



JAPANESE
INDUSTRIAL
STANDARD

Translated and Published by
Japanese Standards Association

JIS A 1967 : 2005

**Indoor air — Sampling and analysis of
volatile organic compounds by sorbent
tube/thermal desorption/capillary gas
chromatography — Diffusive sampling**

ICS 13.040.20

Reference number : JIS A 1967 : 2005 (E)

PROTECTED BY COPYRIGHT

 **Documents**
Document Sharing Hub

28 S

Foreword

This translation has been made based on the original Japanese Industrial Standard established by the Minister of Land, Infrastructure and Transport through deliberations at the Japanese Industrial Standards Committee.

This Standard has been made based on **ISO/FDIS 16017-2 : 2002** *Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography—Part 2 : Diffusive sampling* for the purpose of making it easier to compare this Standard with International Standard; to prepare Japanese Industrial Standard conforming with International Standard; and to propose a draft of an International Standard which is based on Japanese Industrial Standard.

Attention is drawn to the possibility that some parts of this Standard may conflict with a patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have technical properties. The relevant Minister and the Japanese Industrial Standards Committee are not responsible for identifying the patent right, application for a patent after opening to the public, utility model right or application for registration of utility model after opening to the public which have the said technical properties.

Date of Establishment: 2005-11-01

Date of Public Notice in Official Gazette: 2005-11-01

Investigated by: Japanese Industrial Standards Committee
Standards Board
Division Council on Architecture

JIS A 1967 : 2005, First English edition published in 2006-09

Translated and published by: Japanese Standards Association
4-1-24, Akasaka, Minato-ku, Tokyo, 107-8440 JAPAN

In the event of any doubts arising as to the contents,
the original JIS is to be the final authority.

© JSA 2006

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

Printed in Japan

HN

PROTECTED BY COPYRIGHT

Contents

	Page
Introduction	1
1 Scope	1
2 Normative reference	2
3 Principle	2
4 Reagents and materials	2
4.1 Volatile organic compounds (VOC)	2
4.2 Dilution solvent	2
4.3 Sorbents	3
4.4 Calibration standards	3
4.5 Standard atmosphere	3
4.6 Standard atmosphere loaded sorbent tubes	3
4.7 Preparation of solutions for liquid spiking	3
4.8 Standard liquid loaded sorbent tubes	4
5 Apparatus and instruments	5
5.1 Sorbent tubes	5
5.2 Sorbent tube end caps	5
5.3 Diffusion end caps	5
5.4 Syringes	5
5.5 Gas chromatograph	5
5.6 Thermal desorption apparatus	5
5.7 Injection facility for preparing standard tube	6
6 Tube conditioning	6
7 Sampling	6
8 Procedure	7
8.1 Safety precautions	7
8.2 Desorption and analysis	7
8.3 Calibration	9
8.4 Determination of sample concentration	9
8.5 Determination of desorption efficiency	9
8.6 Calibration of uptake rate	9
9 Calculations	10
9.1 Mass concentration of analyte	10
9.2 Volume concentration of analyte	10
9.3 Uptake rate q_v and q_v' relation	10
10 Interferences	11

11	Performance characteristics	11
12	Test report	11
13	Quality control	12
Annex A (informative)	Operating principles of diffusive sampling	26
Annex B (informative)	Description of sorbent types	32
Annex C (informative)	Guidance on sorbent selection	33
Annex D (informative)	Guidance on sorbent use	34
Annex E (informative)	Actual measurement data of diffusive sampling in Japan	36
Annex F (informative)	Summary of data on overall uncertainty, precision, bias and storage	37
Bibliography.....		40
Annex 1 (informative)	Comparison table between JIS and corresponding International Standard	45

Indoor air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography — Diffusive sampling

Introduction This Japanese Industrial Standard has been prepared based on the first edition of **ISO/FDIS 16017-2** *Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography—Part 2 : Diffusive sampling* published in 2002 with some modifications of the technical contents.

The portions given sidelines or dotted underlines are the matters in which the contents of the original International Standard have been modified. A list of modifications with the explanations is given in Annex 1 (informative).

1 Scope This Standard gives general guidance for the sampling and analysis of volatile organic compounds (hereafter referred to as "VOC") in air. This Standard is applicable to indoor air.

