

MDHS 83/2

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Resin acids in rosin (colophony) solder flux fume

**Laboratory method using gas
chromatography**

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Scope

1 This method describes a laboratory method for measurement of exposure to rosin-based solder flux fume, using 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 analysed using GC with a flame ionisation detector (FID). If confirmation of the components' identities is required, samples may also be analysed by GC with a mass spectrometer (MS) detector. But, this is not recommended for quantitative analysis as, unlike the FID, the MS detector gives different responses for the various resin acids.

Recommended sampling

3 For long-term exposures: Maximum sampling time: 8 hours; Sampling rate: 1-2 l/min; Sampled volume: up to 960 l. For short-term exposures: Sampling time: 15 mins; Sampling rate: 2 l/min; Sampled volume: 30 l.

Prerequisites

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

Safety

5 People using this method should be familiar with normal laboratory practice and carry out a suitable risk assessment. The method does not address all the safety problems associated with its use. 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 Sampling pumps: Capable of sampling up to 2 l/min and conforming to the requirements specified of MDHS14.¹

8 Belts/harnesses and tubing: To support the sampling pumps and connect them with the sampling media.

9 Flow meter: Calibrated against a primary standard and conforming to the requirements of MDHS14.¹

10 Volumetric flasks: 10 ml flasks conforming to the requirements of BS EN ISO 1042.²

11 Analytical balance: Capable of weighing to ± 0.1 mg over the range 0-100 g and calibrated against a primary standard.

12 Pipettes: A range of positive displacement micropipettes to measure volumes in the range 100 µl to 3 ml. These should be calibrated against a primary standard conforming to BS EN ISO 8655-6.³

13 Heating block: An electrical heating block with variable temperature adjustment in the range 30-80 °C \pm 5 °C. The block should be equipped with an evaporator to supply dry air or nitrogen for evaporation.

14 GC vials: 2 ml capacity.

15 Septa: Teflon-silicone septa for the GC vials.

16 Pasteur pipettes.

17 Ultrasonic bath.

18 Gas chromatograph: Split/splitless injector and flame ionisation detector.

19 GC vials 250 μ l removable inserts.

Reagents

20 Cyclohexane: HPLC grade (alternatively, diethyl ether may be substituted).

21 Toluene: HPLC grade.

22 Methyl stearate: > 98%.

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

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

Solutions

25 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 the 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.

26 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 freshly immediately before use.

27 Two abietic acid stock solutions (0.01% w/w): Accurately weigh around 70 mg of abietic acid into a 10 ml volumetric flask and make up to volume with cyclohexane to give a 1% w/w solution. Pipette 1 ml of this solution into a 10 ml flask and dilute to volume with cyclohexane to give a 0.1% w/w solution. Pipette

1 ml of this solution into a 10 ml flask and dilute to volume with cyclohexane to give a 0.01% w/w solution. Prepare these six solutions freshly immediately before use.

Sample collection

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

29 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.

30 Attach the sampling head containing the filter to the worker as shown in Figure 1. Position the sampling head on the right side for right-handed workers and the left side for left-handed workers.



Figure 1 Sampling head position

31 After sampling, check the flow rate, switch off the pump and place the sampler in a clean container to prevent contamination.

32 Transport the filters to the laboratory for analysis either in the sampling heads or in a suitable container.

33 Store samples under refrigeration while awaiting analysis and analyse within four weeks.

Sample preparation

- 34 Transfer the filter to a 2 ml GC vial.
- 35 Add 1.2 ml of cyclohexane, cap and place in an ultrasonic bath for 30 seconds.
- 36 Transfer 1.1 ml of the cyclohexane extract from the volumetric flask to a fresh 2 ml GC vial. Place the sample vial in a heating block at 40 °C and evaporate the solvent under a stream of nitrogen. Take care not to lose solution through splashing during the evaporation stage, as this has the potential to be a major source of error.
- 37 Add 200 µl of the dimethylformamide dimethyl acetal methylating reagent to the sample.
- 38 Cap the vial with a Teflon-silicone septum and heat to 75 °C on the heating block for 30 minutes to prepare the derivative.
- 39 Allow the sample to cool to room temperature then transfer to a 250 µl GC vial insert using a glass pipette and re-cap.
- 40 Treat the blanks in the same way as the samples.

Instrument conditions

- 41 Gas chromatograph:
- | | |
|------------------------------|---|
| (a) Column | BP-1; 0.5 µm film thickness |
| (b) Dimensions | 12 m x 0.32 mm |
| (c) Carrier gas/pressure | Hydrogen; 7 psi |
| (d) Split flow/ratio | 10 ml min ⁻¹ ; approx 3:1 |
| (e) Injector temperature | 250 °C |
| (f) Detector temperature | 300 °C |
| (g) Injection volume | 1–2 µl |
| (h) Initial oven temperature | 180 °C for 0 min |
| (i) Oven ramp 1 | 1 °C min ⁻¹ to 195 °C, hold for 0 min |
| (j) Oven ramp 2 | 20 °C min ⁻¹ to 285 °C, hold for 5.5 min |
| (k) Total run time | 25 min |

Calibration

- 42 Prepare six calibration standard solutions to cover the range 0-250 µg/ml total resin acid by accurately pipetting 0-1.5 ml of 0.01% abietic acid solution into separate 2 ml GC vials. Three standards should be

prepared with one abietic acid stock solution and three with the other.

