MDHS 63/2

Methods for the Determination of
Hazardous Substances
Health and Safety Laboratory

HSE

1,3-Butadiene in air

Laboratory method using diffusive samplers, thermal desorption and gas chromatography

February 2005

INTRODUCTION

Note: This method updates and replaces MDHS63 (ISBN 0 11 885950 1, June 1989). The principal changes are (a) to restrict the maximum diffusive sampling time to 10 hours when using Molecular Sieve 13X sorbent; (b) to add validation data for Molecular Sieve 13X; (c) to add uptake rate data for graphitised carbon sorbents.

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health Regulations 2002 (COSHH)[1] are designed to ensure that the exposure of people at work to substances which could damage their health is either prevented or, where that is not reasonably practicable, adequately controlled. Employers are required to make an assessment of the health risk created by such work, and to prevent or control exposure to the substances involved. The COSHH Regulations also require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers must ensure that their responsibilities under the COSHH Regulations are fulfilled before allowing employees to undertake any procedure described in this MDHS.

2 Guidance is given in *Control of substances hazardous to health. The Control of Substances Hazardous to Health Regulations 2002. Approved Code of Practice and guidance* which includes the COSHH Regulations.[2]

Properties and uses

3 1,3-Butadiene, CAS Number 106-99-0, synonym buta-1,3-diene, CH2=CHCH=CH2, is a colourless gas of boiling point -4°C. The liquefied gas has a vapour pressure of 245 kPa at 21°C. 1,3-Butadiene has a characteristic aromatic odour. It is extremely flammable (flash point -76°C; explosive limits approx. 2-11.5% v/v in air).

4 It is produced mainly by dehydrogenation of n-butenes or by thermal cracking of light oil or naphtha. Its principal use is in the manufacture of synthetic rubbers, often in combination with styrene or acrylonitrile. It is a starting material for many organic syntheses.

Health effects

5 1,3-Butadiene is of low acute toxicity following single inhalation exposure. Irritation of the eyes, nose, mouth and respiratory tract occurs at very high concentrations. Animal studies indicate that epoxide metabolites may be genotoxic. 1,3-Butadiene should be regarded as a potential human carcinogen (EU category 2).

Health and safety precautions

6 Prevention and control of exposure, emergency procedures and health surveillance are described more fully in HSE publications on COSHH.[1-4]

7 Under the Chemical Hazard and Packaging (CHIP) Regulations,[5] 1,3-butadiene has been assigned the R-phrases and S-phrases:

R12	Extremely flammable;
R45	May cause cancer;
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible);
S53	Avoid exposure - obtain special instructions before use.

8 Following massive exposure, the patient should be removed to a clean atmosphere, and artificial respiration given if respiration has ceased. Contaminated clothing should be removed. Washouts with cold running water are required after splashes of the liquefied gas in the eye or on the skin. Medical attention should be sought and, if the patient is sent to hospital, it is recommended that the appropriate note on treatment in the series Exposure to Gases and Vapours, published by the Chemical Industry Association Ltd, should be transmitted with the patient (noting that exposure has been to butadiene). For butadiene this is Label 21 in the series.

Exposure limits

9 The COSHH Regulations lay down the requirements for using maximum exposure limits (MELs) and occupational exposure standards (OESs) for achieving adequate control of worker exposure. The critical health effects for the purpose of setting an exposure limit for 1,3-butadiene are mutagenicity and carcinogenicity. Further information is available in *Summary criteria for occupational exposure limits*, EH64/C7.[6]

10 For 1,3-butadiene, the Health and Safety Commission has approved a MEL of 10 ppm (22 mg/m^3), 8-hour time-weighted average. MELs are published in EH40 Table 1.[7]

Analytical methods

11 This is not a 'reference' method in the strict analytical sense of the word. There are alternative methods available for the determination of 1,3-butadiene.[8] The use of methods not included in the MDHS series is acceptable, provided they have been shown to have the accuracy and reliability appropriate to the application.

PRINCIPLE

12 Diffusive samplers consist of a sorbent separated from ambient air by a diffusion resistance, commonly a controlled air gap and draught shield. In this method a tube-type sampler is used. The sampler is exposed to air for a measured time period. Sampling rates are determined by prior exposure in a standard test atmosphere, or they may be determined by laboratory or field comparisons with a reference method. 1,3-Butadiene migrates into the sampler by diffusion and is collected on the sorbent. The adsorbed butadiene is desorbed by heat in thermal desorption (TD) apparatus and is transferred by inert carrier gas into a gas chromatograph (GC) equipped with either flame ionization (FID) or mass spectrometer (MS) detection.

SCOPE

13 The method described is for the determination of time-weighted average concentrations of butadiene gas in workplace atmospheres and can be used for the determination of personal exposure or for fixed location monitoring.

