Introducción a las técnicas instrumentales basadas en desorción térmica y GC/MS aplicadas al análisis de materiales

Development of standard methods for emission testing of materials

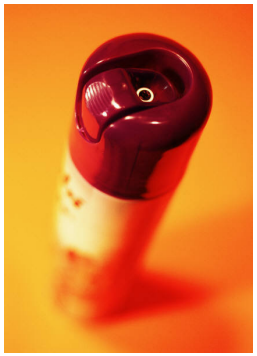
Agilent Technologies

MARKES international

Jaume Santamaria
Responsable de Ventas
Agilent Technologies

Material Emissions – Application Area: Release of VOC and SVOC from……..

- Indoor Air Quality
- Construction Product Manufacturers
  - Flooring (resilient, textile & sports)
  - Insulation materials (thermal & sound)
  - Structural plastics and foams
  - Adhesives & sealants
  - Plaster board (dry wall) and gypsum
  - Paints & varnishes
  - Wall coverings
  - Door & window frames
  - Ceiling materials
- Vehicle Interior Air Quality
- Automotive trim
- Toys
- Packaging
- Cleanroom components
- Electronic computer components
- Cleaning products
- Air Fresheners
- Furniture



Regulations and Market Drivers - Construction Product Regulation

Construction Product Regulation adopted in Feb 2011

- Implemented 1st July 2013
- Mandatory VOC/SVOC emission testing for CE Mark
- Requires '3rd party accreditation and suggests Factory Production Control (**FPC)**

Process to harmonise target compounds and limit levels (LCIs) is in progress

Construction Product Regulation (CPR) 2011

CE

Essential Requirement 3: **Hygiene, health and the environment –** minimise the emissions of dangerous substances, volatile organic compounds (VOC), greenhouse gases or dangerous particles into indoor air

Regulations and Market Drivers - Construction
Product Regulations

Legislation on substances in construction products

The CP-DS database is designed to help all interested parties to identify all relevant regulations in the field of dangerous substances in construction products. More information and disclaimer

General information about the European Union

General information about:

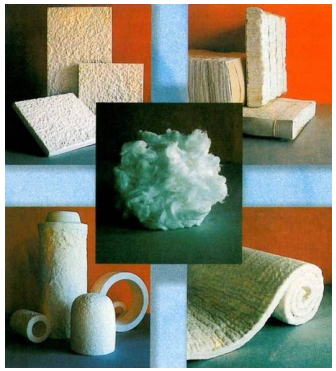
- Austria
- Denmark
- Germany
- Netherlands
- Norway
- United Kingdom

No information is available yet for the following countries:

Belgium, Bulgaria, Cyprus, Czech Republic, Estonia, Finland, France, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden

- Final testing standard (prEN) expected in 2015 or 2016

What is affected…



Emission safety of combustible air fresheners and similar products

- CEN TC421
- Emission safety of combustible air fresheners - test methods
- Emission safety of combustible air fresheners – methodology for the assessment of test results and application of recommended concentration limit
- Chamber TD-GC/MS

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

REACH & SVHC

REACH: Registration, Evaluation, Authorisation and restriction of CHemicals.

Guidance on requirements for substances in articles

Restrictions on the manufacture, placing on the market and use of certain dangerous substances, preparations and articles

Manufacturer responsible for ‘intentional and unintentional release of chemicals’

China implementing Chinese REACH

SVHC - Substances of very high concern
2-Ethoxyethyl acetate
2-Propenamide
2-Pyrrolidinone, 1-methyl-
Anthracene
Benzenamine, 4,4'-methylenebis-
Benzene, 1-methyl-2,4-dinitro-
Benzyl butyl phthalate
Bis(2-ethylhexyl) phthalate
Dibutyl phthalate
Diisoheptyl phthalate
Distannoxane, hexabutyl-
Ethanol, 2-ethoxy-
Ethanol, 2-methoxy-
Propane, 1,2,3-trichloro-

EPHECT

Emissions, Exposure Patterns and Health Effects of Consumer Products in the EU





European collaborative action, which focused on consumer products, known to be potential sources of hazardous and other health relevant air pollutants in dwellings.

- Identify and quantify a set of key indoor air pollutants and emerging pollutants
- Provide applicable tools to reduce the risk associated to the indoor use of consumer products and will lead to a healthier indoor environment for citizens.

