



Health and Safety Executive
Health and Safety Laboratory

MDHS 41/2

Methods for the
Determination of
Hazardous Substances

August 1994

Arsenic and inorganic compounds of arsenic (except arsine) in air

Laboratory method using continuous flow or flow injection analysis hydride generation atomic absorption spectrometry

INTRODUCTION

Note 1: *This method updates and replaces MDHS 41.1. The principal change is that use of continuous flow and flow injection analysis hydride generation systems is now described rather than use of a discrete batch hydride generation system, a technique which has now been largely superseded. Other changes which have been made include (i) use of cellulose ester membrane filters and sodium carbonate-impregnated back-up paper pads rather than cellulose ester membrane filters or sodium hydroxide-impregnated paper filters, and (ii) sample dissolution using nitric acid, sulphuric acid and hydrogen peroxide rather than aqua regia. The procedures given in this method can easily be adapted by laboratories still using discrete batch hydride generation.*

Properties and uses

1 The properties and the various industrial uses of arsenic and inorganic compounds of arsenic are described in HSE Guidance Note EH 8.²

Health effects

2 Health effects of arsenic and inorganic compounds of arsenic are summarised in HSE Guidance Note EH 8² and are described more fully in HSE Toxicity Review TR 16.³

Health and safety precautions

3 HSE leaflet MS(A)8⁴ summarises the risks involved in working with arsenic and what can be done to control them. Control of exposure, emergency procedures and health surveillance are described more fully in HSE Guidance Note EH 8.²

Exposure limits

4 Schedule 1 of the Control of Substances Hazardous to Health (COSHH) Regulations⁵ specifies a maximum exposure limit (MEL),⁶ 8-hour time-weighted average reference period, for arsenic and compounds, except arsine (as As). This limit is reproduced in HSE Guidance Note EH 40.⁷

Analytical methods

5 This is not a 'reference' method in the strict

analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte (eg other methods in the MDHS series). With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

6 This method has been validated⁸ to demonstrate that it complies with the *General requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres* described by the Comité Européen de Normalisation (CEN) in draft European Standard prEN 482.⁹ If an alternative method is used, it is necessary to demonstrate that it also meets these performance requirements.

Requirements of the COSHH Regulations

7 The COSHH Regulations⁵ require that employers make an assessment of the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. The COSHH Regulations also include a requirement that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this method.

SCOPE

Applicability

8 This MDHS describes a method for determination of the concentration of arsenic and inorganic compounds of arsenic (except arsine) in workplace air, using continuous flow or flow injection analysis hydride generation atomic absorption spectrometry. It is applicable to the determination of the majority of arsenic-containing materials in industrial use or occurring in workplace air. However, certain metal arsenides (eg alkali metal, aluminium, calcium and zinc arsenides) decompose in the presence of water or in acid solution to liberate arsine, and these are not determined. High levels of certain transition metals, particularly copper and

nickel, interfere with the hydride generation process (see paragraph 15), and the method is therefore unsuitable for determination of arsenic in dusts and fume containing very high levels of these elements (eg stainless steel welding fume). The method is suitable for sampling over periods in the range 15 minutes to 8 hours.

Note 2: *The analytical procedures described in this method may be easily adapted for use with discrete batch hydride generation atomic absorption spectrometry, hydride generation atomic fluorescence spectrometry, hydride generation inductively coupled plasma atomic emission spectrometry and hydride generation inductively coupled plasma mass spectrometry.*

Note 3: *HSE Guidance Note EH 42¹⁰ advises employers about how they should conduct investigations into the nature, extent and control of exposure to substances hazardous to health which are present in workplace air. The objective of air monitoring is usually to determine worker exposure, and therefore the procedures described in this method are for personal sampling in the breathing zone. The method may be used for background or fixed location sampling, but it should be recognised that due to aerodynamic effects the samplers used do not necessarily exhibit the same collection characteristics as when they are used for personal sampling.*

METHOD PERFORMANCE

Sampling efficiency

9 The sampling efficiency of a similar method has been determined to be 1.00 for laboratory-generated arsenic aerosols and 0.98 for arsenic trioxide vapour.¹¹ Field trials indicate that the sampling method described in this MDHS has equivalent performance.⁸

Effectiveness of sample dissolution procedure

10 The sample dissolution procedure described is effective for arsenic and the majority of inorganic arsenic compounds found in samples of workplace air, except certain metal arsenides (see paragraph 8). However, if there is any doubt about the suitability of this procedure for the dissolution of arsenic compounds in particulate material which may be present in the test atmosphere, its effectiveness should be investigated before proceeding with the method.

Detection limits

11 Detection limits for the determination of arsenic are dependent upon the analytical line at which absorbance measurements are made and upon the hydride generation system and atomic absorption spectrometer used. However, the qualitative and quantitative instrumental detection limits for arsenic, defined as three times and ten times the standard deviation of a blank determination, have been estimated⁸ to be approximately 0.3 ng ml⁻¹ and 1 ng ml⁻¹ for the

197.2 nm arsenic line. For an air sample volume of 960 litres and a sample solution aliquot of 5 ml, this corresponds to arsenic-in-air concentrations of 0.015 µg m⁻³ and 0.05 µg m⁻³. The working range of the method is approximately 100 ng to 125 µg of arsenic per sample for absorbance measurements made at the 197.2 nm arsenic line on test solutions prepared using sample solution aliquots in the range 5 ml to 0.1 ml.

Overall uncertainty

12 Laboratory experiments⁸ indicate that the analytical method does not exhibit significant bias. The mean analytical recovery for dosed filters in the range 5 µg to 100 µg of arsenic was determined to be 100.7% using continuous flow HGAAS and 99.3% using flow injection analysis HGAAS, for a sample solution aliquot of 0.1 ml. The mean analytical recovery for dosed filters in the range 0.5 µg to 10 µg of arsenic was determined to be 98.8% using continuous flow HGAAS and 102.7% using flow injection analysis HGAAS, for a sample solution aliquot of 1 ml.

