

MDHS

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



6/3

Lead and inorganic compounds of lead in air

Laboratory method using flame or
electrothermal atomic absorption
spectrometry

March 1998

INTRODUCTION

Note 1: This method updates and replaces MDHS 6/2.¹ The principal change is that the revised method now recommends use of the sampling procedure for inhalable dust described in MDHS 14/2.² However, existing users may continue to use the single-hole sampler recommended for sampling lead in air in previous HSE guidance,^{1,3} since field comparisons have established that it usually gives equivalent results to inhalable samplers for this application.

Requirements of the Control of Lead at Work (CLAW) Regulations 1998

1 The CLAW Regulations⁴ require employers to assess the risk to employees of their exposure to lead at work, and to take steps to prevent or adequately control exposure. If the employer concludes from the assessment that the exposure of his or her employees to lead is likely to be significant (a term defined in the Regulations), the employer must introduce specific controls such as issuing employees with protective clothing, carrying out air monitoring and placing employees under medical surveillance to monitor the concentration of lead their bodies absorb. Guidance on the CLAW Regulations is given in the supporting Approved Code of Practice.⁵

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

2 Those who carry out and supervise the procedures described in this MDHS could be exposed to various hazardous substances, and therefore should also be aware of the requirements of the COSHH Regulations.⁶ 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.

3 Guidance is given in the Approved Codes of Practices 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.⁷

Occurrence, properties and uses

4 Lead does not occur in the elemental state in nature but mainly as its sulphide ore (galena). It also occurs as the sulphate and carbonate ores, anglesite and cerussite respectively.

5 Lead is a silver grey metal having a melting point of 327°C and a boiling point of 1740°C. It is highly lustrous when freshly cut but tarnishes upon exposure to air. It is very soft and malleable and is easily melted, cast, rolled and extruded. It is widely used in batteries and solders, as an anti-knock additive for motor fuels and also in glasses and glazes in the ceramic industry and as pigments in paints.

Health effects

6 Lead and its inorganic compounds can be hazardous to health, producing a variety of biological effects, depending on the level of lead circulating in the blood. The basis of lead toxicity is its ability to react with cellular macromolecules; it binds to sulphhydryl and other groups on proteins, inhibiting enzyme activity and competing for binding sites with other metals.

7 Lead and its compounds can be absorbed into the body by inhalation of dust, aerosol, fume and vapour, with the degree of absorption dependent on particle size and solubility. There is relatively little absorption from the

gastrointestinal tract following ingestion and absorption through the skin is likely to be negligible. Once absorbed, lead binds strongly to red blood cells, and is then deposited in bone, where it accumulates. The elimination half-life for lead in bone is likely to be in excess of 20 years.

8 There is no useful information about the health effects of single exposure to lead and its compounds. There are no reports of skin, eye or respiratory tract irritation, nor of sensitisation effects.

9 Following repeated exposure, the first symptoms associated with high levels of exposure include headaches, tiredness, stomach pains, constipation and anaemia. Continued exposure, leading to high blood lead levels, can result in central and peripheral nervous system damage, which can be irreversible. In addition, kidney damage, gastrointestinal problems, adverse effects on the developing fetus and breastfed infants and on male fertility have been associated with exposure to lead.

10 There are no relevant human data in relation to genotoxicity and carcinogenicity. However, the results from animal studies raise concerns that lead and its compounds may have the potential to produce genetic damage and cause cancer.

11 Lead compounds (with the exception of those specified elsewhere) are classified as:

R61 Repr. Cat. 1	May cause harm to the unborn child
R62 Repr. Cat. 3	Possible risk of impaired fertility
R20/22	Harmful by inhalation and if swallowed
R33	Danger of cumulative effects

Health and safety precautions

12 HSE leaflet MS(A)¹⁸ summarises the risks involved in working with lead and what may be done to control them. Health and safety precautions are fully covered in the Approved Code of Practice⁵ supporting the CLAW Regulations.⁴

Exposure limit

13 The occupational exposure limits for lead are set out in Regulation 2 of the CLAW Regulations.⁴ They will also be reproduced in Appendix 5 of HSE Guidance Note EH 40.⁹

Analytical methods

14 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.

15 This method has been validated¹⁰ to demonstrate that it complies with BS EN 482 *Workplace atmospheres - General requirements for the performance of procedures for the measurement of chemical agents*.¹¹ If an alternative method is used it is necessary to demonstrate that it also meets these performance requirements.

SCOPE

16 This MDHS describes a method for determination of the concentration of lead and inorganic compounds of lead in workplace air using either flame atomic absorption spectrometry or electrothermal atomic absorption spectrometry. It is applicable to the determination of water-soluble lead salts and the majority of lead-containing materials in industrial use or occurring in workplace air (see paragraph 21).