Products Include:

- All purpose cleaners
- Furniture polish
- Floor polish
- Combustible air fresheners (candles, incense)
- Air fresheners (spray)
- Coating products for (hard surfaces, leather, textiles)
- Hair styling products (sprays, gels,…)
- Deodorants (sprays)
- Perfumes

Consumer Goods - Toys

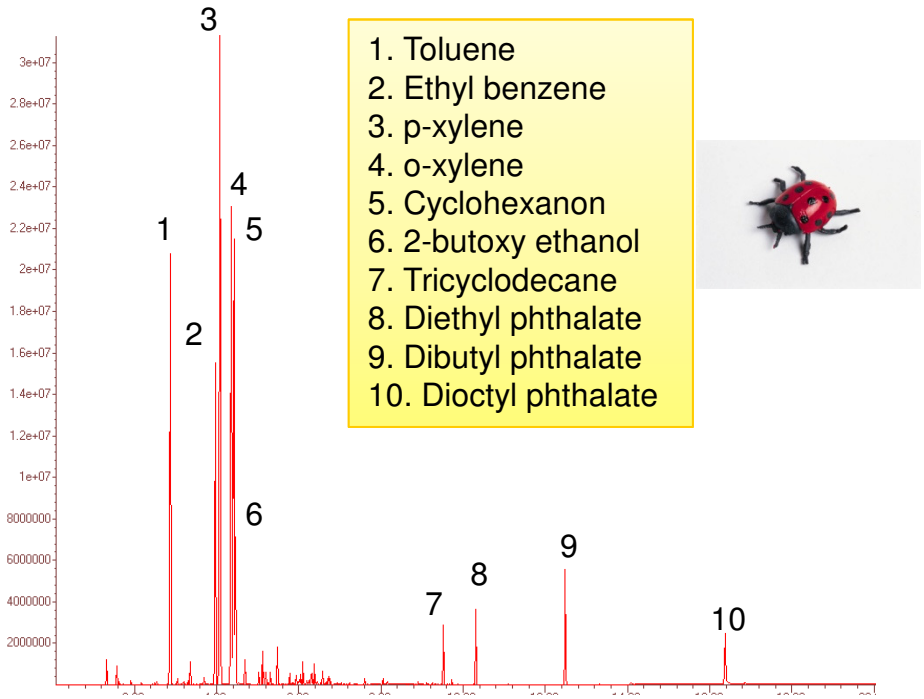
- VOCs from toys may be evaluated using chambers and Thermal desorption in accordance with method prEN 71-11.

- The chemical emission profile gives a comprehensive description of the chemical released.

- Volatiles such as toluene, plus some higher boiling phthalates, which are classified as ‘Substances of Very High Concern’ (SVHC) under REACH (Registration, Evaluation, Authorisation and restriction of CHemicals legislation) in the EU & P.R. China can be determined.

Typical analytical conditions:

- µ-CTE gas flow: 100 mL/min
- µ-CTE temperature: 40.C
- Test time: 20 mins equilibration, 15 mins vapour sampling
- Sorbent tube: Tenax TA or Quartz/Tenax TA/Carbopack X
- TD system: UNITY 2 or TD-100
- Trap: U-T12ME-2S (Material emissions



Migration from food packaging materials

Contaminants arise from an external source such as **packaging**

Off-flavours result from processes taking place in the food itself, such as **microbial action**.

Plastic substances which are restricted by a specific **migration limit** are for instance plasticizers, stabilizers or anti-static agents. Regulation EC (No) 11/2011.

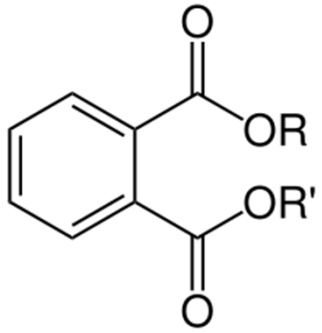
According to the international accepted method EN 13130

Using all kind of food simulants as water, acetic acid, ethanol, iso-Octane, olive oil and Tenax®

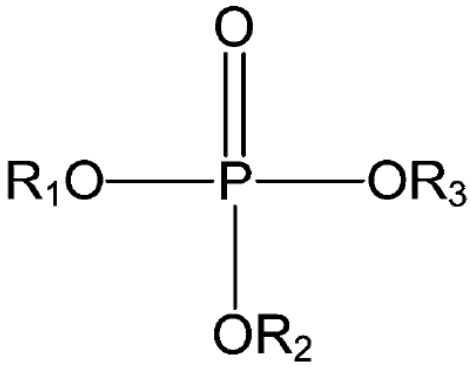
Using all required exposure scenarios as immersion, filling, cell and pouch

Not just volatiles...

