MDHS

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

HSE
Health & Safety Executive

53/2

1,3-Butadiene in air

Laboratory method using pumped samplers, thermal desorption and gas chromatography

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INTRODUCTION

Note: This method updates and replaces MDHS 53 (ISBN 0 11 885643 X, produced in January 1992). The principal changes are (i) to recommend a drying pre-filter when using Molecular Sieve 13X sorbent; (ii) to add new validation data for Molecular Sieve 13X and for graphitised carbon blacks as alternative sorbents.

Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations[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 the Approved Codes of Practice for the Control of Substances Hazardous to Health Regulations, the *General COSHH ACOP*, and the Control of Carcinogenic Substances Regulations, the *Carcinogens ACOP*, which are included in a single publication with the COSHH Regulations.[2]

Properties and uses

3 1,3-Butadiene, CAS Number 106-99-0, synonym buta-1,3-diene, CH_2=CHCH=CH_2, 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 *Chemical Exposure Treatment Cards,* published by the Chemical Industries Association, should be transmitted with the patient (noting that exposure has been to butadiene). For butadiene this is series 3.

Exposure limits

9 Regulation 7 of the COSHH Regulations 1999 lays 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 an MEL of 10 ppm (22 mg/m^3), 8-hour time-weighted average. MELs are published in EH40.[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 A measured volume of sample air is drawn through a metal or glass tube packed with a zeolite (Molecular Sieve 13X) or a graphitised carbon black. The butadiene gas is sorbed and thus removed from the flowing air stream. The collected butadiene is desorbed by heat in thermal desorption (TD) apparatus and is transferred under inert carrier gas into a gas chromatograph (GC) equipped with either flame ionisation (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 10 min to 8 h and concentrations in the range 0.2 to 100 mg/m^3 (about 0.1 to 50 ppm) for samples of 5 l of air. It complies with the European performance standards EN 482:1994[14] and EN 1076:1997[15] for workplace measurements when using Molecular Sieve 13X as sorbent, provided a drying pre-filter is fitted to prevent adsorption of excessive water. Water vapour, 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 sorbent, the type of interface and the GC column. Some older types of thermal desorber, coupled to a packed column with a splitless interface, are less affected by adsorbed water. Carbon dioxide may interfere with MS detection. The addition of a carbon dioxide adsorption layer, eg potassium hydroxide, is optional. Graphitised carbon black sorbents, such as Carbopack X or Carbograph 5-TD are suitable and, based on their performance in laboratory-based tests, the method using Carbopack X and Carbograph 5-TD may also comply with EN 482 and EN 1076. 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 butadiene concentrations typically found in ambient air. The use of larger sampling volumes to achieve greater sensitivity may be subject to interference by water and carbon dioxide. Graphitised carbon black sorbents such as Carbopack X or Carbograph 5-TD may be more suitable, based on their performance in limited laboratory-based tests.

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 0.2 µg/m^3 (0.1 ppb) for a 5 l air sample.

18 HSE Guidance Note 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.

REAGENTS

Butadiene

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

APPARATUS

Molecular Sieve 13X

20 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. Tubes prepacked to customer specification are available commercially from some sources. 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.

Graphitised carbon blacks

21 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 prepacked to customer specification are available commercially from some sources.

Sorbent tubes

22 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. 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 will be within the desorber heated zone.

23 A suggested packing procedure for 5.0 mm ID steel tubes is to attach a small polythene funnel and preweigh an empty tube in a small beaker. Weigh in typically 500-800 mg Molecular Sieve 13X or 400-500 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 clean metal rod about 4 mm in diameter, for example, a sawn-off screwdriver which has been thoroughly degreased and dried. Do not use excessive force or the retaining gauze at the other end may be dislodged. Check for this by tapping a freshly packed tube on a hard surface, when no sorbent particles should fall out.

Pre-drying tube

24 Pre-drying tubes containing sodium sulphate are commercially available. Alternatively, drying pre-filters can be made from 25 mm 3-section filter cassettes. Use glass fibre filters (binder-free) to retain the sodium sulphate. A second CO_2 removal layer of potassium hydroxide is optional. It is not normally necessary to use a pre-drying tube with Carbopack X or Carbograph 5-TD sorbents, although it may be advisable at very high humidity in excess of 80% RH.