Note 2: *Health and Safety Guidance Booklet HS(G) 173*¹² advises employers about monitoring strategies for toxic substances. It describes how they may investigate the nature, extent and control of exposure. The objective of air monitoring is usually to determine the exposure of a worker by inhalation, and therefore the method described in this measuring procedure is written primarily for personal sampling in the breathing zone. However, it may also be used for fixed place or static sampling.

17 The flame atomic absorption spectrometry method is suitable for measuring lead-in-air concentrations between 0.1 and 2 times the occupational exposure limit for lead (see paragraph 13) using sampling times between 30 minutes and 8 hours and a volumetric flow rate of 2 l min⁻¹ (see paragraph 34).

18 The electrothermal atomic absorption spectrometry method is suitable for measuring lower lead-in-air concentrations, or when using shorter sampling times or lower volumetric flow rates (see paragraph 35).

METHOD PERFORMANCE

Detection limits

19 The qualitative and quantitative detection limits for lead, defined as three times and ten times the standard deviation of a blank determination, have been determined¹⁰ to be 0.025 µg ml⁻¹ and 0.084 µg ml⁻¹ for flame atomic absorption spectrometry; and 0.30 ng ml⁻¹ and 1.0 ng ml⁻¹ for electrothermal atomic absorption spectrometry. For an air sample volume of 30 litres and a sample solution volume of 10 ml this corresponds to lead-in-air concentrations of 8.4 µg m⁻³ and 28 µg m⁻³ for flame atomic absorption spectrometry; and 0.10 µg m⁻³ and 0.34 µg m⁻³ for electrothermal atomic absorption spectrometry.

Bias

Sampler bias

20 The bias of inhalable samplers has been shown¹³ to vary considerably. However, a bias of less than ± 5% is

typical for the samplers recommended in MDHS 14/2.² This value was therefore used when estimating the bias of the measuring procedure as a whole using Equation 1.

Analytical bias

21 The sample dissolution procedure has been tested¹⁰ on a range of lead-containing materials in industrial use or occurring in workplace air. The mean analytical recovery of lead was 99.0% ± 1.8% for lead metal, lead monoxide, lead dioxide, lead tetroxide, lead chromate, lead sulphate, lead stearate, European Coal and Steel Community certified reference material 876-1 furnace dust and two glass enamels containing lead pigments.

22 The mean analytical recovery for 130 filters spiked with between 0.9 µg and 288 µg of lead has been determined¹⁰ to be 103.9 ± 4.9% using flame atomic absorption spectrometry; and the mean analytical recovery for 80 filters spiked with between 0.10 µg and 4.5 µg of lead was determined¹⁰ to be 99.5 ± 2.5% using electrothermal atomic absorption spectrometry.

23 Laboratory experiments¹⁰ therefore indicate that the analytical method does not exhibit significant bias. An analytical bias of zero was therefore substituted in Equation 1 when estimating the bias of the measuring procedure as a whole.

Combination of sampling and analytical bias

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

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

Precision

Imprecision of the aerosol sampling process

25 The imprecision of the aerosol sampling process usually depends strongly on the size distribution of the airborne particles sampled, and it can depend on other factors, such as windspeed. Draft European Standard EN (00137009)¹⁴ suggests calculating approximate values of the imprecision of the sampling process relevant to the workplace atmosphere to be sampled, using information given in the sampler test report.

26 However, this approach is not practicable for assessing the performance of a measuring procedure intended for general application. The results of a study to evaluate the performance of inhalable samplers¹³ suggest that the relative standard deviation of the aerosol sampling process is normally less than 5% for inhalable samplers that meet the requirements of draft European Standard EN (00137009).¹⁴ The relative standard deviation of the aerosol sampling process, $RSD_{sampler}$, was therefore taken to be 5% when estimating the imprecision of the measuring procedure as a whole using Equation 2.

Imprecision arising from flow rate variability

27 In the case of aerosol samplers where there is no interaction between particle size selection characteristics and volumetric flow rate, at least for small changes in flow rate, the imprecision arising from flow rate variability can be estimated simply. BS EN 1232 *Workplace atmospheres - Pumps for personal sampling of chemical agents - Requirements and test methods*¹⁵ prescribes a maximum allowable error in the volumetric flow rate of ±5%. Assuming that this is met on 99% of all occasions, the flow-related relative standard deviation, RSD_{flow} , is equal to 0.05/3. This value was therefore used when estimating the imprecision of the measuring procedure as a whole using Equation 2.

