systems.

Note 37: Spray from the gas/liquid separator may be carried into the measurement cell by the argon stream in some cold vapour generation systems. In the case of an atomic absorption system, this is detrimental to the stability of response of the system and damaging to quartz cells. It is recommended that a membrane filter made of

PTFE is inserted into the tubing from the gas/liquid separator to the measurement cell. Alternatively, a tube containing drying granules can be used to remove water droplets in the argon stream. In the case of an atomic fluorescence system, it is essential that water vapour should be removed from the gas entering the measurement cell, otherwise the atomic fluorescence of mercury would be quenched. A drying tube consisting either of drying granules or of a water permeable membrane³⁹ in contact with a stream of dry inert gas is typically used to dry the gas entering the measurement cell.

SAMPLING

Selection of sampling method

Measurement of mercury vapour

108 If it is known that no particulate inorganic mercury compounds are used in the workplace and that none are produced in the processes carried out, use either the diffusive badge method or the pumped sorbent tube method to collect samples of mercury vapour. Refer to Appendix B for guidance on the advantages and disadvantages of the diffusive and pumped sampling methods.

Measurement of particulate inorganic mercury compounds

109 If it is known that no elemental mercury is used in the workplace and that no mercury vapour is produced in the processes carried out, use the filter sampling method to collect samples of particulate inorganic mercury compounds.

Measurement of mercury vapour and particulate inorganic mercury compounds

110 If both mercury vapour and particulate inorganic mercury compounds are believed to be present in significant proportions in the test atmosphere, collect samples of mercury vapour and particulate inorganic mercury compounds with a pumped sorbent tube and prefilter using the method. Then analyse the sorbent tube and filter together.

Note 38: *The prefilter may be omitted if it is believed that particulate inorganic mercury compounds do not make up a significant proportion (eg <10%) of the sum of mercury vapour and particulate inorganic mercury compounds present in the test atmosphere (see note 41).*

Consideration of the effect of temperature and pressure on the uptake rate of diffusive badges

111 The sample uptake rate of diffusive badges is temperature and pressure dependent, but the effect is relatively small. Nevertheless, temperature correction of the sample uptake rate can improve accuracy at extremes of temperature (see paragraph 54). Consider whether the difference between the temperature and pressure at which the nominal sample uptake rate given by the manufacturer of the diffusive badge applies and the atmospheric temperature and pressure during sampling is likely to be great enough to justify applying a correction (see paragraph 206). If a correction is to be made, measure and record the atmospheric temperature and pressure at the start and at the end of the sampling period (see paragraphs 124 and 125). Then calculate a temperature and pressure corrected sample uptake rate following the procedure given in paragraph 207.

Diffusive sampling

Use of diffusive badges for sampling mercury vapour

112 Use diffusive badges (paragraph 79) to measure personal exposure to mercury vapour, or as static samplers to measure background concentrations of mercury vapour in air.

Sampling period

113 Select an appropriate sampling period, taking into account the purpose of the measurement. It is recommended that sampling is carried out for the entire working period, but in any case the sampling time shall not be less than 6 h.

Handling of sorbent capsules

114 To minimise the risk of damage or contamination, only handle sorbent capsules (paragraph 80) using flat-tipped tweezers (paragraph 91) in a clean area where the concentration of mercury vapour is as low as possible.

Cleaning of diffusive badges prior to use

115 Disassemble each diffusive badge (paragraph 79) and place all parts except the attachment clip, two polyethylene mesh discs, retaining internal metal 'O' ring and foam disc in a suitable container. Soak in 1 + 9 nitric acid (paragraph 69) for 1 h.

116 Soak the two polyethylene mesh discs separately in 1 + 9 nitric acid (paragraph 69), ensuring that any traces of Hydrar dust are removed, since these will otherwise trap mercury vapour when the badge is reused, preventing it from entering the capsule.

117 Rinse all parts of the diffusive badge three times in water (paragraph 67). Dry as quickly as possible, then reassemble the badge for storage without a new sorbent capsule or foam disc (see Figure 1). Store in a clean area (where the sampler will not become contaminated with mercury) until ready to use again.

Loading diffusive badges with sorbent capsules

118 Remove the required number of sorbent capsules (paragraph 80) from the pouches in which they were supplied, by carefully cutting one edge off each pouch. Discard any particles of Hydrar that have become dislodged from the sorbent capsule during transit. Load each sorbent capsule into a clean diffusive badge (paragraph 117) with the mesh side facing towards the sampling face (see Figure 1). Place a clean foam disc in the back cover of each sampler and then fit the back cover to the sampler housing (see Figure 1). Label each sampler so that it can be uniquely identified and seal with its protective cover to prevent contamination. Retain the pouches in which the sorbent capsules were supplied for storage of the samples after sampling.

Note 39: *Always use samplers within a few days of loading with sorbent capsules, as the sealing caps do not provide a hermetic seal.*

119 Retain in unopened pouches, four unused sorbent capsules from the same batch used for sample collection. Use these for preparation of calibration solutions (see paragraph 168) so that calibration solutions and sample solutions are matrix-matched.

Blanks

120 Retain as blanks, one unused sorbent badge (paragraph 118) from each batch of ten prepared, subject to a minimum of two. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but do not expose by removing the protective caps.

Note 40: *It has been found that the mercury blank differs very little from one box of sorbent capsules to the next, provided that they have the same batch number. If sorbent capsules from different batches are used, it is necessary to retain blank sorbent capsules from each batch, and to note the batch number of the sorbent capsule used for each sample.*

Sampling position

Personal sampling

121 Remove the diffusive badge from its pouch and position it in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel with the attached clip. Position it in such a way that it is unlikely to get knocked or be contaminated with liquid mercury.

Static sampling

122 Select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by mercury from emission sources. Remove the diffusive badge from its pouch and attach it to a stand or a convenient fixture in a suitable position to monitor the background concentration of mercury in air at breathing height.

123 If the air is very still (air speeds $<7.5 \text{ m min}^{-1}$), use the pumped sorbent tube method or take note of the fact that low results will be obtained (see paragraph B4). In windy conditions (air speed $>230 \text{ m min}^{-1}$), provide some shielding from the wind.

Sample collection

124 Remove the protective cap from the badge and record the time at the start of the sampling period. If appropriate (see paragraph 111), measure the temperature and/or pressure at the start of the sampling period and record the measured values.

125 At the end of the sampling period (see paragraph 113), replace the protective cap, record the time and calculate the duration of the sampling period. If appropriate (see paragraph 111), measure the final temperature and/or pressure and record the measured values.

126 Carefully record the sample identity and all relevant sampling data (see Appendix C).

Transportation of samples

127 Remove the sorbent capsule from the badge, taking care not to contaminate it (see paragraph 114) and place it in the pouch in which it was received. Seal the pouch with the label provided by the manufacturer for this purpose. Write the sample number and other details pertinent to the sample on the label. Follow the same procedure for the blanks (paragraph 120).

128 Transport the sealed plastic pouches (paragraph 127) to the laboratory in a container which has been designed to prevent damage to the samples in transit and which has been labelled to assure proper handling.

129 Follow 'chain of custody' procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

130 Analyse the samples within four weeks of sampling.

Sampling using pumped sorbent tubes

Use of sorbent tubes, prefilters and inhalable samplers

Sampling of mercury vapour

131 Use sorbent tubes (paragraph 81) to collect samples for measurement of personal exposure to mercury vapour or the background concentration of mercury vapour in air. Precede the sorbent tubes with prefilter assemblies (paragraph 83) if the concentration of airborne particles could be sufficiently high that there is a risk of blockage of the glass wool plugs that retain the Hydrar sorbent in the tubes. Use a flow rate within the range recommended by the manufacturer of the sorbent tube, normally 200 ml min^{-1} for a 200 mg tube or 2 l min^{-1} for a 500 mg tube.

Sampling of particulate inorganic mercury compounds

132 Use quartz fibre filters (paragraph 86) mounted in inhalable samplers (paragraph 85) to collect samples for measurement of personal exposure to particulate inorganic mercury compounds or to measure the background concentration of particulate inorganic mercury compounds in air. Use the samplers at their design flow rate and in accordance with the manufacturer's instructions, so that they collect the inhalable fraction of airborne particles.