13 The component of the coefficient of variation of the method that arises from analytical variability, CV(analysis), is dependent upon a number of factors, including the volume of the sample solution aliquot used in preparation of the test solution and whether continuous flow or flow injection analysis hydride generation atomic absorption spectrometry is used. CV(analysis) is at a minimum when the concentration of arsenic in the test solution is in the mid-range of the calibration, and in laboratory experiments⁸ it was estimated to be about 1% using continuous flow hydride generation atomic absorption spectrometry and about 3% using flow injection analysis hydride generation atomic absorption spectrometry, for measurements made at 197.2 nm on test solutions with an arsenic concentration in the range 10 ng ml⁻¹ to 40 ng ml⁻¹.

14 The overall uncertainty of the method, as defined by CEN,⁹ has been shown⁸ to be within the specification of 30% prescribed by CEN for the overall uncertainty of measurements for comparison with limit values, assuming that the coefficient of variation of the method that arises from inter-specimen sampler variability, CV(inter), is negligible and that the coefficient of variation of the method that arises from pump flowrate variability, CV(flow), is limited to 5%.

Interferences

15 A number of transition metals, mainly those of Groups VIII and IB, cause signal depression in the determination of arsenic by hydride generation atomic absorption spectrometry. This interference has been shown to be associated with the reduction of metal ions to the free metal.^{12,13} The resulting finely dispersed metal precipitate captures and decomposes the hydride formed in a secondary reaction. The metal may be slow to redissolve, in which case low results may be obtained when subsequent test solutions are analysed. If high levels of interfering elements may be present, it is advisable to analyse calibration solutions between

sample test solutions to check that signal depression is not occurring. It has been shown that this type of interference is minimised by using a high concentration of hydrochloric acid and a low concentration of sodium tetrahydroborate solution.¹³ The most severe interferences are caused by nickel, copper, and cobalt, but with the reagent concentrations used in this method the signal depression caused by $10 \mu\text{g ml}^{-1}$ of these three metals is less than 10%, for a solution containing 10 ng ml^{-1} of arsenic.¹⁴ Flow injection analysis hydride generation systems are much less affected by metal interferences than continuous flow hydride generation systems.

PRINCIPLE

16 A measured volume of air is drawn through a cellulose ester membrane filter and sodium carbonate-impregnated back-up paper pad, mounted in an inhalable dust sampler. Particulate arsenic and inorganic compounds of arsenic are collected on the cellulose ester membrane filter, and arsenic trioxide vapour is collected by reaction with sodium carbonate on the impregnated back-up paper pad. Arsine is not trapped. The cellulose ester membrane filter, back-up paper pad and collected sample are digested using nitric acid, sulphuric acid and hydrogen peroxide. The nitric acid and hydrogen peroxide are removed by boiling on a hot plate until dense, white fumes of sulphur trioxide are evolved, and the sample solution is allowed to cool and made up to volume with water. Aliquots of the sample solution are prepared for hydride generation by the addition of hydrochloric acid and potassium iodide. The test solution is reacted with sodium tetrahydroborate solution in a continuous flow hydride generation system or flow injection analysis hydride generation system to liberate arsine and hydrogen. These gaseous products are separated from the reaction liquid in a gas/liquid separator and carried by an inert purge gas into a silica or quartz tube. This tube is mounted in the optical path of an atomic absorption spectrometer equipped with an arsenic hollow cathode lamp or electrodeless discharge lamp, and it is heated either electrically or by an oxidising air-acetylene flame. Absorption measurements are made at 197.2 nm or 193.7 nm.

REAGENTS

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

Water

18 Water complying with the requirements of BS 3978¹⁵ grade 2 water (electrical conductivity less than 0.1 mS m^{-1} and resistivity greater than $0.01 \text{ M}\Omega\cdot\text{m}$ at 25°C).

1 mol/l sodium carbonate in 5% (v/v) glycerol solution

19 Weigh 10.6 g sodium carbonate (Na_2CO_3) into a 250 ml beaker. Add 5 ml glycerol and 50 ml of water (paragraph 18) and swirl to dissolve. Quantitatively transfer the solution into a 100 ml volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

Hydrochloric acid (HCl), concentrated, e about 1.18 g ml^{-1} , 35% (m/m) to 36% (m/m)

20 The concentration of arsenic shall be less than $0.01 \mu\text{g ml}^{-1}$.

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, therefore beware of pressure build-up in stoppered flasks when preparing acid/water mixtures.

Hydrochloric acid, diluted 1 + 1

21 Add approximately 900 ml of water (paragraph 18) to a 2 litre volumetric flask. Carefully add 1 litre of concentrated hydrochloric acid (paragraph 19) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

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

22 The concentration of arsenic shall be less than $0.01 \mu\text{g ml}^{-1}$.

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

Sulphuric acid (H_2SO_4), concentrated, e about 1.84 g ml^{-1} , about 98% (m/m)

23 The concentration of arsenic shall be less than $0.05 \mu\text{g ml}^{-1}$.

WARNING - Concentrated sulphuric acid is corrosive and causes burns. Avoid exposure by contact with the skin or eyes. Personal protection (eg gloves, face shield or safety spectacles etc) should be used when working with the concentrated or diluted sulphuric acid. Fumes produced by heating concentrated sulphuric acid are irritant, and this operation should therefore be carried out

in a fume hood. Caution should be exercised if adding water to sulphuric acid, since this reacts violently with water (preferably prepare acid/water mixtures by adding acid to water).

Hydrogen peroxide (H₂O₂), e about 1.10 g ml⁻¹, approximately 30% (m/v) solution

24 The concentration of arsenic shall be less than 0.01 µg ml⁻¹.

WARNING - Hydrogen peroxide is corrosive and oxidising. Avoid exposure by contact with the skin or eyes. Personal protection (eg gloves, face shield or safety spectacles etc) shall be used when working with hydrogen peroxide.