Imprecision arising from analytical variability

28 The relative standard deviation of the analytical method, $RSD_{analysis}$, has been determined¹⁰ to be less than 10% for samples in the range 0.90 µg to 2.25 µg of lead and less than 3% for samples in the range 3.6 µg to 288 µg of lead, using flame atomic absorption spectrometry; and less than 5% for samples in the range 0.10 µg to 4.5 µg of lead, using electrothermal atomic absorption spectrometry. The determined relative standard deviations were substituted in Equation 2 to estimate the imprecision of the measuring procedure as a whole for each mass of lead.

Combination of sampling and analytical precision

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

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

Overall uncertainty

30 The overall uncertainty for a measuring procedure is defined in BS EN 482¹¹ 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:

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

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.

31 Equation 3 can be rewritten as:

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

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

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

32 The overall uncertainty can then be estimated by substituting in Equation 4 the values for bias and relative standard deviation calculated using Equations 1 and 2. In this manner, the overall uncertainty of the measuring procedure described in this method has been estimated¹⁰ to be less than 28% for samples in the range 0.9 µg to 288 µg using flame atomic absorption spectrometry; and less than 20% for samples in the range 0.1 µg to 4.5 µg using electrothermal atomic absorption spectrometry.

33 BS EN 482¹¹ prescribes that the overall uncertainty of procedures for the measurement of chemical agents in workplace air shall be < 50% for measurements in the range 0.1 to 0.5 times the limit value, and < 30% for measurements in the range 0.5 to 2.0 times the limit value.

34 The flame atomic absorption spectrometry method therefore complies with the overall uncertainty requirements of BS EN 482¹¹ when measuring lead-in-air concentrations between 0.1 and 2 times the occupational exposure limit for lead (see paragraph 13) using sampling times between 30 minutes and 8 hours and a volumetric flow rate of 2 l min⁻¹.

35 The electrothermal atomic absorption spectrometry method complies with the overall uncertainty requirements of BS EN 482¹¹ for samples containing at least ten times less lead than when flame atomic absorption spectrometry is used.

Interferences

36 No significant chemical interferences occur when aqueous solutions are aspirated into a fuel-lean air-acetylene flame. However, there is the possibility of non-atomic absorption from the flame and other species when the 217.0 nm line is used. The use of background correction is therefore recommended.

37 No interferences have been reported for the determination of lead by electrothermal atomic absorption spectrometry.

38 Various anions can give a precipitate with lead. Their effect can usually be reduced by making the solutions 0.1 M with respect to ethylene diamine tetra-acetic acid.

PRINCIPLE

39 A measured volume of air is drawn through a filter mounted in an inhalable sampler.

40 The filter and collected sample are treated with 5 ml of 1 + 1 nitric acid and 100 µl hydrogen peroxide solution and heated on a hot plate until about 1 ml of concentrated nitric acid solution remains. This is diluted to 10 ml with water and the resultant solution is analysed for lead by aspirating into the oxidising air-acetylene flame of an atomic absorption spectrometer. Absorbance measurements are made at 217.0 nm with background correction.

41 For more accurate measurements when the concentration of lead in the solution is low, the analysis may be repeated using electrothermal atomic absorption spectrometry. Aliquots of the sample solution and a matrix modifier solution are injected onto a solid, pyrolytic graphite platform mounted in a pyrolytically-coated graphite tube and after drying and ashing stages the sample is atomised electrothermally. Absorbance measurements are made at 283.3 nm with background correction.

REAGENTS

42 During the analysis, use only reagents of recognised analytical grade. Use only distilled or de-ionised water, or water of equal purity (paragraph 43). Do not pipette by mouth.

Water

43 Water complying with the requirements of BS 3978¹⁶ 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)

44 The lead concentration of the acid shall be less than 0.005 µg ml⁻¹.

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

Nitric acid, diluted 1 + 1

45 Carefully add 500 ml of concentrated nitric acid (paragraph 44) to 450 ml of water (paragraph 43) in a 2 litre beaker. Swirl to mix, allow to cool and quantitatively transfer to a 1 litre volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Nitric acid, diluted 1 + 9

46 Add approximately 800 ml of water (paragraph 43) to a 1 litre volumetric flask. Carefully add 100 ml of concentrated nitric acid (paragraph 44) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

Stock standard lead solution, 1000 µg ml⁻¹ of lead

47 Use a commercially available standard solution at a concentration of 1000 µg ml⁻¹ of lead. Observe the

manufacturer's expiry date or recommended shelf life. Alternatively prepare a stock lead standard solution by the following procedure:

48 Accurately weigh 1.598 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) into a 100 ml beaker, add 20 ml of 1 + 1 nitric acid (paragraph 45), cover with a watch glass and heat on a hot plate (paragraph 62) in a fume cupboard until the solid is completely dissolved. Remove the beaker from the hot plate, allow to cool, quantitatively transfer the solution into a 1 litre volumetric flask, dilute to the mark with water (paragraph 43), stopper and mix thoroughly.

