HSE
Health and Safety Executive

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

Laboratory method using sample collection on filters, gravimetric determination and soxhlet extraction

MDHS47/3

Methods for the Determination of Hazardous Substances
Health and Safety Laboratory

Scope

1 This method describes the measurement of time-weighted average concentrations of rubber process dust and rubber fume in air. The following definitions are taken from EH40/2005;[1] 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; rubber fume is fume evolved in the mixing, milling and blending of natural 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.

2 Where necessary, both analytes may be determined from a single sample. If measurement of rubber process dust only is required, there is no need to follow the procedures laid down in this MDHS. The methods detailed in MDHS14[2] are suitable for rubber process dust only. 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. The fraction of dust collected by this sampling technique falls into the category described as inhalable dust, as defined in BS EN 481.[3]

Summary

3 A measured volume of air is drawn through a pre-weighed, pre-extracted filter. The filter is re-weighed to obtain a value for the total mass of inhalable dust deposited on the filter. The filter is soxhlet extracted with cyclohexane, then re-weighed. The quantity of cyclohexane-soluble material, rubber fume, is obtained from the mass loss of the filter during the extraction.

Recommended sampling

4 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 and the procedure is therefore not recommended for short-term (15 min) sampling. Sampling should be carried out as described in MDHS14[2] for inhalable dusts. It is recommended that a minimum of six blank filters should be submitted with each set of samples to obtain with reasonable certainty the detection limit of the method.

Prerequisites

5 Users of this method will need to be familiar with the content of MDHS14.[2]

Safety

6 Users of this method should be familiar with standard laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

7 An inhalable dust sampler as described in MDHS14.[2]

8 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 and stored in a dust-proof container.

9 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).

10 After weighing, filters should be stored individually in clean sample tins, or other suitable containers, which have been marked in such a way as to uniquely identify the filter inside.

11 Personal sampling pumps that meet the requirements of BS EN 13137.[4]

12 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ± 2%.

13 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 site to the analytical laboratory.

Laboratory apparatus and reagents

14 During the analysis, use only reagents of a recognised analytical grade.

15 Cyclohexane (> 99.5% purity).

16 Anti-bumping granules.

17 A laboratory grade detergent suitable for cleaning samplers and glassware, diluted with water according to manufacturer's instructions.

18 Tweezers for all filter handling to prevent transfer of material from human skin to the filters, which would interfere with the analytical result.

19 Soxhlet extraction equipment employing 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. Several 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. The apparatus should be operated in a fume cupboard capable of containment of cyclohexane vapour and liquid in the event of spillage.

20 Cellulose filter, 11 cm diameter (Whatman grade 50 or equivalent).

21 Microbalance, 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

22 Sampling should be carried out in accordance with the procedures described in MDHS14[2] for inhalable dust. It is recommended that a minimum of six blank filters should be submitted with each set of samples (see Appendix 1 paragraphs 1–4). 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.

Sample analysis

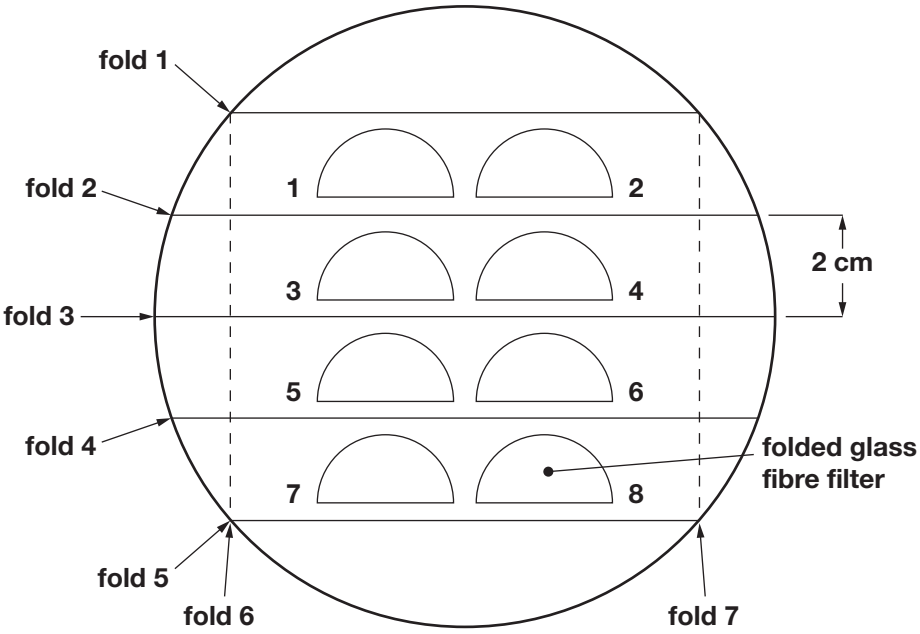
23 Before use, clean all glassware to remove any residual grease or chemicals. Firstly, soak overnight in laboratory detergent solution and then rinse thoroughly with distilled water and allow to dry.

