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*Draft Indian Standard*

**METHODS FOR MEASUREMENT OF AIR POLLUTION**

**PART 27 VAPOUR-PHASE ORGANIC CHEMICALS VINYL CHLORIDE TO nC22 HYDROCARBONS IN AIR AND GASEOUS EMISSIONS – BY DIFFUSIVE (PASSIVE) SAMPLING ONTO SORBENT TUBES OR CARTRIDGES FOLLOWED BY THERMAL DESORPTION (TD) AND CAPILLARY GAS CHROMATOGRAPHY (GC) ANALYSIS.**

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वायु प्रदूषण मापने की विधियाँ

भाग 27 वाष्प-चरण कार्बनिक रसायन विनाइल क्लोराइड से nC22 वायु और गैसीय उत्सर्जन में हाइड्रोकार्बन-सॉर्बेंट ट्यूब या कार्ट्रिज पर डिफ्यूसिव (निष्क्रिय) सैंपलिंग के बाद थर्मल डिऑर्शन (टीडी) और केशिका गैस क्रोमैटोग्राफी (जीसी) विश्लेषण

ICS 685.312.122.6

Air Quality Sectional Committee, CHD 35

Last date of comments: 3<sup>rd</sup> September 2023

**FOREWORD**

(Formal text to be added after finalization of document)

This (draft) Indian Standard addresses a wide range of air monitoring applications and is prepared in two parts. IS 5182 (Part 27) covers diffusive (passive) sampling of vapour phase organic chemicals onto sorbent tubes or cartridges followed by analysis using thermal desorption - gas chromatography (TD-GC). Compatible matrices include ambient air, indoor/in-vehicle air and workplace air. Target compounds include the important pollutants benzene, toluene and xylene, together with industrial solvents, fuel components, odorous compounds and many other volatile and semi-volatile organic compounds. IS 5182 (Part 28) covers pumped sampling of vapour phase organic chemicals onto sorbent tubes followed by analysis using TD-GC and addresses a similar wide range of air monitoring applications plus product emission testing.

Useful additional information is provided in various international standards, referenced in each respective sub-part, but this standard harnesses the measuring techniques available and used in India.

The base draft is given by Dr Sushil K. Tyagi, Former Addl. Director, CPCB Delhi.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022 'Rules for rounding off numerical values (*second revision*)'.

## 1 SCOPE

This method is applicable to measuring the vapour-fraction of target GC-compatible organic compounds in ambient, indoor and workplace air. Compatible compounds range in volatility from vinyl chloride to nC<sub>22</sub> hydrocarbons at concentrations ranging from low micrograms per cubic metre (low ng/l) to milligrams per cubic metre (high µg/l). The list of compounds of interest is given in Annex B III, but other organic vapours within the specified volatility range can also be monitored using this method provided a stable uptake rate can be determined and provided they are readily analysed by gas chromatography. The method involves exposing diffusive (passive) samplers to the atmosphere under test, for fixed lengths of time. The samplers comprise a sorbent tube or cartridge housed in such a way as to define a fixed diffusion barrier – typically a permeable barrier or air gap. Subsequent analysis is by thermal desorption (TD) and gas chromatography (GC) employing a capillary column and a mass spectrometric (MS) detector.

This procedure gives a time-weighted average result. It is not applicable to the measurement of rapid fluctuations in concentration or to instantaneous measurements.

## 2 REFERENCE

The following Indian Standards are referred to in the text in such a way that some or all their content constitutes requirements of this standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

<i>IS No.</i>	<i>Title</i>
5182	Methods for measurement of air pollution:
(Part 11) : 2006	Part 11 benzene, toluene and xylene (BTX) ( <i>Second Revision</i> )
ISO 16017-1 : 2000	Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography — Part 1: Pumped sampling
ISO 16017-2 : 2003	Indoor, ambient and workplace air — Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography — Part 2: Diffusive sampling

## 3 SIGNIFICANCE AND USE

Convenient sorbent-based sampling together with laboratory GC analysis, is extensively used for the collection of time weighted average concentration data for organic vapours in air and gas. It is applied to workplace, indoor and ambient atmospheres. Two categories of sampler are deployed; those containing charcoal (subsequently desorbed with 1-2 ml solvent, typically carbon disulfide) and those compatible with thermal desorption [*see* IS 5182 Part 11)].

Both solvent extraction (desorption) and thermal desorption (extraction) methods have their place. However, as limit levels fall in industrial environments and as interest grows in ppb-level toxic and odorous pollutants in urban and indoor/in-vehicle air, the significant (1 000-fold) sensitivity advantage of thermal desorption is increasingly necessary to deliver accurate results. Generally speaking, either solvent extraction or thermal desorption methods can be applied to workplace air monitoring, but the extra sensitivity of TD methods is usually required for monitoring indoor, in-

vehicle and ambient air. A more detailed comparison of the two approaches is summarized in informative Annex A.

#### 4 RELEVANT STANDARD METHODS

The following national and international standard methods provide useful background information:

- a) **US EPA Method 325A:** Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection
- b) **US EPA Method 325B:** Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis
- c) **ISO 16017:** Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 1: Pumped sampling and Part 2: Diffusive sampling
- d) **EN 14662-4:** Ambient air quality - Standard method for measurement of benzene concentrations - Part 4: Diffusive sampling followed by thermal desorption and gas chromatography.
- e) **ASTM D6196:** Standard practice for choosing sorbents, sampling parameters and thermal desorption analytical conditions for monitoring volatile organic chemicals in air
- f) **UK Health and Safety Executive:** Methods for the Determination of Hazardous Substances #80: Volatile organic compounds in (workplace) air: Laboratory method using diffusive solid sorbent tubes, thermal desorption and gas chromatography

#### 5 TERMS AND DEFINITIONS

##### 5.1 Axial Diffusive Sampler

A tube-form device with precisely controlled dimensions that samples gaseous organic chemicals in air diffusively through one end of the tube onto the sorbent surface held inside the tube at a fixed distance from the sampling end.

##### 5.2 Desorption Efficiency

The ratio of the mass of analyte that actually reaches the analytical GC column from the sorbent tube relative to the mass of analyte that is expected to reach the analytical GC column from the sorbent tube during analysis.

##### 5.3 Diffusive (passive) Sampler

A device which is capable of collecting vapours from the air at a rate controlled by a physical process such as gaseous diffusion through a static air layer or porous material and/or permeation through a membrane, but which does not involve active (pumped) sampling of air through the device.

##### 5.4 Diffusive Uptake Rate or Diffusive Sampling Rate (U)

The constant which links the rate of analyte adsorption/collection to atmospheric concentration, expressed in nanograms per parts per million (volume/volume) per min ( $\text{ng.ppm.min}^{-1}$ ) or picograms per parts per billion (volume/volume) per minute ( $\text{pg.ppb.min}^{-1}$ ). It may also be expressed as cubic centimeters per minute ( $\text{cm}^3/\text{min}$ ).

### 5.5 Field Blank

A conditioned sampler from the batch used for the sampling exercise, subjected to the same handling procedure in the field, including removal and replacement of storage caps/covers, but not used for sample collection. These blanks are analysed with the samples.

### 5.6 Internal Standard

Readily-distinguished compound of known concentration added to a sample to facilitate the qualitative identification and/or quantitative determination of sample components.

### 5.7 Laboratory Blank

Conditioned sampler from the batch selected for each sampling exercise, retained in the laboratory, sealed with long term storage caps or covers throughout the sampling exercise to be used as a blank. These blanks are analysed with the samples.

### 5.8 Radial Diffusive Sampler

A tube form device which allows controlled diffusive sampling around the walls of the sampler; that is parallel to the radius, to increase the sampling surface and rate relative to axial samplers.

### 5.9 Retention Volume

Volume of air or carrier gas that has passed through a sorbent tube pre-loaded with a small aliquot of the organic vapour at the sampling end, at the point when the concentration of organic compound eluting from the far end of the tube reaches a peak.

#### NOTES:

- 1 The retention volume varies with compound, temperature, humidity and with type of sorbent.
- 2 The retention volume is determined chromatographically (*see* ISO 16017-1).

### 5.10 Safe Sampling Volume (SSV)

The volume of sampled air below which there is negligible risk of that compound breaking through during sample collection.

NOTE — This is traditionally calculated as 50 percent of the chromatographically-determined retention volume or 70 percent of the breakthrough volume (*see* ISO 16017-1).

### 5.11 Sorbent Strength

Term to describe the affinity of sorbents for vapour-phase organic chemicals (VOCs); a stronger sorbent is one which offers higher safe sampling volumes for VOCs relative to another, weaker, sorbent.

## 6 PRINCIPLE

Two forms of sampler are applicable for this method:

- a) Axial diffusive (passive) samplers (*see* Fig B1). These comprise standard stainless steel or inertcoated stainless steel sorbent TD tubes, with a well-defined air gap (15 mm long x 5 mm internal diameter) at the sampling end. The dimensions of the air gap are controlled by positioning the sorbent retaining gauze 14 mm from the sampling end of the tube and by fitting a diffusive cap over the sampling end of the tube throughout the exposure period (*see* Fig. B1).

NOTE — TD tubes used for diffusive sampling may be packed with one or a series of sorbents, but only the sorbent at the sampling surface plays any significant part in the sampling process.

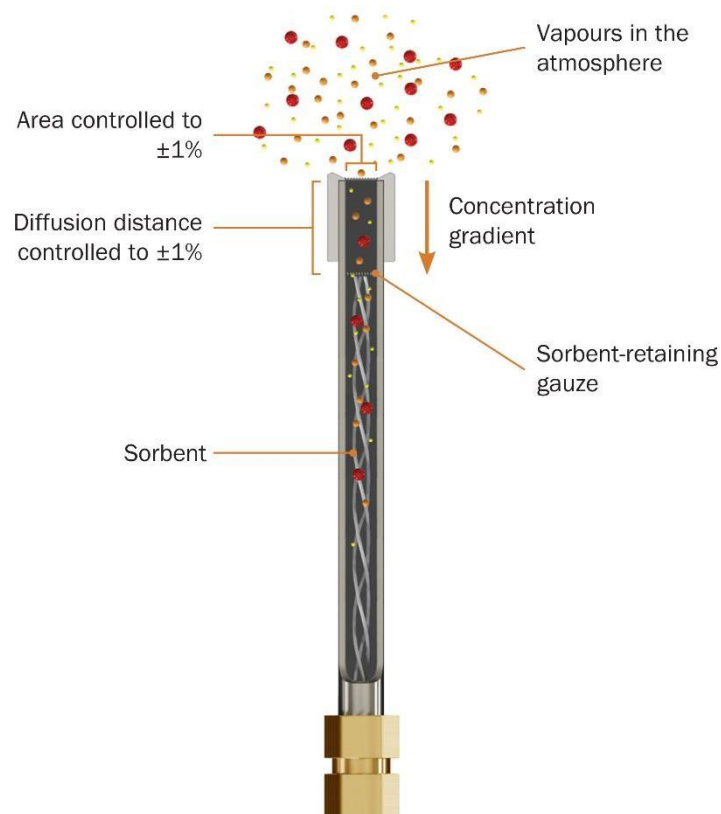


FIG B1 SCHEMATIC OF A TD SORBENT TUBE BEING USED TO SAMPLE DIFFUSIVELY (*SEE ALSO FIG B6 FOR A MORE DETAILED ILLUSTRATION OF THE DIFFUSIVE SAMPLING MECHANISM*)

- b) Radial diffusive (passive) samplers (*see Fig B2*). During sampling, these comprise a sorbent cartridge housed in a permeable diffusive body – typically constructed of sintered metal or porous polymer. The sorbent cartridges are stringently sealed and protected from analyte losses and contamination both before and after sampling. They are transferred to clean, empty TD tubes as soon as possible after sampling to ensure leak-tight storage and to be ready for TD-GC analysis.