Note 3: Lead standard solution prepared according to the instructions in paragraph 48 may be stored in a polypropylene bottle (paragraph 61) for a period of one year without deterioration.

Working standard lead solution, 1.00 $\mu\text{g ml}^{-1}$ of lead

49 Accurately pipette 100 μl of stock lead standard solution (paragraphs 47 or 48) into a 100 ml volumetric flask. Add 1 ml of concentrated nitric acid (paragraph 44), dilute to the mark with water (paragraph 43), stopper and mix thoroughly. Prepare this solution fresh daily.

Hydrogen peroxide (H_2O_2), ρ about 1.10 g ml^{-1} , approximately 30% (m/v) solution

50 The lead concentration of the solution shall be less than 0.01 $\mu\text{g ml}^{-1}$.

WARNING - Hydrogen peroxide solution is a powerful oxidant. 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 hydrogen peroxide solution.

Matrix modifier solution, 0.1% (m/v) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.0% (m/v) $\text{NH}_4\text{H}_2\text{PO}_4$

51 Weigh 0.100 g of magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2.00 g of ammonium di-hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) into a 250 ml beaker. Add 50 ml water (paragraph 43) and swirl to dissolve. Add 10 ml of concentrated nitric acid (paragraph 44), swirl to mix, and quantitatively transfer the solution into a 100 ml volumetric flask. Dilute to the mark with water, stopper and mix thoroughly.

Laboratory detergent solution

52 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water (paragraph 43) according to the manufacturer's instructions.

SAMPLING EQUIPMENT

Inhalable samplers

53 Samplers, with protective covers, designed to collect the inhalable fraction of airborne particles, as defined in BS EN 481,¹⁷ and complying with the

provisions of draft European Standard EN (00137009).¹⁴ Inhalable samplers suitable for personal sampling are described in MDHS 14/2.²

Note 4: Existing users may continue to use the single-hole sampler recommended for sampling lead in air in previous HSE guidance, since field comparisons have established that it usually gives equivalent results to inhalable samplers for this application.

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

Note 6: Some inhalable samplers are designed to collect the inhalable fraction of airborne particles on the filter, and any particulate matter deposited on the internal surfaces of the sampler is not of interest. Other inhalable samplers are designed such that airborne particles which pass through the entry orifice(s) match the inhalable convention, in which case particulate matter deposited on the internal surfaces of the sampler does form part of the sample. (Samplers of this second type generally incorporate an internal filter cassette or cartridge which can be removed from the sampler to enable this material to be easily recovered.) The operating instructions supplied by the manufacturer should be consulted to find out whether particulate matter deposited on the internal surfaces of the sampler forms part of the sample.

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

Filters

54 Filters, of a diameter suitable for use in the samplers (paragraph 53), and with a retentivity of not less than 99.5% for particles with a 0.3 μm diffusion diameter (see subclause 2.2 of BS EN 481¹⁷). The use of filters that are soluble using the sample preparation procedure described is recommended, and mixed cellulose ester membrane filters of 0.8 μm mean pore diameter are considered to be most suitable.

The lead content shall be less than 0.001 μg per filter.

Note 8: Glass fibre or other filters which do not dissolve using the sample preparation procedure described may be used, but extra care needs to be taken to ensure quantitative transfer of sample solutions to volumetric flasks (paragraph 90).

Sampling pumps

55 Sampling pumps, complying with the provisions of BS EN 1232,¹⁵ and compatible with the samplers used (paragraph 53).

Note 9: Existing users may continue to use sampling pumps that do not fully comply with the provisions of

BS EN 1232,¹⁵ provided that they take steps to ensure that the required volumetric flow rate (see paragraph 73) is maintained to within $\pm 5\%$ of the nominal value throughout the sampling period.

56 BS EN 1232¹⁵ 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 10: An integral timer is a highly desirable additional feature.

57 BS EN 1232¹⁵ 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 $\pm 5\%$ 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 $\pm 5\%$ 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 $\pm 5\%$ from the initial value during the operating time.

Flowmeter

58 Flowmeter, portable, capable of measuring the required volumetric flow rate (see paragraph 67) to within $\pm 1\%$, and calibrated against a primary standard, is a flowmeter whose accuracy is traceable to national standards.

Note 11: 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 17), provided they have adequate sensitivity.

Ancillary equipment

59 Flexible tubing, of a diameter suitable for ensuring a leakproof fit, to connect the sampler to the

pump; a belt to which the pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes, or similar, if required (see paragraph 79), in which to transport samples to the laboratory.

LABORATORY APPARATUS

Glassware, made of borosilicate glass

60 A selection of laboratory glassware: including beakers; watch glasses; measuring cylinders; and volumetric flasks, class A, complying with the requirements of BS 1792.¹⁸

Note 12: It is recommended that a set of glassware is reserved for the analysis of lead by this method.