This Standard is applicable to a wide range of VOC, including hydrocarbons, halogenated hydrocarbons, esters, glycol ethers, ketones and alcohols. A number of sorbents⁽¹⁾ are recommended for the sampling of these VOC, each sorbent having a different range of applicability. Very low boiling compounds are only partially retained by the sorbents and can only be estimated qualitatively. Semi-volatile compounds are fully retained by the sorbents, but may only be partially recovered.

Note (1) The sorbents listed in Annex B and elsewhere in this Standard are those known to perform as specified under this Standard (trademarked name). This information is given for the convenience of users to show that they are widely available, however, does not constitute an endorsement of the products. Equivalent products may be used if they can be shown to lead to the same results.

This Standard is applicable to the measurement of airborne vapours of VOC in a mass concentration range of approximately 20 µg/m³ to 1 × 10⁵ µg/m³ for an exposure time of 8 h, or 0.3 µg/m³ to 300 µg/m³ individual organic for an exposure time of four weeks.

The upper limit of the useful range is set by the sorptive capacity of the sorbent used and by the linear dynamic range of the gas chromatograph column and detector or by the sample splitting capability of the analytical instrumentation used. The lower limit of the useful range depends on the noise level of the detector and on blank levels of analyte and/or interfering artefacts on the sorbent tubes. Artefacts are typically sub-nanogram for well-conditioned Tenax GR and carbonaceous sorbents such as Carbotrap/Carbotrap type materials, carbonized molecular sieves such as Spherocharb and pure charcoals. Artefacts are typically at low nanogram levels for Tenax TA and at 5 ng to 50 ng levels for other porous polymers such as Chromosorb and Porapak.

Remarks : The International Standard corresponding to this Standard is as follows :

In addition, symbols which denote the degree of correspondence in the contents between the relevant International Standard and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21**.

ISO/FDIS 16017-2 : 2002 *Indoor, ambient and workplace air—Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography—Part 2 : Diffusive sampling* (MOD)

2 Normative reference The following standard contains provisions which, through reference in this text, constitute provisions of this Standard. The most recent edition of the standard (including amendments) indicated below shall be applied.

JIS A 1960 *Indoor air—General aspects of sampling strategy*

Remarks : **ISO/DIS 16000-1** : 2001 *Indoor air—Part 1 : General aspects of sampling strategy* is identical with the said standard.

3 Principle The diffusive sampler (or samplers) is exposed to air for a measured time period. The rate of sampling is determined by prior calibration in a standard atmosphere (see **8.6**).

The organic vapour migrates down the tube by diffusion and is collected on the sorbent. The collected vapour (on each tube) is desorbed by heat and is transferred under inert carrier gas into a gas chromatograph equipped with a capillary column and a flame ionization detector or other suitable detector, where it is analysed. The analysis is calibrated by means of liquid or vapour spiking onto a sorbent tube.

Information on possible saturation of the sorbent bed, the effect of transients and the effect of face velocity is given in Annex A. The dependence of effective uptake rates on the concentration level of pollutants and the time of diffusive sampling results in different values being given in tables 1 and 2. Further detailed information on the theory of performance of diffusive samplers is given in **prEN 13528-3** [1].

4 Reagents and materials During the analysis, use only reagents of recognized analytical reagent grade. Fresh standard solutions should be prepared weekly, or more frequently if evidence is noted of deterioration, e.g. condensation reactions between alcohols and carboxylic acid.

4.1 Volatile organic compounds (VOC) VOC are required for calibration reagents, using either standard liquid spiking (**4.7** and **4.8**) or standard atmosphere spiking (**4.4** to **4.6**) onto sorbent tubes.

4.2 Dilution solvent Dilution solvent shall be used for preparing calibration blend solutions for standard liquid spiking (**4.7**). The solvent should be of chromatographic quality. It shall be free from compounds co-eluting with the analytes.

Remarks : Methanol is usually used. Alternative dilution solvents can be used, particularly if there is no possibility of reaction or chromatographic co-elution.

4.3 Sorbents Sorbents of particle size 0.18 mm to 0.25 mm (60 mesh to 80 mesh) are recommended. Each sorbent shall be preconditioned under a flow of inert gas by heating it overnight at a temperature at least 25 °C below the published maximum for that sorbent before packing the tubes. They shall be kept in a clean atmosphere during cooling to room temperature, loaded into the sorbent tube, then stored. Wherever possible, analytical desorption temperatures should be kept below those used for conditioning. Tubes prepacked by the manufacturer are also available and as such only require conditioning.