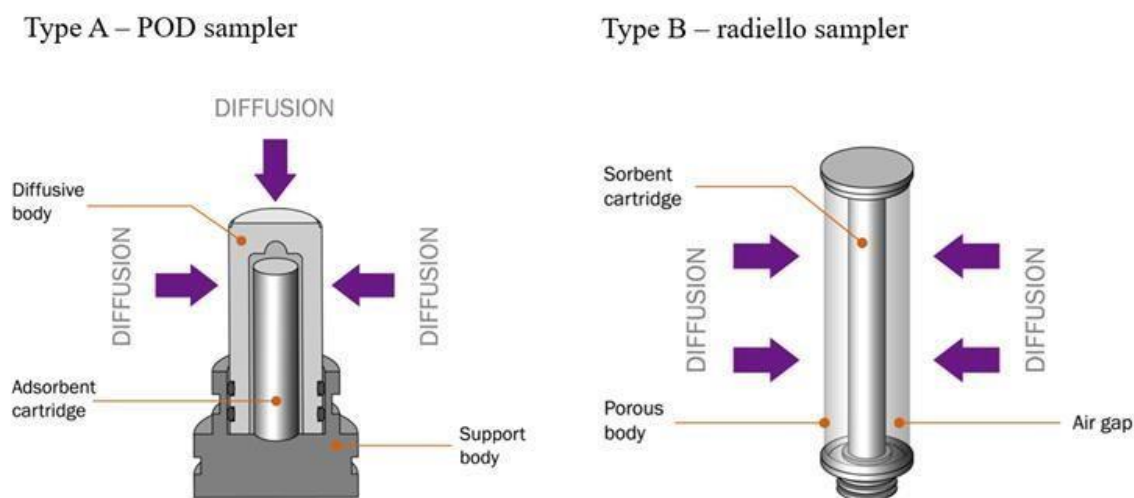


FIG B2 SCHEMATIC OF TYPE A (POD) AND TYPE B (RADIELLO) RADIAL DIFFUSIVE SAMPLERS IN MONITORING MODE

Once sampled and sealed, sorbent tubes and TD tubes containing sampled sorbent cartridges are stored in a clean environment (at or below 25 °C) and analysed within 4 weeks by two-stage thermal desorption (TD) with capillary gas chromatography (GC) using mass spectrometric (MS) detection.

Each tube is loaded into the thermal desorber in turn, checked for leaks and purged of air. It is then heated in a flow of inert carrier gas passing through tube from the sampling end. This releases the retained compounds and sweeps them into an electrically-cooled sorbent focusing trap where they are concentrated. Once primary (tube) desorption is complete, the focusing trap is heated rapidly in a reverse flow of carrier gas to inject the compounds directly into the capillary GC column in a concentrated band of vapour. Desorption from the tube to the focusing trap and from the focusing trap to the column can be split or splitless depending on the air concentrations being monitored and the mass of compounds sampled.

Secondary (focusing trap) desorption and injection of the organic compounds into the capillary GC column triggers the start of the GC program. The desorbed compounds are separated, measured and identified by the analytical system. The concentration of each target compound in the sampled air is then calculated from the measured mass, the respective uptake rate for each compound and diffusive sampling time (exposure period).

## 7 REAGENTS AND MATERIALS

**7.1 Organic Compounds for Calibration** — Must be of chromatographic quality

**7.2 Dilution Solvent** for preparing calibration blend solution for liquid spiking of conditioned sorbent tubes. Shall be of chromatographic quality and free from interfering compounds that could co-elute chromatographically with the compound(s) of interest.

### 7.3 Solid Sorbents

Many types of sorbent, suitable for packing thermal desorption sample tubes, cartridges and focusing traps, are commercially available. Sorbents can be classified by material and the most common types used are as follows:

- a) Graphitised carbon black – examples include Carbograph, Carbopack and Carbotrap sorbents
- b) Poly(diphenyl-p-phenylene oxide) – examples include Tenax TA
- c) Graphitised poly(diphenyl-p-phenylene oxide) – examples include Tenax GR
- d) Carbon molecular sieve – examples include Carboxen, Sulficarb and Carbosieve

They range in strength from very strong (retentive) sorbents, required to quantitatively retain and release very volatile substances such as C<sub>3</sub> hydrocarbons, to very weak sorbents, suitable for quantitative sampling and release of high boiling semi-volatiles such as n-C<sub>30</sub>. The required sorbent particle size is 0.18 mm to 0.60 mm (80 mesh to 30 mesh). Listed in order of increasing sorbent strength starting from the weakest, example TD-compatible sorbents that are suitable for diffusive sampling include:

- a) Tenax TA<sup>®</sup> particle size ~0.25 mm to ~0.6 mm (60 mesh to 30 mesh). Tenax TA is an inert, hydrophobic porous polymer based on 2,6-diphenyleneoxide. Suitable for organic compounds ranging in volatility from n-C<sub>6/7</sub> (depending on air sampling volume) to n-C<sub>26</sub> or more.
- b) Carbon black sorbents, such as Carbopack X<sup>™</sup> or Carbograph 5 TD<sup>™</sup> particle size 0.25 mm to 0.5 mm (60 mesh to 40 mesh). Hydrophobic carbon sorbents suitable for organic compounds with vapour pressures below those for C<sub>4</sub> hydrocarbons and above those for n-C<sub>10</sub>.

NOTE — Weaker types of carbon black sorbent are also commercially available

- c) Carbon molecular sieve sorbents such as Carboxen 1003<sup>™</sup> or Sulficarb<sup>™</sup>. These are very strong and are used for trapping compounds more volatile than C<sub>4</sub> hydrocarbons.

NOTE — Carbon molecular sieve sorbents are not completely hydrophobic. If such sorbents are used, the tube will require dry purging before analysis, to remove residual water.

More information on sorbent selection is given in 8.

### 7.4 Preparing Calibration Standards on Sorbent Tubes

Target compounds should be calibrated using original reference compounds whenever possible. Standards should be introduced to the sampling end of conditioned sorbent tubes using either liquid or gas phase standards. This method is used for calibrating both axial diffusive sorbent tubes and radial diffusive cartridges. Table 1 below shows the various calibration range for workplace, ambient and indoor air monitoring. Calibration solution concentrations will vary depending on the concentration of the atmosphere which is being measured. Additional information and illustrative examples for preparing calibration standards suitable for workplace air monitoring, ambient or indoor air monitoring and for material/product emission testing are all given in Annex B.

NOTE — It is advisable to include toluene as one of the compounds in a calibration mix as unknowns are conventionally ‘semi-quantified’ using the response factor for toluene.

**Table 1 Typical Calibration Ranges for Each Type of Sampler and Type of Atmosphere**  
(Clause 7.4)



Measurement atmosphere  (1)	Typical minimum mass per $\mu\text{L}$  (2)	Typical maximum mass per $\mu\text{L}$  (3)	Section reference  (4)
<i>Using axial samplers</i>			
Workplace air (8 h)	0.5 $\mu\text{g}$	10 $\mu\text{g}$	11.1 and Annex B
Ambient air (14 days)	25 ng	500 ng	11.1 and Annex B
Indoor/in-vehicle air (14 days)	25 ng	500 ng	11.1 and Annex B
<i>Using POD samplers</i>			
Workplace air (4 h)	0.5 $\mu\text{g}$	10 $\mu\text{g}$	11.2 and Annex B
Ambient air (48 h)	25 ng	500 ng	11.2 and Annex B
Indoor air (24 h)	25 ng	500 ng	11.2 and Annex B
<i>Using Radiello samplers</i>			
Workplace air (1 h)	0.5 $\mu\text{g}$	10 $\mu\text{g}$	11.2 and Annex B
Ambient air (24 h)	25 ng	500 ng	11.2 and Annex B
Indoor air (8 h)	25 ng	500 ng	11.2 and Annex B

NOTE — Typical calibration ranges for each type of sampler and type of atmosphere given the duration of passive monitoring specified – See sections **10.4** and **10.5**. See also **Annex B**.

#### **7.4.1 Gas-phase Standards**

Standard atmospheres containing known concentrations of the compound(s) of interest are prepared using a recognized procedure such as ISO 6141<sup>1</sup> or ISO 6145<sup>2</sup>. The concentration(s) of the compounds in the standard atmosphere should be similar to those expected to be collected during the respective field monitoring exercise.

Alternatively, gas standards of appropriate quality shall be sourced commercially. The mass of each compound of interest loaded on to the sorbent tube in the introduced aliquot (volume) of gas standard should be similar to the masses expected to be collected during field monitoring.

#### NOTES

- 1 It is notoriously difficult to produce stable standard atmospheres that are traceable to primary standards, particularly if target compounds include reactive and/or high boiling species. Frequent monitoring of the standard atmosphere is recommended as a check on stability.
- 2 Pressurised commercial gas standards, containing relatively high concentrations of key target compounds are often the most stable and affordable form of gas-phase standard providing the optimum calibration stock for very volatile target analytes, e.g. compounds that are in the gas phase at room temperature.

#### 7.4.2 Loading Sorbent Tubes with Gas-phase Standards

Standard tubes are prepared either by passing a known volume of standard atmosphere through a conditioned sorbent tube from the sampling end (e.g. by means of a pump operating at 50 ml/Min) or by introducing a metered volume of de-pressurised gas standard using a gas syringe or gas sampling valve and mass flow controller. The total volume of gas passing through the sorbent tubes when loading calibration standards shall not exceed the breakthrough volume for any of the compounds of interest. After loading, tubes shall be disconnected and sealed.

Fresh standard tubes should be prepared for each batch of samples.

#### 7.4.3 Liquid Calibration Solutions for Preparing Spiked Sorbent Tubes

A series of liquid standard solutions shall be prepared over a range of concentrations such that injecting 1 µl aliquots of each standard onto respective conditioned sorbent tubes introduces the range of analyte masses that is expected to be collected during field monitoring (*see 9.3*).

The selected compound(s) shall be prepared in chromatographic-grade solvent (e.g. in methanol). Liquid standards shall be maintained at a stable temperature. The stability of calibration solutions shall be monitored and a fresh series of standards shall be prepared if there is evidence of deterioration, e.g. reactions between alcohols and ketones.

#### 7.4.4 Loading Sorbent Tubes with Liquid Standards

The sampling end of a conditioned sorbent tube is fitted to some form of unheated injector through which inert gas is passed at 50-100 ml/Min (*see 8.7*).

A suitably precise micro-syringe (*see 8.6*) shall be used to inject a maximum of 1 µl of standard solution through the septum of the injector and into the tube immediately above the sorbent bed. After 5 minutes, the tube is disconnected and sealed.

#### NOTES

- 1 It is normally recommended to keep injection volumes to 1µl or below to minimize the risk of solvent interference during subsequent analysis.
- 2 Introducing liquid standards onto sorbent tubes in a gas stream via a suitable injector is considered the optimum approach to liquid standard introduction, as volatile components reach the sorbent bed in the vapour phase. However, when preparing standards containing high boiling compounds, analyte transfer is enhanced if the injector allows the tip of the syringe to make gentle contact with the sorbent retaining mechanism (e.g. gauze or quartz wool) at the sampling end of the tube.
- 3 If standard tubes are being prepared by introducing aliquots from more than one standard solution or gas, it is appropriate to introduce the standard(s) containing higher boiling components first and those containing the most volatile organic compounds last. This minimizes risk of analyte breakthrough during the standard tube loading process.
- 4 The purity of the inert carrier gas used to purge sorbent tubes during standard introduction should be such that 0.5 ng toluene can be measured without significant interference. The quality of the carrier gas is of great importance, as any contaminants contained in the gas are enriched on the sorbent together with the substances to be analysed (*see 7.7*).
- 5 For guidance on estimating the mass of analyte that will be collected during diffusive monitoring (*see Annex B*).

Fresh standard tubes shall be prepared for each batch of samples.

## 7.5 Internal Standards

Suitable internal standard compounds should not be present in the sample and should be readily distinguished from sample components. They should also behave in a similar way, chemically, to the compounds of interest. Toluene D-8 is often used, for example, if subsequent analysis is by TD-GCMS.

A gas or liquid-phase internal standard can be added to the sampling end of sample or standard sorbent tubes by mixing with the calibration solution or by spiking separately.

NOTE — Internal standards can be added to tubes just before field monitoring (as an extra check on tube transportation and handling procedures in the field) or immediately before analysis, for analytical quality control.

Some makes of automated thermal desorber allow gas phase internal standard to be introduced to the sampling end of sorbent tubes or focusing traps automatically, as part of the 2-stage thermal desorption process. If available, this facility can be also used to introduce internal standard to the focusing trap during desorption of radial diffusive sampling cartridges.

## 7.6 Certified Standard Tubes Available Commercially

Standard tubes pre-loaded with certified masses of representative compounds of interest are available commercially and can be used for establishing analytical quality control and for routine calibration.