Polypropylene bottle

61 A polypropylene bottle, with leakproof screw cap, for storage of stock standard solution (paragraph 48), cleaned before use by soaking in 1 + 9 nitric acid (paragraph 46) for at least 24 hours and then rinsing thoroughly with water (paragraph 43). A bottle made of an alternative plastic may be used provided that it is suitable for the intended use.

Hotplate

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

Disposable gloves

63 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

64 A set of adjustable micropipettes, complying with the requirements of BS 7653-1 to BS 7653-4,¹⁹⁻²² for the preparation of working standard lead solution (see paragraph 49) and calibration solutions (see paragraphs 91 and 100) and dilution of samples (see paragraphs 97 and 107). A suitable set might include micropipettes covering the ranges 10 μl to 100 μl , 100 μl to 1000 μl and 1000 μl to 5000 μl . Dispensers for dispensing acid.

Atomic absorption spectrometer

65 An atomic absorption spectrometer, fitted with an air-acetylene burner, supplied with compressed air and acetylene, and equipped with either a lead hollow cathode lamp or electrodeless discharge lamp. If electrothermal atomic absorption spectrometry is to be carried out the atomic absorption spectrometer shall be capable of carrying out simultaneous background correction at 283.3 nm, either by using a continuum source such as a deuterium lamp to measure non-specific attenuation, or by using Zeeman or Smith-Hieftje

background correction systems.

Electrothermal atomiser

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

Note 13: *Some manufacturers of atomic absorption spectrometers use an alternative design of electrothermal atomiser to achieve a constant temperature environment during atomisation, and some use aerosol deposition as a means of sample introduction. The use of such accessories is acceptable, but the method performance may be different from that given in paragraphs 19, 28 and 32.*

Disposable autosampler cups

67 Disposable polystyrene autosampler cups for use in the autosampler used with the electrothermal atomiser. Soak in 1 + 9 nitric acid (paragraph 46) before use.

Note 14: *Disposable polystyrene autosampler cups are also useful for containing solutions to be pipetted in microlitre quantities.*

SAMPLING

Preliminary considerations

Use of samplers

68 Use the samplers (paragraph 53) at their design flow rate, and in accordance with the instructions provided by the manufacturer, so that they collect the intended fraction of airborne particles.

Sampling period

69 Select an appropriate sampling period, taking into account the purpose of the measurement. If sampling is carried out in a dusty environment, the sampling time shall not be so long as to risk overloading the filter. (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 40.⁹) Advice on monitoring strategies for toxic substances is given in Health and Safety Guidance Booklet HS(G) 173.¹²

Handling of filters

70 To minimise the risk of damage or contamination, only handle filters using flat-tipped tweezers (paragraph 59), in a clean area. Wear disposable gloves (paragraph 63) to prevent the possibility of contamination.

Preparation for sampling

Cleaning of samplers

71 Clean the samplers (paragraph 53) before use. Disassemble the samplers, soak in laboratory detergent

solution, rinse thoroughly with water (paragraph 43), wipe with absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine.

Loading the samplers with filters

72 Load clean samplers (see paragraph 71) with filters (paragraph 54), label each sampler so that it can be uniquely identified, and seal with its protective cover to prevent contamination.

Setting the volumetric flow rate

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

73 Connect each loaded sampler (paragraph 72) to a sampling pump (paragraph 53) using flexible tubing (paragraph 59), ensuring that no leaks can occur. Remove the protective cover from each sampler, switch on the sampling pump, attach the calibrated flowmeter (paragraph 58) to the sampler so that it measures the flow through the sampler inlet orifice(s), and set the required volumetric flow rate (see paragraph 68). Switch off the sampling pump and seal the sampler with its protective cover to prevent contamination during transport to the sampling position.

Note 15: *If necessary, allow the sampling pump operating conditions to stabilise before setting the volumetric flow rate (refer to the manufacturer's instructions).*

Blanks

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

Sampling position

75 Position the sampler in the worker's breathing zone, as close to the mouth and nose as is reasonably practicable, eg fasten it to the worker's lapel. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, eg to a belt (paragraph 59) around the waist, or place it in a convenient pocket.

Collection of samples

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

Note 16: *If the temperature or pressure at the sampling position is significantly different from that where the volumetric flow rate was set (see paragraph 73), the*

volumetric flow rate could change and it might need to be re-adjusted before sampling.

Note 17: If the sampling pump used does not comply with BS EN 1232¹⁵ (see note 9), monitor its performance frequently, a minimum of once per hour. Measure the flow rate using the calibrated flowmeter (paragraph 58) 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.