- 43 Evaporate the standards to dryness at 40 °C under dry nitrogen then derivatise as described in paragraphs 37-39.
- 44 Once prepared, standards may be re-used for several months if kept refrigerated and quality checked before use. To be acceptable for re-use, the standards must produce both a linear detector response and a response factor no greater than 20% different from the value when the standards were first prepared. If this is not the case, a fresh set of standards must be prepared.
- 45 Analyse the calibration solutions.
- 46 Determine the chromatographic peak areas of methyl stearate (peak 2 in Figure 2) and all the peaks in the resin acid region of the chromatogram (between retention time 5 and 10 minutes).
- 47 Reject any standards where the chromatographic peak area of the methyl stearate peak differs from the mean value by greater than 10%. If more than two standards are rejected then prepare a fresh set.

48 For each valid standard, sum the peak areas from the resin acid region to obtain the total resin acid (TRA) peak area, A_C .

49 Blank correct the calibration data by subtracting the A_C value from the 0 µg standard from each of the other standards.

50 Calculate the resin acid content of each standard, C_C , and plot against the blank corrected A_C values.

51 Construct the line of best fit; the slope of this line is the detector response factor for the resin acids.

Sample analysis

52 Analyse the samples and determine the chromatographic peak area of the methyl stearate peak and all peaks in the resin acid region.

53 Reject any samples in which the peak area of the methyl stearate shows a difference greater than 10% from the mean value obtained in the calibration solutions.

54 Sum all the peaks in the resin acid region of the chromatogram to obtain the TRA area for each sample, A_S and blank, A_B .