Certified reference standards can be purchased from a number of sources including but not limited to the suppliers listed below:

HSL	The HSE Science and Research Centre, Harpur Hill, Buxton, Derbyshire, SK17 9JN, UK <a href="mailto:hseorders@tso.co.uk">hseorders@tso.co.uk</a> +44 333 202 5070
Markes International	Markes International Limited, 1000 Central Park, Western Avenue, Bridgend, CF31 3RH, UK <a href="mailto:enquiries@markes.com">enquiries@markes.com</a> +44 (0)1443 230935
VSL	Thijssseweg 11, 2629 JA Delft, The Netherlands <a href="mailto:vsl@vsl.nl">vsl@vsl.nl</a> *31 15 269 15 00

## 7.7 Carrier Gas

As thermal desorption is a powerful enrichment (concentration) and desorption technique, it is essential to use the highest quality carrier gas installation; 99.9995 percent is an example of a suitable grade of GC carrier gas.

## 8 APPARATUS

Ordinary laboratory apparatus and the following:

## 8.1 Sorbent Tubes — Used both for axial diffusive sampling and for calibration of axial and radial diffusive samplers

Tubes with outside diameter of 6.4 mm (0.25 inch), inside diameter of 5 mm (stainless steel) and of length 89 mm (3.5 inch) have been found to work well for this method and are used in many commercial TD systems (*see* Fig B1). Such ‘industry standard’ tubes typically contain an overall sorbent bed length of 40-60 mm, retained in the central, directly-heated portion of the tube using stainless steel gauzes. A precise 14 mm air space is left free of sorbent at the sampling end to define the diffusive air gap. A similar or longer air gap is left at the other end of the tube to minimize interference from diffusive ingress – e.g. when replacing storage caps with analytical caps.

Inert-coated stainless steel tubes are preferred if reactive organic compounds are of interest.

NOTE — Glass TD tubes are thicker walled and typically have a narrower and more variable internal diameter. It is also more difficult to precisely and repeatably define the air gap in glass tubes. For these reasons, glass tubes are not commonly used for diffusive (passive) sampling.

Each tube requires a unique alphanumeric identification number. Indelible bar codes or some other form of electronically-read label are also useful. Solvent-containing paints and markers or adhesive labels should not be used on the tubes.

Sorbent tubes suitable for diffusive sampling are available commercially or can be filled in the laboratory. Only the sorbent nearest the sampling end of the tube plays a part in the diffusive sampling process so single sorbent tubes are most commonly used for diffusive (passive) sampling.

### NOTES

- 1 There is a strong relationship between sorbent strength, i.e. tube retention volumes and safe sampling volumes in pumped sampling [*see* ISO 16017-1 and IS 5182 (Part 28)], and the stability of the axial diffusive sampling uptake rate over extended time periods<sup>3</sup>. As a general rule, if the retention volume of a given compound on a given single-sorbent tube is in the order of 20 l or more, back-diffusion of the analyte from that sorbent surface during sampling will be negligible. This means that uptake rates will be stable for extended periods (weeks).
- 2 Example axial diffusive sampling uptake rates for a range of compounds using stainless steel or inert-coated stainless steel TD tubes packed with specified sorbents are given in Annex C.

## 8.2 Diffusion Caps

Inert metal caps, fitted with a low-emission o-ring seal and with a fine stainless gauze across the surface (*see* Fig B3). The gauze in the cap defines the fixed air gap between the ambient air and sorbent sampling surface. The gauze in the cap also prevents large particles entering the diffusive tube when sampling in dusty environments.

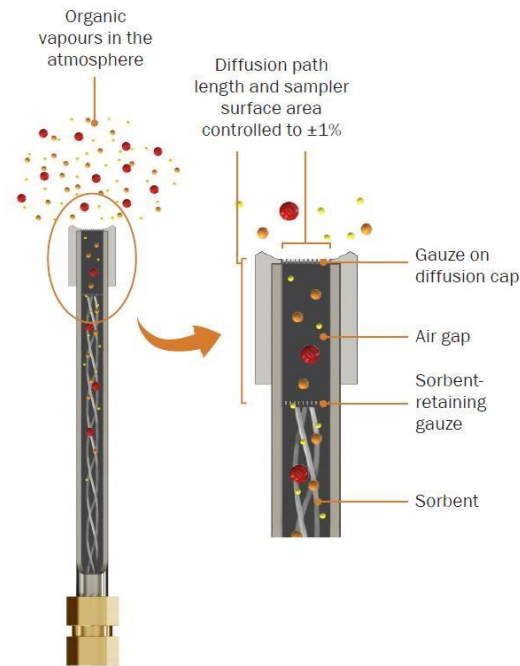
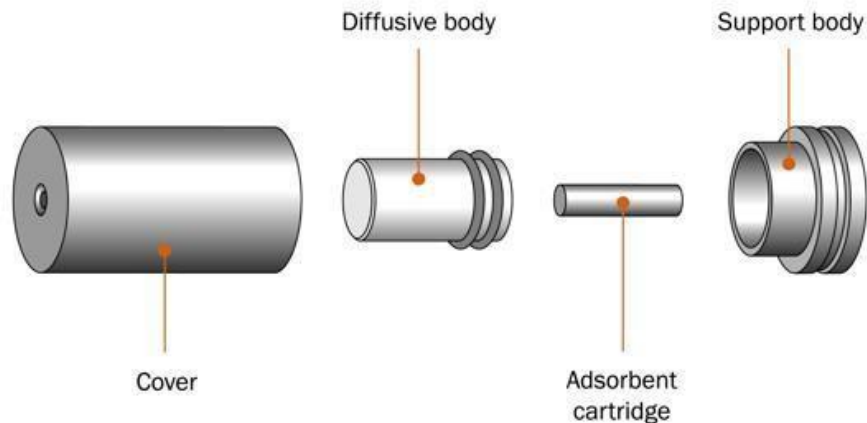


FIG B3 ILLUSTRATION OF A DIFFUSION CAP ON THE SAMPLING END OF A SORBENT TUBE DURING AXIAL DIFFUSIVE (PASSIVE) SAMPLING

### 8.3 Radial Diffusive Samplers and their Key Components

Radial diffusive samplers (*see* Fig. B2) comprise a sorbent cartridge housed in some form of permeable diffusive body. The diffusive body is typically constructed of sintered metal or porous polymer. The sorbent cartridge is packed with TD-compatible sorbent of suitable sorbent strength to retain the target compound or compounds of interest and is sized to fit into an empty TD tube for long term storage and for desorption and analysis. Key components of two example commercial brands of radial sampler are shown in Fig B4.

### Type A – POD sampler



### Type B – radiello sampler

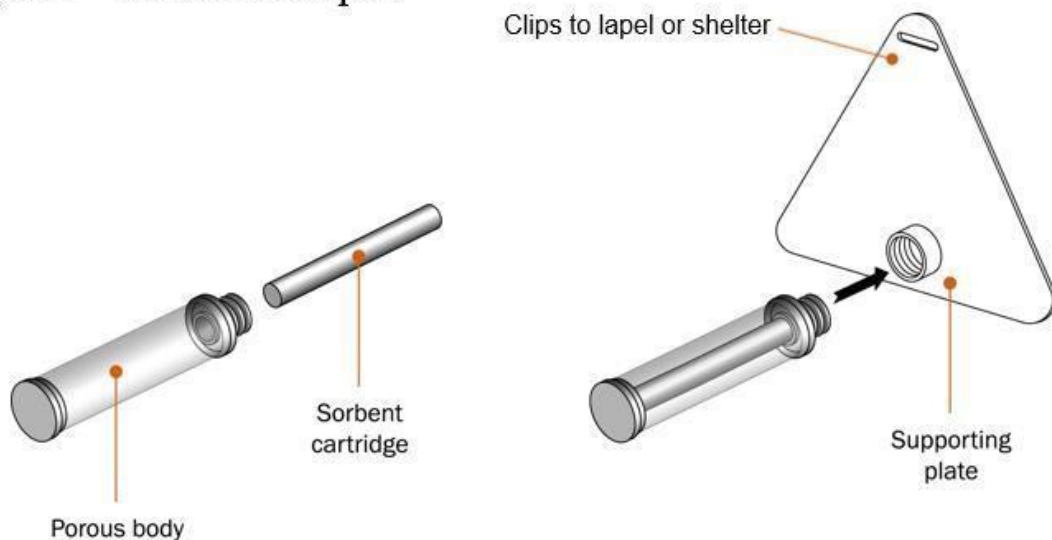


FIG B4 EXPLODED DIAGRAMS OF TYPE A (POD) AND TYPE B (RADIELLO) SAMPLERS SHOWING ALL COMPONENTS AND HOW THEY GO TOGETHER

#### 8.4 Long Term Storage Caps for Conditioned and Sampled Sorbent Tubes/Cartridges

Reliable long-term tube storage caps are a critical component of air monitoring, particularly at trace (ppb and sub-ppb) levels. They are required for transportation and storage of conditioned and sampled sorbent tubes and cartridges to prevent both contaminant ingress and analyte loss. Two-piece metal screw caps fitted with combined polytetrafluoroethylene (PTFE) ferrules have been found to provide the most secure and readily-available option. Validated studies have shown that they remain effective for many months at ambient and refrigerated temperatures (*see* also ISO 16017-1).

#### 8.5 Storage Containers for Conditioned and Sampled Sorbent Tubes and Cartridges

Clean, non-emitting containers made of inert materials such as unused paint cans or aluminium tins and glass jars with an air tight seal are used for storage and transportation of sealed diffusive

(passive) samplers before and after exposure. Suitable containers maintain artefact levels below required levels (*see* 13).

### **8.6 Precision Syringe**

Syringe used for injecting liquid standards shall be readable to at least 0.1 µl.

**8.7 Injection Facility** — for preparing standard tubes by injecting liquid (or gas) standards.

Calibration loading rigs designed specifically for spiking TD tubes with liquid or gas standards in a controlled flow of carrier gas, are commercially available. Alternatively, it is possible to use an unheated packed-column GC injector adapted with a push fit connector and o-ring seal for easy insertion and removal of sorbent tubes without damaging tube ends.

### **8.8 Carrier Gas Installation**

Only high-quality, stainless steel diaphragm regulators shall be used on carrier gas cylinders. Carrier gas lines shall be constructed using medical grade tubing and connected using appropriate swage fittings with no brazed joints. Oxygen and organic filters should be installed in the carrier gas lines and maintained regularly.

### **8.9 Gas Chromatograph (GC)**

Fitted with a mass spectrometric detector capable of detecting target compounds at the lowest levels of interest with a signal-to-noise ratio of at least 5 to 1, preferably 10 to 1 under practical routine operating conditions. The GC may also be fitted with a conventional GC detector such as a flame ionisation detector (FID) for routine operation if required.

### **8.10 Capillary GC Column.**

A polar or moderately polar, bonded capillary columns of 30 m to 60 m length, with an internal diameter 0.25 mm to 0.32 mm and phase thickness 0.25 µm to 1.0 µm are examples of columns proven to be suitable for analysing a wide range of trace organic air pollutants. Polar or more specialist columns may also be required for some applications.

### **8.11 Two-stage Thermal Desorption Apparatus,**

To accommodate one or multiple TD tubes which are uploaded into the carrier gas flow path for analysis. During thermal desorption, sorbent-packed TD tubes and tubes containing sorbent cartridges are heated with inert (carrier) gas flowing from the sampling end. Desorbed vapours swept from the sample tube are focused (concentrated) on a small, electrically-cooled sorbent trap which is then itself desorbed by heating it rapidly with carrier gas flowing in the opposite direction to that used during focusing. This fast secondary (trap) desorption ‘injects’ the analytes into the GC column in a narrow, concentrated band of vapour, compatible with capillary chromatography, and triggers the start of the GC program. (*see* Fig B5)

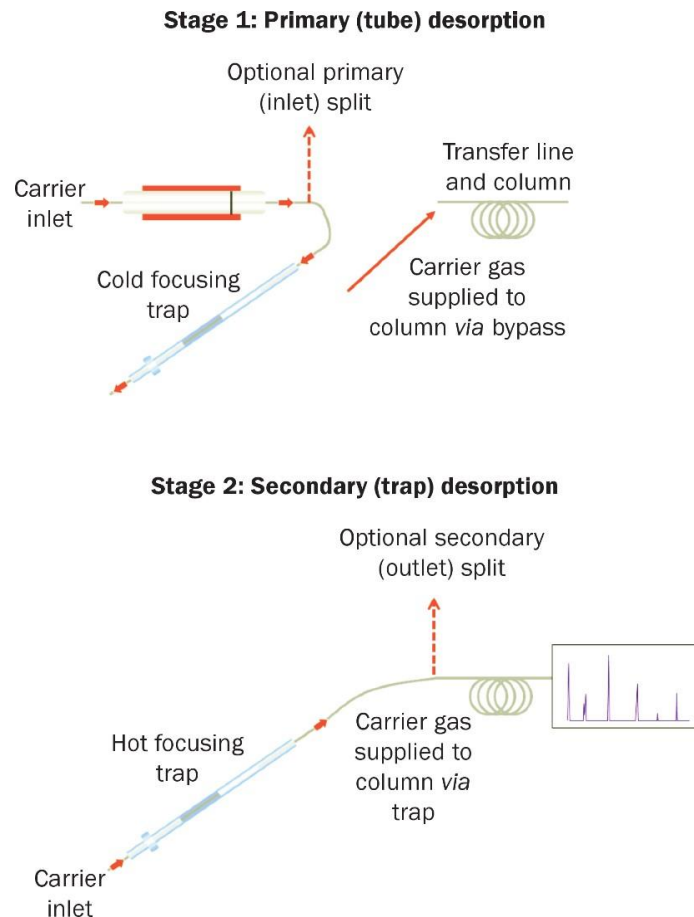


FIGURE B5 TWO MAIN STAGES OF THERMAL DESORPTION

NOTE — Reversing the direction of gas flow through the focusing trap during secondary desorption, allows the use of multiple sorbents and thus extends the volatility range of compounds that can be sampled and analysed in a single cycle.