14 The method is suitable for sampling over periods in the range 30 min to 8 h and concentrations in the range 0.6 to 100 mg/m^3 (about 0.3 to 50 ppm). It complies with the European performance standards EN 838:1995[13] and EN 482:1994[14] for workplace measurements, when using the zeolite Molecular Sieve 13X as sorbent. Measurement of concentrations lower than 0.6 mg/m^3 is feasible, subject to the limitation on long sampling times in paragraph 15. Certain types of graphitised carbon black may also be suitable. Graphitised carbon blacks with specific surface areas reported less than 200 m^2/g, such as Carbopack B and Carbotrap, are not recommended, due to lack of sorption capacity. Graphitised carbon black sorbents, such as Carbopack X or Carbograph 5-TD, may be suitable and, based on its performance in more limited tests than those required in the full standards, Carbopack X may also comply with EN 838[13] and EN 482.[14] Carbon molecular sieves such as Carboxen 1003, Carboxen 569 and Carbosieve SIII are not recommended for butadiene, due to losses that occur in storage.[21]

15 The method with Molecular Sieve 13X sorbent has not been validated for measuring very low ambient butadiene concentrations in the range 0.1 to 3 μg/m.[3] The use of sampling periods longer than 10 hr to achieve greater sensitivity, is not normally recommended with Molecular Sieve 13X. A silicone membrane in the diffusion cap cannot prevent excessive water adsorption over very long sampling periods. Water, if present in sufficient quantity, may change the effective split-ratio of a TD-GC interface. However, the magnitude of the water problem depends on the type of interface and GC column. Some older types of thermal desorber, coupled to a packed column with a splitless interface, are less affected by adsorbed water. Certain types of proprietary graphitised carbon blacks, such as Carbopack X or Carbograph 5-TD, have a lower water uptake than Molecular Sieve 13X and may be suitable for sampling times longer than 10 h.

16 The upper limit of the useful range is determined by the sorption capacity of sorbent, the split-ratio of the TD-GC interface and the linear range of the GC detector.

17 The lower limit of the useful range depends on detector noise, the split-ratio of the TD-GC interface and on blank analyte levels in the sorbent tube. If the blank level is less than 1 ng butadiene, the limit of quantification is about 0.6 mg/m^3 (0.3 ppm) for 30 min and about 0.04 mg/m^3 (0.02 ppm) for 8 h sampling.

18 HSE guidance HSG173 advises employers about how they should conduct investigations into the nature, extent and control of substances hazardous to health which are present in workplace air.[9] The objective of air monitoring is usually to determine worker exposure and therefore the procedure described in this method is primarily for personal sampling in the breathing zone. It may also be used for background or fixed location monitoring. Sampling times shorter than 30 min might be feasible. Where the instantaneous concentration value is fluctuating, measurement of mean concentration is valid, provided the total sampling time exceeds the time constant of the sampler by an adequate margin. For the Perkin-Elmer type sampler described in this method, the lower limit is about 15 min, although 30 min is usually the shortest time used in validation studies. Alternative on-site procedures, such as portable gas chromatography, infra-red spectrophotometry or a total organic analyser, may be used to monitor rapidly changing concentrations.

19 Over the range specified in paragraph 14, the mean uptake rate, or calibration factor, with Molecular Sieve 13X sorbent has been found to be 0.58 cm^3/min or 1.31 ng/ppm/min when the sampler is fitted with a silicone membrane diffusion cap. It does not vary significantly with the time of exposure or with exposure concentration. Samplers without silicone membranes should not be used for this application as they may be adversely affected by high ambient humidity.

20 A full validation for butadiene at workplace concentrations on graphitised carbon sorbents has not been carried out. Over a range of exposure similar to that specified in paragraph 14, one study reported that the uptake rate on Carbopack X sorbent did not vary significantly with the sampling time, concentration or relative humidity.[23] In a laboratory intercomparison over a more restricted range of 1.2 ppm for 2 hours the mean uptake on Carbopack X was found to be 0.59 cm^3/min or 1.33 ng/ppm/min.[25] Ambient or environmental sampling of butadiene is outside the scope of this method and full validation data are not reported here. However, for a sampling period of one week at ambient concentrations in the range 0.1 µg/m^3 to 3 µg/m^3, the mean uptake rate, or calibration factor, with Carbopack X sorbent is reported provisionally by one source as 0.53 cm^3/min or 1.19 ng/ppm/min.[23] Another source has reported butadiene uptake rates on Carbopack X for one-week and two-week sampling as 1.24 ng/ppm/min and 1.02 ng/ppm/min respectively, expressed as the mean of about 35 measurements for each exposure time, over a concentration range of 0.5 µg/m3 to 3 µg/m^3.[24] The difference between one week uptake rates reported by these two sources is not significant.

