HSE
Health and Safety Executive

Aromatic carboxylic acid anhydrides in air

Laboratory method using glass fibre filter with sorbent back-up tube and liquid chromatography

MDHS62/2

Methods for the Determination of Hazardous Substances
Health and Safety Laboratory

Scope

1 This procedure describes a laboratory method for the determination of time-weighted average airborne concentrations of a range of aromatic carboxylic acid anhydrides (ACAs) such as phthalic anhydride (PA, CAS No. 85-45-9), trimellitic anhydride (TMA, CAS No. 55-30-7) and tertrachlorophthalic anhydride (TCPA, CAS No. 117-08-8).

Summary

2 A measured volume of air is drawn through a glass fibre filter and sorbent back-up tube in series (if required) to trap ACA with significant vapour pressure. The filter is desorbed in high performance liquid chromatography (HPLC) mobile phase. The sorbent tube is desorbed with acetone and, after evaporation, dissolved in HPLC mobile phase. Any ACAs are converted to the corresponding aromatic carboxylic acid (ACacid) in the mobile phase and analysed by HPLC with UV detection.

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 Air monitoring should be carried out as described in MDHS14[1] for inhalable particulate using an IOM sampler at 2 litres per minute. For ACA with significant vapour pressures a back-up tube can be placed in series after the filter but the sampling efficiency for inhalable particulate will be compromised if the flow rate of 2 litres per minute is not maintained.

Prerequisites

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

Safety

6 Users 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 IOM inhalable dust sampler or equivalent operated as described in MDHS14.[1]

8 Binder-free glass fibre filters (25 mm GF/A have been found to be suitable for the IOM sampler).

9 Two-section sorbent tube containing Tenax®, 20 mg and 10 mg front and back sections respectively. This can be connected in series to the outlet of the IOM sampler using a short piece of flexible tubing.

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

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

12 Flexible plastic tubing for making a leak-proof connection from the sampling train 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

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

14 Aromatic carboxylic acid anhydride (ACA).

15 Concentrated phosphoric acid (85% aqueous solution).

16 Acetonitrile: HPLC grade.

17 Water: HPLC grade.

18 Acetone.

19 Volumetric flasks, class A, complying with the requirements of BS EN ISO 1042.[3]

20 Piston operated micropipettes complying with the requirements of BS EN 8655-6.[4]

21 Solvent-resistant plastic syringe filters (2 µm pore size) for sample filtration before analysis.

22 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.

23 Wide-necked glass desorption vials capable of accepting 25 mm diameter filters without bending, about 10 ml capacity with PTFE lined screw caps.

24 HPLC mobile phase: Add 840 ml water to 150 ml acetonitrile in a screw-cap flask (1 litre) and mix thoroughly. Add slowly, with shaking, 10 ml of concentrated phosphoric acid and mix thoroughly.

25 HPLC system with UV-detector: Suitable operating conditions are listed below (these may need to be adjusted to achieve optimal separation of the ACAs from other components). The use of other columns and conditions are acceptable provided they have the accuracy and reliability appropriate to the application:

Column dimensions	250 mm x 8 mm ID
Column packing	7 micron Lichosorb RPB18
Mobile phase	15:1:84 acetonitrile/phosphoric acid/water
Flow rate	1.5 $ml.min^{-1}$
Injection volume	20 µl
UV detector	230 nm

Sampling

26 Sampling should be carried out in accordance with the procedures described in MDHS14.[1] Load a glass fibre filter into the filter head. Remove the ends of the sorbent tube before sampling and place in series, behind the filter head, using a short piece of flexible tubing. Draw a measured volume of air through the filter and sorbent tube. If necessary, use two or more consecutive samples to avoid overloading the sampler.

27 In some processes, only TMA is present. In this case, where circumstances suggest that only particulate TMA will be present, then the sorbent tube may be dispensed with.

28 After sampling remove the filter from the sampling head using clean flat-tipped tweezers, place in a labelled transport cassette for transfer to the laboratory. Sorbent tubes should be capped (if used) and transported with the filter cassettes.

29 With each batch of ten samples, submit at least two blank filters and sorbent tubes from the same lot. Subject these blanks to the same handling procedure as the samples, but draw no air through them.