Required features and functions of the thermal desorber:

- a) Leak-tight tube seals or 'analytical' caps to protect sampled and desorbed tubes from analyte loss and contaminant ingress while they are on the analytical system. This is particularly critical for automated operation where multiple tubes may be in situ for extended periods.
- b) Stringent leak testing of each tube after it is loaded into the sample flow path and before heat or gas flow is applied. Any tubes which fail the leak test should not be heated but retained intact for operator attention, while the system continues to analyse subsequent tubes in the sequence.

NOTE — As the carrier gas flow path of the chromatographic system is effectively broken into every time a new sample is uploaded for analysis, leak testing is essential for data confidence.

- c) Exclusion of artefacts from outer tube surfaces - The mechanism for sealing tubes into the sample flow path must exclude external contaminants, e.g. from handling tubes in the field.



- d) Pre-purging of air - Tubes shall be pre-purged with carrier gas (after leak testing and before desorption) to remove residual air, prevent sorbent and analyte oxidation and extend system life
- e) The secondary desorption process must allow quantitative splitting of the sample for compatibility with both trace ambient-level and higher workplace-level air contamination.

Other useful TD options include:

- 1) Cryogen-free (typically electrical) cooling of the focusing trap to controlled sub-zero temperatures – to ensure the repeatable retention of very volatile compounds without liquid cryogen
- 2) Automatic addition of gas-phase internal standard onto a series of pre-conditioned sorbent tubes before field monitoring or onto the sampling end of the sorbent tube or focusing trap immediately before primary desorption. For analytical quality control best practice
- 3) Automatic dry purging of tubes (in the sampling direction) before primary desorption to selectively eliminate water and minimise analytical interference during analysis of humid samples.
- 4) Sample splitting during primary (tube) as well as secondary (trap) desorption to allow quantitative analysis of very high-level samples (e.g. confined work spaces) as well as trace-level monitoring
- 5) Quantitative re-collection of sample split flow for repeat analysis and validation of desorption efficiency and compound recovery (*see 5.2 and 9.1*).

## 9 PREPARING FOR FIELD MONITORING

### 9.1 Developing and Validating the Analytical Method

The approximate masses of each target analyte that will be collected during air monitoring can be estimated from the expected air concentrations (or regulated limit levels), the expected exposure duration and analyte uptake rates (*see Annex B* for more information). Using conditioned sorbent tubes (*see 9.4*) prepare a number of mid-range standards containing these analyte levels (*see 7.4 and Annex B*).

Ensure the mass spectrometer detector is tuned and performing according to manufacturer's specifications. Use the relevant list of target compounds or preliminary screening data to check the suitability of the analyser configuration (choice of capillary GC column, focusing trap sorbents and settings, etc.) and choice of sorbents in the sampling tubes or cartridges (*see 7.3*). Use the mid-range standards to develop and optimize the analytical method – GC program, mass spectrometer settings, TD temperatures and times, desorption flows, split ratios, etc. – and to confirm system stability.

The sensitivity and linearity of the analytical method can then be evaluated by running a multi-level calibration (*see 9.3*).

Desorption efficiency (i.e. the recovery of analytes from the sorbent tube and through the 2-stage TD process to the GC column) must be above 95 percent. This can be tested by re-running desorbed standard tubes to check there is no carryover and comparing the results obtained by thermal desorption with those obtained for a liquid injection of the same standard under the same GC conditions (temperature program, gas flow, split flow, etc). Alternatively, if the selected thermal desorber offers the option of quantitative re-collection of split flow; repeat analysis of the re-collected samples will quickly show if one or more compounds is not being fully recovered as it

passes through the 2-stage TD process, relative to other stable compounds in the mix such as toluene. Parameters can then be amended accordingly.

NOTE — Most TD methods readily offer >99percent recovery. If analyte loss occurs, possible causes include incomplete desorption, thermal degradation and condensation or sorption of compounds within the sample flow path.

## 9.2 Checking System and Sorbent Tube/Cartridge Blanks

Using a clean empty TD tube and analytical conditions, check the TD-GC-MS system blank meets method requirements (*see 9.4*). Repeat this exercise with representative blank sorbent tubes or cartridges from the batch that will be used for field monitoring. These ‘laboratory blank’ tubes must contain the same sorbent as the field monitoring tubes, have been conditioned at the same time and stored in the same container. Ideally they should also have been packed at the same time and had a similar history of use.

If the system or laboratory blank levels do not meet method requirements condition the system and/or tubes using more stringent conditions (temperatures and gas flows) than will be used for analysis, then repeat the above blank analysis.

Take care not to exceed the maximum temperature of the least stable sorbent in the sample tubes.

NOTE — Tubes may need repacking or cartridges might need replacing if they can no longer reach the required cleanliness after extensive conditioning.

## 9.3 Calibration

Prepare conditioned sorbent tubes (*see 9.4*) with standards of the target compounds (*see 7.4*) at 5 different levels (for more information *see Annex B*). The analyte masses introduced in each standard should cover the range expected to be collected during field monitoring with a factor of at least 20 between the analyte masses on the lowest and highest level standards.

A mid-range standard should be analysed at least every ten samples during routine operation and the results compared with the 3 previous mid-range standards to ensure system performance remains stable. A multi-level calibration, with replicates at each level, should be carried out whenever analysis of the single level standards shows system responses have drifted by 10 percent or more. A multi-level calibration, with replicates at each level, should also be repeated whenever the analytical method or target compound list is changed and immediately before analysis of a new batch of samples – ideally as part of the same analytical sequence.

Replicates for at least 4 of the 5 calibration levels, including the lowest and highest levels, should agree within 10 percent or the multi-level calibration exercise shall be repeated. The linear regression coefficient should also be above 0.99 for toluene over the calibration range.

## 9.4 Sorbent Tube or Cartridge Conditioning

Newly-packed sorbent tubes or cartridges should be obtained pre-conditioned from the manufacturer or be stringently conditioned on receipt in the laboratory, following manufacturer’s instructions. Once sorbent tubes and cartridges have been conditioned they should remain sealed with long term storage caps (*see 8.4*), kept in a suitable clean storage container (*see 8.5*) and maintained at a controlled, stable temperature (ideally between 20 °C and 30 °C) at all times when not in use.

The total number of sorbent tubes and diffusion caps or clean sorbent cartridges and radial sampler assemblies required for a field monitoring exercise should be calculated, including those for required for sampling, field blanks and lab blanks.

NOTE — Air monitoring studies carried out using radial diffusive samplers will also require conditioned sorbent tubes for multi-level and single-level calibration.

If a batch of sorbent tubes or cartridges has only just been desorbed and analysed for a previous study (within 2 weeks) and if pollutant levels encountered during the previous study were low, and provided they have been kept properly sealed and stored since their last use, they can be re-used for field monitoring without further conditioning. In all other cases the required batch of sorbent tubes or cartridges should be conditioned within 2 weeks of the start of a field monitoring exercise by desorbing them for 10-15 minutes and at 100 ml/min inert (carrier) gas flow using slightly more stringent conditions than those required for analysis, but taking care not to exceed the safe maximum temperature of any sorbent present.

In either case, a representative selection of the batch of tubes or sorbent cartridges (at least 1 in 10) should be analysed using routine analytical parameters (*see 9.1*), to ensure that the analytical blank is sufficiently small before being sent to the field for air sampling. The blank level is acceptable if interfering peaks are at 10 percent or less of the areas of target compounds at the lowest level interest. If the blank is unacceptable, the sorbent tubes or cartridges should be reconditioned.

At least two of the conditioned tubes or cartridges from each batch shall be retained sealed and stored in the laboratory throughout the field monitoring exercise. These are the laboratory blanks (*see 5.5*).

NOTE — All sorbents are subject to inherent artefacts the level of which will vary with sorbent type and desorption temperature. Follow manufacturer's guidance with respect to conditioning and analysis parameters to keep artefact levels to a minimum. It is normally possible to keep individual artefacts below 5-10 mg on conditioned Tenax tubes/cartridges and around 2 ng on conditioned carbon tubes/cartridges. It is also usually possible to chromatographically separate sorbent artefacts from low level of compounds of interest such that the resultant analytical interference is not significant.

## 10 SAMPLING

### 10.1 General Preparation for Sampling

Before monitoring begins, estimate the ideal exposure time based on study requirements, the relevant uptake rates for the compounds and sampler type selected, the expected concentration range, available analytical detection limits and required reporting limits.

#### NOTES

- 1 Stable uptake rates on axial diffusive tubes packed with an appropriate sorbent tube for the target analytes are typically in the order of 2 ng/ppm/min (or 2 pg/ppb/min) for exposure periods ranging from 8 h to 2 weeks or more (*see Annex C*). This number can be used as a rough guide when calculating the masses expected to be collected during monitoring (*see Annex B*).
- 2 Stable sampling rates on type A radial diffusive samplers housing cartridges packed with an appropriate sorbent tube for the target analytes are typically in the order of 5 – 8 mL/min for exposure periods ranging from 4 h – 3 days (*see Annex C*). This number can be used as a rough guide when calculating the masses expected to be collected during monitoring (*see Annex B*).
- 3 Stable uptake rates on type B radial samplers housing cartridges packed with an appropriate sorbent tube for the target analytes are typically in the order of 20 – 30 mL/min for exposure periods ranging from 8-24 h *see Annex C*. This number can be used as a rough guide when calculating the masses expected to be collected during monitoring (*see Annex B*).

- 4 Quantitative diffusive sampling is robust and reproducible provided a sorbent of sufficient strength is selected for the given target compounds. Using a sufficiently strong sorbent means that the vapour concentration at the surface of the sorbent is maintained at or near zero for the duration of sampling (*see* Fig B6). If the sorbent used is too weak, retained compounds back-diffuse from the sorbent over time causing the concentration of analyte in the air at the sorbent surface to increase. When this happens, the ‘diffusion gradient’ is reduced, lowering the sampling rate (*see* Fig B6) and causing under-reporting.
- 5 Most diffusive samplers only have one sorbent exposed meaning that each sampler addresses a limited analyte volatility range. If the compounds of interest cover a wider volatility range, two or more samplers, packed with different sorbents, can be used in parallel. The samplers described in this standard are re-usable and don’t need a pump so using two or more samplers in parallel remains a cost-effective monitoring option.