21 The mean uptake rate with Carbograph 5-TD sorbent has not been evaluated for workplace sampling. Carbograph 5-TD is a graphitised carbon black said to be similar to Carbopack X.

REAGENTS

Butadiene

22 This is obtainable either as pressurised pure liquefied gas or certified mixture in a cylinder or lecture bottle.

APPARATUS

Molecular Sieve 13X

23 Molecular Sieve 13X, particle size of 0.18-0.25 mm (60-80 mesh), is one option for the sampling tubes. This sorbent should be preconditioned by heating in an inert atmosphere for at least 4 h at 300°C or 16 h at 250°C before packing the tubes. Due to the presence of up to 25% water in untreated zeolites, the use of analytical thermal desorber apparatus is not normally recommended for conditioning packed tubes. Liquid water may condense in valves and traps designed to protect valves from contamination. For conditioning Molecular Sieve 13X packed tubes, use only apparatus that vents water to air without intermediate valves and traps. Examine the bulk sorbent before packing. If there is evidence of ‘fines’ due to mechanical damage, use an appropriate sieve to remove them. Tubes pre-packed to customer specification are available commercially from some sources.

Graphitised carbon blacks

24 Alternatively, Carbopack X or Carbograph 5-TD is used for the sampling tubes. These sorbents do not normally require preconditioning before packing. The bulk sorbent should be supplied in a granular form specified for thermal desorption and it should not be necessary to remove ‘fines’ before packing. Packed tubes may be conditioned before use by heating for at least 4 h at 300°C in a stream of inert gas. Tubes pre-packed to customer specification are available commercially from some sources.

Sorbent tubes

25 Tubes should be compatible with the thermal desorption apparatus to be used. Typically, but not exclusively, they are constructed of stainless steel tubing, 6.4 mm (1/4″ inch) OD, 5.0 mm ID and 89 mm long. Tubes of other dimensions may be used but the uptake rates in paragraphs 19-20 are based on these dimensions. One end of the tube is marked, for example, by a scored ring about 10 mm from the end. The tubes are packed with preconditioned sorbent so that the sorbent is retained within the desorber heated zone. The critical air gap is defined by the distance between an internal stainless steel gauze retaining the sorbent and the end of the tube. Before packing, check that the internal gauze is firmly in position, seated flat and that the air gap meets the intended specification. For the Perkin-Elmer type tube this is 14.0-14.6 mm (without diffusion cap fitted).

26 A suggested packing procedure is to attach a small polythene funnel and pre-weigh an empty tube in a small beaker. Weigh in typically 500-800 mg Molecular Sieve 13X or 300-400 mg Carbopack X or Carbograph 5-TD. Tap the tube gently on a hard surface to settle the particles and press in a glass-wool plug and retaining gauze. Gauze loading rigs capable of applying controlled pressure to the retaining gauze are commercially available. In the absence of a loading rig, use light pressure and a metal rod about 4 mm in diameter, for example a sawn-off screwdriver which has been thoroughly solvent degreased and dried. Do not use excessive force or the retaining gauze at the air gap end may be dislodged. Check for this by tapping a freshly packed tube on a hard surface, when no sorbent particles should fall out.

End-caps

27 Two types of end-cap should be available. One type, used for sealing the tubes when stored, is a closed metal end-cap with PTFE ferrule, eg Swagelok™. End-caps made from solid PTFE with Viton™ O-rings are acceptable for up to three days after sampling (Table 1), but are not recommended for extended storage. The second type, the diffusive end-cap, allows ingress of vapour through a metal gauze backed by a silicone membrane, the size of the opening being the same as the internal cross-section of the tube.

Thermal desorber

28 Apparatus for the thermal desorption of the sorbent tubes and transfer of the desorbed vapours via an inert gas flow into a gas chromatograph will be required. A typical apparatus contains a mechanism for holding the tubes to be desorbed while they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time are adjustable, as is the carrier gas flow rate. The desorbed sample, contained in the purge

gas, is routed to the gas chromatograph via a heated transfer line. Some types of apparatus incorporate additional features, such as automatic sample tube loading, leak-testing and a secondary cold-trap. It is advisable to have some means of controlling the proportion of sample reaching the gas chromatograph inlet (split-ratio). It should be possible, within limits, to control the split-ratio independently of the primary desorption flow. The thermal desorber apparatus must be capable of heating the sample tube to at least 265°C in the primary desorption step (for Molecular Sieve 13X).

Gas chromatograph

29 A gas chromatograph fitted with FID or MS detection is suitable.

30 A wide range of chromatographic columns may be used for this analysis. The choice will depend largely on which compounds are present, if any, that might interfere in the analysis. Polar packed GC columns have been used with some older or home-made thermal desorbers. Examples of packed columns used previously are 30% isodecyl phthalate on Chromosorb™ W and 0.19% picric acid on Carbopack C. Some examples of suitable capillary column phases are:

- thick-film methylsilicone at low or sub-ambient temperature;
- Porous Layer Open Tubular (PLOT) KCL-Al_2O_3;
- GS-GasPro™ PLOT (J&W/Agilent proprietary phase).