Remarks : A guide for sorbent selection is given in Annex C. Equivalent sorbents may be used. A guide to sorbent conditioning and analytical desorption parameters is given in Annex D.

4.4 Calibration standards Calibration standards are preferably prepared by loading required amounts of the analytes on sorbent tubes from standard atmospheres (see 4.5 and 4.6), as this procedure most closely resembles the practical sampling situation.

If this way of preparation is not practicable, standards may be prepared by a liquid spiking procedure (see 4.7 and 4.8) provided that the accuracy is confirmed by either :

- a) the method established by using procedures giving spiking levels fully traceable to primary standards of mass and/or volume
- b) the method confirmed by reference materials
- c) the method confirmed by standards produced using standard atmospheres
- d) the method confirmed results of reference measurement procedures

4.5 Standard atmosphere Prepare standard atmosphere of known concentrations of the analytes by an independent method. Methods described in **ISO 6141** and **ISO 6145** are suitable. If the procedure is not applied under conditions that allow the establishment of full traceability of the generated concentrations to primary standards of mass and/or volume, or if the chemical inertness of the generation system cannot be guaranteed, the concentrations shall be confirmed using an independent procedure.

Information : As for standard atmosphere, see references [59], [60], [61], [62], [63], and [64].

4.6 Standard atmosphere loaded sorbent tubes Prepare standard atmosphere loaded sorbent tubes by passing an accurately known volume of the calibration atmosphere through the sorbent tube, e.g. by means of a pump. The volume of atmosphere sampled shall not exceed the breakthrough volume of the sorbent. After loading, disconnect and seal the tube. Prepare fresh standards with each batch of samples. For example, prepare standard atmosphere equivalent to 10 mg/m³ and 100 µg/m³ of analytes. For workplace air, load sorbent tubes with 100 ml, 200 ml, 400 ml, 1 L, 2 L, 4 L of the 10 mg/m³ atmosphere. For ambient or indoor air load sorbent tubes with 100 ml, 200 ml, 400 ml, 1 L, 2 L, 4 L or 10 L of the 100 µg/m³ atmosphere.

4.7 Preparation of solutions for liquid spiking

4.7.1 Solution containing approximately 10 mg/ml of each liquid component Accurately weigh approximately 1 g of analytes into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

4.7.2 Solution containing approximately 1 mg/ml of each liquid components

Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution in 4.7.1. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

4.7.3 Solution containing approximately 100 µg/ml of each liquid component

Accurately weigh approximately 10 mg of analytes into a 100 ml volumetric flask, starting with the least volatile substance. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

4.7.4 Solution containing approximately 10 µg/ml of each liquid components

Introduce 50 ml of dilution solvent into a 100 ml volumetric flask. Add 10 ml of solution in 4.7.3. Make up to 100 ml with dilution solvent (4.2), stopper and shake to mix.

4.7.5 Solution containing approximately 1 mg/ml of gas components

For gases, e.g. ethylene oxide, a high-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 1 ml gas-tight syringe with 1 ml of the pure gas and close the valve of the syringe. Using a 2 ml septum vial, add 2 ml dilution solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the dilution solvent. Open the valve and withdraw the plunger slightly to allow the dilution solvent to enter the syringe. The action of the gas dissolving in the dilution solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the vial. Flush the syringe twice with the solution and return the washings to the vial. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP (standard temperature and pressure : 273.15 K and 1 013.25 hPa) occupies 22.4 L.

4.7.6 Solution containing approximately 10 µg/ml of gas components

For gases, e.g. ethylene oxide, a low-level calibration solution may be prepared as follows. Obtain pure gas at atmospheric pressure by filling a small plastic gas bag from a gas cylinder. Fill a 10 µl gas-tight syringe with 10 µl of the pure gas and close the valve of the syringe. Using a 2 ml septum vial, add 2 ml dilution solvent and close with the septum cap. Insert the tip of the syringe needle through the septum cap into the dilution solvent. Open the valve and withdraw the plunger slightly to allow the dilution solvent to enter the syringe. The action of the gas dissolving in the dilution solvent creates a vacuum, and the syringe fills with solvent. Return the solution to the vial. Flush the syringe twice with the solution and return the washings to the vial. Calculate the mass of gas added using the gas laws, i.e. 1 mole of gas at STP occupies 22.4 L.

