HSE
Health and Safety Executive

Triglycidyl isocyanurate (and coating powders containing triglycidyl isocyanurate) in air

Laboratory method using sample collection on filters, liquid desorption and liquid chromatography

MDHS85/2

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1 This method describes the measurement of time-weighted average concentrations of triglycidyl isocyanurate (TGIC, CAS No. 2451-62-9) in air and in premix and coating powders containing TGIC. Premix is defined as formulated and mixed coating powder prior to extrusion in manufacture and coating powder as the extruded and milled powder supplied by manufacturers to users. Both 'free' or unbound TGIC and cross-linked TGIC will be present in the coating powders as some TGIC cross-links during the manufacturing process. This method measures only 'free' TGIC in coating powders.

Summary

2 A measured volume of air is drawn through a silanised glass fibre filter mounted in an inhalable dust sampler. After sampling, either of two separate extraction methods optimised to extract TGIC and either premix or coating powder samples are used. The resulting solution is analysed by high performance liquid chromatography (HPLC) with UV detection. The determination of TGIC in occupational hygiene samples other than air has been described elsewhere.[1]

3 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

4 For long-term exposures:

- Maximum sampling time: 100 minutes;
- Sampling rate: 2 l min^{-1};
- Sampled volume: up to 200 litres.

For short-term exposures:

- Sampling time: 15 mins;
- Sampling rate: 2 l min^{-1};
- Sampled volume: 30 litres.

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 Inhalable dust sampler as described in MDHS14.[2]

8 Personal sampling pumps that meet the requirements of BS EN 13137.[3]

9 Binder-free silanised glass fibre filters (eg Whatman GF/A), of appropriate diameter for use in the selected inhalable dust sampler and suitable for the collection and analysis of stable samples of TGIC, premix and cured powder coatings.

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

11 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; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes to transport samples to the laboratory.

Laboratory apparatus and reagents

12 During the analysis, use only reagents of a recognised analytical grade. Use only distilled or deionised water.

13 Cyclohexane.

14 Dichlorodimethylsilane.

15 Methanol: HPLC grade.

16 Acetone: HPLC grade.

17 Tetrahydrofuran (THF): HPLC grade.

18 Acetonitrile: HPLC grade.

19 Silanising solution: 5% w/w dichlorodimethylsilane in cyclohexane.

20 Phosphoric acid 85% w/v.

21 Sodium hydroxide solution in deionised water.

22 Nitrogen: compressed and regulated to a flow suitable for drying samples.

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

24 HPLC mobile phase: Dissolve 1.15 g of phosphoric acid in 1 l de-ionised water and adjust to pH6 with sodium hydroxide solution. Add 900 ml of this solution to 100 ml acetonitrile and mix thoroughly.

25 A selection of laboratory glassware, including pipettes, beakers, measuring cylinders and volumetric flasks, Class A, complying with the requirements of BS EN ISO 1042:2000.[4]

26 Piston operated micropipettes complying with the requirements of BS EN 8655-6:2002.[5]

27 A balance, calibrated against a primary standard, for the preparation of the calibration standards. The balance should be capable of weighing to ± 0.1 mg over the range 0 to 100 g.

28 Sample preparation equipment including: vortex mixer, ultrasonic bath and filter apparatus for pre-filtering aqueous samples before HPLC analysis.

29 HPLC system with auto sampler and UV or diode array detector. The latter detector will improve the accuracy of the analysis by more robustly ensuring peak purity. Suitable HPLC conditions for TGIC are listed below, but the use of other columns and conditions is acceptable provided they have the accuracy and reliability appropriate to the application.