Sampling of mercury vapour and particulate inorganic mercury compounds

133 Use sorbent tubes (paragraph 81) to collect samples of mercury vapour and particulate inorganic mercury compounds for measurement of personal exposure to mercury vapour and particulate inorganic mercury compounds or the background concentration of mercury vapour and particulate inorganic mercury compounds in

air. Precede the sorbent tubes with prefilter assemblies (paragraph 83) if it is believed that particulate inorganic mercury compounds could make up a significant proportion (eg >10%) of the sum of mercury vapour and particulate inorganic mercury compounds present in the test atmosphere (see note 41), using an inhalable sampler (paragraph 85) rather than a plastic sampling cassette (paragraph 84) in the prefilter assembly (see note 42). Use a flow rate within the range recommended by the manufacturer of the sorbent tube, normally 200 ml min⁻¹ for a 200 mg tube or 2 l min⁻¹ for a 500 mg tube.

Note 41: *If prefilters are not used with sorbent tubes, particulate inorganic mercury compounds will be trapped on the glass wool plugs that retain the Hydrar sorbent in the tubes, and on the sorbent itself. Although it is fair to assume that the efficiency with which particulate inorganic mercury compounds are trapped by sorbent tubes will be reasonably high, this has not been confirmed experimentally. Furthermore, the limit value for divalent mercury compounds applies to the inhalable fraction of airborne particles, as defined in BS EN 481,¹⁵ while the sampling characteristics of sorbent tubes for airborne particles are unknown. In consideration of these two sources of potential sampling bias, it is acceptable to analyse the sorbent and glass wool plugs in order to estimate total mercury-in-air concentrations only if it is known that the majority of the mercury sampled is in the vapour state. In this case, the overall bias of the sampling method will be acceptably small.*

Note 42: *As mentioned in note 41, the limit value for divalent mercury compounds applies to the inhalable fraction of airborne particles, as defined in BS EN 481.¹⁵ Under such circumstances, an inhalable sampler should be used in the prefilter assembly. If an inhalable sampler is not available that has a design flow rate compatible with the manufacturer's recommended range of flow rates for the sorbent tube, it will be necessary to collect separate samples for determination of mercury vapour and divalent mercury compounds using the methods referred to in paragraphs 131 and 132.*

Sampling period

134 Select an appropriate sampling period, taking into account the purpose of the measurement. The sampling time shall not be less than 1 h for a 200 mg sorbent tube used at a flow rate of 200 ml min⁻¹. If this minimum sampling time is not short enough for the method to be useful for the intended purpose, use a 500 mg sorbent tube at a flow rate of 2 l min⁻¹. Sampling times may be as short as 10 min for an inhalable sampler used at a flow rate of 2 l min⁻¹.

135 When high concentrations of airborne particles are anticipated, select a sampling period that is not so long as to risk overloading the glass wool plugs that retain the Hydrar sorbent in the tubes with particulate matter, or use a prefilter.

Sample handling

136 To minimise the risk of damage or contamination,

only handle quartz fibre filters (paragraph 86) and sorbent tubes (paragraph 81) in a clean area where the concentration of mercury in air is as low as possible; and only handle quartz fibre filters using flat-tipped forceps (paragraph 91).

Cleaning of inhalable samplers

137 If required (see paragraphs 132 and 133), clean the inhalable samplers (paragraph 85) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 78), rinse thoroughly with water (paragraph 67), wipe with absorbent tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Loading samplers with filters

138 If required (see paragraphs 131 to 133), load plastic filter cassettes (paragraph 84) or clean inhalable samplers (paragraph 137) with filters (paragraph 86). Label each filter cassette or sampler so that it can be uniquely identified, and seal with its plug or protective cover to prevent contamination.

Preparation of sorbent tube sampling assemblies

139 Break the flame sealed ends off the required number of sorbent tubes (paragraph 81) using a special glass cutting tool (paragraph 95) or a glass cutting wheel (paragraph 96). Label each sorbent tube so that it can be uniquely identified and, if desired, mount it in a sorbent tube holder (paragraph 82).

140 If required (see paragraphs 131 to 133), construct a prefilter assembly (see paragraph 83) by connecting a loaded filter cassette or sampler (paragraph 138) to each sorbent tube or sorbent tube holder (paragraph 139) with a minimum amount of inert plastic tubing, eg Tygon[®] or PTFE tubing, ensuring that no leaks can occur.

Note 43: *Alternatively, use a sorbent tube holder to which the sampler can be directly attached.*

141 Seal the exposed end(s) of sorbent tubes with the plastic end caps supplied by the manufacturer.

142 Retain six sorbent tubes from the same batch used for sampling for use in the preparation of calibration solutions (paragraph 178).

Setting the volumetric flow rate

Perform the following in a clean area, where the concentration of mercury is low.

143 Remove the protective cover, plug and/or caps from each loaded sampler (paragraph 138) or sorbent tube sampling assembly (paragraph 140) and connect to a sampling pump (paragraph 87) using flexible tubing (paragraph 91), ensuring that no leaks can occur. Switch on the sampling pump, attach the calibrated flowmeter (paragraph 90) to the sampler or sorbent tube sampling assembly so that it measures the flow through the inlet

orifice(s), and set the required volumetric flow rate (see paragraphs 131 to 133). Switch off the sampling pump and seal the sampler or sorbent tube sampling assembly with its protective cover, plug and/or caps to prevent contamination during transport to the sampling position.

Note 44: *If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).*

Blanks

144 Retain as blanks, one unused loaded sampler (paragraph 138) or sorbent tube sampling assembly (paragraph 141) from each batch of ten prepared, subject to a minimum of two. Treat these in the same manner as those used for sampling in respect of storage and transport to and from the sampling position, but draw no air through them.

Sampling position

Personal sampling

145 Position the sampler or sorbent tube sampling assembly (paragraph 143) in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 91) around the waist, or place it in a convenient pocket.

Note 45: *If a sorbent tube is used without a sorbent tube holder or prefilter (see paragraphs 139 and 140), the open end of the tube should be protected with a minimum length of inert plastic tubing to avoid injury.*

Personal sampling

146 If static sampling is carried out to assess the exposure of a worker in a situation where personal sampling is not possible (eg due to the need to sample at a volumetric flow rate higher than the design flow rate of available personal samplers), position the sampler or sorbent tube sampling assembly in the immediate vicinity of the worker and at breathing height. If in doubt, take the sampling position to be the point where the risk of exposure is considered to be greatest.

Static sampling

147 If static sampling is carried out to characterise the background level of mercury in the workplace, select a sampling position that is sufficiently remote from the work processes, such that results will not be directly affected by mercury from emission sources.

Collection of samples

148 When ready to begin sampling, remove the protective cover, plug and/or caps from the sampler (paragraph 138) or sorbent tube sampling assembly (paragraph 140) and switch on the sampling pump. Record the time and volumetric flow rate at the start of the

sampling period. If the sampling pump is fitted with an integral timer, check that this is reset to zero.

Note 46: *If the temperature at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 143), the volumetric flow rate could change and it might need to be readjusted before sampling.*

Note 47: *If the sampling pump used does not comply with BS EN 1232³³ (see note 25), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 90) 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.*

149 At the end of the sampling period (see paragraphs 134 and 135), record the time and calculate the duration of the sampling period. Check the malfunction indicator and/or the reading on the integral timer, if fitted, and consider the sample to be invalid if there is evidence that the sampling pump was not operating properly throughout the sampling period. Measure the volumetric flow rate at the end of the sampling period using the calibrated flowmeter (paragraph 90), and record the measured value. Disconnect the sampling assembly from the sampling pump.

150 Carefully record the sample identity and all relevant sampling data (see Appendix C).

Transportation

151 If sorbent tube sampling assemblies were used for sampling, disassemble them and seal the sorbent tubes with plastic end caps. If the prefilters were used simply to prevent blockage of the glass wool plugs (see note 20), discard them. If the prefilters were used to collect particulate inorganic mercury compounds (see paragraph 131), unload them from the samplers as described in paragraphs 152 to 154. Follow the same procedure for the blanks (paragraphs 120 and 144).