Sampling pumps

25 Sampling pumps complying with the provisions of BS EN 1232[10] with an adjustable flow rate, incorporating a flow meter or malfunction indicator, capable of maintaining the selected flow rate to within $\pm$5% of the nominal value throughout the sampling period, and which people can wear without impeding their normal work activity. The pump should be safe for use in flammable atmospheres.

Flow meter

26 Flow meter, portable, with an accuracy that is sufficient to enable the volumetric flow rate to be measured to within ±5%. The calibration of the flow meter shall be checked against a primary standard, ie a flow meter whose accuracy is traceable to national standards. It is recommended that the flow meter used should be capable of measuring the volumetric flow rate to within ±2% or better. Flow meters incorporated in sampling pumps are not suitable for accurate measurement of the flow rate. However, they can be useful for monitoring the performance of samplers, provided they have adequate sensitivity.

Tubing

27 Plastic or rubber tubing about 90 cm long of appropriate diameter.

Storage end caps

28 For sealing the tubes when stored, a closed metal end cap with PTFE ferrule (eg Swagelok™) is recommended. End-caps made from solid PTFE with Viton™ O-rings are acceptable for up to 3 days after sampling (Table 2), but are not recommended for extended storage.

Thermal desorber

29 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

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

31 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,[11] 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.[12] Retention times of C_4 hydrocarbons on GS-GasPro were not significantly affected by water.

Injection unit for preparing calibration standards

32 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.

Gas-tight syringe

33 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

34 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 20). 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 – Molecular Sieve 13X sorbent

35 Immediately before sampling, remove the end caps from the sorbent tube and connect to the sampling pump with appropriate tubing. The marked end of the tube should be connected furthest from the pump and the sample tube positioned vertically with air passing downwards to minimise channelling. Using the shortest connection, attach a drying pre-tube to the marked end. When using MS detection it is recommended that carbon dioxide adsorption on Molecular Sieve 13X is minimised by adding a layer of potassium hydroxide in the pre-filter. Ensure that all connections are free from leaks.

Collection of samples – Carbopack X or Carbograph 5-TD sorbent

36 Immediately before sampling, remove the end caps from the sorbent tube and connect to the sampling pump with appropriate tubing. The marked end of the tube should be connected furthest from the pump and the sample tube positioned vertically with air passing downwards to minimise channelling. Pre-drying tubes are not normally required, other than as a precaution when the conditions are very humid (>80% RH).

37 When used for personal sampling, the tube should be mounted in the worker's breathing zone, for example on the lapel. The pump is attached to the worker as appropriate to minimise interference.

38 Draw a measured volume of air (about 5 l) through the sorbent tube, remove the drying pre-tube if fitted and replace the metal storage caps. Make sure that the PTFE ferrules of the metal caps are fully home on the tube before tightening. Note the unique identification number of the tube. The sample volume is not critical, but should not exceed the breakthrough volume of the sorbent tube. A flow rate of 10 ml/min is recommended for 8 h sampling and a flow rate of 200 ml/min is recommended for 10 min sampling. 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. It is recommended to test the tightness of the metal caps after the tubes have cooled to their storage temperature. Prior to analysis, cooled tubes should be allowed to reach ambient laboratory temperature before removing the metal caps.

39 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.

40 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.

Breakthrough volume

41 Sampling efficiency will be 100% provided the sampling capacity of the sorbent is not exceeded. Breakthrough is defined as the point at which the effluent concentration is 5% of the applied test concentration. It may be measured by sampling from a standard atmosphere, while monitoring the effluent air with a flame ionisation or equivalent detector. Alternatively, a simpler procedure is to draw air through a sorbent tube ‘spiked’ with butadiene, directly coupled to a second clean tube. Measurement of butadiene in both tubes, as a function of sample volume, will indicate the breakthrough volume. This procedure, while not as rigorous as the first, is usually adequate for the purpose.