Column dimensions	100 mm x 4.5 mm ID with a 1 cm guard column
Column packing	S3 ODS2
Column temperature	20 °C
Mobile phase	0.01 M phosphate buffer pH 6.0 in 10% acetonitrile
Flow rate	1 ml min^{-1}
Injection Volume	25 µl
UV detector wavelength	205 nm

30 Under the above conditions, the retention time of TGIC was 10.3 minutes.

Preparation and sampling

Silanised filters

31 The glass fibre filters require silanisation before use by immersion in a 5% solution of dichlorodimethylsilane in cyclohexane for five minutes. Decant the excess reagent into methanol in order to deactivate before disposal. Rinse the filters in fresh cyclohexane twice more to remove residual reagent then in methanol and allow to stand in fresh methanol for five minutes. Decant the methanol and rinse in acetone. Finally rinse in deionised water in order to remove hydrochloric acid generated during silanisation. The filters are ready for use after drying in an oven. Load the filters into clean, dry inhalable dust samplers using clean flat-tipped tweezers.

Sampling

32 Sampling should be carried out in accordance with the procedures described in MDHS14[2] for inhalable dusts. A suitable sample volume for airborne concentrations between 0.01 and 0.2 mg m^{-3} pure TGIC is 200 litres.

33 A portion (approximately 20 ml) of every cured powder coating and premix used at the site during the period of sampling should be retained for analysis.

34 Place the exposed filters in sealed, labelled metal tins and the bulk samples in sealed containers for transportation. Keep samples refrigerated and analyse within one week.

Blanks

35 A minimum of two field blanks should be included with each batch of ten samples.

Calibration

36 Prepare at least six standard solutions of TGIC over the range 0.5–40 µg ml^{-1} daily by accurately weighing an aliquot of TGIC into a volumetric flask and diluting as appropriate.

37 Analyse each standard solution in an identical manner to the samples and measure the peak area of the target compound. Plot the peak areas against the corresponding TGIC concentration of the standard, in µg ml^{-1}, and construct the line of best fit. The slope of this line is the detector response factor (RF) for TGIC.

38 Modern HPLC equipment is usually sufficiently stable that a new calibration is not required with each set of samples. However, in order to verify the equipment, a quality assurance (QA) solution of known concentration must be analysed with each set of samples. The QA solution may be prepared using the procedure above (paragraph 36).

Sample analysis

39 Analyse samples and blanks in an identical manner.

40 Before use, clean all glassware by soaking overnight in laboratory detergent, then rinse thoroughly with deionised water.

41 The procedure used to extract the sample is dependent on the type of sample taken. The following methods have been optimised to extract either TGIC and premix or coating powder samples.

Bulk coatings

42 Analysis of either samples of the bulk premix (if available) or coating powder is recommended before desorption of the samples in order to be able to modify the HPLC conditions should interfering peaks occur in the chromatograms. The amount of ‘free’ TGIC measured in the coating powder analysis may also be used in combination with the inhalable dust value as a screening method (Appendix).

43 Samples of premix bulk must be ground up to provide a uniform sample for analysis. Accurately weigh approximately 8 mg of the ground premix into each of six vials containing a silanised glass fibre filter and extract as for samples of TGIC and premix in air (paragraph 45).

44 Coating powders are supplied as a fine powder. Accurately weigh approximately 8 mg of the powder into each of six vials containing a silanised glass fibre filter and extract as for TGIC and coating powders in air (paragraph 46).

Samples of TGIC and premix in air

45 Wet the sample filter with 100 µl acetonitrile, then add 2 ml of mobile phase. Sonicate for one hour and filter.

Samples of TGIC and coating powders in air

46 Place the sample filter in a vial containing 2 ml THF and mix on a vortex mixer to dissolve the polyester coating and TGIC. Add water (0.5 ml) to precipitate the polyester coating and mix thoroughly on the vortex mixer. Repeat with a second portion of water (0.5 ml). Evaporate to dryness under nitrogen and add acetonitrile (2 ml). Sonicate for 30 minutes, then transfer a portion (1 ml) to a fresh vial. Evaporate to dryness under nitrogen, then add HPLC mobile phase (1 ml). Sonicate for 30 minutes and filter.