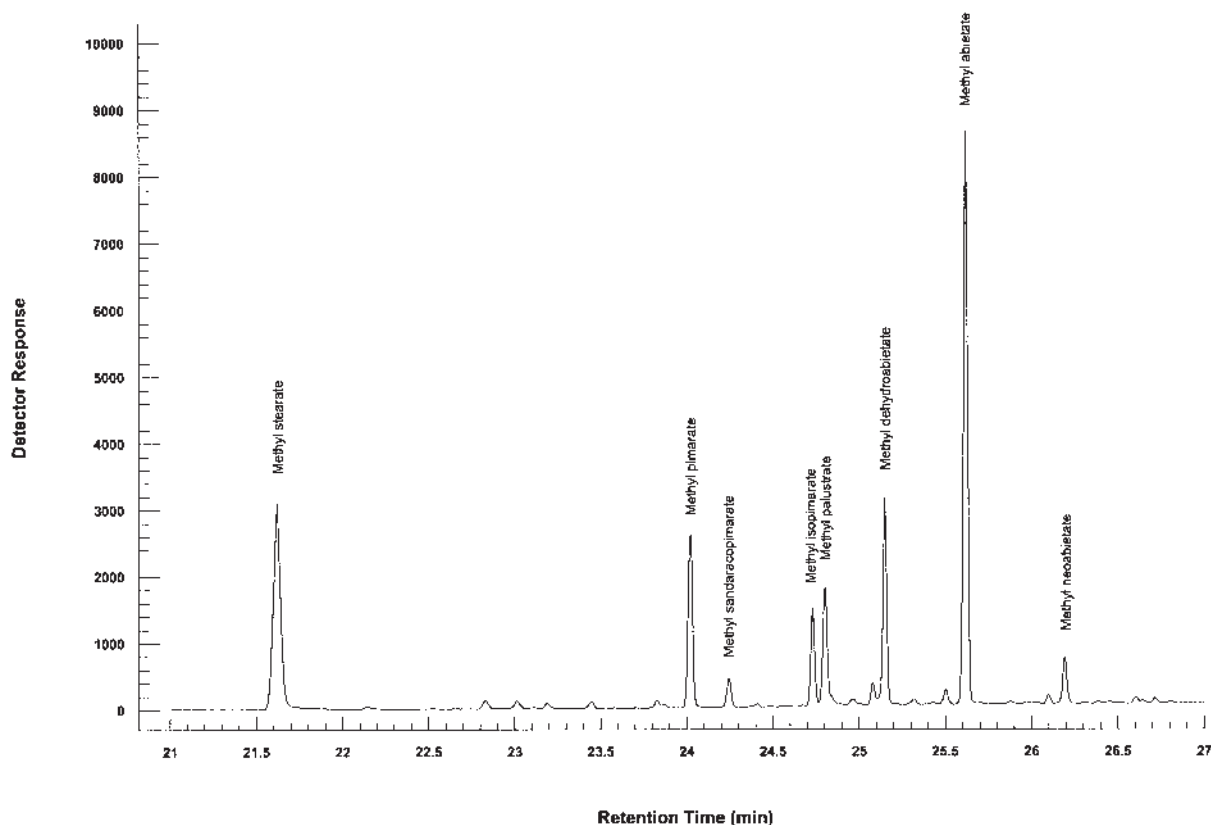


Figure 2 Chromatogram of methyl stearate and resin acid methyl esters

55 Calculate the mean value of A_B and subtract from each of the A_S values.

56 Convert each blank corrected sample value to mass of TRA, m_S μg , using the detector response factor.

57 Where high resin acid concentrations are found, dilute the sample solutions with toluene to bring the concentration within the calibration range.

Calculation of results

58 Calculate the volume of air sampled for each sample, V_S litres.

59 Calculate the TRA concentration $p(\text{TRA})$ in mg m^{-3} using

$$p(\text{TRA}) = m_S/V_S$$

Sources of error

60 If care is not taken during evaporation of the sample solutions (paragraph 36), splashing may occur, leading to loss of sample and low results.

61 Errors will occur if the purity of the abietic acid is not accurately known (paragraph 24).

62 Chromatographic errors, caused, for example, by variations in injection volume or integration of chromatographic peaks, may lead to random errors. The use of an internal standard should help to reduce the former.

63 The presence of other non-resin acid components, for example aliphatic hydrocarbons or phthalate plasticisers, may lead to false positive results if 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.

Appendix 1: Additional information

1 Significant supplementary information can be found below. Other further information can be found in papers in the scientific press⁴ and with accompanying back-up data in reports published online.⁵

Sampling

2 The plume of solder fume generated during soldering operations is often highly directional. Sampling on the lapel, as traditionally done in exposure measurement, gives consistently lower resin acid concentrations than when samples are collected closer to the nose and mouth. It is therefore important when assessing personal exposure to solder fume to position the sampling head as close as possible to the breathing zone. The recommended method is to fix the sampling head to the sidearm of a pair of safety spectacles (see Figure 1). The sampling head should be attached to the right-hand side of the spectacles for right-handed workers and to the left-hand side for left-handed workers.

Evaluation of the method

Overall uncertainty

3 The overall uncertainty for the method, calculated from a combination of bias and precision as in BS EN 482⁶ varies from batch to batch, but is typically between 10 and 25%.

Sampling efficiency

4 The sampling efficiency of the Millipore SMWP (13 mm, 5 µm pore size, mixed cellulose ester) filters was tested using an atmosphere of solder fume at several times the occupational exposure limit. This showed a sampling efficiency of 98–99%.

Detection limits

5 The qualitative and quantitative detection limits for total resin acid, defined as the concentration which gives a signal to noise ratio of 3:1 and 10:1 respectively, are typically around 0.3 µg and 1.0 µg per sample respectively. For an 8-hour sample taken at a flow rate of 2 l/min, these figures correspond to qualitative and quantitative detection limits of 0.3 µg/m³ and 1.0 µg/m³ respectively. For a 15-minute sample at the same flow rate, the corresponding figures are 10 and 30 µg/m³.

Sample stability

6 Sample stability was investigated by spiking filters with a solution containing a mixture of resin acids, placing the filters in sealed containers and determining the analytical recovery after storage. The results indicate a maximum recommended storage time of one week at room temperature or six months, if refrigerated. Once derivatised, the samples are stable for a period of at least two years, if refrigerated.

References

- 1 *General methods for sampling and gravimetric analysis of respirable and inhalable dust* MDHS14/3 (Third edition) HSE Books 2000 Web only version available at www.hse.gov.uk/pubns/mdhs/index.htm*
- 2 BS EN ISO 1042: 2000 *Laboratory glassware. One-mark volumetric flasks* British Standards Institution
- 3 BS EN ISO: 8655-6: 2002 *Piston-operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution
- 4 Pengelly M I, Groves J A, Foster R D et al 'Development of a method for measuring exposure to rosin acids in solder fume' *Ann Occup Hyg* 1994 **38** (5) 765-776
- 5 Pengelly M I and Groves J A *Investigation into the sampling and analysis of solder fume Part V – Development of a Sampling Method for Resin Acids* Health and Safety Laboratory Report 1993 IR/L/SP/93/08 Web only version available at www.hse.gov.uk/research/hsl/_pdf/1993/hsl93-08.pdf
- 6 BS EN 482:1994 *Workplace atmospheres. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

* Amendments may be made occasionally and readers should ensure that they are using the current edition of any method or standard. Current versions of all HSE MDHS methods are available online.

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