152 For inhalable samplers that collect airborne particles on the filter (see note 22), remove the filter from each sampler, place in a labelled filter transport cassette (paragraph 91) and close with a lid. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

153 For samplers that have an internal filter cassette (see note 22), remove the filter cassette from each sampler and fasten with its lid or transport clip.

154 For samplers designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, but which do not have an internal filter cassette (see note 22), transport the samples to the laboratory in the samplers in which they were collected.

155 Transport the sorbent tube samples (paragraph 151) and, if appropriate, the filter samples (paragraphs 152 to

154) to the laboratory in a container that has been designed to prevent damage to the samples in transit and that has been labelled to assure proper handling.

156 Follow 'chain of custody' procedures to ensure sample traceability. Ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

157 Analyse the samples within four weeks of sampling.

ANALYSIS

WARNING – Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc) when working with concentrated or dilute acid, and carry out sample dissolution in a fume cupboard. See the warning notices in paragraphs 68 and 70.

Note 48: *The following procedure is designed so that the complete sample preparation process can be carried out in the same disposable, plastic centrifuge tube. The tube can then be loaded directly into the rack of an autosampler for analysis. This minimises manipulations and reduces the chance of contamination of the sample.*

Note 49: *For samples collected using a sorbent tube and prefilter assembly, the procedure described may be used to analyse the contents of a sorbent tube and its associated prefilter together in order to obtain a combined result for mercury vapour and particulate divalent mercury. The result can then be compared with the occupational exposure limit for mercury and divalent mercury. Alternatively, the procedure may be used to separately analyse samples to determine mercury vapour collected in sorbent tubes and particulate divalent mercury collected on quartz fibre filters.*

Cleaning of glassware

158 Before use, clean all glassware (paragraph 92) to remove any residual grease or chemicals. Firstly, soak overnight in laboratory detergent solution (paragraph 78) and then rinse thoroughly with water (paragraph 67). Alternatively, use a laboratory washing machine.

159 After initial cleaning (paragraph 158), clean all glassware by soaking in 1 + 9 nitric acid (paragraph 69) for at least 24 h and then rinsing thoroughly with water (paragraph 67).

160 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 158 and 159, and which has been reserved for determination of mercury by this method, can be adequately cleaned by rinsing thoroughly with dilute nitric acid (paragraph 69), and then with water (paragraph 67).

Preparation of sample, blank and calibration solutions for analysis of diffusive badges

Preparation of sample and blank solutions

161 Open each sample pouch and remove the sorbent capsule (paragraph 80). Carefully remove the screen from the top of the capsule using pointed tweezers or a needle (paragraph 101). Take care not to lose any sorbent. Carefully pour the sorbent into a disposable 50 ml plastic centrifuge tube (paragraph 94). Discard the screen and empty capsule.

162 Add 2.0 ml concentrated nitric acid (paragraph 68) followed by 2.0 ml of hydrochloric acid (paragraph 70).

Note 50: *It is important that nitric acid is added before hydrochloric acid to ensure that mercury is oxidised to the divalent state. Otherwise mercury left in an elemental state may be lost due to volatilisation.*

163 Tightly seal the centrifuge tubes with their screw caps or push-fit closures, and roll the tubes to wash any Hydrar from the walls. Place the tubes in a test tube rack in a thermostatically controlled water bath (paragraph 97) at 50°C for 1 h, periodically agitating and rolling the tubes to ensure that all hopcalite is dissolved from the ceramic support material of the Hydrar granules.

164 Remove the tubes from the heated water bath and place them to cool in a bath of cold water. When the solutions are cool, carefully unscrew the screw caps from the tubes or remove the push-fit closures and allow any pressure built up due to the formation of oxides of nitrogen to be released.

165 Make up to the 25 ml graduation with water (paragraph 67), reseal the tubes and shake to mix.

Note 51: *Dissolution of the sample yields a dark brown liquid. When diluted to volume with water, this forms a milky blue-green suspension above a white ceramic residue from the Hydrar sorbent.*

166 Centrifuge the sample solutions to remove the ceramic support material from suspension. Alternatively, filter the suspension, having confirmed in tests that the filter used will not contaminate the solution with mercury or remove any mercury from solution.

Note 52: *The use of a centrifuge is preferable to filtration since it enables the sample to be prepared and presented to the instrument without transfer from the centrifuge tube, speeding analysis and making contamination less likely.*

167 Prior to analysis, uncap the centrifuge tubes and let stand in a fume cupboard for at least an hour to allow dissolved oxides of nitrogen to degas from the sample solutions.

Note 53: *Thorough dispersion of oxides of nitrogen from solution is particularly important when CVAFS is used, since they will otherwise quench mercury cold vapour fluorescence. Degassing can be accelerated by passing a stream of an inert gas, such as nitrogen, through the solution prior to centrifugation.*

Preparation of calibration solutions

168 Take four sorbent capsules from the same batch that was used to collect the samples (see paragraph 119) and prepare solutions from them following the procedure in paragraphs 161 to 164. Make up almost to the 25 ml graduation of the centrifuge tubes with water (paragraph 67), and then accurately pipette 0 µl, 125 µl, 250 µl and 500 µl of working mercury standard solution B (paragraph 77) to the solutions. Finally, make up to volume, centrifuge and degas as described in paragraphs 165 to 167. The prepared calibration solutions have mercury concentrations of 0 µg l⁻¹, 5 µg l⁻¹, 10 µg l⁻¹ and 20 µg l⁻¹.

Note 54: *The reason why calibration solutions are prepared by addition of mercury standard solution to blank solutions is because the slope of the calibration is influenced by acid concentration, and the acid concentration of the sample solutions is unknown due to consumption of acid during dissolution of the sorbent. Correspondingly, it has been demonstrated¹⁴ that failure to properly matrix-match calibration and sample solutions can produce high results. On the other hand, some hydride generation systems are believed to be less sensitive to acid concentration than the system used in the validation of this method. In such circumstances, simply matching the acid content of the calibration and sample solutions might be adequate to produce results of sufficient accuracy (ie by preparing calibration solutions in 2 + 2 + 21 nitric acid/hydrochloric acid). Alternatively, for hydride generation systems that are sensitive to acid concentration, it might be possible to obtain satisfactory results by preparing calibration solutions in an intermediate acid concentration (eg 1 + 1 + 23 nitric acid/hydrochloric acid). In both cases, this would reduce the cost of analysis by eliminating the need to use sorbent capsules in the matrix-matching process. However, if the procedure described in paragraph 168 is modified in any way, it should be demonstrated that the results obtained exhibit an acceptable bias, eg <5%.*

Note 55: *An alternative means of reducing the cost of analysis could be to prepare 50 ml of blank solution from just two sorbent capsules and carrying out a standard additions calibration by spiking aliquots of this with appropriate volumes of mercury standard solution.*

Preparation of sample, blank and calibration solutions for analysis of pumped samples

Preparation of sample solutions

169 Remove the plastic end caps from the sorbent tubes. Score each tube with a glass cutting wheel (paragraph 96), approximately halfway across the middle section, where it is packed with glass wool. Then break off the front section of the tube above the glass wool (see note 17). Draw out the glass wool plug using pointed tweezers (paragraph 101), discarding the retaining spring, if present, and place it in a 50 ml disposable centrifuge tube (paragraph 94). Pour the released sorbent granules into the centrifuge tube. Then poke a wire (paragraph 101) into the open end of the remaining section of tube in order to push out the remaining glass wool plug into the centrifuge tube.

Note 56: *Grip the tube with either special rubber tube grips (see paragraph 96) or a cloth to eliminate the chance of being cut by broken glass while breaking open the tube.*

170 If a quartz fibre filter was used to collect particulate divalent inorganic mercury compounds and it is to be analysed together with the contents of the sorbent tube to produce a combined result for mercury vapour and particulate divalent mercury compounds, open the samplers, sampler filter cassettes or transport filter cassettes (see paragraphs 152 to 154), remove the quartz fibre filter using clean flat-tipped forceps (paragraph 91) and place it in the same centrifuge tube as the sorbent and glass wool plug (paragraph 169). Alternatively, if a separate analysis for particulate divalent mercury compounds is required, place the filter in a separate 50 ml disposable centrifuge tube (paragraph 94). Label the centrifuge tubes as appropriate.