Potassium iodide, 0.1% (m/v) solution

25 Weigh 10.0 g of potassium iodide, KI, into a 250 ml beaker. Add 50 ml of water (paragraph 18) and swirl to dissolve. Quantitatively transfer the solution into a 100 ml volumetric flask, dilute to the mark with water, stopper and mix thoroughly.

Sulphuric acid, diluted 1 + 9

26 Add approximately 200 ml of water (paragraph 18) to a 250 ml volumetric flask. Carefully add 25 ml of concentrated sulphuric acid (paragraph 23) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Hydrochloric acid, diluted 1 + 4

27 Add approximately 700 ml of water (paragraph 18) to a 1 litre volumetric flask. Carefully add 200 ml of concentrated hydrochloric acid (paragraph 20) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Stock arsenic standard solution, 1000 µg ml⁻¹ of As(III)

28 Use a commercially available trivalent arsenic standard solution at a concentration of 1000 µg ml⁻¹. Observe the manufacturer's expiry date or recommended shelf life.

29 Alternatively, prepare an arsenic standard solution by the following procedure.

Accurately weigh 1.320 g ± 0.001 g of arsenic trioxide, As₂O₃, into a 50 ml beaker, add 10 ml of concentrated hydrochloric acid (paragraph 20), cover with a watch glass and heat to approximately 150°C on a hot plate in a fume cupboard until dissolution is complete. Quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with 1 + 1 hydrochloric acid (paragraph 21), stopper and mix thoroughly.

WARNING - Arsenic and arsenic compounds are toxic and are recognised as human carcinogens.¹⁶ Avoid any exposure by inhalation. Personal protection (eg an effective respirator) should be used in all cases where exposure to arsenic or arsenic compounds is possible.

Note 4: Arsenic standard solution prepared according to the instructions in paragraph 29 may be stored in a polypropylene bottle (paragraph 44) for a maximum period of one year without deterioration.

Working arsenic standard solution A, 10 µg ml⁻¹ of As(III)

30 Accurately pipette 1.00 ml of stock arsenic solution (paragraph 28 or 29) into a 100 ml volumetric flask, dilute to the mark with 1 + 1 hydrochloric acid (paragraph 21), stopper and mix thoroughly. Prepare this solution fresh weekly.

Working arsenic standard solution B, 1 µg ml⁻¹ of As(III)

31 Accurately pipette 10.0 ml of working arsenic solution A (paragraph 30) into a 100 ml volumetric flask, dilute to the mark with 1 + 1 hydrochloric acid (paragraph 21), stopper and mix thoroughly. Prepare this solution fresh daily.

Sodium tetrahydroborate, between 0.2% (m/v) and 2% (m/v) in 0.1 mol l⁻¹ sodium hydroxide solution

32 Prepare sodium tetrahydroborate solution at the concentration recommended by the manufacturer of the hydride generation system. Weigh between 2 and 20 g of sodium tetrahydroborate, NaBH₄, pellets or powder and 4 g sodium hydroxide, NaOH, pellets into a 1 litre beaker. Add 200 ml of water (paragraph 18) and swirl to mix. Quantitatively transfer the solution into a 1 litre volumetric flask, filtering through a membrane filter using suction filtration apparatus (paragraph 49). Dilute to the mark with water, stopper and mix thoroughly. Prepare this solution fresh daily.

Note 5: Filtration of the solution is necessary to remove undissolved particulate material which might otherwise cause clogging of the tubing or mixing piece of the hydride generation system. The addition of alkali minimises hydrolysis of the sodium tetrahydroborate solution.

Note 6: A few drops of anti-foaming agent may be added to the solution to reduce foaming in the gas/liquid separator of the hydride generation system which may result in a noisy baseline signal.

Note 7: The solution should be stored in a polypropylene bottle if it is not transferred to the reductant reservoir of the continuous hydride generation system immediately after preparation. The top of the bottle should not be fully tightened or pressure will build up due to the slow release of hydrogen.

Sodium hydroxide, 0.5% (m/v) solution

33 Weigh 5.0 g of sodium hydroxide, NaOH, pellets into a 1 litre beaker. Add 250 ml of water and swirl to dissolve. Quantitatively transfer the solution into a 1 litre volumetric flask, make to the mark with water, stopper and mix thoroughly.

Laboratory detergent solution

34 Laboratory detergent solution, suitable for cleaning of samplers and labware, diluted with water (paragraph 18) according to the manufacturer's instructions.

Inert purge gas

35 Inert purge gas, eg argon or nitrogen, cylinder or cryogenic supply.

SAMPLING EQUIPMENT

Samplers for collection of the inhalable fraction of airborne particles

36 Samplers, with protective covers, for collection of the inhalable fraction of airborne particles, as defined in European Standard EN 481.¹⁷ The seven-hole sampling head described in MDHS 14¹⁸ and the IOM (Institute of Occupational Medicine) inhalable dust sampler are suitable for personal sampling. Samplers manufactured in non-conducting plastic shall not be used as these have electrostatic properties which may influence representative sampling.

Note 8: *In general, the collection characteristics of inhalable samplers (eg the seven-hole sampling head) are such that particulate material collected on the filter is the inhalable fraction of the airborne particles, and any deposited on the internal surfaces of the sampler is not of interest. However, some samplers are designed such that airborne particles which pass through the entry orifice(s) constitute the inhalable fraction, in which case any particulate material deposited on the internal surfaces of the sampler is part of the sample. Certain samplers of this type (eg the IOM inhalable dust sampler) incorporate an internal filter cassette which may be removed from the sampler to enable this material to be easily recovered.*

Note 9: *Samplers which are assembled by means of screw threaded fittings may be unsuitable for use with a cellulose ester membrane filter and a back-up paper pad. The high restriction of a cellulose ester membrane filter compared with that of a paper pad means that there is a tendency for air to take the path of least resistance and to be drawn along screw threads and in through the edges of the paper pad, rather than through the cellulose ester membrane filter. Leakage can sometimes be eliminated by tightening screw threaded fittings as much as possible to compress and seal the edges of the paper pads, but this is not fully effective for certain types of sampler. Samplers with push-fit components can, in general, be used more reliably.*

Cellulose ester membrane filters and back-up paper pads

37 Cellulose ester membrane filters and back-up paper pads, of a diameter suitable for use in the selected sampler (paragraph 36). The arsenic content of a cellulose ester membrane filter and back-up paper pad shall be less than 0.01 µg.

