Thermal Desorption Technical Support

Note 56: TD-GC/MS analysis of vapour-phase organic compounds for materials emissions testing

Keywords

certification protocols, (T)(V)(S)VOCs, ULTRA-UNITY, field/laboratory blanks, interferences, artifact, FLEC

Introduction

Manufacturers of construction products, furnishings, furniture, car trim components and consumer products need to monitor emissions of individual and total VOCs to assess the environmental impact of their products indoors and in vehicle cabins. In some cases emissions data are also used for product certification and/or to demonstrate compliance with VOC emission limits – Examples of certification protocols include: (1) The US Greenguard protocol, (2) The German AgBB scheme for flooring materials and (3) The Californian 'High Performance' school initiative. Manufacturers may also use the data to compare and categorize different indoor materials/products of similar function and to develop new types of materials/products with lower emissions and lower potential environmental impact.

This support note describes a specific procedure for identifying and quantifying the masses of individual volatile organic compounds (VOCs) which are emitted into a flow of air from products/materials (flooring, wood panels, paints/coatings, polyurethane foams, *etc.*) and collected on sorbent sampling tubes during emissions testing. It also provides a method of estimating the level of total volatile organic compounds (TVOCs) as compared to a reference compound (toluene). This method should be used in conjunction with procedures for sampling and preparing indoor materials/products for emissions testing and for carrying out emissions testing using chambers or emission cells (for example Markes TDTS 55). It will then form part of an overall material emissions test *i.e.* provide a standardised means of determining the mass of speciated organic compounds and TVOC emitted per unit time from a unit quantity (usually surface area) of the material/product under test.

The method, as described here for individual speciated compounds, can be used for the measurement of vapour-phase organic compounds ranging in volatility from n-hexane to n-hexadecane. It can also be extrapolated to more volatile compounds and less volatile compounds if required. Typical vapour concentrations range from 0.1 - 1 g.m^{-3} in the exhaust air from the emission cell or chamber.

[Note that for materials emissions testing purposes, TVOC is usually measured by summing individual peak areas of compounds between n-hexane and n-hexadecane as they elute on a non-polar (methyl silicone) column (Ref ISO 16000-6, ASTM WK-3464, *etc.*). NOTE also that TVOC should be regarded as a factor specific to the product studied and to the exact monitoring and analytical method used. It should only be used for comparison of products with similar target VOC profiles and can only be used for this provided exactly the same test method has been used for each comparative measurement.]

Method summary

Organic vapours in the exhaust stream of an emission test chamber or cell are pumped onto standard thermal desorption tubes (see ISO 16017 or ASTM D 6196) containing either ~200 mg Tenax TA sorbent or a combination of sorbents comprising a short bed (1-2 cm) of quartz wool at the sampling end backed up by

~200 mg of Tenax TA. A secondary tube containing stronger sorbent(s) may need to be attached, in series, to the non-sampling end of the Tenax/Quartz-Tenax tube if very volatile compounds are of interest or if larger sample volumes are required. The pump flow rate and sampling time must be controlled. The sorbent tubes are then thermally desorbed, in a reverse flow of carrier gas, using an appropriate two-stage thermal desorption (TD) apparatus such as a Markes UNITY (manual) or ULTRA-UNITY (up to 100 tubes) system. During thermal desorption, volatile organic compounds are transferred (injected) efficiently into a capillary GC column for subsequent GC-MS(/FID) analysis.

Individual VOCs ranging in volatility between n-C_6 and n-C_{16} are identified and quantified by gas chromatography/mass spectrometry. Selective ion monitoring, ion extraction or spectral deconvolution is used to quantify specific compounds. Individual components of interest should normally be quantified using authentic standards of that particular compound. Other compounds are usually quantified using toluene.

An estimate of TVOC emissions from the indoor material/product is calculated using GC/MS or GC/FID by integrating the total area of the chromatogram between the elution times of n-hexane and n-hexadecane, subtracting the equivalent sample blank area, and using the response factor for toluene for all compounds. [NOTE that some materials emissions testing practices and/or certification protocols specify whether TVOC should be measured using FID or MS. In either case, the type of detector used for TVOC measurement should be clearly identified in the analysis report.]