47 Analyse the sample filter extracts (or bulk premix/coating powders) by HPLC. Measure the chromatographic peak area of the target compound and convert this peak area to a TGIC concentration, in µg ml^{-1}, by dividing by the RF value obtained from the calibration standards.

48 The chromatogram should be checked for interfering peaks and the recovery of 'free' TGIC calculated in the samples of the bulk materials. If necessary, the HPLC conditions can be modified. Premixes are expected to contain only 'free' TGIC, however some TGIC will be cross-linked in the coating powder and the recovery of 'free' TGIC in coating powders will be less than the total amount added to the coating by the manufacturer.

49 Where high TGIC concentrations are found, dilute the sample solutions with mobile phase to bring the concentration back within the calibration range. Repeat the analysis and record the dilution factor.

50 Calculate the mean concentration of TGIC, in µg ml^{-1}, in the blank filter extracts.

Calculation of results

Mass concentration of analyte in air samples

51 Calculate the volume, V_S, in litres, of each air sample using the procedure described in MDHS14.[2]

52 Calculate the airborne concentration of TGIC, C, in mg^{-3}, using the equation:

$$C = D \times (M_S - M_B) / V_S$$

Where:

M_S = Concentration of TGIC in sample, in µg ml^{-1}

M_B = Mean concentration of TGIC in blanks, in µg ml^{-1}

D = Volume of desorbing solution (2.1 ml for pure TGIC and premix samples; 2 ml for powder coatings)

'Free' or unbound TGIC in bulk samples

53 The 'free' or unbound TGIC in the premix/coating, F, as a % weight/weight, can be calculated using the following equation:

$F = (D \times (M_S - M_B) \times 100) / W$

Where:

W = Weight of bulk premix/coating analysed, in µg

Appendix: Additional information

Gravimetric screening method

1 The gravimetric screening method using MDHS14[2] to collect inhalable dust samples can be used as a preliminary screening method for TGIC levels.

2 The inhalable dust can be assumed to come from 'free' TGIC (alone or in premix) or cured coating powder and used to estimate exposure to TGIC.

3 For air samples containing coating powder only, either the proportion of TGIC added to the coating by the manufacturer or the results of an analysis of a sample of the bulk coating powder can be used to estimate the proportion of TGIC in the particulate. For example, it is assumed that for a coating containing 4% by weight TGIC, 4% of the total particulate measured is assumed to be TGIC. As the amount of TGIC added to the coating by the manufacturer includes both 'free' and cross-linked TGIC, a more accurate estimate of exposure would be obtained using the results of an analysis of the bulk coating powder, ie the proportion of 'free' TGIC only in the powder

Detection limits

4 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) = $M_B + (3 \times SD)$

Limit of quantification (LOQ) = $M_B + (10 \times SD)$

The detection limit for TGIC is typically around 0.18 µg per sample. For a 200 litre air sample, this corresponds to a detection limit of 0.9 µg m^{-3}.

Overall uncertainty

5 The overall uncertainty of the procedure as defined by BS EN 482:2012[6] was calculated to be 23% at loadings above 2 µg. The bias was calculated as the possible bias of the flow meter (2%) and the average difference between the stated and analysed concentration of a series of premixes of known concentration (2%). The precision was calculated using the pump precision (5%) and the average precision of the analysis of a series of premix and cured powders (8%).

Stability

6 Premix and coating powders were stored over three weeks. The recovery did not change over this period or on exposure to humid air.

7 TGIC was spiked onto filters over the range 2 to 40 µg and stored for one week at 4 °C. Over this range, the recovery after one days storage was 100% with a standard deviation of 4%. After storage for one week, recovery at filter loadings of 20 to 40 µg was 94% with a standard deviation of 6%. However, at loadings of 2 µg, recovery was 68% with a standard deviation of 11%.

References

1 White J 'Determination of Triglycidyl Isocyanurate from Powder Coatings in Occupational Hygiene Samples by Gas Chromatography with Mass Spectrometric Detection' *Ann Occup Hyg* 2004 **48** (6) 555–563

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

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

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

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

6 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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