4.8 Standard liquid loaded sorbent tubes

Loaded sorbent tubes are prepared by injecting aliquots of standard solutions onto clean sorbent tubes as follows. A sorbent tube is fitted into the injection unit (5.7) through which inert purge gas is passed and a 1 µl to 4 µl aliquot of an appropriate standard solution injected through the septum. After an appropriate time, the tube is then disconnected and sealed. Prepare fresh standard tubes with each batch of samples. For indoor air, load sorbent tubes with 1 µl to 5 µl of solutions 4.7.3, 4.7.4 or 4.7.6.

Remarks : In the case that the dilution solvent is methanol, a purge gas flowrate of 100 ml/min and a 5 min purge time have been found to be appropriate to eliminate most of the solution solvent from the tube. If other dilution solvents are used, the purge conditions should be determined experimentally.

5 Apparatus and instruments

5.1 Sorbent tubes These tubes shall be compatible with the thermal desorption apparatus to be used (5.6). Typically, but not exclusively, they are constructed of stainless steel tubing of dimensions 6.3 mm outside diameter, 5 mm inside diameter and 90 mm long. Tubes of other dimensions may be used, but the uptake rates given in tables 1 and 2 are based on these tube dimensions. For labile analytes, such as unstable compounds, glass-lined or glass tubes (typically 4 mm inside diameter) should be used.

In this case, care should be taken that the uptake rate is not same as that of stainless tube. It is necessary to obtain the uptake rate of stainless tube separately.

Mark one end of the tube, for example by a scored ring, about 10 mm from the sampling end. The tube is packed with preconditioned sorbents so that the sorbent bed will be within the desorber heated zone and a gap of about 14 mm is retained at the marked end of the tube.

Uptake rates in table 1 are given for tubes with a nominal air gap (between sorbent bed and diffusive end cap) of 15 mm. In practice, packed tube dimensions vary [2].

Tubes contain between 200 mg and 1 000 mg sorbent, depending on sorbent density, which is typically about porous polymer, or carbon molecular sieve or graphitized carbon. The sorbents are retained by a stainless steel gauze or an unsilanized glass wool plug, etc.

5.2 Sorbent tube end caps The tubes shall be sealed, e.g. with metal screw-cap fittings with polytetrafluoroethylene (PTFE) seals.

5.3 Diffusion end caps The diffusion end cap is similar to 5.2, but allows the ingress of vapour through a metal gauze, the size of the opening being the same as the cross-section of the tube.

When a moisture content is high, use the end cap with a silicone membrane next to the gauze. For the case, obtain the uptake rate separately.

5.4 Syringes Use syringes of a precision 10 µl liquid syringe readable to 0.1 µl, a precision 10 µl gas-tight syringe readable to 0.1 µl and a precision 1 ml gas-tight syringe readable to 0.01 ml.

5.5 Gas chromatograph A gas chromatograph shall be fitted with a flame ionization detector, photoionization detector, mass spectrometric or other suitable detector capable of detecting an injection of 0.5 ng toluene with an S/N ratio of at least 5 to 1. A gas chromatograph capillary column shall be capable of separating the analytes from other components.

5.6 Thermal desorption apparatus Thermal desorption apparatus is for the two-stage thermal desorption of the sorbent tubes and transfer of the desorbed vapours via an inert gas flow into a gas chromatograph. A typical apparatus contains a mechanism for holding the tubes to be desorbed whilst they are heated and purged simultaneously with inert carrier gas. The desorption temperature and time is adjustable, as is the carrier gas flow rate. The apparatus should also incorporate additional features, such as automatic sample tube loading, leak-testing, and a cold trap in the transfer line to concentrate the desorbed sample. The desorbed sample, contained in the purge gas, is routed to the gas chromatograph and capillary column via a heated transfer line.

5.7 Injection facility for preparing standard tube A gas chromatographic injection port may be used for preparing standard tube. This can be used *in situ*, or it can be mounted separately. The carrier gas line to the injector should be retained. The back of the injection facility should be adapted if necessary to fit the tube. This can be done conveniently by means of a compression coupling with an O-ring seal.