Sorbent tubes and ancillary vapour sampling apparatus

Materials emissions testing is invariably carried out using personal monitoring pumps to pull vapour from the exhaust stream of the chamber or cell through two or more replicate industry standard-sized sorbent tubes or sorbent tube trains. [NOTE that a sorbent tube 'train' comprises 2 or more tubes linked together in series.] More guidance on sampling from the exhaust of emission cells/chambers is given in TDTS 55 and other materials emissions chamber/cell testing protocols. The primary sample tube should be packed with 200 mg of Tenax TA or with a combination of 1 or 2 cm of loosely packed quartz wool (sampling end) backed up by 200 mg of Tenax TA. All sample tubes should be stringently conditioned (See TDTS 5) and indelibly etched with a unique identification number for tracking purposes.

Carbon black-type sorbents or carbon molecular sieves may be used in a secondary (back-up) tube, connected in series with the primary Tenax or quartz-Tenax tubes, for monitoring more volatile compounds (see Markes TDTS 5 and 20 for advice on sorbent selection). Separate TD-GC/MS(/FID) analysis of the more volatile organic emissions can then be carried out without compromising VOC (n-C_6 to n-C_{16}) or TVOC measurements. If a secondary (back-up) tube is used, this should be attached to the primary sampling tube using an inert connection fitting such as a stainless steel ¼ - ¼ inch union fitted with PTFE ferrules which won't damage the ends of the sample tubes.

In common with all TD standard methods, blank (conditioned) and sampled tubes should be sealed with metal screw-cap fittings with combined (one-piece) PTFE ferrules for storage and transportation.

The number of sample tubes and blanks required for each emissions test will be specified in the emissions protocol of interest, but will normally include:

- Sorbent tubes (or sorbent tube trains) for recovery measurements (*i.e.* for testing sink effects)
- Sorbent tubes or sorbent tube trains for sample collection
- Field blanks – primary tubes and secondary (back-up tubes) if applicable
- Laboratory blanks – primary tubes and secondary (back-up tubes) if applicable

Blank tubes should be packed at the same time and have a similar history (in terms of use) to equivalent sample tubes. All sorbent tubes (primary and secondary – if applicable) should be conditioned using more stringent conditions than those required for analysis to give blank levels below 2 ng for toluene and any individual VOCs of interest plus below 20 ng for TVOC under normal operating conditions. [N.B. Typical conditioning temperatures for Tenax or quartz/Tenax tubes are 320 to 335°C – see manufacturers' guidelines.]. A representative proportion (usually >10%) of the sorbent tubes should be analysed using routine analytical parameters to ensure that these blank levels are met.

Requirements for analytical apparatus

Thermal desorber: Markes TD technology (manual UNITY or 100-tube ULTRA-UNITY) is compatible with industry standard-sized tubes and is fully compliant with the requirements of all materials emissions testing protocols. Mi TD systems also offer the unique benefit of SecureTD-Q (quantitative re-collection for repeat analysis) as recommended for validating desorption efficiency (ASTM D-6196 and ASTM WK 3464).

Gas Chromatograph, fitted with a mass spectrometric detector and additional FID (if required).

Mass Spectrometer Detector, tuned according to manufacturer's instructions and capable of scanning between mass ion 25 and 500.

Gas Chromatographic Column: A 100% methyl silicon fused silica capillary column should be used. Typical dimensions: 50-60 m long with 0.25 to 0.32 mm I.D. and a 0.25 to 1.0 µm film thickness.

Effluent Splitting – If both FID and MS detection is demanded by the emissions testing/certification protocol in use, the outlet of the capillary column should be connected to a conventional, zero-dead-volume, capillary effluent splitting device. Connections from each respective detector to the capillary effluent splitter should ensure that the 50% of the effluent from the capillary analytical column is directed to the FID and 50% to the MS detector, taking into account the fact that the MS detector operates at vacuum.