38 The cellulose ester membrane filters shall have a retentivity not less than 99% for 0.3 µm mass median aerodynamic diameter particles.

39 The back-up paper pads shall be impregnated with sodium carbonate in an area where arsenic contamination is known to be low, using the following procedure:

Place the paper pads on a clean PTFE sheet or similar, inert, flat surface. Establish the volume of sodium carbonate solution required to just wet the entire paper pad after the solution has been allowed to spread for a few minutes. Dispense this volume of sodium carbonate solution onto each paper pad and allow to dry for several hours at room temperature. Store the sodium carbonate-impregnated paper pads in an airtight container and use within one week of preparation.

Note 10: *The volume of sodium carbonate solution required to impregnate the back-up paper pads is typically 175 µl for a 25 mm diameter paper pad or 400 µl for a 37 mm diameter paper pad.*

Note 11: *The drying time may be reduced by placing them in an oven at 40°C for 45 minutes.*

Sampling pumps

40 Sampling pumps, with an adjustable flow rate, incorporating a flowmeter or a flow fault indicator, capable of maintaining the appropriate flow rate (see paragraph 55) to within ± 5% of the nominal value throughout the sampling period (see paragraph 56), and capable of being worn without impeding normal work activity. The pumps shall give a pulsation-free flow (if necessary, a pulsation damper shall be incorporated between the sampling head and the pump, as near to the pump as possible). Flow-stabilised pumps may be required to maintain the flow rate within the specified limits.

Flowmeter

41 Flowmeter, portable, capable of measuring the appropriate flow rate (see paragraph 55) to within ± 5%, and calibrated against a primary standard.

Note 12: *The flowmeter incorporated in the pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded sampler in line, and that it is read in a vertical orientation if it is of the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampling head and the*

flowmeter, since in this event a flowmeter in the pump or elsewhere in line will give an erroneous flow rate.

Note 13: A soap bubble flowmeter may be used as a primary standard, provided its accuracy is traceable to national standards (see Appendix 1).

Ancillary equipment

42 Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sampler to the sampling pump; belts or harnesses to which the sampling pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes or similar, if required (see paragraph 64), to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

43 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS 1792.¹⁹

Note 14: It is recommended that a set of glassware is reserved for the analysis of arsenic by this method.

Polypropylene bottle

44 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 29), cleaned before use by soaking in 1 + 4 hydrochloric acid (paragraph 27) for at least 24 hours and then rinsing thoroughly with water (paragraph 18). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

Hot plate

45 A thermostatically controlled hot plate, capable of maintaining surface temperatures of approximately 150°C (see paragraph 69) and 175°C (see paragraph 74).

PTFE sheet

46 A PTFE sheet or other similar inert flat surface suitable for treatment of filters and paper pads with sodium carbonate solution (see paragraphs 38 and 39).

Disposable gloves

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

Piston operated volumetric apparatus

48 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,²⁰⁻²³ for the

preparation of the working standard solutions (see paragraphs 30 and 31), calibration solutions (see paragraph 77) and test solutions (see paragraph 76). A suitable set might include micropipettes covering the ranges 10 µl to 100 µl, 100 µl to 1000 µl and 1000 µl to 5000 µl. Dispensers for dispensing acids and potassium iodide solution (see paragraphs 74, 76 and 77).

Suction filtration apparatus

49 Filter pump, water-operated or vacuum, connected to a conical flask fitted with the filter funnel/support assembly. Filtration should be through membrane filters of 0.8 µm pore size, made of cellulose ester, PVC or other material not degraded by sodium tetrahydroborate solution.

Atomic absorption spectrometer

50 An atomic absorption spectrometer equipped with an arsenic hollow cathode lamp or electrodeless discharge lamp. If the absorption cell (paragraph 53) is heated by an air-acetylene flame, the atomic absorption spectrometer shall be fitted with an air-acetylene burner assembly, suitable for mounting the absorption cell, and supplied with compressed air and acetylene.

Hydride generation system

Either

51 A continuous flow hydride generation system, set up and operated according to the manufacturer's instructions, incorporating (i) reservoirs for sodium tetrahydroborate solution and acid blank, (ii) an autosampler for presentation of the test solution (optional), (iii) inert switching valve(s), either 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) chemically inert mixing piece(s) to facilitate mixing of acid blank or test solution, sodium tetrahydroborate 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. A schematic diagram of a typical system is given in Figure 1.

Note 15: Continuous flow hydride 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 sodium tetrahydroborate solution is introduced.

or

52 A flow injection analysis hydride generation system, set up and operated according to the manufacturer's

instructions, incorporating (i) reservoirs for sodium tetrahydroborate 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) chemically inert mixing piece(s) to facilitate mixing of acid blank or test solution, sodium tetrahydroborate 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 2.

WARNING - Arsine, AsH_3 , is generated when solutions containing arsenic are reacted with sodium tetrahydroborate. This gas is very toxic, but it will normally be produced only in very small quantities. However, in order to eliminate the possibility of exposure to arsine, 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.

Silica or quartz absorption cell

53 An absorption cell made of silica or quartz, heated either electrically or by an air-acetylene flame, and mounted in the optical path of the atomic absorption spectrometer.

