

MDHS

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



47/2

Determination of rubber process dust and rubber fume (measured as cyclohexane-soluble material) in air

Laboratory method using filters, gravimetric determination and Soxhlet extraction

June 1999

INTRODUCTION

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations¹ are designed to ensure that the exposure of people at work to substances which 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 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 MDHS.

Properties and uses

2 Rubber is widely used in the manufacture of a variety of products. The exact composition of rubber varies and is dependent on the intended usage.

Definitions

The following definitions are taken from EH40/98.²

3 Rubber process dust is dust arising in the stages of rubber manufacture where ingredients are handled, weighed, added to or mixed with uncured material or synthetic elastomers. It does not include dusts arising from the abrasion of cured rubber.

4 Where the airborne material contains a mixture of substances, one or more of which is assigned a maximum exposure limit (MEL) or occupational exposure standard (OES), those limit(s) will apply to the individual substances and at the same time the rubber process dust limit will apply to the dust mix as a whole. Where the airborne material is effectively a single substance with an MEL or an OES, that limit alone will apply.

5 Rubber fume is fume evolved in the mixing, milling and blending of natural rubber and rubber or synthetic elastomers, or of natural rubber and synthetic polymers combined with chemicals, and in the processes which convert the resultant blends into finished products or parts thereof, and including any inspection procedures where fume continues to be evolved.

Health effects

6 Epidemiological studies have shown^{3,4,5} that chronic exposure to dust and fume in rubber factories can cause higher than normal incidence of some types of cancers, across wide sectors of the industry.

Exposure

7 A number of airborne pollutants are evolved during manufacturing processes involving the working of rubber, including dusts and fumes. These materials often fall within the categories of 'rubber process dust' and 'rubber fume', as defined by HSE.

8 A number of workers in the rubber industry, including those involved in the making of rubber blends from raw ingredients and the manufacture and inspection of finished products, have the potential for exposure to either rubber process dust or rubber fume. Some workers may be exposed to both materials.

Analytical methods

9 This method is an empirical method. Other empirical methods with the same precision have been shown to give different results. Deviations from these procedures may lead to the results becoming invalid for the purposes of assessing exposure relative to the maximum exposure limits and for comparison with other results.

Changes from previous MDHS 47

10 This MDHS was last revised in 1987. Essentially there are no changes to the methodology described in this

revision from the previous version. However, this revision does include additional information which post-dates the last version. This is mainly contained in paragraph 1 (COSHH regulations) and paragraphs 15 to 18 (determination of blank value and limit of detection). Also, there is little sampling information contained in this MDHS. For information on sampling, you should refer to the latest issue of MDHS 14.⁶

SCOPE

11 The procedures laid down in this MDHS may be used to determine concentrations of rubber process dust and rubber fume in air. Where necessary, both analytes may be determined from a single sample. Persons using this method should be familiar with the current HSE definitions of rubber process dust and rubber fume and should apply these definitions when deciding whether a sample may contain either, or both, analytes. The fraction of dust collected by this sampling technique falls into the category described as total inhalable, as defined in MDHS 14.

12 If measurement of rubber process dust only is required from a sample, there is no need to follow the procedures laid down in this MDHS. The methods detailed in MDHS 14 are suitable for rubber process dust only.

13 This method measures rubber fume as cyclohexane-soluble material. This is the fraction of the fume that is thought to contain the constituents most likely to be harmful, ie that fraction of fume that is trapped on a filter, but is soluble in cyclohexane. It is essentially a method originally developed by the British Rubber Manufacturers Association.

14 The scope of this MDHS does not include guidance on sampling strategies.

15 HSE guidance note HSG173⁷ 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 also, however, be used for background or fixed location sampling.

Detection limits

16 The qualitative detection limits for rubber process dust and rubber fume are determined by weighing a number of blanks. The detection limit is defined as being three times the standard deviation of the blank values.⁸

17 A blank is defined as a filter which has been subjected to the same treatment as a sample filter, but has had no air drawn through it. For this method the blank filters should be pre-extracted in cyclohexane, pre-weighed and fitted into and removed from a sampling head. These filters are then re-weighed with the sample filters, and the weight changes are used to calculate the

blank value with respect to rubber process dust. Rubber fume blanks must then be folded, re-weighed then soxhlet extracted and re-weighed afterwards.