6 Tube conditioning Prior to use, tubes should be conditioned by desorbing them at a temperature at or just above the analytical desorption temperature (see Annex D) for 10 min with a carrier gas flow of at least 100 ml/min. The carrier gas flow should be in a direction to the sampling end.

Tubes should then be analysed, using routine analytical parameters, to ensure that the thermal desorption blank is sufficiently small. If the blank is unacceptable, tubes should be reconditioned by repeating this procedure.

Once a sample has been analysed, the tube may be reused to collect a further sample immediately. However, it is advisable to check the thermal desorption blank if the tubes are left for an extended period before reuse, or if sampling for a different analyte is envisaged. Tubes should be sealed with metal screwcaps with combined PTFE ferrule fittings and stored in an airtight container when not sampling or being conditioned.

Remarks : The sorbent tube blank level is acceptable if interfering peaks are no greater than 10 % of the typical areas of the analytes.

7 Sampling Select a sorbent tube (or tubes) appropriate for the analytes. Guidance on suitable sorbents is given in tables 1 and 2, and sorbent types are described in Annex B.

Immediately before sampling, remove the storage end cap from the tube and replace it with a diffusion end cap. Make sure the diffusion end cap is properly seated and the other end cap is in place.

When used for personal sampling, the tube(s) should be mounted in the breathing zone. When used for fixed-location sampling, choose a suitable site (for indoor air, see **JIS A 1960**). For ambient air, recommendations for site selection and for the protection of samples from adverse environmental conditions are given in Annex A. See also **prEN 13528-3** as a reference [1].

Attention shall be paid to three main considerations : air velocity, protection from precipitation, and security. More information is given in the next paragraph or later. The operating principle of diffusive sampling is shown in Annex A. See also [1] as a reference.

Expose the tubes only under conditions where the face velocity requirement can be expected to be satisfied. For the tubes with diffusion end caps **5.3**, wind speed (air velocity) has no influence. Other devices may have different requirements, including also a minimum wind speed.

Information : The content of this article is equivalent to **JIS A 1960**.

The user shall be cautioned about the possible influence of very high wind speeds (above 12 m/s) for which performance characteristics are currently unavailable.

Record the times and, if necessary, temperature and the barometric pressure at the start of the sampling period and at the end of the sampling period.

Replace the diffusion end cap with a storage end cap and tighten the seal securely. The tubes should be uniquely labeled. Solvent containing paints and markers or adhesive labels shall not be used to label the tubes.

If samples are not be analysed within 8 h, place them in a clean, uncoated, sealed metal or glass container. Record air temperature and barometric pressure periodically during sampling, if it is desired to express concentrations reduced to specific conditions (9.1).

Field blanks (travel 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.

8 Procedure

8.1 Safety precautions This Standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this Standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

8.2 Desorption and analysis

8.2.1 Desorption The sorbent tube is placed in a compatible thermal desorption apparatus. Air is purged from the tube to avoid chromatographic artefacts arising from the thermal oxidation of the sorbent or gas chromatographic stationary phase. The tube is then heated to displace the organic vapours which are passed to the gas chromatograph by means of a carrier gas stream. The gas flow at this stage shall be towards the diffusive sampling end, i.e. the marked end of the tube should be nearest the gas chromatograph column inlet. The gas flowrate through the tube should be on the order of 30 ml/min to 50 ml/min for optimum desorption efficiency.

For the initial air purge, it is usually necessary to use 10 times as much as the tube volume (i.e. 20 ml to 30 ml) of inert gas to completely displace the volume of air (2 ml to 3 ml) in the tube. However, if strongly hydrophilic sorbents are needed, it is necessary to employ a larger purge to reduce sorbed air and water to prevent ice formation blocking the cold trap. During the purge period, care should be taken to minimize heating of the tube.

The desorbed sample occupies a volume of several ml of gas, so that pre-concentration is essential prior to capillary gas chromatograph analysis. This may be achieved using a small, cooled, secondary sorbent trap, which can be desorbed sufficiently rapidly at low flowrates (< 5 ml/min) to minimize band broadening, and produce capillary-compatible peaks. Alternatively, an empty secondary trap, or one containing an inert material such as glass beads, may be used to preconcentrate the sample, but such traps typically require cooling to below -100 °C. Alternatively, the desorbed sample can be passed directly to the gas chromatograph (single-stage desorption) where it shall be refocused. This typically requires a high phase ratio column (e.g. 5 µm film thickness, 0.2 mm to 0.32 mm internal diameter) and a sub-ambient starting temperature.