Note 16: *Spray from the gas/liquid separator may be carried into the absorption cell by the argon stream in some hydride generation systems. 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 absorption cell.*

WARNING - Arsine, AsH_3 , is passed into the absorption cell. This gas is very toxic, but it will normally be decomposed in the cell. However, in order to eliminate the possibility of exposure to arsine, it is essential that efficient local exhaust ventilation is installed to prevent waste gases entering the general laboratory environment.

Analytical balance

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

SAMPLING

Sampling procedure

55 Select a sampler to collect the inhalable fraction of airborne particles and use at the flow rate at which the sampler (paragraph 36) exhibits the required collection characteristics. Refer to MDHS 14¹⁸ for the flow rate to be used when sampling with a seven-hole sampling head or IOM inhalable dust sampler.

56 Select a sampling period of an appropriate duration, such that the filter does not become overloaded with particulate material. (An 8-hour time weighted average concentration may be derived from the results for two or more consecutive samples, as described in HSE Guidance Note EH 42.¹⁰)

Preparation of sampling equipment

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

57 Clean the samplers (paragraph 36) before use. Disassemble the samplers, soak in laboratory detergent solution (paragraph 34), rinse thoroughly with water (paragraph 18), wipe with absorptive tissue and allow to dry thoroughly before reassembly.

58 Load the sodium carbonate-impregnated back-up paper pads (paragraph 39) followed by the cellulose ester membrane filters (paragraph 38) into clean, dry samplers (paragraph 36) such that the filter is upstream in relation to the back-up paper pad when air is drawn through the sampler. Handle the filters only with clean, flat-tipped tweezers (paragraph 42). Connect each loaded sampler to a sampling pump (paragraph 40) using plastic tubing (paragraph 42), ensuring that no leaks can occur. Switch on the sampling pump, attach the calibrated flowmeter (paragraph 41) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the appropriate flow rate (see paragraph 55) with an accuracy of $\pm 5\%$. Remove the flowmeter and allow the pump to operate for an appropriate period to enable it to warm up and the flow rate to stabilise (follow the manufacturer's recommendations). Then discard the used cellulose ester membrane filter and back-up paper pad and load new ones into the sampler for collection of the sample. Finally, attach the calibrated flowmeter again, readjust the flow rate to the appropriate value with an accuracy of $\pm 5\%$, switch off the pump and seal the sampler with its protective cover to prevent contamination with arsenic during transport to the sampling position.

Collection of samples

59 Fix the sampler to the lapel of the worker, in the breathing zone and as close to the mouth and nose as practicable. Then, either place the sampling pump in a convenient pocket or attach it to the worker in a manner that causes minimum inconvenience, eg to a belt around the waist (paragraph 42). When ready to begin sampling, remove the protective cover from the sampling head and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, set this to zero.

60 Since it is possible for a filter to become clogged, monitor the performance of the sampler frequently, a minimum of once per hour. Measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 41) and record the measured value. Terminate sampling and consider the sample to be

invalid if the flow rate is not maintained to within $\pm 5\%$ of the nominal value throughout the sampling period.

Note 17: *Regular observation of the flow fault indicator is an acceptable means of ensuring that the flow rate of flow-stabilised sampling pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside $\pm 5\%$ of the nominal value.*

61 At the end of the sampling period (see paragraph 56), measure the flow rate with an accuracy of $\pm 5\%$ using the calibrated flowmeter (paragraph 41), switch off the sampling pump, and record the flow rate and the time. Also, observe the reading on the elapsed time indicator, if fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within $\pm 5\%$, since this may suggest that the sampling pump has not been operating throughout the sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

62 Carefully record the sample identity and all relevant sampling data (see Appendix 2). Calculate the mean flow rate by averaging the flow rate measurements taken throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in litres per minute by the sampling time, in minutes.

63 With each batch of ten samples, submit for analysis two unused cellulose ester membrane filters (paragraph 38) and sodium carbonate-impregnated back-up paper pads (paragraph 39) from the same lot used for sample collection. Subject these blanks to exactly the same handling procedure as the samples, but draw no air through them.

Transportation

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

64 For samplers which collect the inhalable fraction of airborne particles on the filter (eg the seven-hole sampling head and cyclone samplers), remove the cellulose ester membrane filter and back-up paper pad from each sampler using clean flat-tipped tweezers (paragraph 42), place in a labelled filter transport cassette (paragraph 42) and close with a lid.

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

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

67 Transport the filter transport cassettes, sampler filter cassettes or samplers to the laboratory in a container which has been designed to prevent damage to samples in transit and which has been labelled to assure proper handling.

ANALYSIS

Wear disposable gloves (paragraph 47) during analysis to reduce the possibility of contamination and to protect the hands from corrosive and oxidising reagents.

Cleaning of glassware

68 Before use, clean all glassware (paragraph 43) to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 34) and then rinse thoroughly with water (paragraph 18).

69 After initial cleaning (paragraph 68), clean all beakers used in the sample dissolution procedure (paragraph 74) with hot nitric acid. Fill to one-third capacity with concentrated nitric acid (paragraph 22), cover with a watch glass, heat to approximately 150°C on the hot plate (paragraph 45) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 18).

70 After initial cleaning (paragraph 68), clean all glassware other than beakers used in the sample dissolution procedure (paragraph 74) by soaking in 1 + 4 hydrochloric acid (paragraph 27) for at least 24 hours and then rinsing thoroughly with water (paragraph 18).

71 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 68 to 70, and which has been reserved for determination of arsenic by this method, can be adequately cleaned by rinsing thoroughly with 1 + 4 hydrochloric acid (paragraph 27) and then with water (paragraph 18).

Preparation of sample and blank solutions

72 Open the filter transport cassettes (paragraph 64), sampler filter cassettes (paragraph 65) or samplers (paragraph 66) and transfer each cellulose ester membrane filter and back-up paper pad into an individual, labelled 50 ml beaker using clean flat-tipped tweezers (paragraph 42).

