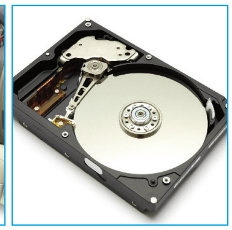
Testing Chemical Emissions from Construction Products and Consumer Goods Using Thermal Desorption with GC/MS

Application Compendium

Abstract

Consumer safety concerns are driving tighter control of chemical release from everyday products such as building materials, furniture and toys. This is creating new markets for low-emission (green) products. Whether you are a test lab or a manufacturer, Agilent Technologies provides the test equipment you need to meet the new regulatory requirements and take advantage of this growing business opportunity.

Agilent Technologies, global leader in GC/MS, has partnered with Markes International, the world's premier provider of analytical thermal desorption (TD) equipment, to bring you the best available technology for materials emissions testing and related applications. In addition to providing flexible, high-performance TD-GC/MS systems for accredited laboratories, Agilent Technologies supplies straightforward emission screening tools for manufacturing industry. Emissions screening technology offers manufacturers a practical and robust solution for routine product conformity checks plus faster development of new low-emission, higher-value products.

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The Measure of Confidence

Agilent Technologies

Introduction

High profile international regulatory developments and increased consumer awareness of green issues are driving global demand for improved assessment and labelling of products in terms of their intentional or unintentional release (emission) of chemicals. The EC Construction Products Directive (CPD - 1989/106/EC), its successor the EC Construction Product Regulation (CPR), the EC Registration, Evaluation, Authorisation and restriction of Chemicals (REACH) Directive (2006/121/EC), Chinese REACH regulations and recent US initiatives to include emission testing within construction codes are key examples of regulatory developments which will increase the need for chemical emissions testing as part of product certification. These new regulations impact much of manufacturing industry with producers of flooring, furniture, toys, domestic goods, cleaning products, woodbased products, insulation materials, coatings, and adhesives/ sealants being in the front line, together with all their suppliers.

'Green' products - A new business opportunity

The changing regulatory landscape and increased awareness of chemical exposure/public health concerns are driving demand for safer 'green' products. Investing in emission testing or screening technology for regulatory compliance equips manufacturers to take advantage of this new market opportunity by developing low-emission, higher-value product formulations.

Product/material testing for chemical release to indoor air is a multistep procedure. It involves putting prepared samples in some form of test chamber or cell, collection of emitted vapors onto sorbent tubes and subsequent analysis by thermal desorption (TD) with GC/MS. Relevant standard methods include: ISO/EN 16000 parts -6, -9, -10, -11 and ASTM D6196, D5116, D6330, D6670, D7143, D7339 & D7706.

Agilent Technologies provides uniquely versatile TD-GC/MS technology for material emissions testing. Systems combine practicality with analytical performance and offer full compliance with the above standards. Manual and automated versions are available and key applications include:

- Certification of products with respect to volatile organic chemical (VOC) emissions using chamber/cell tests
- Fast screening of chemical emissions from products and raw materials for use in:
    - Routine quality control of manufacturing
    - R&D – Aids development of new low emission products
    - Comparing emissions across a product range
    - Addressing customer complaints
    - Comparing products against best-in-class competitors

Other related applications, such as testing emissions of semi-volatile organic chemicals (SVOCs), detection of trace target compounds in complex data sets (for example, carcinogens and odors) indoor air quality assessment and associated ventilation studies can also be accommodated.

The TD-GC/MS technology is further enhanced by a comprehensive portfolio of innovative sampling accessories and data mining tools. Options include Markes' acclaimed Micro-Chamber/Thermal Extractor (µ-CTE) for fast emissions screening and the FLEC cell for testing emissions in field and laboratory locations. Advice on small chambers for emission testing can also be provided.