18 The Royal Society of Chemistry⁸ recommends that a minimum of ten blanks are used with each set of samples in order to have reasonable confidence in the detection limit. This may not always be practical, especially if the number of actual samples in a sample set is small. However, it is recommended that at least six blanks are used in order to determine the detection limit of a gravimetric method.⁶ If fewer blanks than this are used then there will be significant uncertainty attached to the values determined for the mean and standard deviation of the blanks, and hence uncertainty in the results of the analysis.

19 The qualitative detection limits for rubber process dust and rubber fume respectively are typically 90 µg and 60 µg per sample. For a 500 litre air sample these correspond to detection limits of 0.18 mg.m⁻³ for rubber process dust and 0.12 mg.m⁻³ for rubber fume.

Overall uncertainty

20 The overall uncertainty for a measuring procedure is defined in BS EN 482⁹ as 'the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure', and is quoted as a percentage combining bias and precision using the following equation:

$$\text{Overall uncertainty} = \frac{|\bar{x} - x_{\text{ref}}| + 2s}{x_{\text{ref}}} \times 100$$

where:

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

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

s is the standard deviation of measurements.

21 An additional 5% is usually added to the overall uncertainty percentage calculated using the equation above, to allow for the variability of the pump flow rate. The performance requirements quoted in BS EN 482 for overall uncertainty, where the task is 'measurement for comparison with limit values', are ≤50% for samples in the range 0.1 to 0.5 LV and ≤30% for samples in the range 0.5 to 2.0 LV (LV = limit value).

22 The overall uncertainty of this method has not been determined with respect to this definition.

Interferences

23 The soxhlet extraction procedure used to determine rubber fume is designed to measure the amount of cyclohexane-soluble material on a sample filter. However, it is also possible that fine insoluble material may be washed from sample filters during a soxhlet extraction procedure. Thus samples taken in areas with a high level of such dust (eg talc) may show some positive

interference as this material loss will be added to the estimation of cyclohexane-soluble matter.

24 The presence of dust containing material soluble in cyclohexane (eg rubber compounding additives, zinc stearate) will also contribute to the estimation of cyclohexane-soluble matter. In circumstances where significant quantities of such dusts are present, the method will not give a true estimate of rubber fume as such.

25 If there is potential for zinc stearate contamination then a second, parallel sample should be taken and analysed for zinc stearate and the result used to correct the rubber fume result.

Stability

26 The stability of samples taken onto filters as described in this method has not been determined.

PRINCIPLE

27 A known volume of air is drawn through a pre-weighed, pre-extracted filter.

28 The filter is re-weighed to obtain a value for the total weight of material deposited on the filter.

29 The filter is soxhlet extracted with cyclohexane, then re-weighed.

30 The quantity of cyclohexane-soluble material is obtained from the weight loss of the filter during the extraction.

SAMPLING EQUIPMENT

Sampling heads

31 Any sampling head described in MDHS 14 as being suitable for collection of total inhalable dust can be used for this method.

Filters

32 Binder-free glass fibre filters (eg Whatman GF/A), 25 mm diameter, are suitable for this method. A batch of filters should be soxhlet extracted with cyclohexane for 72 hours prior to use. After extraction, the filters should only be handled with tweezers. The filters should be allowed to dry in a gentle stream of clean air, then stored in a dust-proof container.

33 Before initial weighing, the surface of the filter should be lightly brushed with a clean soft brush to remove any loose fibres. Sufficient filters for all samples and blanks should be individually weighed on a microbalance. Filters should be allowed to dissipate electrostatic charges and reach equilibrium with the room atmosphere for a minimum period of 30 minutes before weighing (electrostatic charges may be dissipated by the use of a static eliminator).

Sample tins

34 After weighing, filters should be stored individually in sample tins, or other suitable containers, which have been marked in such a way as to uniquely identify the filter inside. The containers should be rinsed with cyclohexane and dried before use.

Sampling pumps

35 Sampling pumps should meet the requirements laid down in MDHS 14.

Flow-meter

36 A flow-meter which meets the requirements laid down in MDHS 14 is required.

Ancillary equipment

37 Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; belts or harnesses to facilitate attachment of sampling apparatus to sample subjects; containers to allow transportation of samples from sample site to analytical laboratory.