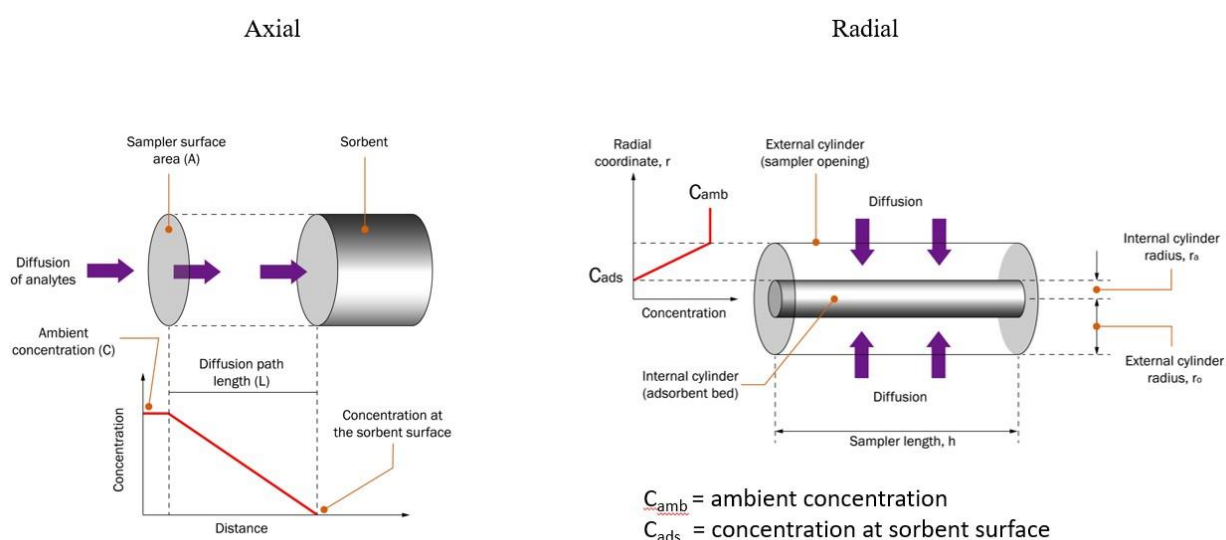


FIG B6 ILLUSTRATION OF THE MECHANISM AND PRINCIPLES OF DIFFUSIVE SAMPLING. EXAMPLES FOR AXIAL AND RADIAL SAMPLERS.

## 10.2 Area Monitoring

Identify representative sampling locations that will not be impacted by exceptional localized pollution sources or ventilation conditions. Moderate air speeds are recommended. Samplers should be protected from particulate ingress by orientating them downwards. They should also be protected from precipitation when monitoring outdoors, using simple, well-ventilated and non-emitting shelters.

## 10.3 Personal Exposure Assessment

When used for personal exposure assessment, diffusive samplers should be positioned near the breathing zone of the wearer (e.g. on a collar or lapel), unimpeded by clothing and with the sampling end of axial tubes pointing down.

## 10.4 Sample Collection with Axial Diffusive Sorbent Tubes

Transport all conditioned sorbent tubes and diffusion caps to the field in clean storage containers (*see* 8.5). Leave tubes capped and in the storage container until they have equilibrated with ambient conditions. The non-sampling end of sorbent tubes remain sealed with long term storage caps (*see*

**8.4)** throughout the diffusive monitoring process. When ready to start sampling, replace the long-term storage cap at the sampling end of the tube with the diffusion cap (*see* Fig B3). Keep the long-term storage caps in the tube storage container (*see* **8.5**) throughout the monitoring exercise.

Note and record the unique identification number of the tube. Check and record the time and date when monitoring starts and again at the end of the monitoring period when the diffusion cap is removed and replaced with a long term storage cap (*see* **8.4**) using appropriate tools. Place the sealed and sampled tubes back into the storage and transportation container without delay. If the container of tubes is to be held under refrigerated conditions, ensure storage caps are retightened once tubes have equilibrated at their minimum storage temperature.

Recommended exposure times for axial diffusive samplers in workplace air are 8 h.

Recommended exposure times for axial diffusive samplers in ambient and indoor air are 7-14 days

For more information (*see* Annex B)

NOTE — Refrigerated storage is not usually necessary provided samples can be maintained at a stable temperature below 25 °C and analysed within 4 weeks.

## **10.5 Sample Collection with Radial Diffusive Samplers**

Follow manufacturer's instructions with respect to preventing contamination and analyte loss when transporting the various components of radial diffusive samplers to and from the field.

NOTE — Some manufacturers specify transporting radial diffusive samplers ready assembled and covered, others recommend completing sampler assembly in the field.

Clean containers (*see* **8.5**) should be used for storing and transporting samplers and their components at all times. Leave the samplers or sampler components sealed and in the storage container until they have equilibrated with ambient conditions. This prevents condensation. Assemble the samplers as quickly as possible at the start of sampling (*see* Fig B2 and B4) and store any unused components in the transport container (*see* **8.5**) throughout the monitoring exercise.

Note and record the sampler's unique identification number and the time and date of monitoring start and end. At the end of the monitoring period follow manufacturer's instructions with respect to sealing the sampler or sampler components to prevent contamination or analyte loss before analysis. Place the sealed samplers or sampler components back into the storage and transportation container without delay. Follow manufacturer's advice with respect to storing samples under refrigerated or ambient conditions.

Recommended exposure times for radial diffusive samplers in workplace air are 1-4 h.

Recommended exposure times for radial diffusive samplers in ambient and indoor air are 8-72 h.

For more information *see* Annex B.

## **10.6 Quality Control during Sampling**

### **10.6.1 Field Blanks**

This should be prepared using devices identical to those used for sampling. They should be transported to the field monitoring location and subjected to the same handling procedure except for the actual period of diffusive sampling. Record these as blanks and analyse them in the same sequence as the samples.

### 10.6.2 Replicate Samples

This should normally be collected in parallel at 10 percent of sampling locations. At least one replicate sample pair should be collected during each monitoring exercise. Replicate samples should be analysed in the same sequence as the samples.

## 11 DESORPTION AND ANALYSIS

### 11.1 Preparing for Analysis

Keep all diffusively sampled sorbent tubes and radial sampler components associated with a monitoring exercise (samples and blanks) sealed and inside the sealed storage/transportation container (*see 8.5*) until ready for analysis. If they have been stored under refrigerated conditions, allow them to equilibrate with the laboratory temperature before removing any caps or seals to minimize risk of condensation which could cause analytical interference.

Quickly transfer sampled or field blank radial sorbent cartridges into clean empty TD tubes if this has not already been done. Ensure the sorbent cartridge is supported within the central, directly heated portion of the TD tube and seal the ends of the tube with long term storage caps or directly with analytical end caps (*see 8.10*) if analysis by automated TD-GC is imminent. Ensure that blank and sampled sorbent tubes and cartridges are not left exposed to lab air contamination for any length of time.

When ready for analysis, replace long-term tube storage caps with analytical end caps and load the sample tubes into the TD autosampler (*see 8.10*). Alternatively, if using a single-tube desorber, only uncap each sample tube immediately before it is sealed into the system for analysis.

Plan the analytical sequence (manual or automated) such that samples are interspersed with calibrants (mid-range and multi-level as required), field blanks, lab blanks and replicate samples.

### 11.2 Analysing Sorbent Tubes and TD Tubes Containing Radial Sorbent Cartridges

Once uploaded and sealed into the TD flow path (manually or automatically as part of a multi-tube sequence), each sample tube proceeds through a series of automatic checks and operations:

While maintained at ambient temperature each tube is first pressurized and subjected to a stringent, no-flow leak test.

#### NOTES

- 1 Without such a test, a leak could go undetected, undermining confidence in data quality.
- 2 Any tubes which fail the leak test should not be analysed, but retained intact for user inspection and intervention to prevent sample loss.

Air is then purged from the tube, to vent, before heat is applied to avoid analyte and sorbent oxidation, artefact formation and degradation of the analytical system.

NOTE — It usually requires 10 x the volume of the tube (i.e. 20 ml to 30 ml of carrier gas) to completely displace air, but larger volumes of carrier gas will be required for complete air displacement when strong sorbents such as carbon molecular sieves are used.

If the selected thermal desorber offers automated dry purging to remove residual water, this step can be included here, if required, and takes place with inert gas flowing through the tube from the sampling end. Similarly, if the TD system offers the option of automated addition of gas-phase internal standard, it is usually introduced onto the sampling end of the sorbent tube at this point or (if analysing radial sorbent cartridges) onto the inlet/outlet end of the focusing trap.

The TD tube is then heated with carrier gas flowing (typically at 20-100 ml/Min) though from the non-sampling end. Organic vapours are desorbed from the sorbent and swept into the cold focusing trap where they are re-concentrated.

NOTE — Some TD systems allow sample splitting during tube desorption such that only a small proportion of the total sample reaches the focusing trap. This facilitates analysis of highly contaminated industrial air samples.

Once primary (tube) desorption is complete, the focusing trap is heated rapidly (typically at 40°C-100°C) in a reverse flow of carrier gas (typically 2-50 ml/Min). This desorbs the organic vapours and transfers (injects) them into the GC column in a narrow, concentrated band of vapour, triggering the start of the GC run. (see Fig B7 to Fig B8) Secondary (trap) desorption can be carried out split or splitless (see Fig B5).

The respective response factors obtained during system calibration can then be applied to the measured peak areas to determine the mass of each analyte in samples and blanks.

Once analysis of each individual tube or sequence of tubes has been completed (manual or automated desorbers respectively), it (they) should be removed from the system, resealed with long-term storage caps (see 8.4) and replaced in the clean storage container (see 8.5). Tube desorption automatically cleans the sorbent tubes and cartridges and leaves them ready for immediate re-use in many cases (see 8.4 for more details.)

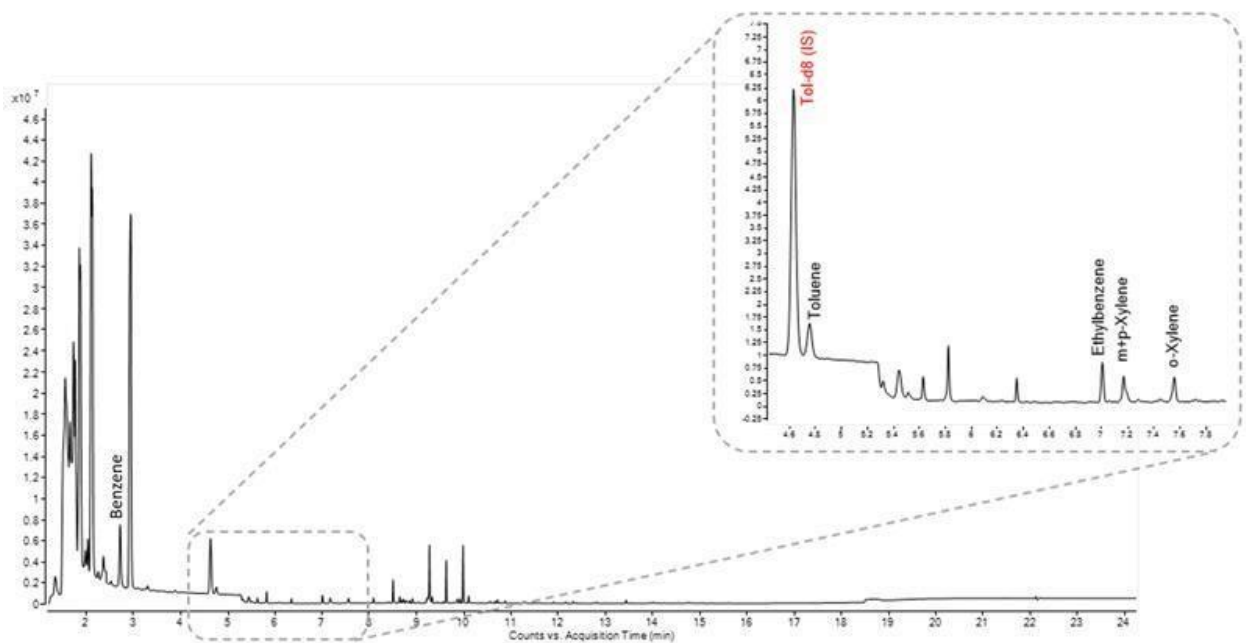


FIG B7: EXAMPLE ANALYSIS OF AN AIR SAMPLE COLLECTED USING A POD RADIAL DIFFUSIVE SAMPLER FROM AN INDOOR ENVIRONMENT AND RUN USING THERMAL DESORPTION GCMS. NOTE THAT ALL IDENTIFIED PEAKS ARE AT OR BELOW LOW PPB-LEVEL

Table 2 Instrument Parameters

(Fig B7)

Sampler	POD	Graphitized carbon
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**Instrumentation - Fig A4**

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Thermal desorber	Two stage system, capable of 'Re-collection', with Peltier cooled backflush trap
Gas Chromatograph	Single Split/Splitless Injector, running in constant flow when Thermal Desorber is interfaced.
Mass spectrometer	Single Quadrupole

