HSE
Health and Safety Executive

Resin acids in rosin (colophony) solder flux fume

Laboratory method using gas chromatography

MDHS83/3

Methods for the Determination of Hazardous Substances
Health and Safety Laboratory

Scope

1 This method describes the measurement of time-weighted average concentrations of rosin (also known as colophony) based solder flux fume collected onto membrane filters with analysis of the resin acid components, after derivatisation, by gas chromatography (GC).

Summary

2 A measured volume of air is drawn through a membrane filter mounted in a sampling head close to the breathing zone. The filter is solvent desorbed, the resin acids derivatised and then quantified using GC with a flame ionisation detector (FID). If confirmation of the resin acid components' identities is required, samples may also be analysed by GC with a mass spectrometer (MS) detector. However, MS is not recommended for quantitative analysis as, unlike an FID, the MS detector gives different response factors for the various resin acids.

The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

3 For long-term exposures: Maximum sampling time: 8 hours; Sampling rate: 1–2 l^{-1}min; Sampled volume: up to 960 litres. For short-term exposures: Sampling time: 15 mins; Sampling rate: 2 $lmin^{-1}$; Sampled volume: 30 litres.

Prerequisites

4 Users of this method will need to be familiar with the content of MDHS14.[1]

Safety

5 Users of this method should be familiar with normal 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

6 Sampling medium: 13 mm diameter, 5 µm pore size, mixed cellulose ester filter (Millipore SMWP found to be suitable) in a Millipore 13 mm Swinnex type sampling head.

7 Personal sampling pumps that meet the requirements of BS EN 13137.[2]

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

Laboratory apparatus and reagents

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

10 Cyclohexane: HPLC grade.

11 Toluene: HPLC grade.

12 Methyl stearate: > 98%.

13 Dimethylformamide dimethyl acetal: > 90% (store under refrigeration).

14 Abietic acid: 90% or better (store under refrigeration).

15 Methyl stearate solution (0.1% w/w): Accurately weigh about 90 mg of methyl stearate into a 10 ml volumetric flask and make up to volume with toluene. Pipette 1 ml of this solution into a 10 ml volumetric flask and dilute to volume with toluene to give a 0.1% w/w solution. The solution can be stored under refrigeration for several months.

16 Methylating reagent: Pipette 8 ml of toluene into a suitable glass bottle. Add 1 ml of the dimethylformamide dimethyl acetal and 1 ml of the 0.1% methyl stearate solution. Prepare this solution immediately before use.

17 A selection of laboratory glassware, including 2 ml vials (with screw-top caps, teflon-silicone septa and 250 µl removable inserts); Pasteur pipettes; and volumetric flasks, Class A, complying with the requirements of BS EN ISO 1042:2000.[3]

18 A balance, calibrated against a primary standard, and capable of weighing to ± 0.1 mg over the range 0 to 100 g.

19 Positive displacement micropipettes complying with the requirements of BS EN 8655-6:2002.[4]

20 A heater block capable of maintaining samples, in 2 ml vials, in the temperature range 30–80 °C, and with a supply of dry air or nitrogen (for evaporation).

21 An ultrasonic bath.

22 A GC system with a split/splitless injector and an FID. Suitable operating conditions are listed below, but the use of other columns and conditions are acceptable provided they have the accuracy and reliability appropriate to the application:

Column	BP-1; 12 m × 0.32 mm; 0.5 µm film thickness
Carrier gas	Hydrogen; 7 psi
Split flow	10 ml/min
Injector temperature	250 °C
Detector temperature	300 °C
Injection volume	1 µl
Oven program	180 °C for 0 mins; ramp at 1 °C min^{-1} to 195 °C, hold for 0 mins; ramp at 20 °C min^{-1} to 285 °C, hold for 5.5 mins

23 Under the above conditions, a typical sample of rosin flux will produce a chromatogram similar to that shown in Figure 1.