TD-GC/MS Technology for Material Emissions Testing

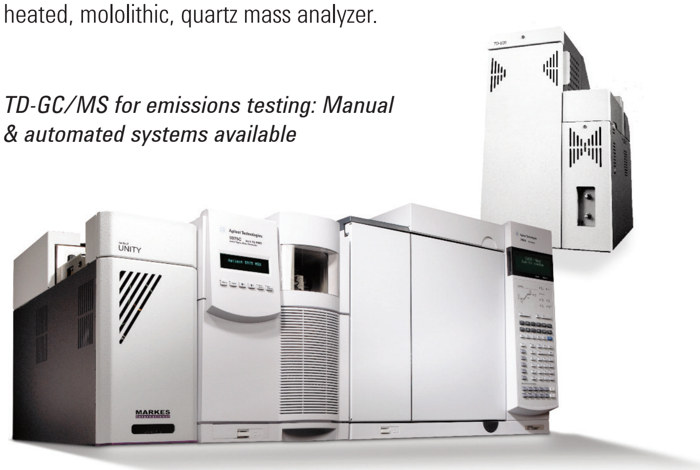
Flexible, high performance thermal desorption

Featuring simultaneous analysis of volatile and semi-volatile organics plus unmatched compatibility with reactive odorous compounds, Agilent TD-GC/MS systems for material emissions testing offer the flexibility and analytical performance you need to meet current and future testing requirements. Cost-effective manual options are based on the single tube thermal desorber UNITY 2, while automated configurations incorporate the robust, 100-tube capacity TD-100. Automation upgrades are available for manual systems to allow you to adapt and expand as demand grows.

GC/MS

Agilent Technologies has established a proven track record for robust, long lasting high-performance GC/MS systems and innovative features that ensure exceptional sensitivity and consistent compound identification in the most difficult matrices. The Agilent 7890A/5975C GC/MSD system represents an optimized union of advanced technologies for GC and MS. Built on the fifth generation of Electronic Pneumatic Control (EPC), the 7890A GC delivers analytes to the MSD with unequalled reproducibility. Improved backflush Capillary Flow Technology (CFT) provides increased protection for the MSD source. For the 5975C MSD, stable, maintenance-free, high sensitivity operation and excellent mass accuracy are the net benefits of three unique components: an inert source, a novel triple-axis HED-EM detector, and the industry's only heated, mololithic, quartz mass analyzer.

TD-GC/MS for emissions testing: Manual & automated systems available



Chamber Test for VOC Emissions from Products and Materials

Application Brief

Many key test protocols and reference methods (notably CEN TC351 standards, ISO 16000-9, ASTM D5116 and the AgBB scheme) specify 'small' test chambers for certification of VOC emissions from construction products and furnishings. Definitions vary, but test chambers are typically constructed of non-sorptive, non-emitting materials such as glass or stainless steel and range in size from 20 L to 5 m^3.

The concept of chambers is that they should simulate the product/material in use in a model (reference) room. To this end, samples are prepared such that only the surface that is exposed to indoor air in real use is exposed in the chamber (Figure 1). The amount of product/material that can be placed in the chamber (the 'loading factor') is also based on the sample surface area to air volume ratio of the product installed in a model room.

Throughout operation, the test chamber is maintained at nominal ambient temperature (23 °C (Europe/US), 25 °C (Korea) and 28°C (Japan)) and under a flow of pure, humidified air (50% R.H.). Vapor phase organics, emitted by the product or material, are pumped onto duplicate sorbent tubes attached to the chamber exhaust at specified intervals - typically 3, 10 to 14 and/or 28-days after the sample is first placed in the chamber. Sampled sorbent tubes are subsequently analysed by TD-GC/MS/(FID).

TD-GC/MS technology supplied by Agilent for emission testing, uniquely features quantitative sample re-collection for repeat analysis on both manual and automated system configurations.

This simplifies validation of analyte recovery per standard methods such as ASTM D6196 and eliminates any risk of having to repeat lengthy/expensive small chamber tests.