Thick-film methylsilicone capillary columns may require sub-ambient operation for adequate resolution of interfering C_4 hydrocarbons. PLOT capillary columns do not normally require sub-ambient operation for resolution of C_4 hydrocarbons. Retention times on KCl-Al_2O_3 PLOT columns are affected by water in the samples. The problem can be circumvented by adding a backflushable pre-column,[10] although this is difficult to manage with conventional automated thermal desorbers. A recent study of the effect of water on butadiene recovery used the GS-GasPro PLOT column.[11] Retention times of C_4 hydrocarbons on GS-GasPro were not significantly affected by water.

Injection unit for preparing calibration standards

31 A 1/4″ packed GC column injector may be used, either in situ, or mounted separately. The purge gas line to the injector should be retained. If no spare commercial injector is available then a septum holder could be fabricated and attached to metal or glass tubing capable of accommodating the 1/4″ calibration tube and a purge gas line. One end must be threaded to take a compression fitting with ferrule or O-ring that will secure the calibration tube during spiking. The injection facility must allow 'on-column' injection, ie the syringe needle must penetrate inside the calibration tube to at least the depth of the fixed gauze (if fitted), but by design the calibration tube must not be permitted to press against the rubber septum, otherwise the purge gas flow may be restricted. The injection unit does not have to be heated. Suitable injection units are also available commercially.

Gas-tight syringe

32 Gas-tight syringes are required for injecting butadiene gas onto the calibration tubes. These are available typically with PTFE-tipped plungers and push button valves. Syringes must be in good condition and free of PTFE flakes and particles capable of blocking the valve or needle. This is particularly important for syringes of 100 µL capacity or less.

PROCEDURE

Sorbent tubes

33 Prior to use, these should be conditioned for at least 16 h at 250°C or at least 4 h at 300°C under inert carrier gas. When conditioning Molecular Sieve 13X, use only apparatus venting to direct air without intermediate valves and traps; analytical thermal desorbers are not recommended if vented water vapour must pass through valves and traps (paragraph 23). Tubes should then be analysed to ensure that the thermal desorption blank is acceptable for the intended application. If the blank is unacceptable, the tubes should be reconditioned. Before Molecular Sieve 13X tubes are reused for sampling it is recommended that a full thermal conditioning be carried out as described. The primary thermal desorption step in the analysis is not guaranteed to remove all water adsorbed by Molecular Sieve 13X in sampling. It is also advisable to check the thermal desorption blank if the tubes are left for an extended period before use. For long-term storage of conditioned tubes use metal end-caps and PTFE compression fittings (ferrules), rather than press-fit end-caps with Viton O-rings.

Collection of samples

34 Immediately before sampling, remove the end-cap from the marked end of the sample tube and replace it with the diffusion cap (Molecular Sieve 13X tubes should be fitted with the silicone membrane version of the diffusion cap). The diffusion cap is usually a tight fit. Use a twisting motion to make sure it is properly seated, otherwise the air gap will be larger than the value specified.

35 When used for personal sampling the tube should be mounted in the worker's breathing zone, for example on the lapel. The orientation of the tube is not critical; however, if outdoors or otherwise exposed to rain, expose the tube with the diffusion cap downwards. When used for fixed location monitoring, a suitable sampling site is chosen. In either case the diffusion cap should be freely open to the sampled atmosphere, ie it should not be obscured by clothing or other objects.

36 At the end of the measured exposure time, remove the diffusion cap and replace the metal storage cap. Make sure that the PTFE ferrules of the metal cap are fully home on the tube before tightening. Note the unique identification number of the tube. If the sample is not to be

analysed immediately, store in a clean area away from source contamination. If it is not practicable to remove the tubes from source contamination immediately after sampling then they should be placed in clean, uncoated sealed metal or glass containers. Marker pens and adhesives containing solvents should not be used to label the tubes or any containers for storing the tubes. Do not keep sample tubes in ambient temperatures above 30°C for more than 1-2 days. Remove to an area not exceeding 20°C and preferably below 5°C as soon as possible, but it is not necessary to store sample tubes in a freezer.

37 Field blanks should be prepared by using tubes identical to those used for sampling and subjecting them to the same handling procedure as the sample tubes, except for the actual period of sampling. Label these as blanks.

38 When interfering compounds are known or suspected to be present in the air, the identity of the compounds should be transmitted with the sample. If possible, potential interferences for a given situation should be checked before routine monitoring is carried out.