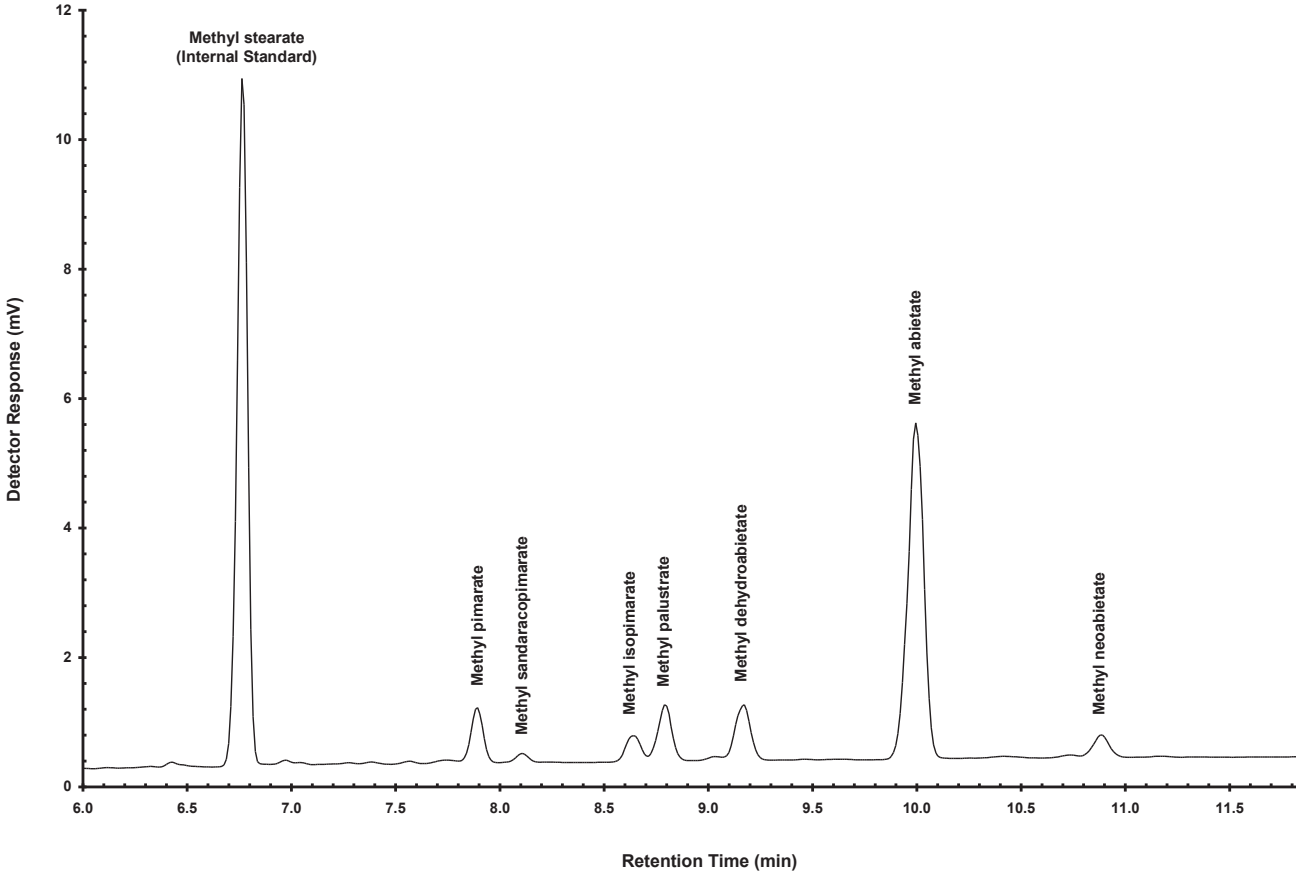

Figure 1 Chromatogram of methyl stearate and resin acid methyl esters

Preparation and sampling

24 Load the filter into the sampling head and accurately set the flow rate to between 1 and 2 l min^{-1}. The higher flow rate should be used for 15-minute samples and/or when it is suspected that sample loadings might be low.

25 Set aside a minimum of three unused filters as blanks for each batch of ten samples collected. Ensure that the blanks are handled in the same way as the samples but without drawing air through them.

26 Attach the sampling head containing the filter to the worker as shown in Figure 2. Position the sampling head on the right side for right-handed workers and the left side for left-handed workers.

Figure 2 Sampling head position

27 After sampling, place the samples in a clean container to prevent contamination. Keep samples refrigerated prior to analysis. If kept under these conditions, samples may be stored for up to four weeks.

Calibration

28 Prepare two abietic acid stock solutions, at a concentration of 0.01% w/w, as follows (these should be freshly prepared immediately before use).

- Accurately weigh around 70 mg of abietic acid into a 10 ml volumetric flask and make up to volume with cyclohexane.
- Pipette 1 ml of this solution into a second 10 ml volumetric flask and dilute to volume with cyclohexane.
- Pipette 1 ml of this solution into a third 10 ml flask and dilute to volume with cyclohexane to give the final 0.01% w/w solution.

28 Prepare a minimum of four calibration standards by accurately weighing aliquots of 0.01% abietic acid stock solution into separate 2 ml vials (prepare half the standards from one stock solution and half from the other). A typical calibration range is 0 to 100 µg (requiring aliquots of 0 to 1.5 ml).

29 Evaporate the standards to dryness at 40 °C under dry nitrogen then derivatise as described in paragraph 35.

30 Analyse the standards in an identical manner to the samples and measure the chromatographic peak areas of the methyl stearate (internal standard) and the total chromatographic peak area of all the peaks in the resin acid region of the chromatogram (see Figure 1).