LABORATORY APPARATUS

Reagents

38 During the analysis, use only reagents of a recognised analytical grade. Appropriate personal protective equipment should be used when handling the reagents listed below.

39 Cyclohexane, >99.5% purity.

40 Anti-bumping granules.

41 A laboratory grade detergent suitable for cleaning of samplers and labware, diluted with water according to the manufacturer's instructions.

Tweezers

42 All filter handling subsequent to the initial soxhlet extraction should be performed with tweezers to prevent transfer of material from human skin to the filters, which would interfere with the analytical result.

Disposable gloves

43 Solvent resistant disposable gloves, to avoid the possibility of contamination from the hands and to protect them from contact with harmful substances. Nitrile gloves are suitable.

44 The gloves used should be talc-free, to prevent the possibility of sample filters being contaminated.

Soxhlet extraction equipment

45 This includes round bottomed flasks (250 ml), soxhlet funnels and condensers, fitted with ground glass

joints to facilitate adequate sealing of the system. Failure to seal the soxhlet extraction apparatus may lead to loss of cyclohexane and subsequent 'boiling dry' of the apparatus. This is particularly important in view of the fact that a 16 hour extraction is required, hence, the apparatus will be left unsupervised for considerable periods of time. A small amount of anti-bumping granules should be added to the solvent reservoir before beginning the extraction. An electrical heating mantle should be used to heat the solvent during the extraction.

Fume cupboard

46 The soxhlet extraction process should be carried out in a fume cupboard which has been shown to provide adequate containment of cyclohexane vapour during the extraction. The fume cupboard should also be capable of containment in the event of a spillage of cyclohexane.

Balance

47 A balance, calibrated against a primary standard, for the weighing of filters. The balance should be capable of weighing to a precision of at least 10 µg, and preferably 1 µg.

SAMPLING

48 Sampling should be carried out in accordance with the procedures described in MDHS 14 for sampling total inhalable dusts.

49 Blank filters should be submitted with each set of samples (see paragraphs 16 to 19).

50 The sensitivity of the method is dependent on the volume of air sampled. For quantification of rubber fume a minimum sampling volume of 500 litres is recommended.

ANALYSIS

Cleaning of glassware

51 Before use, clean all glassware to remove any residual grease or chemicals. Firstly soak overnight in laboratory detergent solution and then rinse thoroughly with distilled water.

Balance calibration

52 The balance calibration should be checked with a calibrated standard weight before and after weighing the filters and, in a long weighing sequence, at the intervals recommended by the balance manufacturer. The calibration procedure should be applied at each weighing stage. For maximum accuracy the same balance should be used at each stage of the determination.

Samples

53 For a 'total particulates' figure, the filters and sample blanks are left to equilibrate for a minimum period

of thirty minutes in the balance room in their holders, or in their tins with the lids raised at one side. Filters and blanks are weighed on a microbalance.

54 Fold the filter in half, using clean tweezers and probe, with the deposit inside. Take care to avoid skin contact with the filter at this stage, and all other stages of the analytical process. Re-weigh the filters and folded blanks since folding may have caused a small weight loss due to fracture of glass fibres.

55 A number of folded glass fibre filters may now be mounted into an envelope formed from an 11 cm diameter cellulose filter (Whatman grade 50 or equivalent), folded in the manner depicted in Figure 1. The cellulose filter is folded to contain the glass fibre filters, then its ends folded over to form an envelope (Figure 2). Care should be taken to avoid folding or damaging the glass fibre filters when doing this. The envelope should be held together with paper clips during the extraction. If space permits, more than one such envelope may be placed in each soxhlet thimble. The soxhlet apparatus is assembled and approximately 150 ml of cyclohexane is added. The samples (including blanks) are then soxhlet extracted for at least 16 h. The blanks should be distributed between different envelopes and soxhlet thimbles.

56 After extraction, envelopes are removed from the soxhlet and hung in a fume cupboard draught for at least 4 hours. Do not attempt to open an envelope while it is wet with cyclohexane. When thoroughly dry, the envelope may be opened. The glass fibre filters should then be allowed to equilibrate in the balance room atmosphere for at least thirty minutes, before re-weighing.