Preparation of standard ‘spiked’ calibration standards

39 Calibration standards are preferably prepared by loading required amounts of butadiene on the sorbent tubes from standard atmospheres using calibrated sampling pumps, or by metering known volumes from a certified gas mixture, as this procedure most closely resembles the practical sampling situation. If this is not practicable, standards may be prepared by a gas syringe spiking procedure, provided that the accuracy of the spiking technique is established by using procedures giving spiking levels traceable to primary standards of mass and/or volume, or it is confirmed with reference materials, if available, or with results of reference measurement procedures.

40 In the gas syringe spiking procedure, pure butadiene gas is obtained from a cylinder or lecture bottle by cautiously releasing some gas into an evacuated plastic bag fitted with a septum and flushing with gas two or three times. Alternatively, release some gas through a length of flexible silicone tubing (in a fume hood and away from sources of ignition), again making sure the tubing is adequately flushed with gas. Samples are then taken with a gas-tight syringe, either through the septum of the bag or wall of the silicone tubing. These samples will be used to load sorbent tubes with known volumes of butadiene, the mass of which can be calculated.

41 Standard ‘spiked’ calibration tubes are prepared by injecting known amounts of butadiene gas onto clean sorbent tubes as follows. A sorbent tube is fitted into the injection unit (paragraph 31) through which inert purge gas is flowing at 50-100 mL/min. Pure butadiene gas, or a mixture of known composition, is injected through the septum using a gas-tight syringe (paragraph 32). After purging for 1 min the tube is disconnected and sealed. Prepare at least three standards at each loading level. Prepare fresh standards with each batch of samples. The experimental vapour density of pure butadiene gas at 0°C and 101.3 kPa pressure is 2.476 mg/mL.[12] 10 µL butadiene at 25°C is equivalent to 22.7 µg which represents the uptake of 8 h diffusive sampling at 36 ppm.

Analysis

42 The sorbent tube is placed in a compatible TD apparatus. Air is purged from the tube to avoid chromatographic artefacts arising from the thermal oxidation of sorbed gases and vapours. The tube is then heated to displace the adsorbed compounds which are passed to the GC by means of a carrier gas stream. Generally the gas flow at this stage is the reverse of that used during sampling, ie the backflush direction. In the special case of butadiene on Molecular Sieve 13X it is recommended that the forward flush direction be used in the primary desorption step. The sampling recommendations (paragraph 14) restrict the mass of adsorbed water within acceptable limits, but desorption in the forward flush direction, while not essential, reduces accumulation of water in the TD-GC system still further. Note that higher boiling materials are not removed in this procedure and the desorbed Molecular Sieve 13X tubes must be conditioned in a separate apparatus before reuse (paragraph 23).

43 The desorbed gas sample occupies a volume of several mL and may need to be concentrated if good chromatographic peak shape and resolution are to be obtained. This may be achieved by using a secondary cold trap external to the GC. Alternatively, the desorbed sample can be passed directly to the GC where it is concentrated by holding the column initially at a low temperature, typically about 10°C.

44 Desorption conditions should be chosen such that desorption from the sample tube is complete and no sample loss occurs in the secondary trap, if fitted. Typical parameters for the Perkin-Elmer ATD-400 are:

Desorb temperature	265°C (Mol Sieve 13X); 150°C (Carbopack X, Carbograph 5-TD)
Desorb time	10 min
Desorb flow	20 ml/min helium
Split ratio	30:1
Valve/Transfer line	225°C
Cold trap low	-30°C
Cold trap high	300°C
Cold trap sorbent	Tenax GR (70 mg) or Carbopack B/CMS dual-bed
Cold trap configuration	backflush

Cold traps tested with ozone precursor hydrocarbons, and equivalent to Carbopack B/carbon molecular sieve, are commercially available pre-packed.

45 Set up the GC for the analysis of butadiene. A variety of chromatographic columns may be used (paragraph 30). A suitable choice might be a 60 m x 0.32 mm GS-GasPro capillary column (J&W/Agilent). Typical operating conditions for this column are:

Carrier gas	helium at 140 kPa
Temperature programme	90°C for 4 min, 4°C/min to 250°C
Detector	flame ionization

46 The elution order of some C2-C6 hydrocarbons on GS-GasPro under the specified operating conditions is given in Table 1.

Table 1 Elution order of some C2-C6 hydrocarbons on GS-GasPro, operated as specified in paragraph 45

Compound	**Retention time - min**
Ethane	8.1
Propane	10.0
Isobutane	13.8
n-Butane	14.6
1-Butene	18.0
1,3-Butadiene	19.0
trans-2-Butene	19.3
Isobutylene (2-methylpropene)	19.3
cis-2-Butene	19.9
n-Pentane	21.5
1-Butyne (ethylacetylene)	25.7
n-Hexane	28.0

47 Correspondence of retention time on a single column should not be regarded as proof of identity.

Calibration

48 Analyse each calibration standard tube by TD-GC. Prepare a calibration graph by plotting the $_{10}$logarithm of the areas of the butadiene peaks, corrected for blank levels, on the vertical scale, against the $_{10}$logarithm of the mass of butadiene loaded on the tube.