ISO 16000-33 Indoor Air: Determination of Phthalates with gas chromatography mass spectrometry



ISO 16000-31: Indoor Air – Measurement of flame retardants and plasticizers based on organophosphorus compounds – Phosphoric acid ester



ISO 12219 Interior air of road vehicles

ISO 12219-1:2012 Interior air of road vehicles -- Part 1: Whole vehicle test chamber -- Specification and method for the determination of volatile organic compounds in cabin interiors

ISO 12219-2:2012 Interior air of road vehicles -- Part 2: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials -- Bag method

ISO 12219-3:2012 Interior air of road vehicles -- Part 3: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials -- Micro-scale chamber method

ISO/FDIS 12219-4 *Interior air of road vehicles -- Part 4: Method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials -- Small chamber method*

ISO/DIS 12219-5 *Interior air of road vehicles -- Part 5: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials -- Static chamber method*

ISO/AWI 12219-6 *Interior air of road vehicles -- Part 6: Method for the determination of the emissions of semi-volatile organic compounds from vehicle interior parts and materials -- Small chamber method*

ISO/AWI 12219-7 *Interior air of road vehicles -- Part 7: Odour determination in interior air of road vehicles and test chamber air of trim components by olfactory measurements*

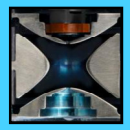
Agilent Technologies: Solutions in GC/MS

6850/MSD

5977E GC/MS

5977C GC/MS

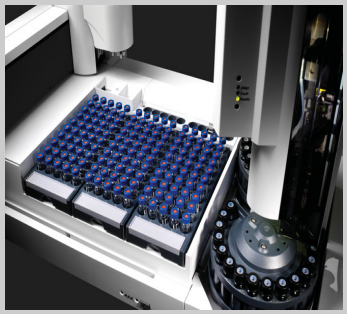
5977T (Transportable)



240 MS Ion Trap

7000C QQQ

Agilent Technologies: Sampling



Inyector ALS 7693

*CombiPal- ALS-HS-SPME

LíQUIDOS (Semivolátiles-Volátiles*)

HEADSPACE 7697

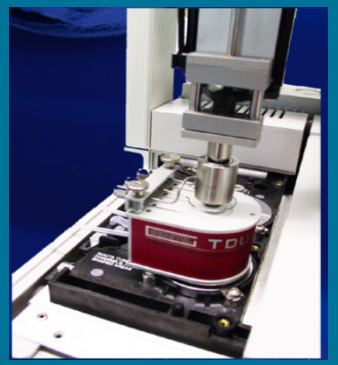
PURGA Y TRAMPA Stratum PTC

LÍQUIDOS-SÓLIDOS (Volátiles)

Markes TD100

Markes CIA8

GASES-MATERIALES (Volátiles)



Twister-Gerstel

SPE AUTOMATIZADA

LÍQUIDOS (Semivolátiles-Volátiles)

Sampling → Thermal desorption → GC/MS → Data analysis

ActiVOC

EasyVOC

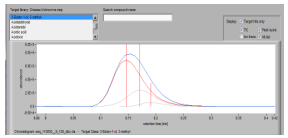
Canisters

Dynamic Headspace - Microchamber

Unity 2 **TD-100**

- Cryogen-free
- Universal: C_2 to C_{40} + reactive compounds
- Repeat analysis
- TD-100:100 tubes

- GC/MS Agilent
- Complete system support
- Check standard for auditing



- Data processing software – TargetView, Mass Hunter or DRS

UNITY 2™

A universal platform for single tube thermal desorption

Accommodates **every TD application on a single platform** (C_2-C_{40} *AND* reactive compounds)

Cryogen-free operation

Compatible with electronic carrier gas control (ECC) to stabilise retention times