73 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 8), wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 18). Follow the same procedure for the blanks (paragraph 63).

74 Add 5 ml of concentrated nitric acid (paragraph 22) and 1 ml of concentrated sulphuric acid (paragraph 23) to each beaker, cover with a watch glass, and heat to approximately 175°C (see note 18) on the hot plate

(paragraph 45) in a fume cupboard. When the initial vigorous reaction has subsided, slide back the watch glasses so that the beakers are only partially covered. Continue to heat each beaker until the solution volume has been reduced to approximately 1 ml, and then remove from the hot plate. Allow the solutions to cool and then carefully add 2 ml of hydrogen peroxide (paragraph 24) to each beaker. Replace the beakers on the hot plate, again covering with the watch glasses, and when the initial vigorous reaction has subsided, slide back the watch glasses so that the beakers are only partially covered. Continue to heat until dense white fumes of sulphur trioxide are evolved (raise the temperature of the hot plate to 200°C, if necessary). If the solution becomes discoloured due to charring of residual organic material, carefully add hydrogen peroxide dropwise until a clear solution is obtained, and then evaporate again until the appearance of dense white fumes. Remove the beakers from the hot plate and allow the solutions to cool.

Note 18: *The exact temperature of the hot plate is not critical. A temperature of 175°C is suggested because it is not so high as to evaporate the nitric acid and hydrogen peroxide at a rate at which there is insufficient time available for oxidation of organic matter, but it is high enough to evaporate all nitric acid and hydrogen peroxide to leave a fuming sulphuric acid solution.*

75 Carefully rinse the watch glass and the sides of each beaker with a small volume of water (paragraph 18), and transfer each solution quantitatively to a 10 ml volumetric flask. If necessary, remove any undissolved particulate material by filtering through a cellulose (paper) filter which has been pre-washed with 1 + 9 sulphuric acid (paragraph 26) and then with water (paragraph 18). Finally, dilute to the mark with water, stopper and mix thoroughly.

76 Prepare blank and sample test solutions for analysis. Transfer an aliquot, V_a ml (see note 19), of solution (paragraph 75) and $(5 - V_a)$ ml of 1 + 9 sulphuric acid (paragraph 26) to a 25 ml volumetric flask. Add 12.5 ml of concentrated hydrochloric acid (paragraph 20) and 2.5 ml of potassium iodide solution (paragraph 25), dilute to the mark with water (paragraph 18), stopper and mix thoroughly. Record the dilution factor, $25/V_a$, used for blank solutions (DF_0) and sample solutions (DF_1). Allow 1 h for reduction of pentavalent arsenic to take place before analysis (see note 20).

Note 19: *The aliquot volume used may be varied up to a maximum of 5 ml, in order to bring the arsenic concentration of the test solution within the calibration range (see paragraph 77). An aliquot volume of 0.1 ml is suggested for comparison of arsenic-in-air concentrations with the MEL of $0.1 \mu\text{g m}^{-3}$, but for the lowest detection limit (see paragraph 11) an aliquot volume of 5 ml should be used.*

Note 20: *Pentavalent arsenic gives a lower analytical response than trivalent arsenic because it is less rapidly converted to arsine. Arsenate, AsO_4^{3-} , is therefore reduced to arsenite, AsO_2^- , prior to hydride generation by reaction with potassium iodide.*

Note 21: *The test solution matrix is 1 + 1 hydrochloric acid, 1 + 49 sulphuric acid and 1% (m/v) potassium iodide.*

Preparation of calibration solutions

Note 22: *Laboratory experiments⁸ have shown that the sensitivity of the hydride generation atomic absorption measurements of arsenic are affected significantly by variation in the sulphuric acid and hydrochloric acid concentration of the solution presented for hydride generation. Therefore it is important to match sample and standard matrices as far as is reasonably practicable.*

77 Prepare at least six calibration solutions to cover the range 0 ng ml^{-1} to 50 ng ml^{-1} of arsenic when the 197.2 nm arsenic line is used, or 0 ng ml^{-1} to 25 ng ml^{-1} of arsenic when the 193.7 nm arsenic line is used (see paragraph 78). Add approximately 50 ml of 1 + 1 hydrochloric acid (paragraph 21) to separate, labelled 100 ml volumetric flasks, add 2 ml of concentrated sulphuric acid (paragraph 23) and then wash down the necks of the flasks with a little more 1 + 1 hydrochloric acid. Add 10 ml of concentrated hydrochloric acid (paragraph 20), 10 ml of potassium iodide solution (paragraph 25), swirl to mix and allow to cool. Accurately pipette the appropriate volume of working arsenic standard solution B (paragraph 31) to each flask, dilute to the mark with 1 + 1 hydrochloric acid, stopper and mix thoroughly. Prepare these calibration solutions fresh daily. Allow 1 h for reduction of pentavalent arsenic to take place before analysis (see note 20).

Note 23: *The range of the set of calibration solutions is given as a guide. The upper limit of the working range is dependent upon the performance characteristics of the hydride generation system (paragraph 51 or 52) 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 note 31.*

Selection of analytical line

78 Select an analytical line for making absorbance measurements. The 197.2 nm arsenic line shall be used unless the highest sensitivity is required.

Note 24: *The 193.7 nm arsenic line is approximately twice as sensitive as the 197.2 nm arsenic line, but use of the latter is preferable since the calibration obtained at this wavelength has a greater linear range.*

Setting up the instrument

79 If the hydride generation system (paragraph 51 or 52) has not been used for some time, clean the gas/liquid separator and the silica or quartz absorption cell (paragraph 53) before use following the procedure described in paragraph 105.

80 Prepare the hydride generation system (paragraph 51 or 52) for operation following the manufacturer's instructions. Fill the reservoir for reductant with sodium tetrahydroborate solution (paragraph 32) and the reservoir for acid blank with 1 + 1 hydrochloric acid (paragraph 21).