Determination of sample concentration

49 Analyse the samples and blanks as described for the calibration standards. Determine the peak response and read from the calibration graph the mass of the analyte in the desorbed sample. The sorbent tube blank level for butadiene is acceptable for workplace sampling if less than 5 ng. Typical levels on Molecular Sieve 13X and Carbopack X are much less than this.

Determination of desorption efficiency

50 Ideally, the efficiency of desorption should be checked by injecting known amounts of butadiene directly onto the secondary trap of the TD apparatus (or directly onto the GC column) and comparing a calibration graph with one prepared from loaded calibration tubes. The desorption efficiency is the response of a calibration standard divided by the corresponding response from a direct injection. If the desorption efficiency is less than 95%, change the desorption parameters accordingly. In practice, the equivalence of the two methods is unlikely to be achieved unless the TD-GC interface is splitless and mass flow-controlled, as in some older types of apparatus with packed columns.

51 Where the TD apparatus does not have a direct injection facility, desorption efficiency of butadiene could be estimated by an indirect method, using n-pentane as an internal standard. It is assumed for the purpose of this test that the desorption efficiency of n-pentane is 100%. One method might be to measure the GC detector response factor of butadiene, relative to n-pentane, by 'spiking' a series of butadiene/pentane mixtures on tubes packed with an alternative carbon sorbent, such as the Air Toxics™ dual-bed tube, then comparing relative response factors obtained by spiking the sample tubes with the same butadiene/pentane mixtures.

Calibration of uptake rate

52 The uptake rates for Molecular Sieve 13X given in paragraph 19 are for tubes specified in paragraph 25, fitted with silicone membrane diffusion caps. The uptake rates for Carbopack X given in paragraph 20 are for tubes specified in paragraph 25, fitted with diffusion caps without a silicone membrane. For other tube specifications it may be necessary to follow the protocol[13] to determine the uptake rate and the range of applicability.

CALCULATION OF RESULTS

Mass concentration of analyte

53 Calculate the mass, in µg, of butadiene in the sample by using the calibration graph prepared for the standard solutions. Also calculate the mass of butadiene in the blank samplers.

Then:

$$\text{Concentration of butadiene in air (mg/m}^3\text{)} = \frac{1000\,(m - m_{blank})}{U \times t}$$

where

m = mass (µg) of butadiene on sample tube;
m_{blank} = mass (µg) of butadiene on blank tube;
U = uptake rate (cm^3 /min);
t = exposure time (min).

Note: If it is desired to express concentrations reduced to specified conditions, eg 25°C and 101 kPa, then:

$$C_{corr} = C \times \frac{101}{P} \times \frac{T}{298}$$

Where:

C = the concentration (mg/m^3) at sampling conditions P, T;
P = the actual pressure of the air sampled, in kPa;
T = actual temperature of the air sampled, in Kelvin.

Volume concentration of analyte

54 Alternatively, the concentration of butadiene in the sampled air may be expressed in ppm.

$$\text{Concentration of butadiene in air (ppm)} = \frac{1000\,(m - m_{blank})}{U' \times t}$$

where U' = uptake rate (ng/ppm/min)

55 Uptake rates in cm^3 /min and ng/ppm/min are related by:

$$\underset{(cm^3/min)}{U} = \underset{(ng/ppm/min)}{U'} \times \frac{24.5}{54.1} \times \frac{T}{298} \times \frac{101}{P}$$

where

24.5 = molar volume (litres) at 298K and 101 kPa;
54.1 = molecular weight of butadiene;
T = temperature of sampled air in Kelvin;
P = pressure of sampled air in kPa.

Note that the current definitions of U (SI unit cm^3/min) and U' (derived unit ng/ppm/min) comply with ISO and CEN practice. Some earlier MDHS methods defined U as ng/ppm/min and U' as cm^3/min.

METHOD PERFORMANCE

Overall uncertainty

56 The overall uncertainty for a measuring procedure is defined in BS EN 482[14] as ‘the quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure’, and is quoted as a percentage combining bias and precision using the following equation where:

$$\text{Overall uncertainty} = \frac{|\bar{x} - x_{ref}| + 2s}{x_{ref}} \times 100$$

$\bar{x}$ = the mean value of results of a number n of repeated measurements;
x_{ref} = the true or accepted reference value of concentration;
s = the standard deviation of measurements.