77 At the end of the sampling period (see paragraph 69), 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 58), and record the measured value. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

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

Transportation

79 For samplers which collect airborne particles on the filter (see note 6), remove the filter from each sampler, place in a labelled filter transport cassette (paragraph 61) and close with a lid. Take particular care to prevent the collected sample from becoming dislodged from heavily loaded filters. Alternatively, transport samples to the laboratory in the samplers in which they were collected.

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

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

82 Transport the samples (paragraphs 79-81) 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.

83 When appropriate, ensure that the documentation which accompanies the samples is suitable for a 'chain of custody' to be established.

ANALYSIS

Wear disposable gloves (paragraph 63) during analysis to protect the hands from toxic, corrosive and oxidising reagents.

Cleaning of glassware

84 Before use, clean all glassware (paragraph 60) to

remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution (paragraph 52) and then rinse thoroughly with water (paragraph 43).

85 After initial cleaning (paragraph 84), clean all beakers used in the sample dissolution procedure (see paragraph 88) with hot nitric acid. Fill to one-third capacity with concentrated nitric acid (paragraph 44), cover with a watch glass, heat to approximately 150°C on the hot plate (paragraph 62) in a fume cupboard for 1 hour, allow to cool, and then rinse thoroughly with water (paragraph 43).

86 After initial cleaning (paragraph 84), clean all glassware other than beakers used in the sample dissolution procedure (see paragraph 88) by soaking in 1 + 9 nitric acid (paragraph 46) for at least 24 hours and then rinsing thoroughly with water (paragraph 43).

87 Glassware which has been previously subjected to the cleaning procedure described in paragraphs 84-86, and which has been reserved for determination of lead by this method, can be adequately cleaned by rinsing thoroughly with 1 + 9 nitric acid (paragraph 46) and then with water (paragraph 43).

Preparation of sample and blank solutions

88 Open the filter transport cassettes (see paragraph 79), sampler filter cassettes (see paragraph 80) or samplers (see paragraph 81) and transfer each filter into an individual, labelled 50 ml beaker (paragraph 60) using clean flat-tipped tweezers (paragraph 59). Follow the same procedure for the blanks (paragraph 74).

89 If the sampler used was of a type in which airborne particles deposited on the internal surfaces of the filter cassette or sampler forms part of the sample (see note 6), carefully wash any particulate material adhering to the internal surfaces into the beaker using a minimum volume of water (paragraph 43).

90 Add 5 ml of 1 + 1 nitric acid (paragraph 45) plus 100 μ l hydrogen peroxide solution (paragraph 50) to each beaker, partially cover with a watch glass, and heat to approximately 150°C on a hot plate (paragraph 62) in a fume cupboard until the filter has dissolved and the solution has been reduced to approximately 1 ml. Remove each beaker from the hotplate and allow to cool.

Note 18: If there is a requirement to determine exposure to other metals, in addition to lead, and the relevant methods in the MDHS series also prescribe dissolution using 1 + 1 nitric acid, the procedure described in paragraph 90 should be used for preparation of sample solutions.

Note 19: Hydrogen peroxide is used to assist dissolution of lead dioxide. It need not be added if lead dioxide is not present in the test atmosphere.

91 Carefully rinse the watch glass and the sides of each beaker with water (paragraph 43), and quantitatively transfer each solution to a labelled 10 ml volumetric flask (paragraph 60). If necessary, remove any undissolved particulate material by filtering through a cellulose (paper)

filter which has been pre-washed with 1 + 9 nitric acid (paragraph 46) and then with water (paragraph 43). Finally, dilute to the mark with water, stopper and mix thoroughly.

Analysis by flame atomic absorption spectrometry

Note 20: *Laboratory experiments¹⁰ have shown that flame atomic absorption measurements of lead are not affected significantly by variation in the nitric acid concentration within the range 5% to 25% (v/v). However, it is good laboratory practice to match sample and standard matrices as far as is reasonably practicable.*

Preparation of calibration solutions

92 Prepare at least six calibration solutions to cover the range 0 $\mu\text{g ml}^{-1}$ to 5 $\mu\text{g ml}^{-1}$ of lead. Add 20 ml of 1 + 1 nitric acid (paragraph 45) to separate, labelled 100 ml volumetric flasks (paragraph 60). Accurately pipette the appropriate volume of stock standard lead solution (paragraphs 47 or 48) into each flask, dilute to the mark with water (paragraph 43), stopper and mix thoroughly. Prepare these solutions fresh daily.

Atomic absorption measurements

93 Set up the atomic absorption spectrometer (paragraph 65) to determine lead at a wavelength of 217.0 nm using an oxidising air-acetylene flame. Follow the manufacturer's recommendations for specific operating parameters, and use background correction. The sensitivity, defined as the concentration required to produce a signal of 1% absorbance or 0.0044 absorbance units, is about 0.09 $\mu\text{g ml}^{-1}$ of lead.