Calculation of results

Volume of air sample

57 Calculate the volume, V_s , in m^3 , of each air sample.

Total particulate material

$$\text{Total particulate material} = \frac{(m_2 - m_1) - b_1}{V_s} \text{ mg.m}^{-3}$$

were:

m_1 = initial weight of filter before sampling (mg);

m_2 = weight of filter after sampling (mg);

b_1 = mean weight change of all blanks (mg).

Cyclohexane-soluble material

$$\text{Cyclohexane-soluble material} = \frac{(m_3 - m_4) - b_2}{V_s} \text{ mg.m}^{-3}$$

were:

m_3 = weight of folded filter before extraction (mg);

m_4 = weight of filter after extraction (mg);

b_2 = mean weight change of all blanks after extraction (mg).

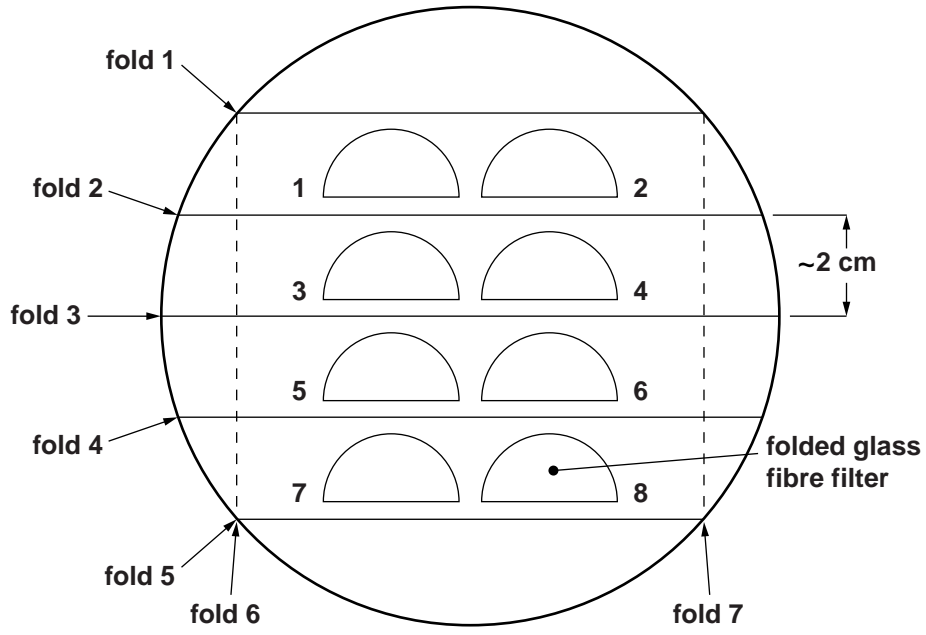


Figure 1 Initial layout of extraction envelope

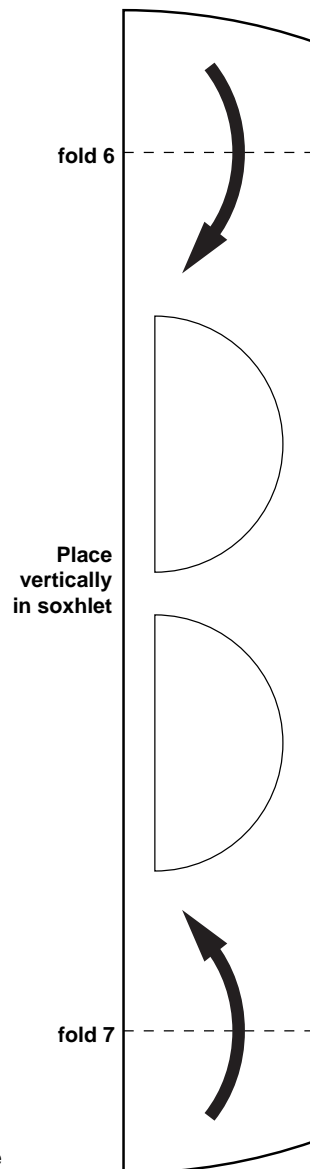


Figure 2 Completed envelope

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 (tel: 0114 2892000).

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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*This is the present edition. Amendments may be made occasionally and readers should ensure that they are using the current edition.

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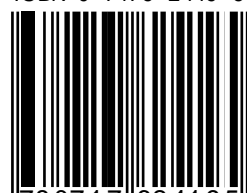
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