31 Calculate the mean peak area of the methyl stearate in the standards and use this value to normalise the total resin acid (TRA) peak area for each standard using the equation:

$A_N = A_S \times (A_1/A_2)$

Where:

A_S = TRA peak area

A_N = Normalised TRA peak area

A_1 = Methyl stearate peak area

A_2 = Mean methyl stearate peak area of the standards

32 Plot the normalised TRA peak areas against the corresponding resin acid contents of the standards, in µg, and construct the line of best fit. The slope of this line is the detector response factor (RF) for TRA.

Sample analysis

33 Analyse samples and blanks in an identical manner.

34 Transfer the sample filter to a 2 ml vial. Add 1.2 ml of cyclohexane, cap and extract in an ultrasonic bath for five minutes. Transfer 1.1 ml of the extract to a fresh 2 ml vial, place in a heating block at 40 °C and evaporate to dryness under a stream of nitrogen. After drying, add 200 µl of methylating reagent, then cap with a teflon-silicone septum and heat to 75 °C for 30 minutes.

35 Cool the samples to room temperature, then transfer to a 250 µl glass insert using a glass Pasteur pipette, re-cap and analyse by GC. Measure the methyl stearate (internal standard) and total resin acid chromatographic peak areas. Normalise the TRA peak area using the equation in paragraph 31 and convert the normalised peak area into a TRA content, in µg, by dividing by the RF value obtained from the calibration standards.

36 Calculate the mean mass of TRA, in µg, in the blanks.

Calculation of results

37 Calculate the volume of air sampled for each sample, V_S, in m^3.

38 Calculate the airborne TRA concentration, C, in µg m^{-3}, using the equation:

$C = (M_S - M_B)/V_S$

Where:

M_S = Mass of TRA in sample, in µg

M_B = Mean mass of TRA in blanks, in µg

Appendix 1 Additional information

Detection limit

1 The estimated limits of detection and quantification may be calculated from the mean and standard deviation (SD) of the blanks using the following formulae:

Limit of detection (LOD) = M_B + (3 × SD)

Limit of quantification (LOQ) = M_B + (10 × SD)

2 Under the stated analytical conditions, the LOD is typically around 0.3 µg, which for an 8-hour air sample at 1 l min^{-1}, equates to around 0.6 µg m^{-3}, and for a 15-minute sample at 2 l min^{-1}, equates to around 10 µg m^{-3}.

Overall uncertainty

3 The overall uncertainty for the method, as defined by BS EN 482:2012[5] varies from batch to batch, but is typically between 10 and 25%.

Sample stability

4 If kept in a sealed container, the maximum recommended storage time for an exposed sample filter is one week, if stored at room temperature, or six months, if refrigerated.[6]

Sampling efficiency

5 The sampling efficiency for the recommended 13 mm, 5 µm pore size, mixed cellulose ester filter has been found to be around 98–99%.[6]

Sources of error

6 Care must be taken during evaporation of the standard/sample solutions to avoid splashing, as this will lead to loss of sample and low results.

7 Errors will occur if the purity of the abietic acid is not accurately known (see paragraph 14).

8 Resin acid compounds other than those shown in Figure 1 may be present in some solder fume samples, in particular dihydro- and tetrahydro- resin acids. These should be quantified as normal. However, non-resin acid components, eg aliphatic hydrocarbons or dialkyl phthalates may also be present, leading to false positive results where such peaks are not correctly identified. Where doubt exists, it is recommended that at least one sample is analysed by mass spectrometry to confirm peak identities.

References

1 *General methods for the sampling and gravimetric analysis of respirable, thoracic and inhalable dust* MDHS14/4 HSE 2014 www.hse.gov.uk/pubns/mdhs/pdfs/mdhs14-3.pdf*

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

3 BS EN ISO 1042:2000 *Laboratory glassware. One-mark volumetric flasks* British Standards Institution

4 BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric methods for the determination of measurement error* 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

6 Pengelly M I, Groves J A, Foster R D et al. 'Development of a method for measuring exposure to resin acids in solder fume' *Ann Occup Hyg* 1994 **38** (5) 765–776

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.

British Standards can be obtained in PDF or hard copy formats from BSI: http://shop.bsigroup.com or by contacting BSI Customer Services for hard copies only Tel: 020 8996 9001 email: cservices@bsigroup.com.

This guidance is issued by the Health and Safety Executive. Following the guidance is not compulsory, unless specifically stated, and you are free to take other action. But if you do follow the guidance you will normally be doing enough to comply with the law. Health and safety inspectors seek to secure compliance with the law and may refer to this guidance.

This MDHS is available at: www.hse.gov.uk/pubns/mdhs

For further information about this method or other MDHS methods, please visit HSL's website: www.hsl.gov.uk or email: hslinfo@hsl.gov.uk