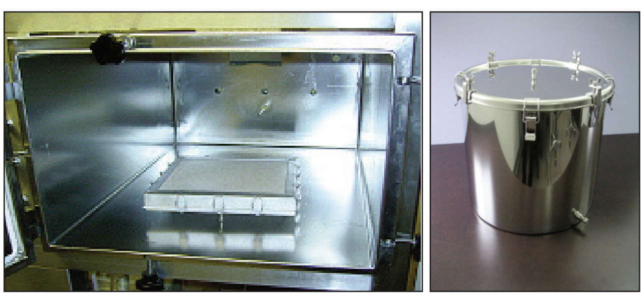


Figure 1. Example prepared flooring sample placed in a typical 500 L small chamber, with inset of 20 L 'ADPAC™' chamber

Construction products - adhesives and sealants

Indoor air contaminants emitted by some adhesives and sealants are odorous and potential throat and airway irritants. Manufacturers are developing water-based, low emission products to minimize chemical emission levels.

The Agilent TD-GC/MS system with 100-tube autosampler is used with Tenax TA tubes for testing chemical emission levels from adhesives using small chambers. In this case an industry-specific method EN 13999, based on ISO EN 16000 parts -6 and -9, is applied. The results show emissions after 10 days (Figure 2).

Sampling	60 mins x 50 mL/min using Tenax TA tubes
Tube desorption	10 mins at 280 °C
Focusing trap	-10 °C to 300 °C (5 mins) at max rate
Split ratio	5:1 during tube desorption only
Carrier gas	He ~20 psi
GC column	HP-5, 50 m x 0.32 mm x 1.05 µm
GC oven	35 °C to 320 °C, multi ramp. 61 mins total
MS: source	230 °C, quad: 150 °C, transfer line: 315 °C
Full scan	28 – 400 amu

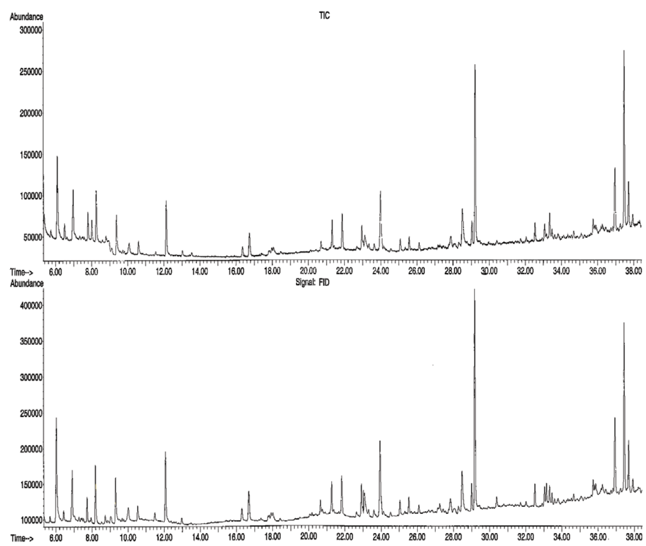


Figure 2. New, very low-emission adhesives (as shown) release less than 500 µg/m3 after 10 days. Vapors collected on Tenax TA tubes. (Reproduced with kind permission from Dr ssa Decio, Dr Cerulli, Dr Leoni and colleagues at MAPEI S.p.A., Milan, Italy)

Emission Test Cells (FLEC) for (S)VOC Emissions from Product and Materials

Application Brief

Some methods for certifying VOC emissions from construction products and furnishings (notably ISO EN 16000-10 and ASTM D7143) specify test cells such as the Field and Laboratory Emission Cell; FLEC. FLEC is a small portable device which differs from small chambers because it is open on one side. The open side is placed onto the surface of planar materials such as wall coverings, flooring materials, textiles, applied paint, timber products, etc. It is used for both laboratory studies and non-destructive field experiments i.e. identifying the source of odor or contaminants in a building.