Unrestricted upgrades (*e.g.* 100-tube automation, canisters, online)

Fully **compliant with standard methods** including stringent leak test, purge to vent, backflush trap, etc

SecureTD-Q™: Quantitative re-collection of all split flow for repeat analysis

Uniquely-wide concentration range (sub-ppt to %)

Versions for **3.5- & 4.5-inch tubes**. Interchangeable

Compatible with RFID **tagged** or untagged tubes

TD-100™

Automated TD system for up to 100 RFID-tagged or untagged tubes

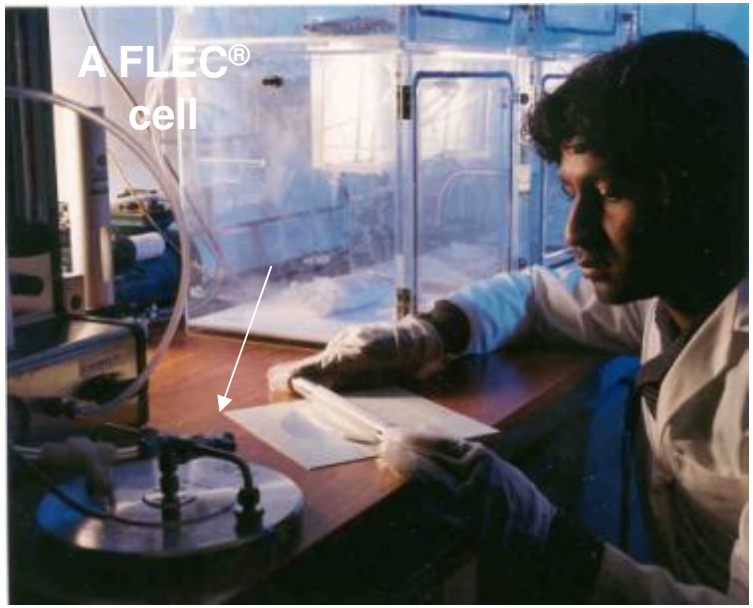
- Incorporates all the advantages of **UNITY 2** and **automated sampling** in a single unit
- Capacity for up to **100** sorbent tubes allows unattended operation all week end
- **Automated re-collection** available factory fitted or for easy field upgrade
- **DiffLok™** tube capping technology for safe and reliable operation
- RFID tag (**TubeTAG™**) read/write capability as standard for tracking tube history
- Tube pressure ratio testing – monitors tube packing integrity
- **Internal standard addition** / dry purge option available for sampled and/or blank tubes

Reference methods for testing chemical emissions from products

ISO 16000-series methods (or Ca01350 based on ASTM stds in the US)

1. Place the material in a test chamber or cell.
2. Collect the vapours
3. Analyse by TD-GC/MS (VOCs) or HPLC (formaldehyde)
4. Evaluate data versus target compound lists and limit levels

Step 1: Place the material in a test chamber or cell



The sample is incubated at 23ºC under a flow of clean air at 50% relative humidity