42 The breakthrough volume as defined above varies with ambient temperature and the concentration of butadiene and other pollutants. It is also affected by humidity and, to some extent, by flow rate. To allow a suitable margin of safety, it is recommended that sample volumes of not more than 70% of the breakthrough volume be taken. For butadiene on Molecular Sieve 13X, the breakthrough volume is in excess of 100 l, even in humid air, so that breakthrough is unlikely to occur in practice. For butadiene on Carbopack X, the breakthrough volume has not been determined exactly, but is not less than 25 l. For Carbograph 5-TD, the breakthrough volume is about 10 l.

Preparation of standard ‘spiked’ calibration standards

43 Calibration standards are preferably prepared by loading required amounts of butadiene on the sorbent tubes from standard atmospheres using calibrated sampling pumps, 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.

44 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.

45 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 32) 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 33). 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.[13] 10 µl butadiene at 25°C is equivalent to 22.7 µg.

Analysis

46 Graphitised carbon blacks adsorb a little water if no drying pre-tube is used in sampling. Before thermal desorption analysis, it is advisable to remove most of the water from Carbopack X or Carbograph 5-TD by a dry purge of 0.5 l nitrogen or helium at ambient temperature. The sorbent tube is then placed in a compatible TD apparatus. In some types of TD apparatus, air is purged from the tube to avoid chromatographic artefacts arising from the thermal oxidation of sorbed gases and vapours. The length of this purge step can be varied in some models, but since the secondary cold-trap is normally designed to be in-line at this stage, it is not as effective in removing water from the system as dry purging off-line (it is not possible to dry purge Molecular Sieve13X at ambient temperature).

47 The tube is then heated to displace the sorbed 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) and the drying pre-filter 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 tubes must be conditioned in a separate apparatus before reuse (paragraph 20).

48 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.

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

Oven	>265°C (Mol Sieve 13X); >150°C (Carbopack X, Carbograph 5-TD)
Desorb time	10 min
Desorb flow	20 ml/min helium
Split ratio	200:1
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

ATD traps tested with ozone precursor hydrocarbons, and equivalent to Carbopack B/carbon molecular sieve, are commercially available pre-packed. This type of cold-trap may be operated at up to +25°C to allow selective elimination of water. Some experimentation with the effects of flow rate and temperature on the recovery of butadiene will be necessary to establish limits.

50 In the thermal desorption step, butadiene and n-pentane (if used as internal standard) are fully recovered from Carbopack X over the temperature range 150-350°C.[22] When using desorption temperatures at the lower end of this range, less volatile hydrocarbons accumulate on graphitised carbon blacks with repeated use, unless the tubes are conditioned at >350°C after each application. Butadiene is fully recovered from Carbograph 5-TD over the temperature range 150-350°C.[24] n-Pentane on Carbograph 5-TD requires a desorption temperature >200°C.[24]

51 Set up the GC for the analysis of butadiene. A variety of chromatographic columns may be used (paragraph 31). 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 ionisation

52 The elution order of some C_2-C_6 hydrocarbons on GS-GasPro under the specified operating conditions is given in Table 1.

Table 1 Elution order of some C_2-C_6 hydrocarbons on GS-GasPro, operated as specified in paragraph 51

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

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

Calibration

54 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

55 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 if it is no greater than 5 ng. Typical levels on graphitised carbon blacks and Molecular Sieve 13X are much less than this.

Determination of desorption efficiency

56 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.

57 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.

CALCULATION OF RESULTS

Mass concentration of analyte

58 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:

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

where:

m = mass (µg) of butadiene on sample tube;
m_{blank} = mass (µg) of butadiene on blank tube;
V = volume of air sampled (litres).

If it is desired to express concentrations reduced to standard conditions, eg 20°C and 101 kPa, then:

$$C_{corr} = C \times \frac{101}{P} \times \frac{T}{293}$$

where:

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

Volume concentration of analyte

59 Alternatively, the concentration of butadiene in the sampled air may be expressed in ppm v/v.

$$C_v \text{ (ppm)} = C \times \frac{24.5}{54.1} \times \frac{T}{298} \times \frac{101}{P}$$

where:

C_v = concentration of butadiene in air (ppm) corrected to standard conditions;
C = concentration of butadiene in air (mg/m^3) at actual sampling conditions P, T;
24.5 = molar volume (litres) at standard conditions 293K and 101 kPa;
54.1 = molecular weight of butadiene.