Calibration

30 ACA stock solution (0.1 g per litre): Accurately weigh approximately 10 mg of ACA and transfer to a 100 ml volumetric flask with mobile phase and make up to the mark. Shake to mix.

31 Prepare at least five standards of ACA by serial dilution of the ACA stock solution.

32 Analyse each standard solution by HPLC in an identical manner to the samples and measure the peak area of the target compound. Plot the peak areas against the corresponding ACA concentration of the standard, in $\mu g.ml^{-1}$, and construct the line of best fit. The slope of this line is the detector response (R_F) of the ACA compound.

33 Modern HPLC equipment is usually sufficiently stable that a new calibration is not required with each set of samples. However, to verify the equipment, a quality assurance (QA) solution of known concentration, must be analysed with each set of samples.

Sample analysis

34 Analyse samples and blanks in an identical manner.

Desorption of filters

35 Remove sample and blank filters from sample tins with tweezers and place each flat in the bottom of a desorption vial.

36 Add 2 ml of HPLC mobile phase to each vial, ensuring that each filter is completely covered, and cap. Allow the vials to stand for at least 60 minutes.

37 Filter and transfer an aliquot of each sample to an HPLC vial for analysis.

Desorption of sorbent tubes

38 Position the tube vertically in a suitable stand, large sorbent section uppermost.

39 Add 4 ml of acetone drop wise to each tube and collect the eluate in a desorption vial. Add 0.2 ml of mobile phase to each vial, allow to stand for 60 minutes and then evaporate to dryness. Dissolve the residue in 0.5 ml mobile phase. The addition of mobile phase converts the ACA to ACacid and helps to reduce evaporative losses (particularly phthalic anhydride, if present).

40 Analyse the sample and blank solutions by HPLC in an identical manner to the standards.

41 Measure the peak area of the target compound and convert this peak area to an ACA concentration, in µg.ml-1, by dividing by the R_F value obtained from the calibration standards.

Calculation of results

42 Calculate the volume, VS, in litres, of each air sample using the procedure described in MDHS14.[1]

43 Calculate the airborne concentration of ACA, C, in $\mu g.m^{-3}$, using the equation:

$$C = (D \times (M_F - M_{FB})) + (D \times (M_T - M_{TB})) \times (1000 / V_S)$$

Where:

M_F = Concentration of ACA in sample filter, in $\mu g.ml^{-1}$

M_{FB} = Mean concentration of ACA in blank filters, in $\mu g.ml^{-1}$

M_T = Concentration of ACA in sample sorbent tube, in $\mu g.ml^{-1}$

M_{TB} = Mean concentration of ACA in blank sorbent tubes, in $\mu g.ml^{-1}$

D = Desorption volume, in ml (2 ml for filters; 0.5 ml for sorbent tubes)

Appendix: Additional information

Detection limit of the method

1 The qualitative and quantitative detection limits for ACA can be estimated from three times and ten times the standard deviation of the blank determinations respectively.

Overall uncertainty

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

Analytical recovery

3 Determine the analytical recovery of ACA from filters and sorbent tubes from the same batch as the samples by spiking six replicates of each with a solution of ACA in acetonitrile at appropriate target levels. Allow the filters to dry in air and pass a gentle steam of air through the sorbent tube for about 5 minutes to remove the acetonitrile before desorption.

4 The mean analytical recovery of TMA on 30 spiked filters over the range 0.81–81 µg was 95% (CV of 7%). The mean analytical recovery of PA loaded onto sorbent tubes was 91%.

Interferences

5 Any compound that co-elutes with the ACA (as ACacid); changing the composition of the mobile phase or changing the separating column may remove this interference. Resorcinol is a possible interference with TMA.

6 The method does not distinguish between ACA and ACacid. Possible conversion of ACA to ACacid may occur in the ambient air prior to the ACA being sampled.

Stability

7 The desorbed solutions are stable for at least 30 days, so that the vials may be left to stand for longer than 60 min if convenient.

8 Spiking solutions in acetonitrile used for recovery determinations are stable at room temperature for at least 80 days when stored in the refrigerator.

References

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

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

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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