* 28 ºC in Japan, 25 ºC in Korea

Photo: Eurofins Environment A/S

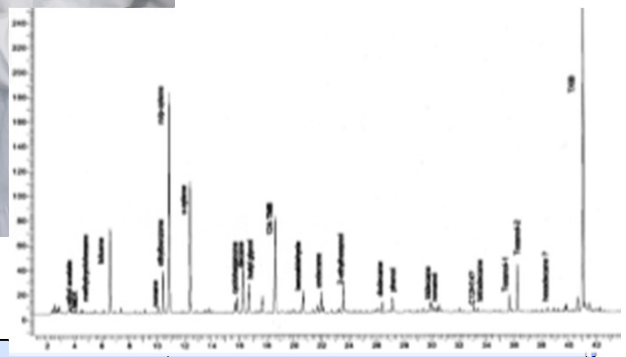
Step 2: Collect the vapours

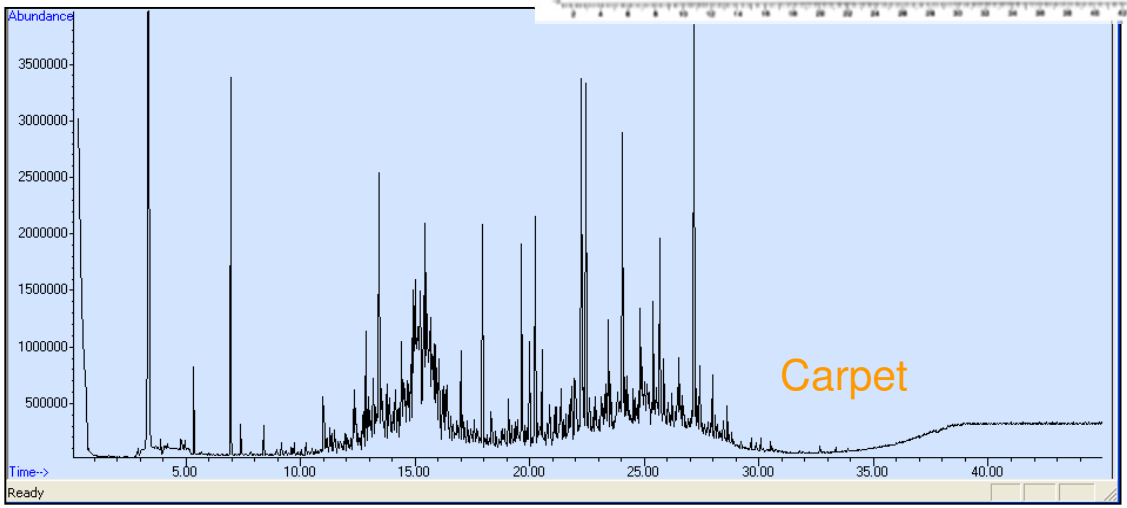
Vapour sampling: 3 & 28 days or at 10 to 14 days
(**this is a long test!**)

2 sorbent tubes in series + **2** tube sets in parallel = **4** tubes per measurement + blanks

Steps 3 & 4: Sample and data analysis

- **TD-GC/MS/FID:** Markes & Agilent versatile TD-GC/MS technology is uniquely suitable for emission testing. Volatile, semi-volatile AND reactive species can be handled in one run.
- **HPLC:** is used for formaldehyde and carbonyls
- **TD-GC/MS:** emission profiles can be very complex. DRS & TargetView can simplify & enhance data processing





Thermal desorption – One versatile technique for all vapour-phase air monitoring applications