---

**Instrument parameters – Thermal desorber**

---

Focusing trap	Capable of collecting compounds from C-4 to C-30	Quartz wool/Porous polymer/Graphitised carbon
Flowpath temperature	180 °C	
Tube prepurge	50ml/Min	1 min
Tube desorb	350 °C	10 min
Trap low temperature	-30 °C	
Trap desorb	300 °C	3 min
Outlet split	5 ml/Min	

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**Instrument Parameters - Gas Chromatograph**

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Carrier gas	Helium	
Column	(5percent-phenyl)-methylpolysiloxane	30 m × 0.25 mm × 0.25 µm
Column flow	1.5 ml/Min	Constant flow mode
Oven ramp	40°C (5 min), 20°C/min to 325°C (5 min)	
Inlet temperature	210 °C	

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**Instrument Parameters - Mass spectrometer**

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MS source temperature	250 °C	
MS quad temperature	200 °C	
MSD transfer line temperature	335 °C	
Data acquisition mode	Full scan	m/z 30 – 350



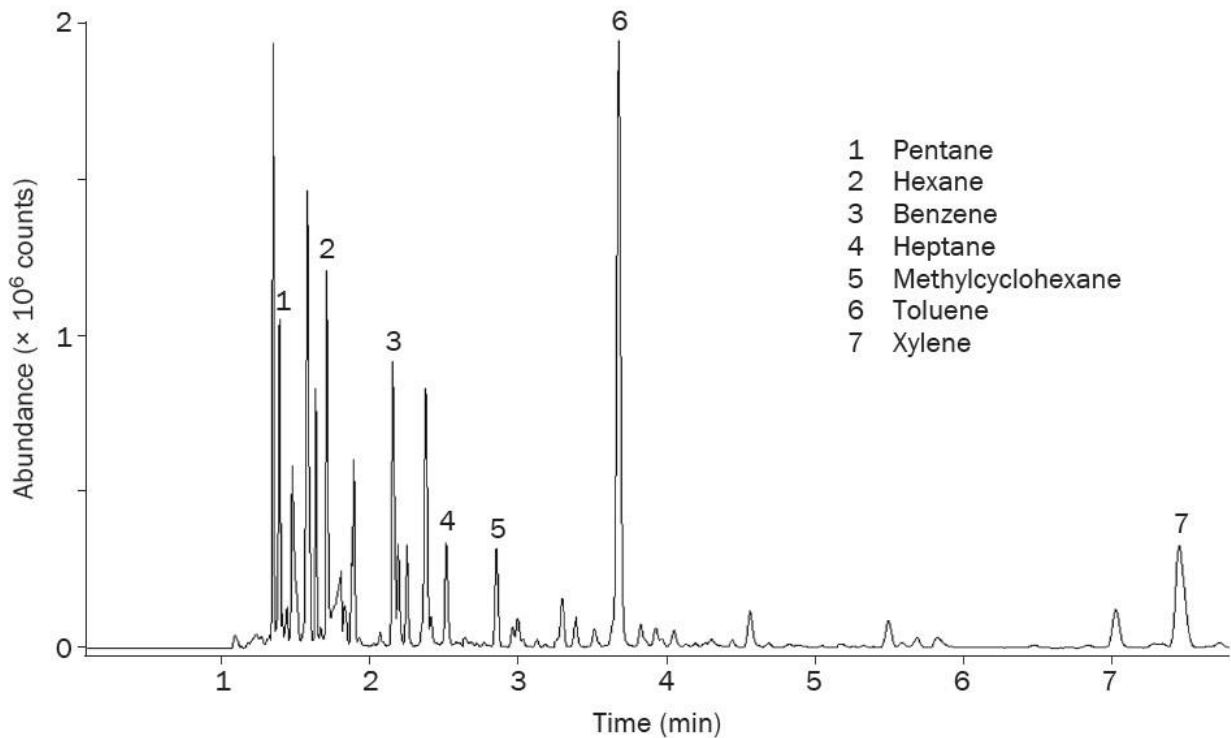


FIG B8: EXAMPLE ANALYSIS OF AN AIR SAMPLE COLLECTED USING AN AXIAL DIFFUSIVE SAMPLER FROM AN INDUSTRIAL LOCATION OVER A TWO WEEK PERIOD AND RUN USING THERMAL DESORPTION GCMS.

**Table 3 Instrument Parameters**

(Fig B8)

**Instrumentation – Figure A4**

Sorbent tube	Compliant with USEPA Method carbon 325	Graphitised
Thermal desorber	Two stage system, capable of ‘Re-collection’, Peltier cooled backflush trap	
Gas Chromatograph	Single Split/Splitless Injector, running in constant flow when Thermal Desorber is interfaced.	
Mass spectrometer	Single Quadrupole	

**Instrument parameters – Thermal desorber**

Focusing trap	Capable of collecting ‘Air Toxics’	Porous polymer/Graphitised carbon/Carbonised molecular sieve
Flowpath temperature	150°C	

Tube prepurge	50ml/Min	1 min
Tube desorb	350°C	10 min
Trap low temperature	25°C	
Trap desorb	320°C	3 min
Outlet split	5 ml/Min	

---

**Instrument parameters – Gas Chromatograph**

---

Carrier gas	Helium	
Column	(5percent-phenyl)-methylpolysiloxane	30 m × 0.25 mm × 0.25 µm
Column flow	1.5 mL/min	Constant flow mode
Oven ramp	40°C (5 min), 20°C/min to 325°C (5 min)	
Inlet temperature	210 °C	

---

**Instrument parameters – Mass spectrometer**

---

MS source temperature	250 °C	
MS quad temperature	200 °C	
MSD transfer line temperature	335 °C	
Data acquisition mode	Full scan	m/z 30 - 350

---

## 12 CALCULATIONS

### 12.1 Axial samplers

The concentration of each analyte in the sampled air,  $C_m$ , can then be calculated in ppm or ppb as follows:

$$C_m(ppm) = \frac{(M_s - M_b)ng}{U \times t}$$

Or

$$C_m(ppb) = \frac{(M_s - M_b)pg}{U \times t}$$

Where

$M_s$  is the mass of analyte measured on the sample tube in nanograms or picograms

$M_b$  is the mass of that analyte detected on the field blank in nanograms or picograms

$U$  is the uptake rate constant for the analyte ( $\text{ng.ppm}^{-1}.\text{min}^{-1}$  or  $\text{pg.ppb}^{-1}.\text{min}^{-1}$ )

And  $t$  is the time of exposure in mins

#### *Example calculation ambient air*

Ambient air was monitored for compound X, with an uptake rate of 2.0 pg/ppb/min ( $\text{ng/ppm/Min}$ ), over a 14 days period. This equates to 20,160 min

142,500 pg of compound X were detected on the sample tube and 2,500 pg were detected in the field blank.

$$C_m (\text{ppb}) = (142,500 \text{ pg} - 2,500 \text{ pg}) / 2 \times 20,160$$

$C_m$  = approximately 3.5 ppb

#### *Example calculation workplace air*

Workplace air was monitored for compound Y, with an uptake rate of 2.5 ng/ppm/min ( $\text{pg/ppb/Min}$ ), over an 8 h period. This equates to 480 mins

2410 ng of compound Y were detected on the sample tube and 10 ng in the field blank.

$$C_m (\text{ppm}) = (2410 \text{ ng} - 10 \text{ ng}) / 2.5 \times 480$$

$C_m$  = approximately 2 ppm

Concentrations stated in Vol/vol (ppm or ppb) terms can readily be converted to mass per unit volume terms ( $\mu\text{g}/\text{m}^3$ ) using the molecular weight of the relevant compound (*see* Annex B for more example calculations and information).

NOTE — To apply uptake rates quoted in  $\text{ml}.\text{min}^{-1}$  ( $\text{cm}^3.\text{min}^{-1}$ ) and for other supportive information, please (*see* ISO 16017-2)

## 12.2 Radial Samplers

NOTE — Uptake rates for radial samplers are typically quoted in units of  $\text{ml}.\text{min}^{-1}$  not  $\text{ng.ppm}^{-1}.\text{min}^{-1}$

The average concentration,  $C_m$ , of each analyte in the sampled air can be calculated in  $\mu\text{g}/\text{m}^3$  as follows:

$$(\mu\text{g m}^{-3}) = \frac{(M_s - M_b)\mu\text{g}}{U_k \times t} \times 1,000,000$$

Or

$$(\mu\text{g m}^{-3}) = \frac{(M_s - M_b)\text{ng}}{U_k \times t} \times 1,000$$

Where

$M_s$  is the mass of analyte measured on the sample tube in micrograms

$M_b$  is the mass of that analyte detected on the field blank in micrograms

$U_k$  is the uptake rate at temperature K for the analyte

And t is the exposure time in mins

*Example calculation indoor air*

Indoor air was monitored for compound X using a POD sampler with an uptake rate of 8 ml/min over a 24 h period. This equates to 1440 minutes

235 ng of compound X were detected on the sample cartridge and 5 ng were detected in the field blank.

$$C_m (\mu g m^{-3}) = [(235 \text{ ng} - 5 \text{ ng}) / 8 \times 1440] \times 1,000$$

$$C_m = \text{approximately } 20 \mu g m^{-3}$$

*Example calculation workplace air*

Workplace air was monitored for compound Y using Radiello sampler with an uptake rate of 20 ml/Min, over a 1 h period. This equates to 60 minutes.

1210 ng of compound Y were detected on the sample cartridge and 10 ng in the field blank.

$$C_m (\mu g m^{-3}) = [(1210 \text{ ng} - 10 \text{ ng}) / 20 \times 60] \times 1000$$

$$C_m = \text{approximately } 1000 \mu g m^{-3} \text{ or } 1 \text{ mg m}^{-3}$$

Concentrations stated in mass per unit volume terms ( $\mu g/m^3$ ) can readily be converted to vol/vol (ppm or ppb) terms using the molecular weight of the relevant compound (*see* Annex B for more example calculations and supportive information).

### 13 QUALITY CONTROL

The following quality control criteria shall be met:

- a) The desorption efficiency shall be >95 percent (>99 percent should be readily achievable) (*see 9.1*)
- b) The linear regression co-efficient shall be above 0.99 for toluene across the calibration range (*see 9.3*)
- c) The chromatographic system and method must be capable of detecting target compounds at the lowest levels of interest with a signal-to-noise ratio of at least 5 to 1, preferably 10 to 1.
- d) The blank level is acceptable if interfering peaks are below 10 percent of the areas of target compounds at the lowest level interest (*see 9.4*).
- e) If field blank chromatograms reflect the same profile of organics as on the samples, and if the levels of these components are 5 percent or more of the sampled compounds, this must be noted in the final report (*see 14*). If levels are 10 percent or more of those on samples, the sample data are invalid.
- f) Replicate mid-level standards should agree within 10 percent.
- g) Replicate samples (*see 10.6.2*) should agree within 15 percent for >80 percent of reported analytes.

NOTE — Replicate samples provide a measure of the precision achievable for the entire monitoring procedure including the sampling and analysis.

## 14 TEST REPORT

The laboratory test reports should contain the details specified for the respective monitoring campaign. The sort of information which may be required includes:

- a) Details of the sampler (unique identification number, sampler type, sorbents, etc), analytical system used and associated data file identification;
- b) Chain of custody information (e.g. details of who collected the samples and who ran the analysis)
- c) Reference to this standard and any supplementary standards referenced
- d) The sampling location, sampling start and end times/dates and the total duration of sampler exposure.
- e) The test results for each sample, including target compounds (calibrated using reference compounds) and any unknowns present in significant concentrations (>5 percent of the total peak area) calibrated using the response factor for toluene.

### NOTES

- 1 When reporting results for locations that were monitored using replicate samples, the mean result should be reported for all analytes that agree within 15 percent (*see 12*). Only the higher result should be reported for all other analytes. (see also below)
  - a) Other relevant test results – including:
    - 1) the most recent multi-level calibration (report and example chromatogram from the lowest level standard),
    - 2) any mid-range, single-level standards analysed during the sample sequence (reports and chromatograms)
    - 3) any field and/or laboratory blank tubes analysed during the sample sequence (reports and chromatograms)
  - b) Identify any monitoring locations where replicate samples were collected and where most of the measured target compound concentrations differ by more than 15 percent
- 2 In this situation, results from the whole study should be regarded as semi-quantitative unless there is evidence to the contrary (e.g. several other replicate samples collected in the same monitoring exercise which agree within 15 percent).
  - a) Any unusual features noted during sample collection or analysis
  - b) Any operation not included in this standard.