If a secondary sorbent cold trap is not available and if sub-zero capillary cryofocusing temperatures are used to preconcentrate the analytes, water should be completely eliminated from the sample tube prior to desorption in order to prevent ice formation which can block the capillary tubing and stop the thermal desorption process.

Remarks : If a secondary cold trap is not available and optimum sample tube desorption flowrates of 30 ml/min to 50 ml/min are used, a minimum split ratio of 30 : 1 to 50 : 1 is typically required for operation with high-resolution capillary columns. Single-stage thermal desorption may thus limit sensitivity.

Desorption conditions should be chosen such that desorption from the tube is complete, and no sample loss occurs in the secondary trap, if used. Typical parameters are as follows.

Cold trap sorbent	typically same as tubes, 40 mg to 100 mg, if used
Cold trap temperature	-180 °C to +20 °C, depending on type of cold trap
Desorption temperature	250 °C to 325 °C
Desorption time	5 min to 15 min
Desorption flow rate	30 ml/min to 50 ml/min
Carrier gas	helium
Split ratios	Split ratios between the sample tube and secondary cold trap and between the secondary cold trap and analytical column (if applicable) shall be selected dependent on expected atmospheric concentration. (See guidance from respective manufacturers of the thermal desorption apparatus.)

Remarks : The desorption temperature depends on the analyte and the sorbent used. Recommendations are given in tables 1 to 6, but the maximum desorption temperatures for particular sorbents are given in Annex B and Annex C. Due to their potential thermal instability, secondary and tertiary volatile amines and some polyhalogenated compounds having one or two carbon atoms specially brominated compounds may suffer some thermal degradation.

8.2.2 Analysis Set the sample flowpath temperature (transfer line temperature) high enough to prevent analyte condensation but not so high as to cause degradation. Analytes sufficiently volatile to be present in the vapour phase in air at ambient temperature do not usually require flowpath temperatures above 150 °C. However, some types of apparatus may require higher temperatures.

Set up the gas chromatograph for the analysis of volatile organic compounds. A variety of chromatographic columns may be used for the analysis of these compounds. The choice depends largely on which compounds, if any, are present that might interfere in the chromatographic analysis.

Remarks : Typical examples are 50 m length × 0.22 mm internal diameter fused silica columns with thick-film (1 µm to 5 µm) dimethylsiloxane or a 50 m length 7 % cyanopropyl, 7 % phenyl, 86 % methyl siloxane stationary phase. Typical operating conditions for these columns are a temperature programme from 50 °C to 250 °C at 5 °C/min, with an initial hold time of 10 min at 50 °C.

The capillary column, or preferably a length of uncoated, deactivated fused silica, should be threaded back through the transfer line from the thermal desorption apparatus to the gas chromatograph such that it reaches as close as possible to the sorbent in the cold trap, or as close as possible to the tube in a single-stage desorber.

Internal tubing shall be inert and dead volumes shall be minimized. A split valve(s) is conveniently placed at the inlet and/or outlet of the secondary trap. The split valve on the outlet of the secondary trap may be located either at the inlet or the outlet of the transfer line. Split ratios depend on the application.

- Remarks 1 Lower split ratios are suitable for ambient (typically 1 : 1 to 10 : 1) and indoor air measurements (typically 1 : 1 to 20 : 1); higher split ratios for workplace air measurements (typically 100 : 1 to 1 000 : 1).
- 2 Correspondence of retention times on a single column should not be regarded as proof of identity.

8.3 Calibration Analyse each standard tube (4.6 or 4.8) by thermal desorption and gas chromatography.

Prepare a calibration graph by plotting the base-ten logarithm of the areas of the analyte peaks corrected for blank levels on the vertical scale against the base-ten logarithm of the mass of the analyte, in µg, on the standard tube corresponding to the standard solutions in 4.7 or standard atmospheres in 4.5.

Remarks : If the calibration range is less than one order of magnitude, it is not necessary to take logarithms of the data.

8.4 Determination of sample concentration Analyse the samples and travel blanks as described in 8.3. Determine the peak area and read from the calibration graph the mass of the analyte in the desorbed sample [3].