At the time of publication BS EN 482 is under revision. The concept of **overall uncertainty** will be replaced by **combined expanded uncertainty**, where bias (systematic error) with respect to the true value is corrected if known. If bias is unknown it is estimated and treated in the same way as any random error component, but in practice the numerical performance requirements of the standard are unchanged. The performance requirements quoted in BS EN 482 for overall uncertainty, where the task is 'measurement for comparison with limit values', are $\leq$50% for samples in the range 0.1 to 0.5 LV and $\leq$30% for samples in the range 0.5 to 2.0 LV (LV = Limit Value).

57 The method performance standard BS EN 838[13] recommends that, in thermal desorption, desorption efficiency be at least 95% initially and at least 90% after two weeks’ storage. Table 1 shows recovery data from two independent studies of butadiene spiked on Molecular Sieve 13X. The sample tubes were stainless steel, sealed with Swagelok caps and PTFE ferrules.

58 The method has been examined following a diffusive sampler evaluation protocol,[13] using a Perkin-Elmer diffusive tube containing Molecular Sieve 13X sorbent and a silicone membrane in the diffusion cap.[15,16] The results of this evaluation are summarised in paragraphs 59-65. Different uptake rates may be given by other makes of diffusive tube, or if a silicone membrane is not employed, or if a different sorbent is used, but the general performance of other systems is expected to be similar to that described here.

59 The variation of uptake rate (mean value, 0.58 cm^3/min or 1.31 ng/ppm/min) determined in separate multiple experiments with Molecular Sieve 13X was 15% expressed as a relative standard deviation. Within the ranges tested (1-50 ppm, 0.5-8 hours) the concentration and time dependence of the uptake rate were not significant compared to the overall error. Since the method is unbiased (paragraphs 63-64) the overall uncertainty is 30%, and meets the requirements of BS EN 482 over the range 0.1-2 LV (paragraph 56). No additional error is implied by the field experiments with Molecular Sieve 13X (paragraphs 63-64).

60 The uptake rate of the sampler is not significantly affected by ambient air movement, provided a minimum of about 0.01 m/s is maintained.

61 The temperature-dependence of mass uptake is expected to be small (+0.2% per °C increase in ambient temperature), if non-ideal sorption effects are ignored.

62 An accelerated Molecular Sieve 13X storage test at 40°C for 10 days[11] showed significant losses of butadiene if the tubes were purged with pure oxygen at the start of the test. No significant losses were observed after purging tubes with air or nitrogen and storing at 40°C for 10 days. About 20% butadiene was lost in 7 days at 20°C when PTFE analysis caps (Perkin-Elmer ATD-400) were used for storage. If using the PTFE analysis caps for temporary storage in place of metal Swagelok, no more than 3 days should elapse between sampling and analysis.[11] Another study reported that when Molecular Sieve 13X was loaded with 90-180 µg butadiene, recovery was as low as 60%. Since back-diffusion was measured and found to be negligible it was concluded that at very high loadings partial polymerisation might occur on the sorbent.[17] In diffusive sampling these loadings are equivalent to more than 150 ppm butadiene for 8 h. There is no evidence of a similar effect at the lower levels appropriate to monitoring compliance at around the MEL. Storage stability data for Molecular Sieve 13X are summarised in Table 2.

Table 2 Butadiene storage tests: % recovery from spiked Molecular Sieve 13X tubes sealed with Perkin-Elmer PTFE or Swagelok end-caps (± s d, n = 6)

Storage end-cap	Amount µg	Temp °C	Storage time - days 0	3	7	14	28	Refs
PTFE	4.0	20	100 ± 4	93 ± 3	77 ± 10	-	-	11
Swagelok	1.3	4	100 ± 4	-	-	95 ± 3	96 ± 4	11
Swagelok	1.3	20	100 ± 4	-	-	96 ± 10	95 ± 4	11
Swagelok	6.7	4	100 ± 1	-	-	97 ± 4	95 ± 5	11
Swagelok	6.7	20	100 ± 1	-	-	102 ± 3	97 ± 2	11
Swagelok	38	4	100 ± 6	-	102 ± 10	-	-	16

63 In a field evaluation,[15] in which paired sets of diffusive samplers and pumped Molecular Sieve 13X tubes were exposed simultaneously on the lapels of people at work, the following results were obtained on plotting log-transformed data:

y = diffusive sampler result (log ppm);

x = pumped tube result (log ppm);

Slope ± standard error = 0.937 ± 0.083;

Intercept ± standard error = -0.065 ± 0.042;

Correlation coefficient = 0.937;

Range of exposure concentration = 0.2 - 18 ppm.

A value of 1 is included in the 95% confidence limits of the slope; a value of 0 is included in the 95% confidence limits of the intercept, indicating that there is no significant difference between the results given by the two methods.