The entire analytical system should be conditioned using an empty sample tube and more stringent parameters of gas flow, desorption time and temperature than are normally required for analysis. Typical TD conditioning parameters are:

Flow path:	200°C
Primary desorption:	15 mins at 300°C
Focusing trap cold temperature:	+30°C
Flow through the trap when cold:	10 ml/min
Split flow during primary desorption:	90 ml/min
Secondary (trap) desorption temp:	320°C for 5 mins
Split flow during secondary desorption:	90 ml/min

It is recommended to keep the GC column at a constant high temperature and the MS ionisers switched off during system conditioning.

Key considerations for reducing artifacts/interferences

The analytical system and all sorbent tubes should be stringently conditioned before analysis – see above. Careful attention should also be paid to routine/user maintenance issues such as regular cold trap replacement, GC column replacement and cleaning the MS source/detector components as per manufacturers' instructions.

Organic components, that have the same or nearly the same retention time as the analyte of interest, will interfere during gas chromatographic analysis. High resolution capillary columns are required to minimize these issues. Analytes and artifacts can be

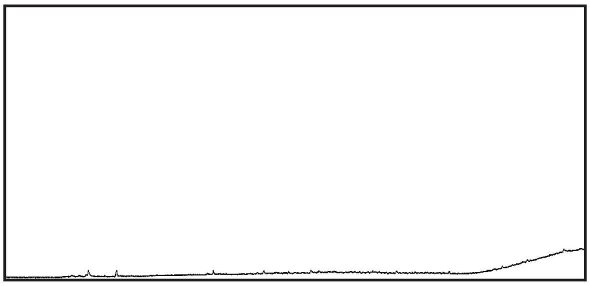

Figure 1: Minimum system background - Markes TD systems incorporate a patented heated valve which eliminates carrier gas artefacts and prevents air/water from reaching the capillary system.
This analysis shows <1 ng total VOC using an optimised system under typical analytical conditions

generated during sampling and analysis (4, 5). Interferences can be minimized by proper selection of gas chromatographic columns and conditions, and by stringent conditioning of both the sorbent tubes and the analytical system before use. Artifacts may be formed during storage of blank sorbent tubes. This is minimized by correctly sealing and storing blank and sampled tubes using ¼-inch metal screw caps with PTFE ferrules as recommended by international standard methods such as ISO 16017 and ASTM D6196 (See TDTS 19).

[NOTE that all sorbents do have an 'inherent' artifact level and that minor peaks will invariably be observed if the system is operated at optimum sensitivity (Figure 1). Inherent artifact levels vary from sorbent to sorbent but are generally at sub-nanogram levels for quartz wool, Tenax TA and for carbon-black type sorbents (6, 7) – see Markes TDTS 5 and 19.]

When using FID, co-eluting peaks are difficult to resolve. Selectivity is enhanced by using a mass spectrometer detector in selected ion monitoring (SIM) mode or in SCAN mode with additional post-run processing using spectral deconvolution to identify co-eluting compounds. Note that, even with spectral deconvolution, it may not be possible to uniquely identify individual compounds when they co-elute exactly (co-maximize) under the analytical conditions selected.

The method is suitable for sampling and analyzing vapour samples ranging up to 95% relative humidity for all hydrophobic sorbents such as quartz wool, Tenax TA and graphitized carbon blacks. When less hydrophobic, strong sorbents such as carbonized molecular sieves are used in a secondary (back-up) tube, care must be taken to reduce the mass of water retained from humid samples (see Markes TDTS 26).

Calibration of the TD-GC/MS(/FID) Analytical System

Follow guidance given in TDTS 7 for calibration of the analytical system using a Markes Calibration Solution Loading rig or equivalent tube injection system. Standard MS calibration curves will be required for toluene and each compound of interest [NOTE that an FID calibration curve for toluene is also required by some protocols]. Calibration curves should typically comprise at least 5 points within the range 20 to 2500 ng. Single level (midpoint) calibrations of all compounds of interest should be carried out frequently (at least once per day) to monitor the stability of the response. The multi-level calibration should be repeated whenever the mid-point calibration of any given compound deviates significantly from that obtained during the last multi-level calibration. MS (and FID) response factors for any given compound should agree across all calibration levels.