8.5 Determination of desorption efficiency The efficiency of desorption is determined by comparing the chromatographic peak area or height of the standard tube (8.3) with that obtained by injecting aliquots of the standard solutions or the standard atmospheres directly into the gas chromatograph. The desorption efficiency is the peak area or height of the standard tube divided by that of the corresponding liquid standard injected directly. If the desorption efficiency is less than 95 %, change the desorption parameters accordingly.

Some makes of thermal desorber do not have a direct liquid injection facility. In these cases, and when standard tubes are prepared from a calibration blend atmosphere, desorption efficiency should be checked by comparing the calibration graph of the analyte (4.1) with that of *n*-hexane. The ratio of the slope of the calibration graph of the analyte relative to that of *n*-hexane should be the same as the relative response factor for that compound. Response factors for other compounds may be calculated approximately from effective carbon numbers [1]. If the ratio of the slopes of the calibration graphs do not agree with the relative response factor within 10 %, change the desorption parameters accordingly.

8.6 Calibration of uptake rate The uptake rates given in tables 1 and 2 are for tubes with the dimensions given in 5.1 without a membrane in the diffusion end cap (5.3). For other specifications, it may be necessary to follow EN 838 [4] or EN 13528-2 [5] to determine the uptake rate.

Remarks : Diffusive uptake rate is sometimes dependent on the choice of sorbent (see **prEN 13528-3** [1]).

9 Calculations

9.1 Mass concentration of analyte Calculate the mass concentration of the analyte in the sample air by means of equation (1).

$$\rho = \frac{m_a - m_b}{q_v \times t} \times 10^6 \dots\dots\dots (1)$$

where, ρ : the mass concentration of analyte in sample air ($\mu\text{g}/\text{m}^3$)
 m_a : the mass of analyte present in the actual sample obtained according to **8.4** (μg)
 m_b : the mass of analyte present in the blank tube (μg)
 q_v : the diffusive uptake rate (cm^3/min) (table 1 or **8.6**)
 t : the exposure time (min)

- Remarks 1 If m_a and m_b are expressed in mg, the resultant mass concentration ρ will be in mg/m^3 .
- 2 If it is desired to express mass concentrations reduced to specified conditions, use equation (2) (e.g. 101.3 kPa at 25 °C)

$$\rho_c = \rho \times \frac{101.3}{P} \times \frac{T + 273}{298} \dots\dots\dots (2)$$

where, ρ_c : the mass concentration of the analyte in air, reduced to specified conditions ($\mu\text{g}/\text{m}^3$)
 P : the pressure at sampling (kPa)
 T : the temperature at sampling (°C)

9.2 Volume concentration of analyte Alternatively, calculate the volume concentration of the analyte in air by means of equation (3).

$$\phi = \frac{m_a - m_b}{q_v \times t} \times 10^6 \dots\dots\dots (3)$$

where, ϕ : the volume concentration of the analyte in air ($\mu\text{l}/\text{m}^3$)
 q_v : the diffusive uptake rate [$\text{ng}/\mu\text{l}/\text{L}/\text{min}$ (table 1 or **8.6**)]
 t : the exposure time (min)

Remarks : If m_a and m_b are expressed in mg, the resultant volume concentration ϕ will be in ml/m^3 .

9.3 Uptake rate q_v and q_v relation Uptake rates q_v (cm^3/min) and q_v [$\text{ng}/\mu\text{l}/\text{L}/\text{min}$] are related by equation (4).

$$q_v = \frac{q_v \times M \times 293 \times P}{24.5 \times T \times 101.3} \dots\dots\dots (4)$$

where, M : the molar mass of the analyte
24.5 : the molar volume at 25 °C and 101.3 kPa

10 Interferences Organic compounds which have the same, or nearly the same, retention time as the analyte will interfere during the gas chromatographic analysis. Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by proper conditioning of both the sorbent tubes and analytical system before use.

The method is suitable for use in atmospheres of up to 95 % relative humidity for all hydrophobic sorbents such as porous polymers and Carbopack/Carbotrap.

Remarks : When less hydrophobic, strong sorbents such as pure charcoals or carbonized molecular sieves are used in atmospheres with humidity in excess of 65 % relative humidity, care shall be taken to prevent water interfering with the analytical process. Suitable water elimination or reduction procedures include sample splitting, "dry purging" of moisture from the secondary cold trap, use of a diffusion end cap (5.3) with silicone membrane and reducing the time of sampling.