171 If a quartz fibre filter was used in an inhalable sampler to determine particulate divalent mercury compounds only, open the samplers, sampler filter cassettes or filter transport cassettes (see paragraphs 152 to 154), remove the quartz fibre filter using clean flat-tipped tweezers (paragraph 91) and place in a 50 ml disposable centrifuge tube (paragraph 94).

172 Add 2.0 ml of concentrated nitric acid (paragraph 68) followed by 2.0 ml of concentrated hydrochloric acid (paragraph 70) to each centrifuge tube.

Note 57: *It is important that nitric acid is added before hydrochloric acid to ensure that mercury is oxidised to the divalent state. Otherwise, mercury left in an elemental state may be lost due to volatilisation.*

Note 58: *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 22), use the nitric acid to carefully wash any particulate material adhering to the internal surfaces into the centrifuge tube, utilising a polypropylene filter funnel (paragraph 102) to avoid spillage.*

173 Tightly seal the centrifuge tubes with their screw caps or push-fit closures, and roll the tubes to wash any Hydrar from the walls. Place the tubes in a test tube rack in a thermostatically controlled water bath (paragraph 97) at 50°C for 1 h, periodically agitating and rolling the tubes to ensure that all hopcalite is dissolved from the ceramic support material of the Hydrar granules.

174 Remove the tubes from the heated water bath and place them to cool in a bath of cold water. When the solutions are cool, carefully unscrew the screw caps from the tubes or remove the push-fit closures and allow any pressure built up due to the formation of oxides of nitrogen to be released.

175 Make up to the 50 ml graduation with water (paragraph 67), reseal the tubes and shake to mix.

Note 59: Dissolution of the sample yields a dark brown liquid. When diluted to volume with water, this forms a milky blue-green suspension above a white ceramic residue from the Hydrar sorbent. The sample tubes will also contain glass wool from the sorbent tube plugs and the quartz fibre prefilter (if used).

176 Centrifuge the sample solutions to remove the ceramic support material from suspension and to drive the glass wool and quartz fibre filter to the bottom of the tubes. Alternatively, filter the suspension, having confirmed in tests that the filter used will not contaminate the solution with mercury or remove any mercury from solution.

Note 60: The use of a centrifuge is preferable to filtration since it enables the sample to be prepared and presented to the instrument without transfer from the centrifuge tube, speeding analysis and making contamination less likely.

177 Prior to analysis, uncap the centrifuge tubes and stand in a fume cupboard for at least an hour to allow dissolved oxides of nitrogen to degas from the sample solutions.

Note 61: Thorough dispersion of oxides of nitrogen from solution is particularly important when CVAFS is used, since they will otherwise quench mercury cold vapour fluorescence. Degassing can be accelerated by passing a stream of an inert gas, such as nitrogen, through the solution prior to centrifugation.

Preparation of calibration solutions

178 Take six sorbent tubes from the same batch that was used to collect the samples (see paragraph 142) and prepare solutions from them following the instructions given in paragraphs 169 and 172 to 174. Make up almost to the 50 ml graduation of the centrifuge tube with water (paragraph 67) and then 0 µl, 100 µl, 200 µl, 300 µl, 400 µl and 500 µl of working mercury standard solution A (paragraph 76) to the six solutions. Finally, make up to volume and centrifuge as described in paragraphs 175 to 177. The prepared calibration solutions have mercury concentrations of 0 µg l⁻¹, 20 µg l⁻¹, 40 µg l⁻¹, 60 µg l⁻¹, 80 µg l⁻¹ and 100 µg l⁻¹.

Note 62: The reason why calibration solutions are prepared by addition of mercury standard solution to blank solutions is because the slope of the calibration is influenced by acid concentration, and the acid concentration of the sample solutions is unknown due to consumption of acid during dissolution of the sorbent. Correspondingly, it has been demonstrated¹⁴ that failure to properly matrix-match calibration and sample solutions can produce high results. On the other hand, some hydride generation systems are believed to be less sensitive to acid concentration than the system used in the validation of this method. In such circumstances, simply matching the acid content of the calibration and sample solutions might be adequate to produce results of sufficient accuracy (ie by preparing calibration solutions in 1 + 1 + 23 nitric acid/hydrochloric acid). This would reduce the cost of analysis by eliminating the need to use

sorbent tubes in the matrix-matching process. However, if the procedure described in paragraph 178 is modified in any way, it should be demonstrated that the results obtained exhibit an acceptable bias, eg <5%.

Note 63: An alternative means of reducing the cost of analysis could be to prepare 50 ml of blank solution from a single sorbent tube and carrying out a standard additions calibration by spiking aliquots of this with appropriate volumes of mercury standard solution.

Note 64: The range of the set of calibration solutions is given as a guide. It is generally appropriate for sampling times of 4 h to 8 h at a flow rate of 200 ml min⁻¹. Lower concentrations may be more appropriate if sampling for shorter periods. The upper limit of the working range is dependent upon the performance characteristics of the cold vapour generation system (paragraph 105 or 106) used and other instrumental factors, which affect sensitivity, and the linearity of the calibration. Accordingly, the range of the set of calibration solutions may be varied, but when making any changes, ensure that the response of the spectrometer over the alternative range of concentrations selected is such that it complies with the limitations on curvature specified in the note in paragraph 198.

Setting up the instrument

Setting up the mercury cold vapour system

179 Prepare the mercury cold vapour generation system (paragraph 105 or 106) for operation following the manufacturer's instructions. Fill the reservoir for reductant with tin (II) chloride solution (paragraph 74). If analysing sorbent tube samples, fill the blank acid reservoir with 1 + 1 + 23 nitric acid/hydrochloric acid (paragraph 71). If analysing diffusive badge samples, fill the blank acid reservoir with 2 + 2 + 21 nitric acid/hydrochloric acid (paragraph 72).

180 Set the purge gas flow rate to the value recommended for the application by the manufacturer of the mercury cold vapour generation system (paragraph 105 or 106).

Note 65: Optimum concentrations of reagents, liquid flow rates, purge gas flow rate etc may vary somewhat according to the exact configuration of the system.

Note 66: Mercury cold vapour generation systems are sensitive to change in temperature. Reagents and test solutions should therefore be allowed to equilibrate to room temperature before commencing analysis.

Note 67: The length of tubing connecting the measurement cell to the outlet of the gas/liquid separator of the mercury cold vapour generation system (paragraph 105 or 106) should be kept to a minimum.

Setting up the spectrometer

181 Set up the spectrometer (paragraph 103 or 104) to make either atomic absorbance measurements or atomic

fluorescence measurements at the 253.7 nm mercury line following the manufacturer's recommendations for specific instrument operating parameters.

Presentation of solutions

182 Present the calibration, sample and blank solutions to the mercury cold vapour generation system (paragraph 105 or 106) by placing the sample uptake tubing into the solution concerned. This may be carried out manually or using an autosampler.

183 Start with the mercury cold vapour system in the configuration in which blank acid is pumped to the mixing piece.

184 In the case of a continuous flow system, change the configuration so that the test solution is pumped to the mixing piece until a maximum atomic spectrometer signal is obtained (see Figure 5b).

185 In the case of a flow injection system, operate the sample injection valve so that a precise volume of the test solution is injected into the acid blank stream, resulting in a peak in the atomic spectrometer signal (see Figure 3b).

186 In the case of a discrete injection system, change the configuration to pump test solution, for a precise period of time, so that a precise volume of test solution is delivered to the mixing piece, resulting in a peak in the atomic spectrometer signal (see Figure 4b).

Note 68: Blockages are likely to occur if ceramic residue, glass fibre or quartz fibre driven to the bottom of the centrifuge tubes is drawn up into the uptake tubing. Care should be taken that this undissolved material is not disturbed during analysis. When using an autosampler, it is important that the tip of the sample probe is positioned well away from the bottom of the tube during solution uptake.