Chambers

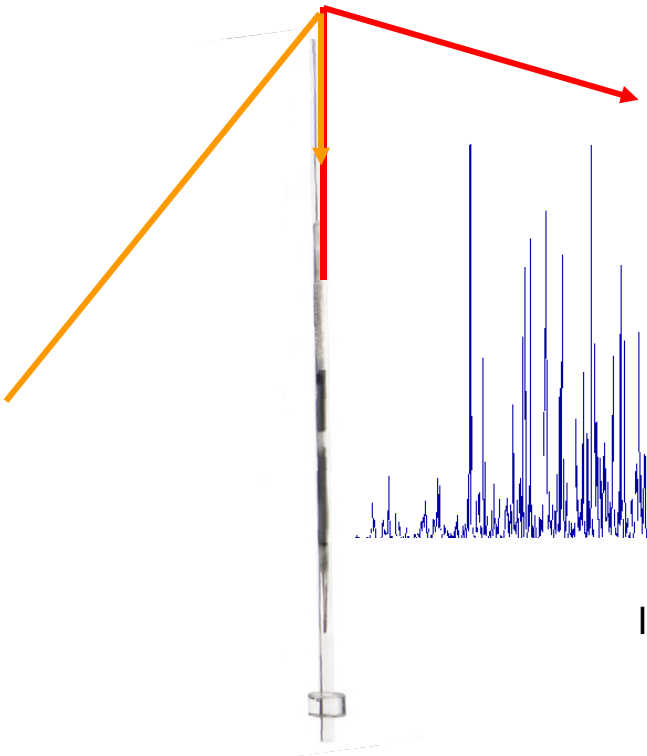
Canisters/bags

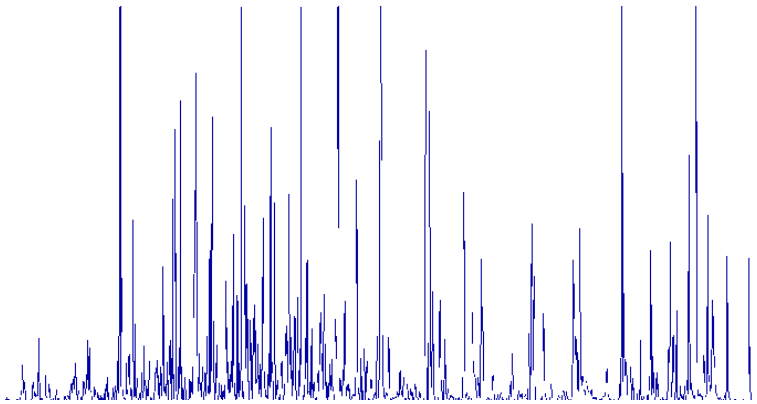
Sorbent tubes

Direct

Active

Electrically-cooled focusing trap





Injection of 100–200 µL vapour into GC(MS)

Water and volatile interferences can be purged to vent

What can be analyzed by TD?

Yes

- Any organic compound more volatile than n-C_{40} (b.p. <500 °C) which is easily gas chromatographed.

  N.B. Vapour-phase organics in normal ambient air typically range up to n-C_{16}

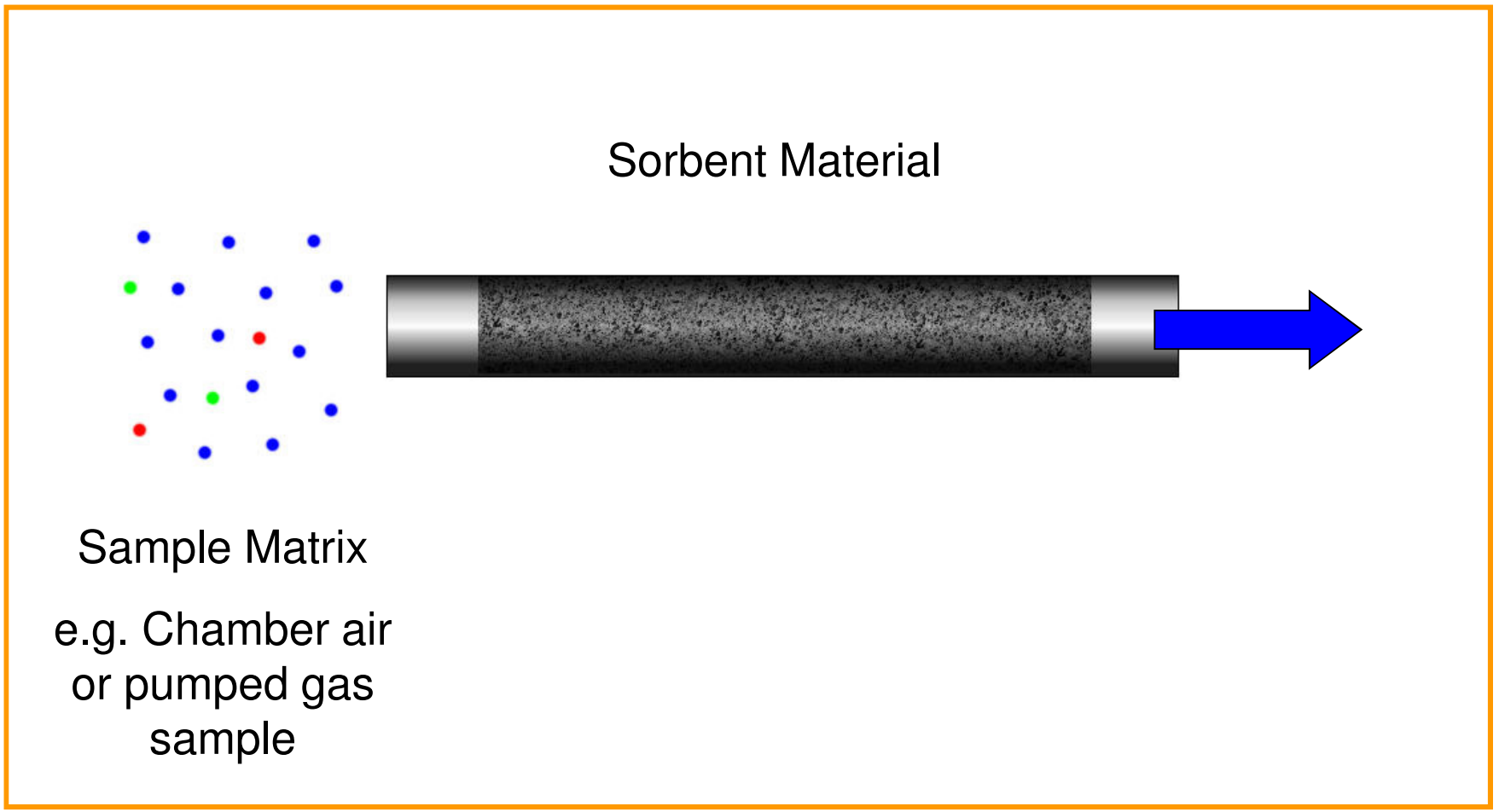
  NB The sorbent or matrix containing the analytes must be compatible with the high temperatures required for quantitative desorption.