Note 25: *Optimum concentrations of reagents, liquid flow rates, purge gas flow rate etc, may vary somewhat according to the exact configuration of the system. This may also influence the magnitude of interference effects (see paragraph 15).*

Note 26: *Hydride 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 27: *Sodium tetrahydroborate solution gradually becomes saturated with hydrogen which may then degas when the solution is pumped. If bubbles of hydrogen reach the mixing piece, there will be a transient change in signal which will affect the analytical result, and this may not necessarily be evident for flow-injection systems. Bubble formation becomes more likely after the sodium tetrahydroborate solution has been standing for several hours, but it may be alleviated by degassing using an ultrasonic bath, or by continuously stirring the reservoir. It may also be helpful to insert a bubble trap in the tubing leading to the mixing piece. If bubble formation is still a problem, consider replicate analysis of the test solutions.*

81 Install the silica or quartz absorption cell (paragraph 53) in the optical path of the spectrometer following the manufacturer's instructions.

Note 28: *The length of tubing connecting the absorption cell to the outlet of the gas/liquid separator of the hydride generation system (paragraph 51 or 52) should be kept to a minimum.*

82 Set up the atomic absorption spectrometer (paragraph 50) to make absorbance measurements at either the 197.2 nm or 193.7 nm arsenic line (see paragraph 78), following the manufacturer's recommendations for specific instrument operating parameters. If an air-acetylene flame is used to heat the silica or quartz absorption cell (paragraph 53), use an oxidising flame.

Presentation of solutions

83 The calibration, sample test or blank test solution is presented to the hydride generation system (paragraph 51 or 52) by placing the sample uptake capillary in the solution concerned. This may be carried out manually or using an autosampler.

84 For continuous flow hydride generation systems, the configuration is such that initially the acid blank solution is pumped to the mixing piece. When ready to analyse the test solution, the configuration is changed so that this is pumped to the mixing piece.

85 For flow injection analysis hydride generation systems, the acid blank solution is continuously pumped to the mixing piece and a precise volume of the test solution is injected into the acid blank stream for analysis.

Conditioning the hydride generation system

86 Condition the hydride generation system before use in order to ensure that a stable signal is obtained before proceeding to carry out a calibration.

87 Place the reductant, acid blank, and sample uptake capillaries in a container of water (paragraph 18), and allow the pump(s) to operate for five minutes for the flow rates to stabilise. Fill a 10 ml measuring cylinder to a convenient mark with water (paragraph 18) and determine each flow rate in turn by placing the appropriate uptake capillary in the measuring cylinder of water and observing the volume of water pumped out in one minute. Verify that the flow rates are within the nominal specification recommended by the manufacturer of the hydride generation system (paragraph 51 or 52) and adjust the pressure exerted on the peristaltic pump tubing by the pump head and/or install new pump tubing as necessary. Replace the uptake capillaries for reductant and acid blank in the appropriate reservoirs.

Either

88 For continuous flow hydride generation systems, alternately pump acid blank (paragraph 21) and the high calibration solution (paragraph 77) to the mixing piece of the continuous flow hydride generation system (paragraph 51 or 52), and make repeat absorbance 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 hydride generation system used. In particular, 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. Record both of these delay times. If the continuous flow hydride generation system is interfaced to the atomic absorption spectrometer for automatic operation, set the necessary parameter(s) to the appropriate value(s).

or

89 For flow injection analysis hydride generation systems, fill the sample loop by pumping the high calibration solution (see paragraph 77) through it, and then inject into the acid blank stream. Note the delay time before an atomic absorbance peak is obtained. Optimise integration or peak height measurement parameters, and then make repeat injections until a repeatable analytical response is obtained.

Note 29: *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 (paragraph 53) following the procedure described in paragraph 105.

Determination of reagent blank

90 Place the reductant, acid blank and sample uptake capillaries in a container of water (paragraph 18) and, after allowing sufficient time for flushing out the system, adjust the spectrometer zero.

91 Replace the uptake capillaries for reductant and acid blank in the appropriate reservoirs. Pump acid blank (paragraph 21) and reductant to the mixing piece and measure the absorbance after allowing sufficient time for the water to be replaced.

Note 30: *If the reagent blank is higher than normal, 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, new sodium tetrahydroborate solution and 1 + 1 hydrochloric acid (paragraph 21) should be prepared. If it is considered that contamination of the system is the likely cause of the high blank, the gas/liquid separator and the silica or quartz absorption cell (paragraph 53) should be cleaned following the procedure described in paragraph 105. The reagent blank should then be redetermined by repeating the procedure given in paragraph 90 or 91.*

Spectrometric measurements

92 Adjust the spectrometer zero while pumping the acid blank (paragraph 21) to the mixing piece of the hydride generation system (paragraph 51 or 52).

Either

93 For continuous hydride generation systems, pump each calibration solution (see paragraph 77) in turn through the sample uptake tubing to the mixing piece, and measure its absorbance after the determined stabilisation delay time (see paragraph 88). Pump acid blank (paragraph 21) to the mixing piece in between each calibration solution and wait for the determined baseline delay time (see paragraph 88) before proceeding to measure the next calibration solution.

or

94 For flow injection analysis hydride systems, inject each calibration solution (see paragraph 77) in turn into the blank acid stream and measure the peak height or peak area of the atomic absorption signal.

95 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 of the calibration solutions versus the

concentration of arsenic, in nanograms per millilitre, in the respective solutions.