Conditioning the mercury cold vapour generation system

187 Condition the mercury cold vapour system before use in order to ensure that a stable signal is obtained before proceeding to carry out a calibration.

188 Place the reductant, acid blank, and sample uptake tubing in a container of water (paragraph 67), and allow the pump(s) to operate for 5 min for the flow rates to stabilise. Fill a 10 ml measuring cylinder (paragraph 92) to a convenient mark with water and determine each flow rate in turn by placing the appropriate uptake tubing in the measuring cylinder of water and observing the volume of water pumped out in 1 min. Verify that the flow rates are within the nominal specification recommended by the manufacturer of the mercury cold vapour generation system (paragraph 105 or 106) and adjust the pressure exerted on the peristaltic pump tubing by the pump head and/or install new pump tubing if necessary. Replace the uptake tubing for reductant and acid blank in the appropriate reservoirs.

Either

189 For continuous flow and discrete injection mercury cold vapour generation systems, alternately pump acid blank (paragraph 71 or 72) and the high calibration solution (paragraph 168 or 178) to the mixing piece of the continuous flow mercury cold vapour generation system (paragraph 105 or 106), and make repeat absorbance or fluorescence measurements with a suitably short integration period. Continue this sequence until a repeatable analytical response is obtained, and record the parameters necessary for operation of the continuous cold vapour system used. In the case of continuous flow systems, record the stabilisation delay time, which is the time taken for the analytical response to reach a stable value when a solution is presented to the system, and the baseline delay time, which is the time taken for the signal response to return to the baseline when the acid blank is pumped again. In the case of discrete injection systems, select a suitable injection period during which sample solution is pumped to the mixing piece in order to obtain an output signal peak of the required height. Note the peak delay time, which is the time taken for the peak maximum to be obtained, and the baseline delay time, which is the time taken for the signal response to return to the baseline when the acid blank is pumped again.

or

190 For flow injection analysis mercury cold vapour generation systems, fill the sample loop by pumping the high calibration solution (paragraph 168 or 178) through it, and then inject into the acid blank stream. Note the peak delay time and the baseline delay time.

191 Optimise integration or peak height measurement parameters, and then make repeat injections until a repeatable analytical response is obtained.

Note 69: If a repeatable analytical response is not obtained, this is likely to be due to contamination of the system. In this case, suspend further operations and clean the gas/liquid separator and the silica or quartz absorption cell.

192 If the cold vapour/atomic spectrometer system is interfaced to a microprocessor or personal computer for automatic control, set the necessary delay times and other parameters to the appropriate value(s).

Determination of reagent blank

193 Place the reductant, acid blank and sample uptake tubing into a container of water (paragraph 67) and, after allowing sufficient time for flushing out the system, adjust the spectrometer zero.

194 Replace the uptake tubing for reductant and acid blank in the appropriate reservoirs. Pump acid blank (paragraph 71 or 72) and reductant (paragraph 74) to the mixing piece and measure the atomic absorbance or fluorescence signal after allowing sufficient time for the water to be replaced.

Note 70: *If the reagent blank is higher than normal, then the analytical performance of the system will be degraded, and in particular the detection limit will be poorer. A high blank may be due to contamination of one or more of the reagents or to contamination of the system. If it is considered that contamination of the reagents is the likely cause of the high blank, then new tin (II) chloride solution (paragraph 74) and 1 + 1 + 23 nitric acid/hydrochloric acid (paragraph 71) or 2 + 2 + 21 nitric acid/hydrochloric acid (paragraph 72) should be prepared. If it is considered that contamination of the system is the likely cause of the high blank, then the gas/liquid separator should be cleaned. The reagent blank should then be redetermined by repeating the procedure given in paragraphs 193 and 194.*

Calibration

195 Adjust the spectrometer zero while pumping acid blank (paragraph 71 or 72) and reductant (paragraph 74) to the mixing piece of the cold vapour generation system (paragraph 105 or 106).

Either

196 For continuous flow and discrete injection cold vapour generation systems, pump each calibration solution (paragraph 168 or 178) in turn through the sample uptake tubing to the mixing piece, and take the maximum atomic absorbance or atomic fluorescence reading after the determined stabilisation delay time or peak delay time (see paragraph 189). Pump acid blank (paragraph 71 or 72) to the mixing piece in between each calibration solution and wait for the determined baseline delay time (see paragraph 189) before proceeding to measure the next calibration solution.

or

197 For flow injection cold vapour generation systems, inject each calibration solution (paragraph 168 or 178) in turn into the blank acid stream, measure the peak height or peak area of the atomic absorbance or atomic fluorescence signal, and wait for the determined baseline delay time (see paragraph 190) before proceeding to measure the next calibration solution.

198 For instruments controlled by a microprocessor or personal computer, use a suitable algorithm to generate the calibration function. For instruments without this capability, prepare a calibration graph by plotting the absorbance or fluorescence of the calibration solutions versus the concentration of mercury, in nanograms per millilitre, in the respective solutions.

Note 71: *In general, it is best to work in the linear range of an atomic absorption calibration, where absorbance is proportional to the concentration of mercury in solution. A certain amount of curvature can be tolerated, and ideally the slope of the top 20% of the calibration curve should be not less than 70% of the slope of the bottom 20% calculated in the same manner. Discretion should be exercised in assessing whether recalibration over a lower concentration range is necessary. Mercury cold vapour atomic fluorescence calibration curves are, by contrast,*

typically close to linear over several orders of magnitude of concentration.

Determination

Either

199 For continuous flow or discrete injection cold vapour generation systems, adjust the spectrometer zero while pumping the acid blank (paragraph 71 or 72) to the mixing piece. Pump the sample and blank solutions (paragraphs 167 or 177) in turn through the sample uptake tubing to the mixing piece, and take the maximum atomic absorbance or atomic fluorescence reading after the determined stabilisation delay time or peak delay time (see paragraph 189). Pump acid blank to the mixing piece in between each test solution and wait for the determined baseline delay time (see paragraph 189) before proceeding to measure the next test solution.

or

200 For flow injection cold vapour generation systems, pump the sample and blank solutions (paragraphs 167 or 177) sequentially through the sample valve, inject into the acid blank stream (paragraph 71 or 72), and measure the peak height or peak area of the atomic absorbance or atomic fluorescence signal. Pump acid blank to the mixing piece in between each test solution and wait for the determined baseline delay time (see paragraph 190) before proceeding to measure the next test solution.

201 If baseline drift is observed while pumping acid blank, then readjust the spectrometer zero.

202 For instruments controlled by a microprocessor or personal computer, use the calibration function (see paragraph 198) to calculate the concentration of mercury in the sample and blank solutions, and obtain a direct read-out of the results in concentration units. For instruments without this capability, determine the concentration of mercury in the sample solution from the peak height or peak area measurements using the calibration graph (see paragraph 198).

203 Analyse a mid-range calibration solution after each five to ten test solutions. If the absorbance reading indicates that the sensitivity has changed by more than $\pm 5\%$, take one of the following 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 paragraphs 195 to 198. In either case, reanalyse the test solutions, which were analysed during the period in which the sensitivity change occurred.

204 If the concentration of mercury found is above the upper limit of the calibration range, dilute the sample solution by a suitable factor and repeat the analysis. Record the dilution factor.

205 Calculate the mean mercury concentration of the blank solutions.

CALCULATIONS

Air sample volumes

Diffusive sampling

206 Calculate the volume, in litres, of the air sampled by multiplying the nominal sample uptake rate of 20.0 ml min⁻¹ by the sampling time, in minutes, and dividing by 1000.