Emission test cells like FLEC are typically constructed of stainless steel with pure, humidified air entering from a baffle around the perimeter and flowing over the sample surface. Temperature, flow and humidity conditions are maintained as described for chambers (see previous page.) Emitted vapors are swept to the exhaust point in the center of the cell, sampled onto one or two sorbent tubes and then analysed by TD-GC/MS/(FID). Vapor sampling is typically carried out at any time from 2 hours to 56 days after the cell is placed on the sample surface.

Emission test cells complement small chambers and many national and international laboratory ‘round-robin’ studies have shown good correlation between the two[1-3]. Test cells are not as universally applicable as small chambers but offer some advantages for compatible planar products/materials. These include; speed (typical equilibration times are 15 to 30 minutes), field portability and ease of cleaning between tests. Cells are also less prone to sink effects and may give better analyte recovery than small chambers.

Agilent Technologies has partnered with Markes to make the FLEC product range available to its TD-GC/MS customers. Contact your local Agilent representative for more details.

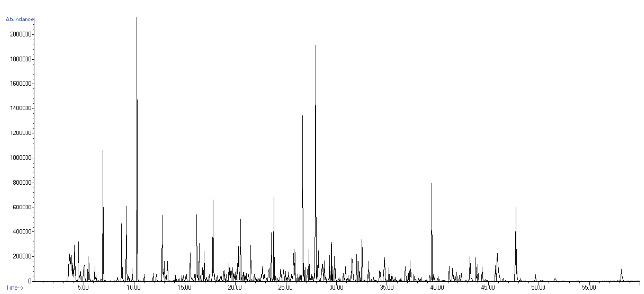


Figure 1. Testing VOC emissions from carpet using FLEC with Tenax tubes and TD-GC/MS analysis. (Reproduced with the kind permission of VITO, Belgium.)

Using FLEC to test carpet emissions

Carpet emissions were tested using a FLEC and a base unit with variable depth designed to accommodate carpet. Analytical conditions were as follows:

Vapor sampling	20 mins at 100 mL/min using Tenax TA tubes
Tube desorption	15 mins at 280 °C
Focusing trap	-10 °C to 275 °C (5 mins) at max rate
Split ratio	40:20 during tube desorption only
Flow path	175 °C
Carrier gas	He. Constant pressure: 10 psi
GC column	5% phenyl, 95% dimethylpolysiloxane, 60 m x 0.32 mm x 0.25µm
GC oven	30 °C (1 min), 5 °C/min to 320 °C (1 min)
MS: source	230 °C, quad: 150 °C, transfer line: 275 °C
Full scan	35 – 250 amu.

Example references for FLEC and chamber correlation:

1. Jahn et al (2000) ECO-label for low emission wood products and wood base products (RAL-UZ 38) – Part 2: Test procedure and results, Healthy Buildings 2000, Vol 4, pp 593-598.

2. Roache et al (1996) Comparing the FLEC with traditional emission chambers. In: Tichenor B, ed. Characterising sources of indoor air pollution and related sink effects. Philadelphia: ASTM STP 1287; pp98-111.

3. Risholm-Sundman (1999) Determination of HCO emissions with the FLEC and correlation to chambers. Indoor Air, 9, pp268-272.

Figure 2. FLEC accessories for accommodating various material / product types

Micro-chamber for Quality Control of VOC Emissions from Products and Raw Materials

Application Brief

Quality control (QC) of chemical emissions from materials requires much faster and lower cost tests than the 3- and 28-day reference methods typically used for product certification. The Micro-Chamber/Thermal Extractor (µ-CTE) was designed by Agilent's partner Markes International specifically for inhouse screening of product emissions – either for factory production control or research & development.

µ-CTEs comprise 4 or 6 individual inert micro-chambers with 114 mL and 44 mL volume respectively. These micro-chambers allow surface or bulk emissions to be tested from 4 or 6 samples simultaneously at ambient or elevated temperatures. A controlled flow of pure air or gas passes into each micro-chamber and is directed onto the surface of the sample. Emitted vapors are then swept into attached sorbent tubes (or DNPH cartridges for formaldehyde). Pumps are not required. Subsequent analysis requires an Agilent TD-GC/MS system (or an Agilent HPLC system for formaldehyde).