For TVOC determination, quantitation is usually carried out using toluene as the reference compound and by taking the average MS (or FID) response factor for the 5 standards.

Certified reference standard tubes pre-loaded with toluene and other VOCs are available commercially and should be used as an independent check on analytical quality assurance on a quarterly basis.

Sampling and related considerations

Sorbent tubes to be used as blanks should be packed and conditioned at the same time and in the same way as those to be used for sample collection. Tubes to be used as laboratory blanks should be retained in the laboratory, and kept sealed until the sampled tubes are ready for analysis. Laboratory blanks should be analysed using standard analytical operating conditions and respective artifact levels should be well below 2 ng for individual VOC and well below 20 ng for TVOC.

Field blanks are also required by a number of emissions testing protocols – these are tubes which undergo the entire test procedure (conditioning, storage, transport to the emissions test chamber, *etc.*) – but which are not actually used to collect sample. Field blanks should also be analysed under normal operating conditions. Most materials emissions protocols prescribe performance criteria for field blank tubes. Typically, these are 2 ng/L (2 $\mu g.m^{-3}$) for individual VOCs and 10-20 ng/L (10-20 $\mu g.m^{-3}$) for TVOCs. If the field blank shows the same pattern of VOCs as on the sample tubes, and if these components are present at 5% or more of those on the sampled tubes, careful attention must be paid to methods of sealing the tubes and other storage procedures in any future studies. If the profile of the VOCs on the field blanks matches that of the sampled tubes and if these components are present at 10% or more of those on the sampled tubes, the sampled tube data are invalid.

Sampling pumps should be calibrated in accordance with manufacturer's instructions and in compliance with relevant standards. A true constant flow pump (such as the FLEC pump available from Markes) will automatically adjust for the varying impedance of different sorbent tubes and does not need to be recalibrated for each individual sorbent tube/sorbent tube train.

Pump flow rates are typically set between 50 ml/min and 500 ml/min for a total sample volume of 5.0 L or less. Larger sample volumes may be used, but this can result in the breakthrough of more volatile compounds such as n-hexane. Tests for breakthrough, using two tubes in series, are described in standard methods such as US EPA TO-17 and ASTM D-6196. If larger sample volumes are required or if there is a requirement to quantify the levels of very volatile organic compounds (*i.e.* compounds more volatile than n-hexane), a secondary (back-up) tube containing a stronger sorbent, such as one of the graphitized carbon blacks or carbon molecular sieves (see Markes TDTS 5), should be attached to the primary Tenax or quartz/Tenax tube using a ¼ - ¼ inch stainless steel straight through union fitted with one-piece PTFE ferrules.

Batches of sealed sampled tubes should be stored and transported in clean, airtight, non-outgassing containers such as uncoated paint cans or Tupperware®-type containers. Tenax TA or quartz/Tenax sample tubes do not require refrigerated storage [8]. Controlled recovery studies have shown ~99% recovery for VOCs from Tenax TA after 11 months storage at ambient temperature. If refrigerated storage conditions are used, tube seals must be retightened once the tubes have reached minimum storage temperatures and tubes must be allowed to re-equilibrate with room temperature before seals are removed immediately prior to analysis. This prevents humidity from the laboratory air condensing inside the cold tube and interfering in the subsequent analysis. Samples comprising chemically stable compounds of interest should be analyzed within 30 days. If target compounds include more reactive species, samples should be analyzed as soon as possible.

Analysis Method

The analytical parameters should be selected such that desorption efficiency exceeds 95% for all analytes. Typical analytical thermal desorption parameters are given in table 1.

A typical GC programme for general VOC analysis (n-C_6 to >n-C_{16}) runs from 50 to 250°C at 5 or 10°C/min, with an initial hold time of 5 or 10 mins at 45°C and a final hold time of 5 or 10 minutes at 250°C.

Desorption efficiency can be checked using SecureTD-Q *i.e.* quantitative re-collection of the split flow for repeat analysis. Data from repeat analysis of the re-collected sample should match that predicted from the split ratio without bias (discrimination) (Figure 2).