METHOD PERFORMANCE

Overall uncertainty

60 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:

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

where:

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

An additional 5% is usually added to the overall uncertainty percentage to allow for the variability of pump flow rate. The performance requirements quoted in EN 482 for overall uncertainty, where the task is 'measurement for comparison with limit values', are ≤50% for samples in the range 0.1 to 0.5 LV and ≤30% for samples in the range 0.5 to 2.0 LV (LV = limit value). From laboratory experiments, the within-laboratory repeatability of replicate measurements was 4-6% expressed as a relative standard deviation. Bias with respect to the true or accepted reference value was not determined directly, but was estimated at up to 8% from bias due to uncorrected desorption efficiency. Taken together with the variability of pump flow rate, the method overall uncertainty does not exceed ±25% in the range 0.5 to 2.0 LV.

61 The method performance standard EN 1076[15] recommends that, in thermal desorption, desorption efficiency be at least 95% initially and at least 90% after 2 weeks' storage.

62 An accelerated Molecular Sieve 13X storage test at 40°C for 10 days[12] 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.[12] Another study reported that when Molecular Sieve 13X was loaded with 90-180 µg butadiene, recovery was as low as 60%. It was concluded that at very high loadings, partial polymerisation might occur on the sorbent.[17] 90-180 µg is equivalent to 5-10 ppm butadiene for a 5 l sample. Similar losses could not be confirmed at a loading of 38 µg in another Molecular Sieve 13X study where the recovery was about 100% after 7 days.[16] Molecular Sieve 13X storage tests in the range 1-38 µg are summarised in Table 2. Carbopack X and Carbograph 5-TD storage tests are summarised in Tables 3 and 4.

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					Refs
			0	3	7	14	28	
PTFE	4.0	+20	100 ± 4	93 ± 3	77 ± 10	-	-	12
Swagelok	1.3	+4	100 ± 4	-	-	95 ± 3	96 ± 4	12
Swagelok	1.3	+20	100 ± 4	-	-	96 ± 10	95 ± 4	12
Swagelok	6.7	+4	100 ± 1	-	-	97 ± 4	95 ± 5	12
Swagelok	6.7	+20	100 ± 1	-	-	102 ± 3	97 ± 2	12
Swagelok	38	+4	100 ± 6	-	102 ± 10	-	-	16

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			Refs
		0	7	14	
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			Refs
		0	7	14	
0.4	+20	100 ± 4	-	92 ± 4	22
8.0	+20	100 ± 2	-	99 ± 5	22

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

Interferences

64 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.

65 Water is a potential interferent (paragraph 14) unless adsorption is prevented with a drying pre-filter (for Molecular Sieve 13X) or removed by dry purging before analysis (for graphitised carbon blacks). Water adsorption data for selected sorbents are summarised in Table 5.

QUALITY CONTROL MEASURES

66 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 MDHS 71.[20]

67 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/pt/pt.htm.

Table 5 Water adsorption from actively sampled air by selected sorbents packed in Perkin Elmer-type thermal desorption tubes (refs 22, 24)

Sorbent	Temp °C	% rel hum	Vol litres	mg water adsorbed	% water adsorbed
Mol Sieve 13X	20	42	10	66	95
	20	100	6	97	93
Carbopack X	20	47	6	0.03	0.04
	4	80	6	2.3	6.2
	20	100	6	9.8	9.6
Carbograph 5-TD	20	50	10	<0.2	<0.2
	20	100	6	6.8	5.6

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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, Broad Lane, Sheffield, S3 7HQ, UK (tel: 0114 2892000; fax: 0114 2892500; 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 type of pre-filter used, if appropriate;

e) the make and type of sampling pump and flow meter used, the primary standard against which it was calibrated, and the range of flow rates for which the flow meter was calibrated;

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

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

h) the overall uncertainty of the method;

i) the mean temperature and pressure during the sampling period, if appropriate (paragraphs 58 and 59);

j) the name of the person who collected the sample;

k) the name of the analyst;

l) the date of the analysis;

m) any unusual features noted during the determination.

If necessary data (eg the volume sampled) 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

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