## 15 TRADEMARKS

Listed products are included to aid readers of this standard and do not indicate an endorsement. Equivalent products may be used.

- a) Tenax TA<sup>®</sup> is a registered trademark of Buchem BV, the Netherlands
- b) Carbpac X<sup>™</sup> and Carboxen 1003<sup>™</sup> are trademarks of Supelco Inc., USA
- c) Carbograph 5 TD<sup>™</sup> is a trademark of LARA s.r.l., Italy
- d) Sulficarb<sup>™</sup> is a trademark of Markes International Ltd., UK

- e) Fast-PAS is a trademark of Markes International Ltd., UK
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## ANNEX A

(Clause 3)

### COMPARING THERMAL DESORPTION (TD) WITH SOLVENT EXTRACTION (SE) FOR AIR MONITORING

#### A-1 SENSITIVITY

Solvent extraction typically involves 1-2 µl GC injections of 1-2 ml solvent extracts taken from the charcoal tubes. In contrast, TD enables 100percent transfer of collected compounds to the GC column. This factor alone means TD is 1000 times more sensitive – compatible with ppb and sub-ppb detection limits as well as higher level samples.

#### A-2 DESORPTION/EXTRACTION EFFICIENCY

National and international standard methods specifying thermal desorption (*see A-3*), including this standard, require at least 95percent desorption efficiency from the sorbent sampling tube and, in practice, complete extraction/desorption and transfer of target analytes to the GC in a single desorption cycle is invariably straightforward. This is because TD is a dynamic process, with gas continually purging compounds away from the sorbent or sample matrix as soon as they are released into the vapour phase by the rising temperature. In contrast, typical solvent extraction procedures are static, with analytes partitioning, in equilibrium, between the sorbent, solvent and vapour (headspace) phases. Standard solvent extraction methods therefore typically require only 75 percent recovery and even this can be difficult to achieve reliably in practice (*see A-3*).

#### A-3 DESORPTION/EXTRACTION REPEATABILITY

Desorption efficiencies have been reported to drop below 30percent when charcoal tubes and CS<sub>2</sub> extraction are used for polar compounds in humid air. This compromises repeatability and can lead to significant under-reporting, as the analyst may not be aware of field/sample conditions.

#### A-4 EXPOSURE RISK

The solvent most commonly used for charcoal tube extraction is CS<sub>2</sub>. CS<sub>2</sub> is toxic, odorous and presents a potential health and safety hazard to laboratory staff. Thermal desorption procedures often require the preparation of a liquid standard for calibration, but no hazardous extraction solvent.

#### A-5 COSTS

Cost should only be taken into consideration if both methods work equally well for the given air monitoring application. However, as a general rule, thermal desorption costs less per sample unless operation is infrequent, in which case solvent extraction is more cost effective.

The initial investment required for TD operation is typically higher than that for solvent extraction, even allowing for installation of a solvent fume hood in the laboratory to extract CS<sub>2</sub>. TD tubes are also more expensive than charcoal tubes, but as they are re-usable (typically at least 100 or 200 times)

the cost per sample is much lower than one-use charcoal tubes. TD can also be fully automated, reducing errors and cost relative to labour-intensive solvent extraction.

#### **A-6 ANALYTICAL INTERFERENCE**

One of the reasons CS<sub>2</sub> was originally selected as a preferred solvent for charcoal-based air sampling methods is that it gives little or no signal on a GC flame ionization detector (FID). However, this advantage does not hold for GC-MS detection. Common solvent interference concerns include masking of peaks of interest, signal quenching (for components co-eluting with the solvent) and baseline disturbances. All these make peak integration difficult and more prone to error. TD is inherently free from solvent and other chromatographic interference (*also see A-7*).

#### **A-7 SELECTIVE ELIMINATION OF INTERFERENTS**

Depending on the sorbent and compounds of interest, TD procedures can generally be optimized to selectively purge air, water and other volatile interferences while target species are retained and enriched/concentrated. This is rarely possible for charcoal tube and CS<sub>2</sub> extraction methods.

#### **A-8 VERSATILITY**

TD sorbent tubes can be used for pumped sampling or in axial diffusive (passive) mode.

#### **A-9 REPEAT ANALYSIS**

Historically, the main advantage of solvent extraction vs TD methods was that each liquid extract could be analysed several times whereas thermal desorption was a one-shot technique. However, most commercial TD systems now offer quantitative re-collection of samples for repeat analysis, meaning the one-shot limitation no longer applies.

### **ANNEX B**

*(Clause 1, Clause 7.4, Table 1, Clause 7.4.4, Clause 9.1, Clause 9.3, Clause 10.1, Clause 10.4, Clause 10.5, Clause 12.1, Clause 12.2 )*

#### **GUIDANCE ON ESTIMATING THE MASS OF ANALYTE THAT WILL BE COLLECTED ON A SORBENT TUBE OR CARTRIDGE DURING DIFFUSIVE (PASSIVE) AIR MONITORING**

#### **AND**

#### **GUIDANCE ON THE RELATIONSHIP BETWEEN CONCENTRATION EXPRESSED IN VOL/VOL TERMS (PPM OR PPB) AND CONCENTRATION EXPRESSED AS MASS PER UNIT VOLUME**

#### **B-1 ESTIMATING THE MASS OF ANALYTE THAT WILL BE RETAINED DURING MONITORING**

The approximate mass of target analyte that will be retained during diffusive (passive) monitoring can be derived from the expected atmospheric concentration or (alternatively) the safe air limit level (if applicable), the exposure (monitoring) period and the uptake rate for that compound on the type of diffusive monitor selected. Example calculations for nominal compounds are presented in Section 11. Additional real world examples for specified compounds are presented here.

**Example 1:** monitoring benzene in urban air for 2 weeks using axial diffusive tubes packed with Carbopack X and an uptake rate of 2 pg/ppb/min, where the limit level is 5 µg/m<sup>3</sup> or 1.6 ppb.

In this case the expected mass of benzene retained can be estimated as follows:

t = Two weeks = 20,160 mins

If 2 = pg adsorbed per ppb per min of exposure:  $2 = \frac{pg}{ppb \times t(mins)}$

Therefore pg benzene expected = 2 x 1.6 (ppb) x 20,160 = 64512 pg which is roughly 65 ng

**Example 2:** monitoring 1,1-dichloroethene (vinylidene chloride) in workplace air for 8 h using axial diffusive tubes packed with Sulficarb and an uptake rate of 2.5 ng/ppm/min, where the limit level is 4 mg/m<sup>3</sup> or 1 ppm.

In this case the expected mass of 1,1-dichloroethene retained can be estimated as

follows: t = 8 h = 480 mins

If 2.5 = ng adsorbed per ppm per min of exposure:  $2.5 = \frac{ng}{ppb \times t(mins)}$

Therefore ng 1, 1-dichloroethene expected = 2.5 x 1 (ppm) x 480 = 1200 ng which is 1.2 µg

**Example 3:** monitoring toluene for 48 h using radial Fast-PAS diffusive samplers packed with Carbopack X and an uptake rate of 6.04 (cm<sup>3</sup>/min), in an ambient environment where the usual concentration is known to be around 10 µg.m<sup>-3</sup>.

In this case the expected mass of toluene retained can be estimated by applying the equation shown in Section 11.2 as follows:

t = 48 h = 2880 mins

$$\frac{10 \mu\text{g.m}^{-3} \times 6.04 \text{ cm}^3/\text{min} \times 2880 \text{ min}}{1,000,000} = \text{mass in } \mu\text{g}$$

Therefore the mass of toluene expected = 0.172 µg which is 172 ng

## **B-2 BRIEF GUIDANCE ON CONVERTING CONCENTRATION EXPRESSED AS MASS/UNIT VOLUME TO PPM OR PPB**

**B-2.1** Go back to first principles and apply the gas laws as follows:

**B-2.1.1** A mole of pure vapour occupies ~25 l at room temperature and pressure

**B-2.1.2** For a nominal compound x with molecular weight 100, this means that a mole (100 g) of pure x vapour occupies ~25 l at room temperature and pressure.



**B-2.1.3** Therefore a cubic meter (m<sup>3</sup>) of pure x vapour would contain around 4,000 g (4 kg) of x

**B-2.1.4** Therefore 1 m<sup>3</sup> of air with x at 1 ppm would contain 4 mg of x

Or 1 ppm x equates to 4 mg/m<sup>3</sup>

**B-2.1.5** Therefore 1 m<sup>3</sup> of air with x at 1 ppb would contain 4 µg of x

Or 1 ppb x equates to 4 µg/m<sup>3</sup>

And so on.

## ANNEX C

(Clause 8.1, Clause 10.1)

### EXAMPLE UPTAKE RATES FOR EXAMPLE TARGET ORGANIC VAPOURS USING DIFFUSIVE SAMPLERS AT 20 °C

Sources used in this Annex are denoted by the superscript IIIx and are listed at the bottom of each table.

**Table 4 Uptake rates on industry standard stainless steel tube-based axial samplers packed with specified sorbents (available from standard sources)**  
(Annex C)

Compound name	B.pt (°C)	Sorbent	Uptake rate	Exposure time	Sources
<b>Aliphatic hydrocarbons</b>					
1,3-butadiene	-4.5 °C	Carbopack X	0.61 ml/min	24 h 1	9
		Carbopack X	1.24 ng/ppm/min	week	9,10,12
		Carbopack X	0.55 ml/min	1 week	10
		Carbopack X	0.45 ml/min	2 weeks	10
n-butane	-0.5 °C	Carbopack X	1.3 ng/ppm/min*	2 week	8
i-butane	-12 °C	Carbopack X	0.8 ng/ppm/min*	2 week	8
		Carbopack B	0.60 mL/min	8 h	13
		Carbopack B	1.77 ng/ppm/min*	8 h 2	13
		Carbopack B	1.34 ng/ppm/min*	week	8
n-pentane	36 °C	Carbopack X	1.8 ng/ppm/min*	2 week	8
		Carbopack X	1.8 ng/ppm/min*	2 week	8
i-pentane	28 °C	Carbopack X	1.6 ng/ppm/min*	2 week	8
n-hexane	69 °C	Carbopack X	2.0 ng/ppm/min*	2 week	8
		Carbopack B	1.75 ng/ppm/min*	2 week	8
n-heptane	98 °C	Tenax TA	1.77 ng/ppm/min	8 h	13
		Tenax TA	0.43 ml/min	8 h	13
		Tenax TA	0.26 ml/min	1 week	12

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n-octane	126 °C	Tenax TA	2.00 ng/ppm/min	8 h	13
		Tenax TA	0.43 ml/min	8 h	13
		Tenax TA	0.27ml/min	1 week	12
n-nonane	150 °C	Tenax TA	2.40 ng/ppm/min	8 h	13
		Tenax TA	0.46 mL/min	8 h	13
		Tenax TA	0.34ml/min	1 week	12
n-decane	174 °C	Tenax TA	2.3 ng/ppm/min	8 h	13
		Tenax TA	0.40 ml/min	8 h	13
		Tenax TA	0.51ml/min	4 weeks	5
n-undecane	196 °C	Tenax TA	0.53ml/min	4 weeks	5
n-dodecane	216 °C	Tenax TA	0.26ml/min	1 week	12
Cyclohexane	81 °C	Tenax TA	0.25ml/min	1 week	12
Methylcyclohexane	101 °C	Tenax TA	0.20ml/min	1 week	12

**Aromatic hydrocarbons**

Benzene	80 °C	Tenax TA	1.3 ng/ppm/min	8 h	13		
		Tenax TA	0.41 mL/min	8 h	13		
		Tenax GR	1.81 ng/ppm/min	8 h	13		
		Tenax GR	0.57 mL/min	8 h	13		
		Carbopack X	0.67ml/min	24 h	9		
		Tenax TA	0.27ml/min	1 week	12		
		Carbopack X	1.85 ng/ppm/min	1 week	10		
		Carbopack B	0.42ml/min	1 Week	2		
		Carbograph 1 TD or Carbopack B	2.14ng/ppm/min	1 week	6		
		Carbograph 1 TD or Carbopack B	2.16ng/ppm/min	1 week	11		
		Carbopack X	2.1ng/ppm/min*	2 weeks	8		
		Carbopack X	1.98ng/ppm/min***	2 Weeks	3		
		Carbopack X	1.93 ng/ppm/min	2 weeks	10		
		Carbograph 1 TD or Carbopack B	1.75ng/ppm/min*	2 weeks	8		
		Carbograph 1 TD or Carbopack B	2.03ng/ppm/min	2 weeks	6		
		Carbograph 1 TD or Carbopack B	2.00ng/ppm/min	2 weeks	11		
		Carbograph 1 TD or Carbopack B	1.83ng/ppm/min	4 weeks	11		
		Carbograph 1 TD or Carbopack B	1.85ng/ppm/min	4 weeks	6		
		Toluene	110.6 °C	Tenax TA	1.67 ng/ppm/min	8 h	13
				Tenax TA	0.44 mL/min 2.12	8 h	13
	Tenax GR	ng/ppm/min		8 h	13		
	Tenax GR	0.56 mL/min		8 h	13		
	Carbopack B	2.06 ng/ppm/min		8 h	13		