207 If appropriate (see paragraph 111), calculate the mean atmospheric temperature and pressure by averaging the measurements taken at the start and end of the sampling period and apply a temperature and pressure correction using the following equation:

$$U_{\text{corr}} = U \times \left(\frac{T_1}{T_2} \right)^{1.5} \times \left(\frac{P_2}{P_1} \right) \quad \text{Equation 3}$$

| | | |
|-------|-------------------|--|
| where | U_{corr} | is the calculated temperature corrected sample uptake rate, in millilitres per minute; |
| | U | is the nominal sample uptake rate, in millilitres per minute, given by the manufacturer of the diffusive badge, ie 20.0 ml min ⁻¹ ; |
| | T_1 | is the mean atmospheric temperature, in kelvin, during the sampling period; |
| | T_2 | is the temperature at which the sample uptake rate given by the manufacturer of the diffusive badge applies, in kelvin, ie 293 K (20°C); |
| | P_1 | is the mean atmospheric pressure, in kilopascals, during the sampling period; and |
| | P_2 | is the pressure at which the sample uptake rate given by the manufacturer of the diffusive badge applies, in kilopascals, ie 101.3 kPa. |

Pumped sampling

208 Calculate the mean flow rate 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 mercury in air

Calculation when using active sampling

209 Calculate the concentration of mercury in air, $\rho(\text{Hg})$, in milligrams per cubic metre (mg m⁻³), using the equation:

$$\rho(\text{Hg}) = \frac{[\rho(\text{Hg})_1 \times V_1 \times \text{DF}_1] - [\rho(\text{Hg})_0 \times V_0 \times \text{DF}_0]}{V} \quad \text{Equation 4}$$

where $\rho(\text{Hg})_1$ is the concentration, in $\mu\text{g ml}^{-1}$, of mercury in the sample solution (see paragraph 202);

$\rho(\text{Hg})_0$ is the mean concentration, in $\mu\text{g ml}^{-1}$, of mercury in the blank solutions (see paragraph 205);

V_1 is the volume, in ml, of the sample solution, ie 25 ml or 50 ml;

V_0 is the volume, in ml, of the blank solutions, ie 25 ml or 50 ml;

DF_1 is the dilution factor for the sample solution (see paragraph 204);

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

V is the volume, in litres, of the air sample (see paragraph 208).

210 For normal use, the volume of sample and blank solutions is 25 ml for the diffusive badge method and 50 ml for the pumped sorbent tube method, and the dilution factor for sample and blank measurements is 1. In the case of the diffusive badge method, Equation 4 is therefore reduced to:

$$\rho(\text{Hg}) = \frac{[\rho(\text{Hg})_1 - \rho(\text{Hg})_0] \times 25}{V} \quad \text{Equation 5}$$

and in the case of the pumped sorbent tube method to:

$$\rho(\text{Hg}) = \frac{[\rho(\text{Hg})_1 - \rho(\text{Hg})_0] \times 50}{V} \quad \text{Equation 6}$$

TEST REPORT

211 Appendix C gives recommendations for information to be included in the test report.

QUALITY CONTROL MEASURES

212 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 71.⁴⁰

213 If mercury analysis is performed frequently, it is recommended that internal quality control is performed. The use of stored quality control solutions is inappropriate since mercury solutions of low concentration are not stable. Also, the result would vary dependent on the blank value of the batch of sorbent tubes or batches used. It is therefore recommended that a quality control solution prepared from the batch of sorbent tubes or diffusion badge capsules used to collect the samples is prepared at the same time as the samples. The concentration of this should correspond to approximately 50% of the calibration range. Analyse this a suitable number of times (eg twenty) on separate occasions, and calculate the mean and standard deviation of the measured mercury concentration for each quality control solution. Assuming that the distribution of these values is Gaussian, construct a Shewhart chart for each quality control solution with warning and action limits at ± 2 SD and ± 3 SD respectively. Subsequently, analyse the quality control solutions with each analytical batch and plot the result on the Shewhart charts. Compare the internal quality control results with the target values and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.⁴⁰

214 It is recommended that all laboratories undertaking the determination of mercury 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 71.⁴⁰ However, at present the WASP scheme does not encompass mercury.

ADVICE

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

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

APPENDIX A - OPERATING PARAMETERS FOR DETERMINATION OF MERCURY USED AT HSL

A.1 Flow injection CVAAS

| | |
|------------------------|--|
| AAS instrumentation | Perkin Elmer PE 5100 AA spectrometer with mercury hollow cathode AAS lamp and heated quartz gas cell |
| Flow injection | Perkin Elmer FIAS 200 flow injection analysis equipment system with 500 µl injection loop, 300 µl reaction coil, a gas/liquid separator fitted with PTFE filter to prevent spray contaminating gas cell. |
| Pump speed | 120 revs min ⁻¹ |
| Acid/sample steam flow | 12 ml min ⁻¹ |
| Reductant steam flow | 5.5 ml min ⁻¹ |
| Argon carrier gas flow | 70 ml min ⁻¹ |
| Gas cell temperature | 100°C |
| Wavelength | 253.7 nm |
| Slit width | 0.7 nm |
| Mode | Peak height |
| Wavelength | 253.7 nm |
| Mode | Peak height |
| Read time | 40 sec |

A.2 Discrete injection CVAFS

| | |
|-------------------------------|---|
| AFS instrumentation | PS Analytical Merlin Millennium discrete injection CVAFS system with high intensity mercury lamp |
| Discrete injection equipment | Gas/liquid separator switching valve to divert sample solution into acid stream for a timed period, and internal Permapure dryer system to remove water from carrier gas entering AFS cell. |
| Pump speed | half of maximum |
| Acid/sample steam flow | 4.5 ml min ⁻¹ |
| Reductant steam flow | 4.5 ml min ⁻¹ |
| Argon carrier gas flow | 300 ml min ⁻¹ |
| Argon AFS detector sheath gas | 300 ml min ⁻¹ |
| Compressed air drier gas air | 2.5 l min ⁻¹ |
| Wavelength | 253.7 nm |
| Mode | Peak height (ratio) |
| Delay time | 15 sec |
| Sample injection time | 20 sec |
| Maximum read time | 120 sec |

APPENDIX B - GUIDANCE ON SELECTION OF A SAMPLING METHOD FOR MERCURY VAPOUR

The following guidance is intended to help the user choose whether to collect samples of mercury vapour using diffusive badges or pumped sorbent tubes.

Advantages and disadvantages of diffusive sampling

B1 Diffusive badges used for collection of mercury vapour are small, lightweight, and require no sampling pump. Samples are stable for at least 30 days if the sorbent capsules are stored in the plastic pouches in which they are supplied. Sampling can therefore be carried out with the minimum of equipment, and samples can easily be sent for analysis by mail. Also, the sampler is reusable, so that consumable costs are kept to a minimum.

B2 While eminently suitable for sampling throughout the entire working period, the diffusive badge method is not suitable for sampling periods <6 h.

B3 The diffusive badge method is not suitable for measuring particulate inorganic mercury compounds.

B4 The uptake rate of diffusive badges is dependent upon face velocity (see paragraph 56). In particular, the uptake rate drops off in still air conditions. For personal sampling this is not a problem, since body movements and convection currents due to body heat provide sufficient air movement. However, diffusive badges should be used with caution for static (area) sampling (see paragraph 123). At very high wind speeds, erratic increases in sampling rate can occur and additional shielding is necessary (see paragraph 123).

B5 Diffusive badges are not suitable for use if they could become contaminated with liquid mercury, or if the badges could be subject to frequent knocks or vibration which might pulverise the sorbent, allowing it to escape from the capsules.

Advantages and disadvantages of pumped sampling

B6 An advantage of pumped sampling is that mercury vapour and particulate may be collected simultaneously for comparison with a limit value for mercury and inorganic compounds. This can be achieved by sampling with a sorbent tube alone when particulate mercury compounds are present in the air at low concentrations, eg in chloralkali processes. However, when high concentrations of particulate mercury compounds could be present, it is necessary to use a quartz fibre prefilter and analyse it together with the contents of the sorbent tube to obtain a total mercury-in-air concentration.

B7 When it is known that all the airborne mercury is present in particulate form, sampling may be carried out using a quartz fibre filter alone. This is analysed using an analytical technique that is essentially identical with that described for sorbent tube samples.

B8 Pumped sampling can be used for sampling times as short as 1 h using the 200 mg sorbent tube, or 15 min using the 500 mg sorbent tube. It can be used in still air and windy conditions since the sampling rate is independent of air speed.