A tube which at first showed a good level of blank values may give rise to formation of artefacts later. Ozone [6] and nitrogen oxides in the presence of water [7] may damage Tenax TA. Benzaldehyde and acetophenone are possible products of these reactions.

As ozone and nitrogen oxides may react with the analytes, this shall be considered by choosing sampling volumes as small as possible if gases of this kind are to be expected in larger amounts in the air sampled. If Tenax TA does not show the necessary stability because of the presence of aggressive gases, Carbopack may be used as a sorbent [8], [9], [10].

For environmental applications (table 2), the procedure has been tested mainly for stable compounds. Artefact formation or degradation of collected susceptible VOC can occur, particularly in very warm weather and at high ozone concentrations [4]. In such circumstances, the user is cautioned to perform collected sampling with an alternative procedure not so affected, e.g. a pumped sorbent tube with an oxidant pre-trap, to demonstrate suitability.

11 Performance characteristics Examples of the performance characteristics, including overall uncertainty, precision, bias, storage and blank levels obtained when testing the procedure described in this Standard are given in Annex F and tables 3 to 8.

12 Test report The test report shall contain at least the following information.

- a) complete identification of the sample
- b) reference to this Standard or any supplementary standard

- c) sampling location, sampling time period and exposure time
- d) barometric pressure and temperature, if required
- e) test result
- f) any unusual features noted during the determination
- g) any operation not included in this Standard or in standards to which reference is made, or regarded as optional

13 Quality control An appropriate level of quality control should be employed (reference [18] or equivalent).

The tube blank is acceptable if artefact peaks are no greater than 10 % of the typical areas of the analytes.

The uptake rates given in tables 1 and 2 are expected to remain constant during the lifetime of the tubes. However, the tubes can become unpacked due to excessive vibration or the sorbent can eventually deteriorate. Tubes should therefore be visually examined frequently, and repacked with fresh sorbent after approximately 100 uses or 2 years, whichever comes first.

**Table 1 Diffusive uptake rates on sorbent tubes
(without membrane as specified in 5.1)
(applicable to sampling of 4 h to 8 h)**

Compound	Sorbent	Level (¹)	Uptake rate (²)	
			cm ³ /min	ng/μl/L/min
Hydrocarbons				
1,3-Butadiene	Molecular Sieve 13X	A	0.59	1.30
<i>n</i> -Pentane	Chromosorb 106	A	0.50	1.46
	Carbopack B (³)	B	0.60	1.77
<i>n</i> -Hexane	Chromosorb 106	A	0.50	1.77
Benzene	Tenax TA (⁴)	A	0.41	1.3
	Porapak Q	A	0.42	1.37
	Tenax GR	B	0.57	1.81
	Chromosorb 106 (⁵)	B	0.54	1.72
<i>n</i> -Heptane	Chromosorb 106	A	0.48	1.95
	Tenax TA (⁵)	A	0.43	1.77
	Carbotrap B	B	0.47	1.94
Toluene	Tenax TA (⁵)	B	0.44	1.67
	Tenax GR	B	0.56	2.12
	Chromosorb 106	B	0.52	1.94
	Carbopack B	B	0.55	2.06
<i>n</i> -Octane	Chromosorb 106	A	0.46	2.13
	Tenax TA (⁵)	A	0.43	2.00
Xylene	Tenax TA (⁵)	B	0.42	1.82
	Chromosorb 106	B	0.48	2.10
	Tenax GR	B	0.57	2.48
Ethylbenzene	Tenax TA (⁵)	B	0.46	2.0
	Tenax GR	B	0.56	2.43
	Chromosorb 106	B	0.44	1.9
	Porapak Q	D	0.55	2.38
Stylene	Tenax TA (⁵)	A	0.47	2.0
	Chromosorb 106	B	0.51	2.15
<i>n</i> -Nonane	Chromosorb 106	A	0.46	2.40
	Tenax TA (⁵)	A	0.40	2.12
Isopropylbenzene	Chromosorb 106	C	0.46	2.26
	Tenax TA (⁵)	C	0.46	2.26
	Porapak Q	D	0.51	2.5