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		Carbopack B	0.55 mL/min	8 h	13
		Tenax TA	1.82 ng/ppm/min	8 h	13
		Tenax TA	0.42 mL/min	8 h	13
Xylene	138 - 144 °C	Tenax GR	2.48 ng/ppm/min	8 h	13
		Tenax GR	0.57 mL/min	8 h	13
m,p-Xylene	138 - 139 °C	Carbopack B	0.47ml/min	1 Week	2
		Tenax TA	2.0ng/ppm/min	8 h	13
		Tenax TA	0.46 mL/min 2.38	8 h	13
		Tenax GR	ng/ppm/min	8 h	13
Ethyl benzene	136 °C	Tenax GR	0.55 mL/min	8 h	13
		Tenax TA	0.35ml/min	1 week	12
		Carbopack B	0.47ml/min	1 Week	2
Trimethylbenzene	165 -176 °C	Tenax TA	2.37 ng/ppm/min 0.48	8 h	13
		Tenax TA	mL/min	8 h	13
1,2,4-trimethylbenzene	169 °C	Tenax TA	0.54ml/min	4 weeks	5
1,3,5-trimethylbenzene	165 °C	Carbopack X	0.41 ml/min	24 h	9
		Tenax TA	2.0 ng/ppm/min 0.47	8 h	13
Styrene	145	Tenax TA	mL/min	8 h	13
Naphthalene	218 °C	Tenax TA	0.41ml/min	8 h	7
		Tenax TA	2.26 ng/ppm/min 0.46	8 h	13
Cumene	152.4 °C	Tenax TA	mL/min	8 h	13
4-ethyltoluene	162 °C	Carbopack X	0.41 ml/min	24 h	9
<b>Halocarbons</b>					
Carbon tetrachloride	77 °C	Carbopack X	0.51ml/min	24 h	9
1,1-dichloroethane	57 °C	Carbopack X	0.57ml/min	24 h	9
Cis-1,2-dichloroethene	55 °C	Carbopack X	0.58ml/min	24 h	9
1,2-dichloroethane	83.5 °C	Carbopack X Tenax	0.57ml/min	24 h	9
	83.5 °C	TA	0.20ml/min	1 week	12
1,1,1-trichloroethane	74 °C	Carbopack X	0.51ml/min	24 h	9
1,1,2 trichloroethane	114 °C	Carbopack X	0.49ml/min	24 h	9
1,2-dichloro, 1,1,2,2tetrafloroethane	4 °C	Carbopack X	0.44ml/min	24 h	9
1,1,2-trichloro, 1,2,2trifloroethane	48 °C	Carbopack X	0.46ml/min	24 h	9
Hexachloroethane		Tenax TA	2.4ng/ppm/min	4 Weeks	1
1-chloropropene	45 °C	Carbopack X	0.51ml/min	24 h	9
1,2-dichloropropane	95.5 °C	Carbopack X	0.52ml/min	24 h	9
Hexachlorobutadiene	215 °C	Tenax TA	3.5ng/ppm/min	4 Weeks	1
Chlorobenzene	132 °C	Carbopack X	0.46ml/min	24 h	9
<b>Other</b>					
Benzaldehyde	179 °C	Tenax TA	0.41ml/min	1 week	12
Ethylacetate	77 °C	Tenax TA	0.23ml/min	1 week	12
Alpha-pinene	156 °C	Tenax TA	0.20ml/min	1 week	12
Limonene	176.0 °C	Tenax TA	0.27ml/min	1 week	12

\*Average of 2 numbers at different percent RHs

\*\* Average of 3 different locations

\*\*\* Average of varying dates of test

**Table 5 Uptake rates for Fast-PAS radial samplers**

(Annex C)

Compound name	B.pt (°C)	Sorbent	Uptake rate	Exposure time	Sources
<b>Aliphatic hydrocarbons</b>					
n-butane	-0.5	Carbopack X	4.94 (cm <sup>3</sup> /min)	72 h	1
1-butene	-6.3	Carbopack	3.01 (cm <sup>3</sup> /min)	72h	1
1, 3-butadiene	-4.5	Carbopack X	4.29 (cm <sup>3</sup> /min)	72h	1
trans-2-butene	0.9	Carbopack X	5.97 (cm <sup>3</sup> /min)	72h	1
cis-2-butene	3.73	Carbopack X	4.13 (cm <sup>3</sup> /min)	72h	1
2-methylpropane	-12	Carbopack X	1.28 (cm <sup>3</sup> /min)	72h	1
			8.47 (cm <sup>3</sup> /min)	24h	2
n-pentane	36	Carbopack X	8.59 (cm <sup>3</sup> /min)	72h	1
1-pentene	29.9	Carbopack X	9.55 (cm <sup>3</sup> /min)	72 h	1
trans-2-pentene	36.3	Carbopack X	8.83 (cm <sup>3</sup> /min)	72 h	1
2-methyl-butane	27.8	Carbopack X	8.56 (cm <sup>3</sup> /min)	72 h	1
isoprene	34	Carbopack X	9.89 (cm <sup>3</sup> /min)	72h	1
n-hexane	68.7	Carbopack X	8.1 (cm <sup>3</sup> /min)	72h	1
2-methylpentane	60.2	Carbopack X	9.9 (cm <sup>3</sup> /min)	72h	1
2,2-dimethyl-butane	49.7	Carbopack X	6.76 (cm <sup>3</sup> /min)	72h	1
2,3-dimethyl-butane	57.9	Carbopack X	6.76 (cm <sup>3</sup> /min)	72h	1
			6.82 (cm <sup>3</sup> /min)	24h	2
n-heptane	98.5	Carbopack X	7.13 (cm <sup>3</sup> /min)	72h	1
2-methylhexane	90	Carbopack X	5.77 (cm <sup>3</sup> /min)	72h	1
3-methylhexane	91	Carbopack X	5.77 (cm <sup>3</sup> /min)	72h	1
			6.58 (cm <sup>3</sup> /min)	24h	2
n-octane	125.6	Carbopack X	6.29 (cm <sup>3</sup> /min)	72h	1
n-decane	174.1	Carbopack X	3.73 (cm <sup>3</sup> /min)	72h	1
methylcyclopentane	71.8	Carbopack X	7.89 (cm <sup>3</sup> /min)	72h	1

cyclohexane	80.7	Carbopack X	6.84 (cm <sup>3</sup> /min)	72h	1
methylcyclohexane	100.9	Carbopack X	6.79 (cm <sup>3</sup> /min)	72 h	1
1,3-dimethylcyclohexane	122.4	Carbopack X	6.8 (cm <sup>3</sup> /min)	72h	1
1,4-dimethylcyclohexane	120	Carbopack X	6.78 (cm <sup>3</sup> /min)	72h	1
2,2,4-trimethylpentane	99.2	Carbopack X	5.5 (cm <sup>3</sup> /min)	72h	1
<b>Aromatic hydrocarbons</b>					
benzene	80	Carbopack X	8.15 (cm <sup>3</sup> /min)	24 h	2
			8.89 (cm <sup>3</sup> /min)	72h	1
toluene	110.6	Carbopack X	6.04 (cm <sup>3</sup> /min)	24h	2
			8.1 (cm <sup>3</sup> /min)	72h	1
ethyl-benzene	136	Carbopack X	5.96 (cm <sup>3</sup> /min)	24h	2
			6.92 (cm <sup>3</sup> /min)	72h	1
m,p-xylene	138 - 139	Carbopack X	5.28 (cm <sup>3</sup> /min)	24 h	2
			5.93 (cm <sup>3</sup> /min)	72h	1
o-Xylene	144.5	Carbopack X	7.67 (cm <sup>3</sup> /min)	24h	2
			5.69 (cm <sup>3</sup> /min)	72h	1
cumene	152.4	Carbopack X	5.29 (cm <sup>3</sup> /min)	72h	1
1,3,5-trimethylbenzene	165	Carbopack X	5.5 (cm <sup>3</sup> /min)	72h	1
1,2,4-trimethylbenzene	169	Carbopack X	5.85 (cm <sup>3</sup> /min)	72h	1
1,2,3-trimethylbenzene	176.1	Carbopack X	5.85 (cm <sup>3</sup> /min)	72h	1

**Table 6 Uptake rates for Radiello radial samplers**

(Annex C)

Compound name	B.pt (°C)	Sorbent	Uptake rate	Maximum Exposure time	Sources
<b>Aliphatic hydrocarbons</b>					
n-hexane	68.7	Carbograpgh 4TD	25.5 (mL/min)	7 days	1
n-heptane	98.5	Carbograpgh 4TD	25.3 (mL/min)	14 days	1
n-octane	125.6	Carbograpgh 4TD	24.1 (mL/min)	14 days	1
n-nonane	150	Carbograpgh 4TD	21 (mL/min)	14 days	1
n-decane	174.1	Carbograpgh 4TD	22.3 (mL/min)	14 days	1
n-undecane	196	Carbograpgh 4TD	12.0 (mL/min)	14 days	1

cyclohexane	80.7	Carbograpgh 4TD	27.6 (mL/min)	7 days	1
<b>Aromatic hydrocarbons</b>					
benzene	80	Carbograpgh 4TD	27.8 (mL/min)	7 days	1
toluene	110.6	Carbograpgh 4TD	30 (mL/min)	14 days	1
m,p-xylene	138-139	Carbograpgh 4TD	26.6(mL/min)	14 days	1
o-xylene	144.5	Carbograpgh 4TD	24.6 (mL/min)	14 days	1
ethylbenzene	136	Carbograpgh 4TD	25.7 (mL/min)	14 days	1
styrene	145	Carbograpgh 4TD	27.1 (mL/min)	14 days	1
1,2,4 trimethylbenze	169	Carbograpgh 4TD	21.9 (mL/min)	14 days	1
<b>Halocarbons</b>					
1,1,1-trichloroethane	74	Carbograpgh 4TD	20 (mL/min)	7 days	1
trichloroethylene	87.2	Carbograpgh 4TD	27.1 (mL/min)	7 days	1
tetrachloroethylene	121.3	Carbograpgh 4TD	25.4 (mL/min)	7 days	1
1,4-dichlorobenzene	174	Carbograpgh 4TD	22 (mL/min)	14 days	1
<b>Alcohols</b>					
2-butoxyethanol	168.4	Carbograpgh 4TD	19.4 (mL/min)	14 days	1
2-ethyl-1-hexanol	184.6	Carbograpgh 4TD	14.3 (mL/min)	14 days	1
2-ethoxyethanol	135	Carbograpgh 4TD	26.0 (mL/min)	14 days	1
2-methoxyethanol	124.1	Carbograpgh 4TD	4.0 (mL/min)	14 days	1
1-methoxy-2propanol	119	Carbograpgh 4TD	26.6 (mL/min)	14 days	1
<b>Esters and Ethers</b>					
methyl-tert-butyl ether (MTBE)	55.2	Carbograpgh 4TD	30 (mL/min)	7 days	1
ethyl-tert-butyl ether (ETBE)	73.1	Carbograpgh 4TD	30 (mL/min)	7 days	1
butyl acetate	126.1	Carbograpgh 4TD	24.5 (mL/min)	14 days	1
2-methoxyethyl acetate	143	Carbograpgh 4TD	21.0 (mL/min)	7 days	1
2-ethoxyethyl acetate	156.4	Carbograpgh 4TD	20.9 (mL/min)	14 days	1
isopropyl acetate	88.6	Carbograpgh 4TD	25.8 (mL/min)	7 days	1
<b>Other</b>					
dimethyl disulfide	109.8	Carbograpgh 4TD	23.7 (mL/min)	7 days	1
limonene	176	Carbograpgh 4TD	12.8 (mL/min)	14 days	1
a-pinene	156	Carbograpgh 4TD	6.4 (mL/min)	7 days	1