94 Adjust the spectrometer zero while aspirating the blank calibration solution (paragraph 92). Repeat this procedure regularly throughout the analysis and readjust the zero if the baseline drifts.

95 Aspirate the calibration solutions (paragraph 92) into the flame in order of increasing concentration and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, generate a calibration for lead by carrying out a linear regression. For instruments without this capability, prepare a calibration graph by plotting the absorbance of the calibration solutions versus the lead concentration.

96 Aspirate the sample and blank solutions (paragraph 91) into the flame and make absorption measurements for each solution. For instruments controlled by a microprocessor or personal computer, use the calibration function (see paragraph 95) to determine the concentration of lead in the sample and blank solutions and obtain a direct readout of the results in $\mu\text{g ml}^{-1}$ of lead. For instruments without this capability, determine the concentration of lead in $\mu\text{g ml}^{-1}$ from the calibration graph (see paragraph 95).

97 Aspirate a mid-range standard into the flame after each five to ten sample solutions and make an absorption measurement. If this indicates that the sensitivity has changed by more than $\pm 5\%$, take one of the following appropriate corrective measures: either use the available

software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis, recalibrate the spectrometer as described in paragraph 95; and in either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

98 If high concentrations of lead are found, dilute the sample solutions to bring the concentration within the calibration range, and repeat the analysis. Make all dilutions so that the final nitric acid concentration is 1 + 9. Record the dilution factor.

99 Calculate the mean lead concentration of the blank solution in $\mu\text{g ml}^{-1}$.

100 If the concentration of lead in the sample solutions is less than 0.5 $\mu\text{g ml}^{-1}$ consider repeating the analysis using electrothermal atomic absorption spectrometry (see paragraphs 101-109) since this technique gives more precise measurements at low concentrations.

Analysis by electrothermal atomic absorption spectrometry

Note 21: *Lead is present at a low level in the environment and it is essential that strict standards of cleanliness are observed to avoid contamination of labware. This is particularly important when carrying out electrothermal atomic absorption spectrometry since the technique exhibits a very low detection limit. Ensure that all glassware is cleaned thoroughly before use in accordance with paragraphs 84-87, and that autosampler cups (paragraph 67) are stored in 1 + 9 nitric acid (paragraph 46) until required.*

Preparation of working calibration solutions

101 Prepare a working calibration solution at a concentration of 50 ng ml^{-1} of lead. Accurately pipette 50 μl of working standard lead solution (paragraph 49) into a 10 ml volumetric flask. Add about 5 ml of water (paragraph 43) and 2 ml of 1 + 1 nitric acid (paragraph 45) and swirl to mix. Dilute to the mark with water (paragraph 43), stopper and mix thoroughly. Prepare this solution fresh daily.

102 Prepare a working calibration blank solution following the procedure in paragraph 101, but omitting the 50 μl of working standard lead solution.

Atomic absorption measurements

103 Set up the atomic absorption spectrometer (paragraph 65) and electrothermal atomiser (paragraph 66) to determine lead at a wavelength of 283.3 nm using background correction. Follow the manufacturer's recommendations for specific operating parameters.

Note 22: *The operating parameters for electrothermal atomic absorption spectrometry vary considerably between different instruments, much more so than for flame atomic absorption spectrometry. A Perkin-Elmer 5100PC atomic absorption spectrometer with Zeeman HGA-600 graphite furnace module and AS-60 autosampler was used in the validation of this method,¹⁰ and the*

operating parameters used are given in Appendix B. The characteristic mass for lead, defined as the number of picograms required to give 0.0044 absorbance-seconds, was determined to be 13 pg for this analytical system. This is equivalent to a sample solution concentration of 0.65 ng ml⁻¹ of lead for a 20 µl sample solution injection volume.

104 Program the autosampler to prepare matrix-modified calibration, sample solutions and blank solutions in situ on a pyrolytic graphite platform mounted in the pyrolytically-coated graphite tube of the electrothermal atomiser. Prepare at least six matrix-modified calibration solutions to cover the range 0 ng ml⁻¹ to 50 ng ml⁻¹ using the working calibration solution (paragraph 101), the working calibration blank solution (paragraph 102) and the matrix modifier solution (paragraph 51). Prepare matrix-modified sample and blank solutions using the sample and blank solutions (paragraph 91) and the matrix modifier solution (paragraph 51); see Table B2 for typical autosampler injection volumes.

Note 23: The procedure described above may be varied to accommodate the use of electrothermal atomisers of alternative design (see note 13).

Note 24: Matrix-modified calibration and test solutions may be prepared in volumetric flasks as an alternative to preparation in situ using the autosampler.