Analysis of VVOC compounds and simultaneous analysis of VOC and Semi-VOCs

Tubes packed with 200 mg of Tenax TA will allow quantitative recovery of compounds boiling up to n-C_{22} or slightly higher. Tubes packed with 1 or 2 cm of quartz wool in front of the 200 mg of Tenax TA will allow quantitative recovery of higher boiling compounds, including longer chain phthalate plasticisers (Figure 2). The Markes ULTRA-UNITY automated TD system facilitates simultaneous analysis of volatile and semi-volatile organics because the focusing trap desorbs in backflush mode (See TDTS 64). This means that high boilers are trapped and efficiently desorbed from the weaker sorbents in the front of the trap while more volatile species are quantitatively retained and released from stronger sorbents at the back of the trap.

Higher flow path temperatures (*e.g.* 200°C) and extended GC run times are required for the simultaneous analysis of VOC and semi-VOC (*i.e.* compounds higher boiling than n-C_{22}), but most other TD analytical conditions can remain

Parameter	Settings
Pre-purge time (min)	1
Desorption temperature (°C)	280 Suitable for tubes packed with Tenax TA or quartz plus Tenax TA. [Note that other sorbents, which may be used in secondary (back-up) tubes for sampling VVOCs, may require different desorption conditions.]
Desorption time (min)	5-15
Desorption flow rate	30 to 80 ml/min passing through the sample tube in the reverse direction to that used for sampling. The tube desorption flow rate is the sum of the flow through the cold focusing trap and the split flow (if any) during tube desorption
Cold trap low temperature (°C)	Between -15 and +30 [higher temperatures are used for water management (see Markes TDTS Note 26)]
Flow rate through trap for desorption ($mL.min^{-1}$)	3 to 50 in the reverse direction to that used for focusing. The trap desorption flow rate is the sum of the flow through the analytical column and the split flow (if any) during trap desorption
Cold trap high temperature	Heated as fast as possible (*e.g.* $100°C.s^{-1}$) to 300°C for 3 minutes
Cold trap sorbent	Quartz and Tenax TA (backed up by a stronger carbon black or carbon molecular sieve adsorbent if VVOCs also of interest)
Flow path temperature (°C) (transfer line and main valve)	150 (Flow path temperature must be set high enough to prevent analyte condensation, but not so high as to cause degradation. N-hexadecane and more volatile analytes do not require flow path temperatures above 150°C. For the analysis of compounds less volatile than n-C_{22} flow path temperatures of 200°C will be required.
Carrier gas	Helium. Ideally use back-pressure regulated electronic pneumatic control of the carrier gas head pressure through the entire TD-GC-MS(/FID) analytical system, so that stable retention times are maintained independent of split flow, trap temperature, *etc*.
Gas flows and split ratios	Split ratios between the sample tube and secondary trap, and between the secondary trap and analytical column should be selected dependent on expected vapour concentrations in the chamber/cell exhaust and the volume of gas sampled onto each sorbent tube. Typical desorption and split flows for vapour samples comprising 200 - 1000 ng per IVOC would be 50 ml/min tube desorption flow (comprising 30 ml/min flow through the cold focusing trap and 20 ml/min inlet split flow) and 22 ml/min trap desorption flow (comprising 2 ml/min column flow and 20 ml/min outlet split flow). This gives and inlet split ratio of 50:30, an outlet split ratio of 22:2 and an overall split ratio of 18:1.

Table 1: Typical analytical thermal desorption parameters

the same (see above table). The analysis of higher boiling compounds will not compromise the analysis of (T)VOC data provided the GC programme is maintained as standard during elution of n-C_6 to n-C_{16} compounds, but is then subsequently extended to higher temperatures for elution of the higher boiling species.