Recent studies have shown that microchamber emissions data, obtained within a few minutes of sample preparation, correlate with that from longer term small chamber reference methods [1-3]. This means micro-chambers can be used to monitor chemical emissions from products as part of routine QC of manufacturing. To support this, micro-chamber technology is now the subject of extensive method development for rapid emissions screening within key standards agencies [4-6].

Test conditions

Tests were carried out on vinyl floor tiles using the µ-CTE at 40°C with 50 mL/min flow of air, 30 mins equilibration and 15 mins vapor sampling, into Tenax TA tubes (Figure 1).

Tube desorption	10 mins at 300 °C
"Mat Ems" focusing trap	-10 °C to 300 °C (5 mins) at max rate
Split ratio	20:1
GC column	DB-5, 60 m x 0.25 mm x 0.25 µm
Oven programme	45 °C with multi ramp to 300 °C
MS temps: Source	230 °C, quad: 150 °C, transfer line: 280 °C
Full scan	45 – 450 amu.

Example references and draft standard activity

1. T. Schripp, B. Nachtwey, J. Toelke, T. Salthammer, E. Uhde, M. Wensing, M. Bahadir, Journal of Analytical and Bioanalytical Chemistry, 387, 5, 1907-1919, (2007).

2. PARD Report: Correlation between the VDA 276 test and microchamber testing. Issued by WMG, University of Warwick, UK. G J Williams, M Pharoah (2009).

3. Prof. Mangoo Kim, Kangwon, National University, Korea.(2010) Presentation to ISO TC146 SC6 WG13 (Document # N0087)

4. VDI 2083-17 (Draft) Clean room technology – Compatibility with required cleanliness class and surface cleanliness.

5. ASTM D7706 standard practice for micro-scale test chambers for rapid assessment of vapor-phase organic compounds (VOC) emitted by materials.

6. ISO DIS 12219-3 (Indoor air of road vehicles) Part 3: Screening method for the determination of the emission of VOCs from car trim components - Micro-scale chamber method.

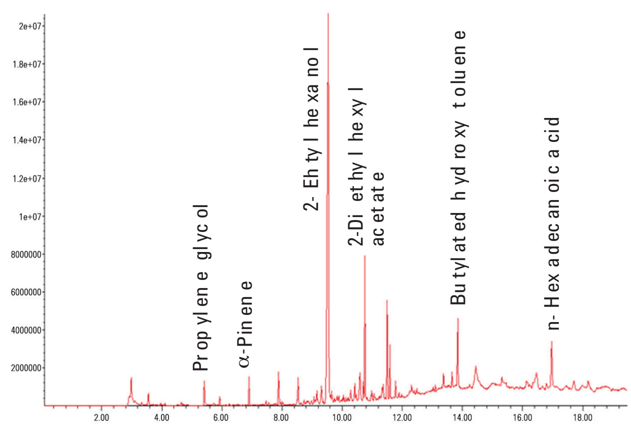


Figure 1. Chromatogram of emissions from a vinyl floor tile carried out using the micro-chamber at 40°C

Figure 2. (Left) µ-CTE with 6 x 44 mL micro-chambers. Max. temp: 120°C. (Right) µ-CTE with 4 x 114 mL micro-chambers. Max. temp: 250°C

Micro-chamber for Testing Semi-VOC Emissions from Products and Raw Materials

Application Brief

The combination of an Agilent TD-GC/MS system and a Micro-Chamber/Thermal Extractor (µ-CTE) accessory facilitates measurement of vapor-phase SVOC emissions in conjunction with volatiles.