Note 25: Sample test solutions should be diluted (see paragraph 108) before analysis by electrothermal atomic absorption spectrometry if results obtained by flame atomic absorption spectrometry (see paragraph 100) indicate that the lead concentration is above the upper limit of the calibration range for electrothermal atomic absorption spectrometry (see paragraph 104).

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

106 Place the working calibration solution (paragraph 101), the working calibration blank solution (paragraph 102), the matrix modifier solution (paragraph 51), and the sample and blank solutions (paragraph 91) in separate acid-washed autosampler cups (paragraph 67) and position as appropriate in the autosampler carousel. Analyse the matrix-modified calibration, sample and blank solutions, using the microprocessor or personal computer software to generate a calibration and obtain a direct read-out of sample and blank results in ng ml⁻¹ of lead.

107 If significant baseline drift is observed during the course of the analysis, or if the sensitivity changes by more than ±5%, take one of the following appropriate corrective measures: either use the available software facilities of the microprocessor or personal computer to correct for the sensitivity change (reslope facility); or suspend analysis, recalibrate the spectrometer as

described in paragraph 105. In either case reanalyse the solutions which were analysed during the period in which the sensitivity change occurred.

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

109 Calculate the mean lead concentration of the blank solutions in ng ml⁻¹.

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 lead in air

111 Calculate the concentration of lead in air, ρ(Pb), in milligrams per cubic metre (mg m⁻³), using the equation:

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

where

ρ(Pb)₀ is the mean concentration, in µg ml⁻¹, of lead in the blank solutions (see paragraphs 99 and 109);

ρ(Pb)₁ is the concentration, in µg ml⁻¹, of lead in the sample solution (see paragraphs 96 and 106);

V is the volume, in litres, of the air sample (see paragraph 110);

V₀ is the volume, in ml, of the blank solutions, ie 10 ml (see paragraph 91);

V₁ is the volume, in ml, of the sample solution, ie 10 ml (see paragraph 91);

DF₀ is the dilution factor for the blank solutions, ie 1; and

DF₁ is the dilution factor for the sample solutions (see paragraphs 98 and 108).

Note 26: For low concentrations of lead in air determined by electrothermal atomic absorption spectrometry, calculate results in micrograms per cubic metre by using solution concentrations in ng ml⁻¹ in the above equation.

TEST REPORT

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

QUALITY CONTROL MEASURES

113 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 71.²³

114 If lead analysis is performed frequently it is recommended that internal quality control is performed. In such instances, prepare quality control samples by spiking a large number of filters with microlitre volumes of a solution of known lead concentration. Randomly select a suitable number (eg twenty) of quality control samples, analyse them on separate occasions, and calculate the mean and standard deviation of the measured lead concentrations. Assuming that the distribution of results is Gaussian, construct a Shewhart chart with warning and action limits at ± 2 SD and ± 3 SD respectively. Subsequently, analyse a quality control sample 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 71.²³ Take care to ensure that the quality control samples are stored under conditions which ensure maximum stability.

115 It is strongly recommended that all laboratories undertaking the determination of lead 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 71.²³

ADVICE

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

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

APPENDIX A Recommendations for the test report

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

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

APPENDIX B Typical operating parameters for determination of lead by electrothermal atomic absorption spectrometry

Mode: Peak area
 Integration time: 5 seconds
 Background correction: Zeeman
 Injection volumes: 20 μl of calibration, sample or blank solution and 10 μl of matrix modifier solution

Table B1 - Typical temperature profile for determination of lead using electrothermal atomic absorption spectrometry

Step	Ramp time (sec)	Hold time (sec)	Furnace temp ($^{\circ}\text{C}$)	Argon flow (ml min^{-1})	Read
1 Dry	1	50	120	300	
2 Ash	1	30	850	300	
3 Cool down	1	15	20	300	
4 Atomise	0	5	1800	0	*
5 Clean	1	5	2600	300	

Table B2 - Typical autosampler injection volumes for the in-situ preparation of matrix-modified calibration, sample and blank solutions

Matrix-modified solution	Volume of working calibration solution (μl)	Volume of working calibration blank solution (μl)	Volume of matrix modifier solution (μl)	Volume of sample or blank solution (μl)
0 ng ml^{-1} calibration solution	-	20	10	-
10 ng ml^{-1} calibration solution	4	16	10	-
20 ng ml^{-1} calibration solution	8	12	10	-
30 ng ml^{-1} calibration solution	12	8	10	-
40 ng ml^{-1} calibration solution	16	4	10	-
50 ng ml^{-1} calibration solution	20	-	10	-
Sample or blank solution	-	-	10	20
Sample solution dilution	-	(20 - x)	10	x

The lead concentrations in the matrix-modified calibration solutions are notional, in that they relate to the 20 μl volume of sample or blank solution (ie the 10 μl volume of matrix-modifier solution is ignored).

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