Note 31: *In general, it is best to work in the linear range of an atomic absorption calibration, where absorbance is proportional to the concentration of arsenic 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. However, hydride generation atomic absorption calibrations are more curved than flame atomic absorption calibrations, and discretion should be exercised in assessing whether recalibration over a lower concentration range is necessary.*

Determination

Either

96 For continuous flow hydride generation systems, adjust the spectrometer zero while pumping the acid blank (paragraph 21) to the mixing piece of the continuous hydride generation system (paragraph 51 or 52). Pump each sample and blank test solution (paragraph 76) in turn through the sample uptake tubing to the mixing piece, and make absorbance measurements after the determined stabilisation delay time (see paragraph 88). Pump the acid blank to the mixing piece in between each test solution and wait for the determined baseline delay time (see paragraph 88) before proceeding to measure the next test solution.

or

97 For flow injection analysis hydride generation systems, pump each sample and blank test solution (paragraph 76) sequentially through the sample valve, inject into the acid blank stream, and measure the peak height or peak area of the atomic absorption signal.

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

99 For instruments controlled by a microprocessor or personal computer, use the calibration function (see paragraph 95) to calculate the concentration of arsenic in the sample and blank test solutions, and obtain a direct read-out of the results in concentration units. For instruments without this capability, determine the concentration of arsenic in the sample and blank test solutions (paragraph 76) from the calibration graph (see paragraph 95).

100 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 paragraph 92 to paragraph 95. In either case, re-analyse the test solutions which were analysed during

the period in which the sensitivity change occurred.

101 If high concentrations of arsenic are found, repeat the analysis on a new test solution (paragraph 76) prepared using a smaller aliquot of the sample solution, to bring the concentration within the range of the calibration. Alternatively, if using the 193.7 nm arsenic line, change to the less sensitive 197.2 nm arsenic line.

102 Calculate the mean arsenic concentration of the blank test solutions.

Close down procedure

103 Switch off the flame or electricity supply to the heating coil of the silica or quartz absorption cell (paragraph 53).

104 Place the reductant, acid blank, and sample uptake capillaries in a container of water (paragraph 18), and allow the pump to operate for five minutes to flush out the system.

105 Disconnect the tube connecting the gas/liquid separator of the hydride generation system (paragraph 51 or 52) and the silica or quartz absorption cell (paragraph 53). Disconnect other inlets and outlets to the gas/liquid separator, and remove it and the silica or quartz absorption cell from their mountings. Soak the gas/liquid separator, the silica or quartz absorption cell, and the tube which connects the two pieces of apparatus in sodium hydroxide solution (paragraph 33) for at least 30 minutes. Remove, wash thoroughly with 1 + 1 hydrochloric acid (paragraph 21), and rinse thoroughly with water (paragraph 18). Reassemble the system.

106 Follow any other aspects of close-down procedure recommended by the manufacturer.

QUALITY CONTROL MEASURES

107 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 71.²⁴

108 If arsenic analysis is performed frequently, it is recommended that internal quality control is performed. In such instances, prepare quality control samples by spiking a large batch of cellulose ester membrane filters with microlitre volumes of a solution of known arsenic concentration. Analyse a random selection of at least 20 filters, each along with a different analytical batch, and calculate the mean value and standard deviation of the readings. Assuming that the distribution of these values is Gaussian, construct a Shewhart chart with warning and action limits at ± 2 SD and ± 3 SD respectively. Subsequently, analyse a quality control filter with each analytical batch, and plot the result on the Shewhart chart. Compare the internal quality control result with the target value and take appropriate action if the warning or action limits are exceeded, as recommended in MDHS 71.²⁴ Take care to ensure that the quality

control samples are stored under conditions which ensure maximum stability.

109 It is strongly recommended that all laboratories undertaking the determination of toxic elements in workplace air should participate in an external quality assessment scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP), details of which are given in MDHS 71.²⁴ At present, the WASP scheme does not cover arsenic.

CALCULATIONS

Volume of air sample

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

Concentration of arsenic in air

111 Calculate the mass concentration of arsenic in the air sample, $e(\text{As})$, in milligrams per cubic metre, at ambient conditions, using the equation:

$$e(\text{As}) = \frac{[e(\text{As})_1 \cdot V_1 \cdot \text{DF}_1 - e(\text{As})_0 \cdot V_0 \cdot \text{DF}_0]}{1000 \cdot V}$$

where

$e(\text{As})_0$ is the mean concentration, in nanograms per millilitre, of arsenic in the blank solutions (see paragraph 102);

$e(\text{As})_1$ is the concentration, in nanograms per millilitre, of arsenic in the sample solution (see paragraph 99);

V is the volume, in litres, of the air sample (see paragraph 62);

V_0 is the volume, in millilitres, of the blank solution, ie 10 ml (see paragraph 75);

V_1 is the volume, in millilitres, of the sample solution, ie 10 ml (see paragraph 75);

DF_0 is the dilution factor used in the preparation of the blank test solution (see paragraph 76);

DF_1 is the dilution factor used in the preparation of the sample test solution (see paragraph 76);

1000 is the factor to convert the result to milligrams per cubic metre.

TEST REPORT

112 Appendix 2 gives recommendations for information to be included in the test report.

APPENDIX 1

Primary standard for calibration of portable flowmeter

The primary standard should preferably be a flowmeter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flowmeter may be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A one litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with water (paragraph 18), allowing temperatures to stabilise, drawing off a known volume and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol and four parts water. The burette must be thoroughly wetted with the solution and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. (Traceability of the calibration will require checking of the clocks and use of certificated weights.)

APPENDIX 2

Recommendations for the test report

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

- (a) a complete identification of the air sample, including the date of sampling, the place of sampling, and the identity of the individual whose breathing zone was sampled;
- (b) a reference to this MDHS and a description of any deviation from the procedures described;
- (c) the type and diameter of cellulose ester membrane filter and back-up paper pad used;
- (d) the type of sampler used;
- (e) the type of sampling pump used;
- (f) the type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
- (g) the time at the start and at the end of the sampling period, and the duration of the sampling period in minutes;
- (h) the volume of air sampled, in litres;
- (i) the name of the person who collected the sample;
- (j) the time-weighted average mass concentration of arsenic found in the air sample, in milligrams per cubic metre;
- (k) the name of the analyst;
- (l) the date of the analysis.

Advice

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

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

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