No

- Compounds which are not compatible with standard GC or which require special care during GC analysis, *e.g.* cold on-column injection
- Methane
- Compounds less volatile than n-C_{40} (non-volatiles)
- Most inorganic (permanent) gases - O_2, O_3, CO_2, SO_2, NO_2, *etc;* however, **exceptions include H_2S, CS_2, N_2O & SF_6 which all work well with TD**

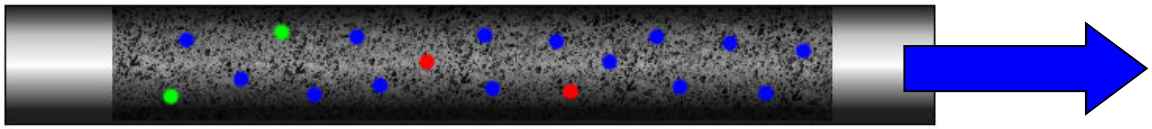
Sampling and analytical techniques for determining volatiles and semi-volatiles

What is Thermal Desorption?



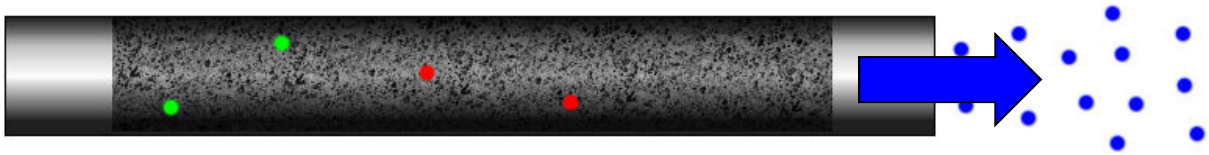
What is Thermal Desorption?

Sample passes onto the sorbent



Compounds of interest are adsorbed on the sorbent surface

What is Thermal Desorption?



Lighter gases such as nitrogen pass through the sorbent

What is Thermal Desorption?

Sorbent is now heated in a reversed flow of clean carrier gas (back flushed)

What is Thermal Desorption?

Compounds are released from the sorbent into the flow of carrier gas

It is a simple extension of the technique of Gas Chromatography and is a **sample introduction technology** for difficult or real-world samples