64 The results of the field evaluation of Molecular Sieve 13X have also been examined by a paired t-test. For the 24 comparisons, the distribution of (y-x) has mean 0.35 and standard deviation 1.6. The t-test indicates that this mean is not significantly different from zero, ie it indicates that there is no significant difference between the results given by the two methods. The tests described here are designed to demonstrate whether or not, on average, the diffusive results are unbiased, relative to the pumped sampler results, within the random errors associated with the methods. Estimates of the random error of each individual method cannot be obtained directly from these experiments (since both methods are subject to error) but are given in the next paragraph.

65 In a static sampling exercise involving replicates of seven Molecular Sieve 13X samplers of each type (three sets in all), the diffusive sampler and pumped sampler results were very similar.[15] The mean coefficient of variation of the pumped results was 20% and that of the diffusive results was 16%.

66 Full validation data, including both laboratory and field comparisons, are only available for Molecular Sieve 13X sorbent. More limited studies of diffusive uptake rates and storage stability have been carried out on the carbon sorbent Carbopack X [21-23] and of storage stability on Carbograph 5-TD.[22] Storage stability data for Carbopack X and Carbograph 5-TD are summarised in Tables 3 and 4. An uptake rate on Carbopack X has been determined over a period of two hours at 1.2 ppm (0.59 cm^3/min or 1.33 mg/ppm/min).[25] The provisional uptake rate on Carbopack X determined in another study was not significantly affected by exposure times of 0.5-8 hours or humidity over the range 20-80% RH.[23]

Table 3 Butadiene storage tests: % recovery from spiked Carbopack X tubes sealed with Swagelok caps (± s d, n = 5)

Amount µg	Temp °C	Storage time - days 0	7	14	Refs
0.005	20	-	95 ± 3	-	21
0.4	4	100 ± 4	-	101 ± 5	22
0.4	20	100 ± 4	-	96 ± 3	22
8.0	4	100 ± 4	-	101 ± 3	22
8.0	20	100 ± 4	-	100 ± 10	22

Table 4 Butadiene storage tests: % recovery from spiked Carbograph 5-TD tubes sealed with Swagelok caps (± s d, n = 6)

Amount µg	Temp °C	Storage time - days 0	7	14	Refs
0.4	20	100 ± 4	-	92 ± 4	22
8.0	20	100 ± 2	-	99 ± 5	22

67 Precision and related terms: repeatability, reproducibility, relative standard deviation and bias are defined in ISO 5725-1[18] or IUPAC.[19]

Interferences

68 Any compound that co-elutes with butadiene at the operating conditions chosen by the analyst is a potential interferent; changing the polarity of the GC column stationary phase or use of a mass selective detector may remove this interference.

QUALITY CONTROL MEASURES

69 An appropriate level of quality control should be employed when using this method. Analytical quality

requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assurance schemes are described in MDHS71.[20]

70 It is strongly recommended that all laboratories undertaking the determination of hazardous substances in workplace air should participate in an external quality assurance scheme such as HSE's Workplace Analysis Scheme for Proficiency (WASP). Details of WASP are available from the HSL website at http://www.hsl.gov.uk/proficiency-testing/index.htm.

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ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN, UK, Tel: 01298 218000 Fax: 01298 218986; e-mail: hslinfo@hsl.gov.uk

The Health and Safety Executive wishes, where possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

APPENDIX 1: RECOMMENDATIONS FOR THE TEST REPORT

It is recommended that the test report should include the following information:

(a) a complete identification of the sample, including the date and place of sampling;

(b) reference to this MDHS and a description of any deviation from the procedures described;

(c) the type and size of sample tube used;

(d) the duration of the sampling time in minutes and/or the time at the start and the end of the sampling period;

(e) the time-weighted average concentration found in the air sample, in milligrams per cubic metre or parts per million;

(f) the overall uncertainty;

(g) the mean temperature and pressure during the sampling period, if appropriate (paragraphs 53 and 61);

(h) the name of the person who collected the sample;

(i) the name of the analyst;

(j) the date of the analysis;

(k) any unusual features noted during the determination.

Note: If necessary data (eg the duration of the sampling time) are not available to the laboratory for the above calculations to be carried out, the test report may contain the result in micrograms of butadiene per sample.

APPENDIX 2: DESCRIPTION OF SORBENT TYPES

Molecular Sieve 13X	sodium aluminosilicate zeolite
Carbopack X	graphitised carbon black
Carbograph 5-TD	graphitised carbon black
Carbopack B	graphitised carbon black
Carbotrap	graphitised carbon black
Air Toxics dual-bed	graphitised carbon black + carbon molecular sieve
Carboxen 1003	carbon molecular sieve
Carboxen 569	carbon molecular sieve
Carbosieve SIII	carbon molecular sieve

Carbopack™, Carbosieve™, Carbotrap™ and Carboxen™ are trade marks of Sigma-Aldrich (Supelco). Carbograph™ is a trade mark of Alltech Associates.

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