24 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.

25 For determination of inhalable dust, the filters and sample blanks must be left to equilibrate for a minimum period of 30 minutes in the balance room in their holders, or in their tins with the lids raised at one side.

26 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.

Figure 1 Initial layout of extraction envelope



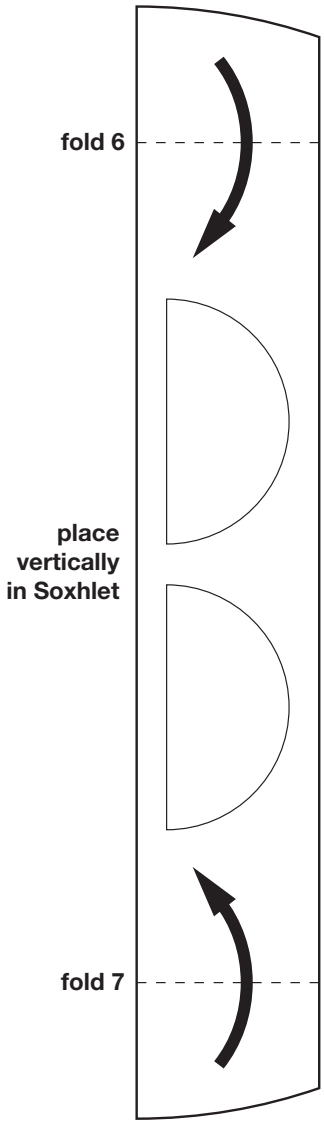


Figure 2 Completed envelope

27 A number of folded glass fibre filters may now be mounted into an envelope formed from an 11 cm diameter cellulose filter 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 hours. The blanks should be distributed between different envelopes and soxhlet thimbles.

28 After extraction, envelopes are removed from the soxhlet apparatus and hung in a fume cupboard draught for at least four hours. Do not attempt to open an envelope until thoroughly dry. The glass fibre filters should then be allowed to equilibrate in the balance room atmosphere for at least 30 minutes, before re-weighing.

Calculation of results

Volume of air sample

29 Calculate the volume, V_S, in m^{-3}, of each air sample as outlined in MDHS14.[2]

Total particulate material

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

where:

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

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

where:

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).

Appendix 1 Additional information

Detection limit of the method

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

2 For this method, the blank filters should be 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.

3 It is recommended that at least six blanks are used in order to determine the detection limit of a gravimetric method. 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.

4 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

5 The overall uncertainty for this measurement procedure as defined in BS EN 482[5] has not been determined.

Interferences

6 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. Therefore, 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.

7 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.

8 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

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

References

1 *EH40/2005 Workplace exposure limits: Containing the list of workplace exposure limits for use with the Control of Substances Hazardous to Health Regulations 2002 (as amended)* Environmental Hygiene Guidance Note EH40 (Second edition) HSE Books 2011 ISBN 978 0 7176 6446 7 www.hse.gov.uk/pubns/books/EH40.htm

2 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable dust* MDHS14/4 HSE 2014 www.hse.gov.uk/pubns/mdhs/index.htm

3 BS EN 481:1993 *Workplace atmospheres. Size fraction definitions for measurement of airborne particles* British Standards Institution

4 BS EN 13137:2013 *Workplace atmospheres. Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution

5 BS EN 482:2012 *Workplace exposure. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

You should use the most current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

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