The analysis of VVOCs (very-volatile organic compounds) requires the addition of a secondary (back-up) tube packed with stronger sorbents (See TDTS 5 and 20). Such tubes can be analysed separately using the same TD system and analytical conditions as described above. Some compounds will only partially break through the primary Tenax/quartz-Tenax tube and will therefore occur in the analysis of both the primary and secondary tubes. The peak areas for these compounds must then be of

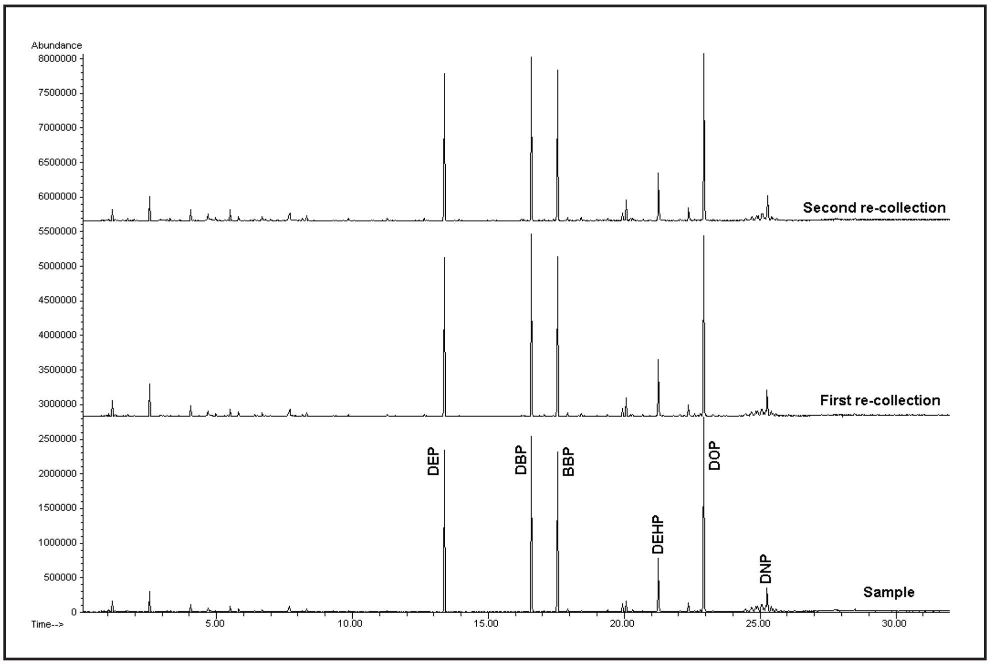

Fig. 2: Mixed phthalate standard (di-ethylphthalate to di-nonylphthalate) analysed, quantitatively re-collected and re-analysed twice. No bias or selective loss of one or more analytes, was observed across the volatility range

summed from each chromatogram to give a total area for every affected compound.

[Note that multiple sorbents can be packed into a single tube if one analysis is preferred, but that this could compromise the mass of Tenax used and thus affect (T)VOC data.]

Confirmation of component identity

Generally speaking compounds are only reported as positively identified if both the retention time and the mass spectrum match that of a standard of that VOC analysed under identical conditions. If a component of interest co-elutes chromatographically with another compound, spectral deconvolution can be used to separate the mass spectral data for that compound from interfering mass ions before a spectral comparison or standard library search is carried out (see Markes TDTS 66).

Measurement of individual VOCs

Selective ion monitoring is normally used to quantify individual components. Spectral deconvolution should be used to remove the contribution from interfering components with similar mass ions if necessary. Required limits quantitation for toluene are usually in the order of 0.5-1 ng which represents a vapour concentration of 0.1-0.2 ng.L^{-1} (0.1 – 0.2 µg.m^{-3}) for a 5 L sample of exhaust gas.

The number of individual VOCs of interest will be defined by the requirements of the specific testing protocol, the type of product being tested, and the defined needs of the user. Approaches include:

a) measure all detected compounds between n-C_6 and n-C_{16}

b) quantify and identify the largest compounds eluting in this range (*e.g.* the 10 biggest peaks)

c) quantify and identify the largest peaks corresponding to at least 90% of the overall chromatographic area between n-C_6 & n-C_{16}

d) quantify and identify specific target analytes only

Individual, identified VOCs should be quantified by comparing peak areas from the sample with those of authentic standards wherever possible. These should be analysed under the same conditions and quantified using the same mass ions. Other compounds detected in the n-C_6 to n-C_{16} volatility range (*i.e.* minor components or non-target compounds) are usually quantified using the MS (or FID) response factor for toluene. It should always be made clear in the report which compounds were quantified with authentic standards and which were quantified using toluene response.