APPENDIX C - 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, either the identity of the individual whose breathing zone was sampled or the location at which a fixed point measurement was made, a very brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;
- b) a reference to this MDHS, including information about which analytical technique was used, and a description of any deviation from the procedures described;
- c) the make and type of sorbent badge or sorbent tube and/or sampler used;
- d) the make, type and diameter of filter used, if appropriate;
- e) the make and type of sampling pump used, and its identification (for pumped samples only);
- f) the type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, and the range of flow rates over which the calibration of the flowmeter was checked (for pumped sampling only);
- g) the time at the start and at the end of the sampling period, and the sampling time in minutes;
- h) the mean flow rate during the sampling period, in litres per minute (for pumped sampling only);
- i) the mean temperature and pressure during the sampling period, if appropriate (see paragraph 111);
- j) the volume of air sampled, in litres;
- k) the name of the person who collected the sample;
- l) the time-weighted average mass concentration of mercury vapour and/or divalent mercury compounds found in the air sample, in milligrams per cubic metre;
- m) the analytical variables used to calculate the result, including the concentrations of mercury in the sample and blank solutions, the volumes of the sample and blank solutions, and the dilution factor, if applicable;

Note: *If necessary data (eg the volume of air sampled) are not available to the laboratory for the above calculations to be carried out, the laboratory report may contain the analytical result in micrograms of mercury per sample.*

- n) the type(s) of instrument(s) used for sample preparation and analysis;
- o) the name of the analyst;
- p) the date of the analysis; and
- q) any inadvertent deviations, unusual occurrences or other notable observations.

REFERENCES

- 1 Health and Safety Executive *Mercury vapour in air: Laboratory method using hopcalite adsorbent tubes and acid dissolution with cold vapour atomic absorption spectrometric analysis using atomic absorption spectrometry* MDHS 16 HSE Books 1983 ISBN 0 7176 0110 2
- 2 International Standards Organisation *Workplace air: Determination of mercury and inorganic mercury compounds: Method by cold vapour atomic absorption spectrometry or atomic fluorescence spectrometry* ISO 17733 (in draft)
- 3 *Control of Substances Hazardous to Health Regulations 1999* SI 1999/437 The Stationery Office 1999 ISBN 0 11 082087 8
- 4 Health and Safety Commission *General COSHH ACOP (Control of Substances Hazardous to Health) and Carcinogens ACOP (Control of Carcinogenic Substances) and Biological Agents ACOP (Control of Biological Agents): Control of Substances Hazardous to Health Regulations 1999: Approved Codes of Practice L5* (Third edition) HSE Books 1999 ISBN 0 7176 1670 3
- 5 Chipman JK, Cross HJ, Fletcher AC, Levy LS, Smillie MV, Spurgeon A, Fairhurst S, Howe A, Mason H, Northage C and Wright AL *Mercury and its divalent compounds* Health and Safety Executive Contract Research Report No 76/1995 HSE Books 1995 ISBN 0 7176 0930 8
- 6 Health and Safety Executive *Mercury: Medical guidance notes* Guidance Note MS 12 (Revised) HSE Books 1996 ISBN 0 7176 1252 X
- 7 Health and Safety Commission *Approved Supply List (6th edition): Information approved for the classification and labelling of substances and preparations dangerous for supply* HSE Books 2000 ISBN 0 7176 1832 3
- 8 *Chemicals (Hazard Information and Packaging for Supply) Regulations 1994 (CHIP 2)* SI 1994/3247 The Stationery Office 1994 ISBN 0 11 043877 9, as amended by the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 1996 (CHIP 1996)* SI 1996/1092 The Stationery Office 1996 ISBN 0 11 054570 2, the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 1997 (CHIP 1997)* SI 1997/1460 The Stationery Office 1997 ISBN 0 11 063750 X, the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 1998 (CHIP 1998)* SI 1998/3106 The Stationery Office 1998 ISBN 0 11 079931 3, the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 1999 (CHIP 1999)* SI 1999/197 The Stationery Office 1999 ISBN 0 11 080410 4, and the *Chemicals (Hazard Information and Packaging for Supply) (Amendment) Regulations 2000 (CHIP 2000)* SI 2000/2381 The Stationery Office 2000 ISBN 0 11 099805 7
- 9 Health and Safety Executive *Mercury and its inorganic divalent compounds* Guidance Note EH 17 (Revised) HSE Books 1996 ISBN 0 7176 1127 2
- 10 Health and Safety Executive *Occupational exposure limits 2002* EH40/2002 (updated annually) HSE Books 2002 ISBN 0 7176 2083 2
- 11 Health and Safety Executive *Mercury and its inorganic divalent compounds: Criteria document for an occupational exposure limit* EH 65/19 HSE Books 1995 ISBN 0 7176 1014 4
- 12 Health and Safety Executive *Criteria document summaries: Synopses of the data used in setting occupational exposure limits* EH 64 (1995 Supplement) HSE Books 1995 ISBN 0 7176 0883 2
- 13 Foster RD, Howe AM and Gardiner PHE *Measurement of mercury in workplace air: Part 1: General information: Development of MDHS 16/2 and investigations into alternative methods* HSL Internal Report IR/L/IS/98/07 2001
- 14 Foster RD, Howe AM and Gardiner PHE *Measurement of mercury in workplace air: Part 2: Development and validation of MDHS 16/2* HSL Internal Report IR/L/IS/98/08 2001
- 15 British Standards Institution *Workplace atmospheres: General requirements for the performance of procedures for the measurement of chemical agents* BS EN 482:1994 BSI ISBN 0 580 23644 7
- 16 Rathje AO, Marcero DH and Dattilo D Personal monitoring technique for mercury vapor in air and determination by flameless atomic absorption *Am Ind Hyg Assoc J* 1974 **35** 571-574
- 17 Rathje AO and Marcero DH Improved hopcalite procedure for the determination of mercury vapor in air by flameless atomic absorption *Am Ind Hyg Assoc J* 1976 **5** 311-314
- 18 British Standards Institution *Workplace atmospheres: Size fraction definitions for measurement of airborne particles* BS EN 481:1993 BSI ISBN 0 580 22140 7
- 19 Health and Safety Executive *Monitoring strategies for toxic substances* Health and Safety Guidance Booklet HSG173 HSE Books 1997 ISBN 0 7176 1411 5
- 20 US Occupational Safety and Health Administration *OSHA Analytical Methods Manual 2nd Edition* Method ID-140 *Mercury vapor in workplace atmospheres* and associated back-up report *Evaluation of a solid sorbent passive dosimeter for collecting mercury vapor* USDOL/OSHA 1991 <http://www.osha.gov/>
- 21 Cee RJ, Ku JC, Zimowski SL, Edwards SL and Septon JC An evaluation of mercury vapour sampling devices *Proceedings of the mercury in mining conference* USDOL/MSHA Nevada State Division of Mine Inspection and the Nevada Mining Association August 1987