Emissions of semi-volatiles (fogging compounds), traditionally defined as chemicals less volatile than n-hexadecane, are prone to condensation and can present a challenge to quantitative analysis. Micro-chamber components are heated to ensure quantitative transfer of SVOC emissions from sample materials to the attached sorbent tube. Efficient recovery was demonstrated by comparing TD-GC/MS data for an alkane test mix (C9 to C24) spiked onto a sorbent tube with that from the same standard introduced to a micro-chamber maintained at 120 °C (Figure 1.)

The Agilent TD-GC/MS system and µ-CTE combination can also be used to monitor volatile and semi-volatile emissions, including phthalate plasticizers, from children's toys (Figure 2.) The toy samples in this case were small plastic animals which were tested whole using the µ-CTE at 40 °C.

Markes supplies two µ-CTE options; one with 6 x 44 mL chambers and a maximum temperature of 120 °C and the other with 4 x 114 mL chambers and a max temperature of 250 °C. The latter is suitable for use with ISO 16000-25; Determination of SVOC emissions - micro-chamber method.

Example µ-CTE applications for SVOC emisssions

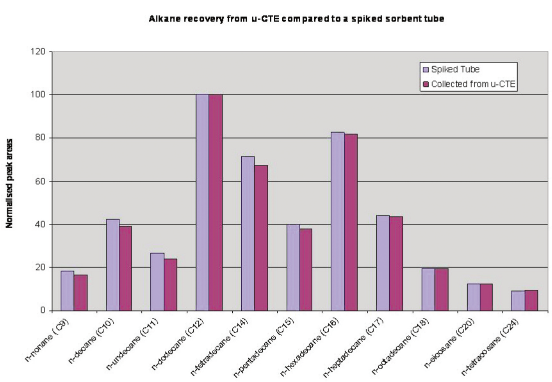


Figure 1. 1 µL mixed alkane standard (C_9 to C_{24}) thermally desorbed from a sorbent tube (blue bars) and a µ-CTE at 120 °C (purple bars)

The manual or automated sample re-collection feature of every Agilent TD-GC/MS offers simple validation of SVOC recovery through the analytical system per standard method recommendations.

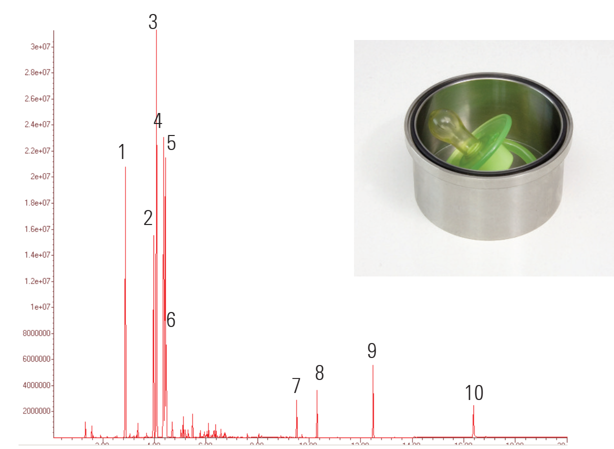
Test conditions

Tests were carried out using the µ-CTE at:

- 120 ° with 50 mL/min for 10 mins (Figure 1)
- 40 °C with 100 mL/min flow for 15 mins (Figure 2)

Sample collection: IAQ tube

Tube desorption	10 mins at 300 °C
"Mat ems" focusing trap	-10 °C to 300 °C (5 mins) at max rate
Split ration	20:1
GC Column	DB-5, 30 m x 0.25 mm x 0.25 µm
Oven program	45 °C with multi ramp to 300 °C
MS temps – source	230 °C, quad: 150 °C, transfer line: 280 °C
Full scan	45 – 450 amu.



1 Toluene
2 Ethyl benzene
3 m/p-Xylene
4 o-Xylene
5 Cyclohexanone
6 2-Butoxy ethanol
7 Tricyclodecane
8 Diethylphthalate
9 Dibutylphthalate
10 Dioctylphthalate

Figure 2. VOCs and SVOCs sampled from a child's plastic toy using the µ-CTE at 40 °C with TD-GC/MS analysis

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