If a measurable mass of one or more of the individual VOCs of interest occurs in the field blank, this mass should be subtracted from the mass found in the sample to give a corrected VOC mass in ng. [Note that if the mass of one or more compounds on the field blank tube exceeds 10% of that found in the sample tube, this invalidates the data for that compound.]

The area specific emission rate for each identified VOC can then be calculated for the material/product under test using procedures described in relevant practices and protocols for emissions testing.

The Markes ULTRA-UNITY automated thermal desorption system offers the option of Internal Standard Addition (ISDP Accessory). The ISDP allows a fixed volume of a gas phase internal standard to be automatically introduced onto the sampling end of the sorbent tube immediately after the leak test and before tube desorption. This is recommended as a check on analytical system stability. Deuterated toluene is commonly used as a gas-phase internal standard because it is not present naturally.

Estimating TVOC

TVOC estimates are only meaningful for comparison of products with very similar emission profiles *e.g.* different manufacturing batches of the same product. Comparing TVOC data is also dependent upon all analyses being carried out using identical analytical parameters including sorbent selection, GC column selection, method conditions (TD and GC/MS), selected target analyte range and choice of calibrant (usually toluene).

Normally the area of the chromatogram to be included in the TVOC measurement is that from the retention time of n-hexane to that of n-hexadecane inclusive, and should be calculated using baseline-to-baseline chromatographic integration methods. The total area of peaks in this part of the chromatogram, FID or MS-SCAN (mass 45-450), should be used to calculate the TVOC result. The mass of TVOC (ng) (TVOCSAMPLE) can then be calculated using the average FID or MS response factor for toluene as specified in the protocol being followed. The FID or MS response factor for toluene should then be used to calculate TVOCBLANK from the total peak area (FID or MS-SCAN) for the same region of the relevant field blank tube analysis. TVOCBLANK should then be subtracted from TVOCSAMPLE to give a corrected TVOC mass in ng.

The area specific TVOC emission rate for the material/product under test can then be calculated from the TVOC mass as described in relevant practices and protocols for emissions testing.

References

(1) GREENGUARD^{TM} Certification – www.greenguard.org

(2) AgBB protocol: Health-related evaluation procedure for VOC and SVOC emissions from building products - July 2004. Available from DIBT (German Institute of Building Technology, Berlin) (Also see prEN 15052 available from European National Standards Institutes.)

(3) The Collaborative for High Performance Schools (CHPS) – Section 01350 – Special Environmental Requirements (www.chps.net)

(4) Clausen, P.A. and Wolkoff, P. (1997) Degradation Products of Tenax TA Formed during Sampling and Thermal Desorption Analysis: Indicators of Reactive species Indoors. *Atmospheric Environment* **31**:715-725.

(5) Ciccioli, P. *et al*. (1986) GC Evaluation of Organic Components Present in the Atmosphere at Trace Levels with the Aid of Carbopack B for Preconcentration of the Sample. *J. Chrom*. **351**: 433-449.

(6) De Bortoli, M. *et al*. (1992) Comparison of Tenax and Carbotrap for VOC Sampling of Indoor Air. *Indoor Air* **2**: 214-216.

(7) Helmig, D. (1996) Artifact-free Preparation, Storage and Analysis of Solid Adsorbent Sampling Cartridges in the Analysis of Volatile Organic Compounds in Air. *J. Chrom*. **732**: 414–417.

(8) Vandendriessche, S., Griepink, B., Hollander, J. C. Th., Gielen, J. W. J., Langelaan, F. G. G. M., Saunders K. J. and Brown R. H. (1991) Certification of a Reference Material for Aromatic Hydrocarbons in Tenax Samplers. *Analyst* **116**: 437-441.