- 22 Schroeder WH, Keeler G, Kock H, Roussel P, Schneeberger D and Schaedlich F International field comparison of atmospheric mercury measurement methods *Water, air and soil pollution* 1995 **80** 611-620
- 23 SKC *Operating instructions: Passive sampler for mercury Catalog No. 520 Series Form No 3758 - Rev 9706* SKC Inc 1997
- 24 British Standards Institution *Workplace atmospheres: Diffusive samplers for the determination of gases and vapours: Requirements and test methods* BS EN 838:1996 BSI ISBN 0 580 26240 5
- 25 British Standards Institution *Workplace atmospheres: Pumped sorbent tubes for the determination of gases and vapours: Requirements and test methods* BS EN 1076:1997 BSI ISBN 0 580 28358 5
- 26 British Standards Institution *Workplace atmospheres: Procedures for measuring metals and metalloids in airborne particles: Requirements and test methods* BS EN 13890:2002 BSI
- 27 Menke R and Wallis G Detection of mercury in air in the presence of chlorine and water vapour *Am Ind Hyg Assoc J* 1980 **41** 120-124
- 28 West CD Relative effect of molecular absorption on atomic absorption and atomic fluorescence *Anal Chemistry* 1974 **46** 797-799
- 29 British Standards Institution *Water for analytical laboratory use: Specification and test methods* BS EN ISO 3696:1995 BSI ISBN 0 580 16312 1
- 30 British Standards Institution *Workplace atmospheres: Assessment of performance of instruments for measurement of airborne particles* BS EN 13205:2002 BSI ISBN 0 580 39193 0
- 31 Health and Safety Executive *General methods for sampling and gravimetric analysis of respirable and total inhalable dust* MDHS 14/3 HSE Books 2000 ISBN 0 7176 1749 1
- 32 US Occupational Safety and Health Administration *OSHA Analytical Methods Manual 2nd Edition Method ID-145 Particulate mercury in workplace atmospheres* USDOL/OSHA 1991 <http://www.osha.gov/>
- 33 British Standards Institution *Workplace atmospheres: Pumps for personal sampling of chemical agents: Requirements and test methods* BS EN 1232:1997 BSI ISBN 0 580 28328 3
- 34 British Standards Institution *Laboratory glassware: One-mark volumetric flasks* BS EN ISO 1042:2000 BSI ISBN 0 508 30111 7
- 35 British Standards Institution *Piston-operated volumetric instruments: Part 1: Terminology, general requirements and user recommendations* BS EN ISO 8655-1 BSI (in press)
- 36 British Standards Institution *Piston-operated volumetric instruments: Part 2: Piston pipettes* BS EN ISO 8655-2 BSI (in press)
- 37 British Standards Institution *Piston-operated volumetric instruments — Part 5: Dispensers* BS EN ISO 8655-5 BSI (in press)
- 38 British Standards Institution *Piston-operated volumetric instruments: Part 6: Gravimetric test methods* BS EN ISO 8655-6 BSI (in press)
- 39 Corns WT, Ebdon L, Hill SJ and Stockwell PB Effects of moisture on the cold vapour determination of mercury and its removal by use of membrane dryer tubes *Analyst* 1992 **117** 717-720
- 40 Health and Safety Executive *Analytical quality in workplace air monitoring* MDHS 71 HSE Books 1991 ISBN 0 7176 1263 5

TITLES IN THE MDHS SERIES

- | | | | |
|------|---|------|--|
| 1 | Acrylonitrile charcoal tube/gas chromatography (GC) | 54 | Protocol for assessing the performance of a pumped sampler for gases and vapours |
| 2 | Acrylonitrile pumped thermal desorption/GC | 55 | Acrylonitrile diffusive/thermal desorption/GC |
| 3 | Standard atmospheres syringe injection | 56/2 | Hydrogen cyanide ion-selective electrode |
| 4 | Standard atmospheres permeation tube | 57 | Acrylamide liquid chromatography |
| 5 | On-site validation of methods | 59 | Manmade mineral fibres |
| 6/3 | Lead atomic absorption (AA) | 60 | Mixed hydrocarbons |
| 10/2 | Cadmium AA | 61 | Total hexavalent chromium compounds in air colorimetric |
| 12/2 | Chromium AA | 62 | Aromatic carboxylic acid anhydrides |
| 14 | Total inhalable and respirable dust gravimetric | 63 | Butadiene diffusive/thermal desorption/GC |
| 15 | Carbon disulphide charcoal tube/GC | 64 | Toluene charcoal diffusive/solvent desorption/GC |
| 16 | Mercury adsorbent tube (Hydrar) AA | 65 | Mine road dust: determination of incombustible matter |
| 17 | Benzene charcoal tube/GC | 66 | Mixed hydrocarbons (C ₅ to C ₁₀) in air diffusive/thermal desorption/GC |
| 18 | Tetra alkyl lead continuous monitoring | 67 | Total (and speciated) chromium in chromium plating mists colorimetric (1,5-diphenylcarbazine) |
| 19 | Formaldehyde colorimetric (Chromotropic acid) | 68 | Coal tar pitch volatiles |
| 20 | Styrene pumped charcoal tube/GC | 69 | Toluene diffusive/solvent desorption/GC |
| 21 | Glycol ethers charcoal tube/GC | 70 | General methods for sampling airborne gases and vapours |
| 22 | Benzene thermal desorption/GC | 71 | Analytical quality in workplace air monitoring |
| 23 | Glycol ethers thermal desorption/GC | 72 | Volatile organic compounds in air |
| 24 | Vinyl chloride charcoal tube/GC | 73 | Measurement of air change in factories and offices |
| 25/2 | Organic isocyanates reagent bubbler/HPLC | 74 | n-Hexane in air diffusive/solvent desorption/GC |
| 26 | Ethylene oxide charcoal tube/GC | 75 | Aromatic amines solid sorbent/thermal desorption/GC |
| 27 | Diffusive sampler evaluation protocol | 76 | Cristobalite in respirable dusts X-ray diffraction (direct method) |
| 28 | Chlorinated hydrocarbons charcoal tube/GC | 77 | Asbestos in bulk materials |
| 29/2 | Beryllium AA | 78 | Formaldehyde diffusive/solvent desorption/liquid chromatography |
| 30/2 | Cobalt AA | 79 | Peroxodisulphate salts mobile phase ion chromatography |
| 31 | Styrene pumped thermal desorption/GC | 80 | Volatile organic compounds diffusive/thermal desorption/GC |
| 32 | Phthalate esters solvent desorption/GC | 81 | Dustiness of powders and materials |
| 33 | Adsorbent tube standards | 82 | The dust lamp |
| 35/2 | HF and fluorides ion-selective electrode | 83 | Resin acids GC |
| 36 | Toluene charcoal tube/GC | 84 | Oil mist from mineral oil-based metalworking fluids |
| 37 | Quartz in respirable airborne dust direct infra-red | 85 | Triglycidyl isocyanurate in air pumped filter/desorption/liquid chromatography |
| 38 | Quartz in respirable airborne dust KBr disc technique | 86 | Hydrazine in air |
| 39/4 | Asbestos fibres light microscopy (European reference version) | 87 | Fibres in air |
| 40 | Toluene thermal desorption/GC | 88 | Volatile organic compounds in air diffusive/solvent desorption/GC |
| 41/2 | Arsenic AA | 89 | Dimethyl sulphate and diethyl sulphate thermal desorption/GC-mass spectrometry |
| 42/2 | Nickel AA | 90 | Alkyl 2-cyanoacrylates liquid chromatography |
| 43 | Styrene diffusive/thermal desorption/GC | 91 | Metals and metalloids XRF |
| 44 | Styrene diffusive/solvent desorption/GC | 92 | Azodicarbonamide high performance liquid chromatography |
| 45 | Ethylene dibromide solvent desorption/GC | 93 | Glutaraldehyde HPLC |
| 46/2 | Platinum AA | 94 | Pesticides pumped filters/sorbent tubes/GC |
| 47 | Rubber fume in air measured as total particulates and cyclohexane soluble material | 95 | Metalworking fluid AA/plasma-atomic emission spectrometry |
| 48 | Newspaper print rooms: measurements of total particulates and cyclohexane soluble material in air | 96 | Volatile organic compounds in air pumped solid sorbent/solvent desorption/GC |
| 49 | Aromatic isocyanates acid hydrolysis/ diazotisation | 100 | Asbestos-containing materials |
| 50 | Benzene diffusive/thermal desorption/GC | | |
| 51/2 | Quartz in respirable dusts X-ray diffraction (direct method) | | |
| 52/3 | Hexavalent chromium in chromium plating mists colorimetric (1,5-diphenylcarbazine) | | |
| 53 | 1,3 Butadiene thermal desorption/GC | | |

©Crown copyright 2002

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

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

First published 2002

£17.50



MAIL ORDER HSE priced and free publications are available from:
HSE Books, PO Box 1999, Sudbury, Suffolk CO10 2WA Tel: 01787 881165
Fax: 01787 313995 Website: www.hsebooks.co.uk

RETAIL HSE priced publications are available from bookshops

HEALTH AND SAFETY ENQUIRIES HSE InfoLine Tel: 08701 545500
Fax: 02920 859260 e-mail: hseinformationservices@natbrit.com or write to:
HSE Information Services, Caerphilly Business Park, Caerphilly CF83 3GG
Website: www.hse.gov.uk

ISBN 0-7176-2348-3



9 780717 623488