2 Stage Thermal Desorption

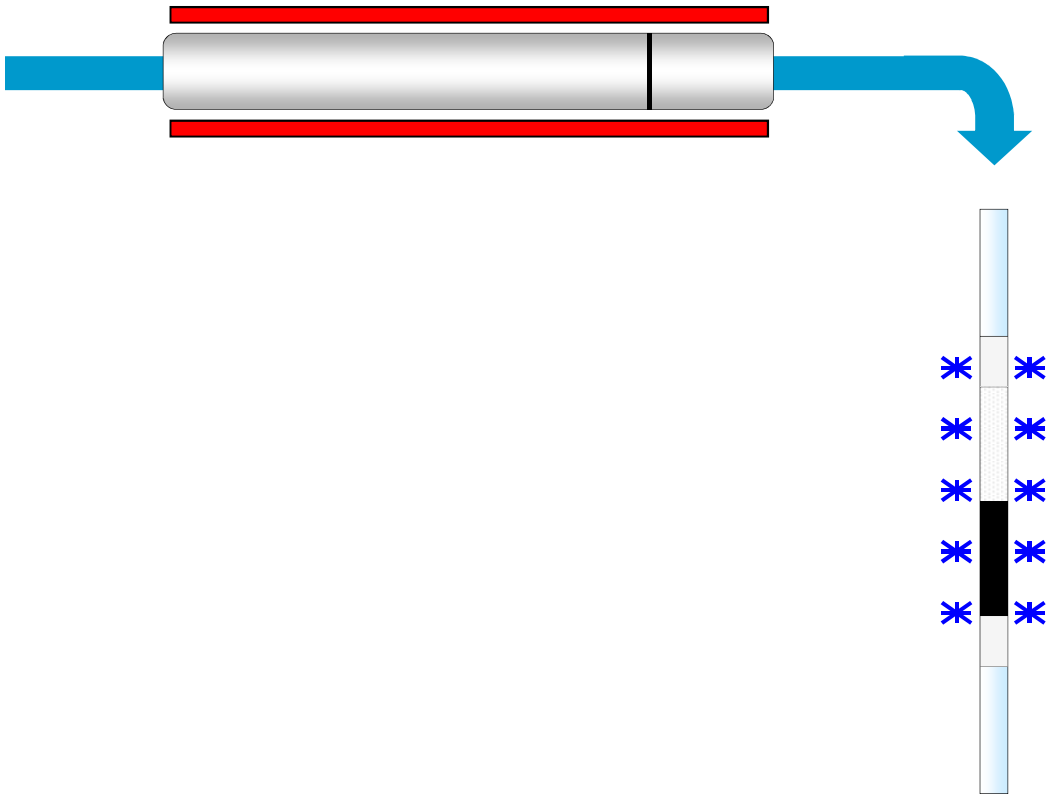
PROBLEM: Compounds are released SLOWLY from the sorbent tube

Would lead to **very wide** chromatographic peaks and low sensitivity

2 Stage Thermal Desorption

STAGE 1

Transfer compounds from tube to secondary trap

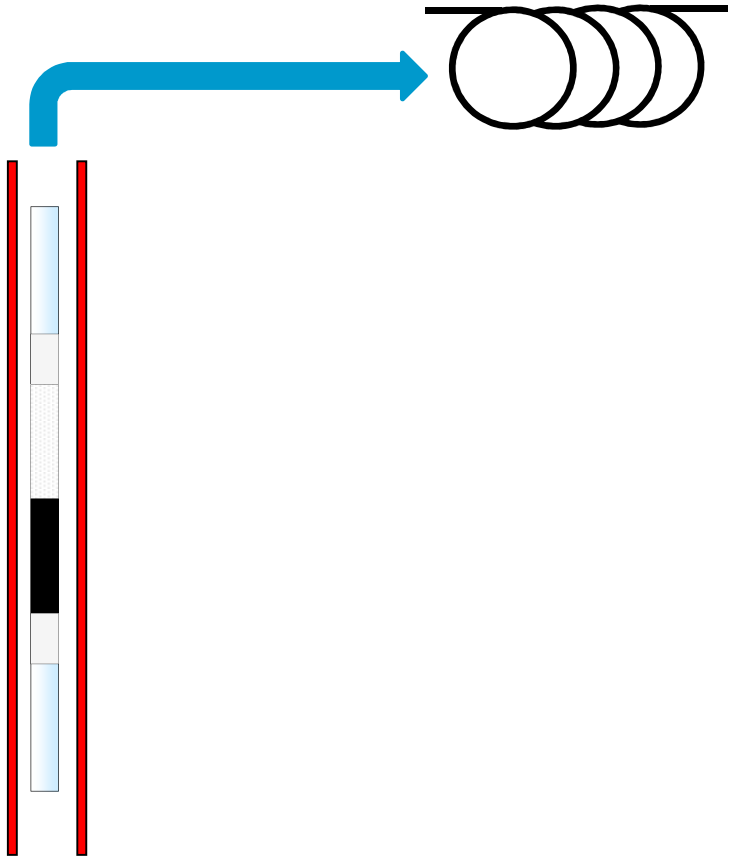


Electrically cooled narrow bore cold trap

2 Stage Thermal Desorption

STAGE 2

Rapid transfer of compounds from cold trap to GC

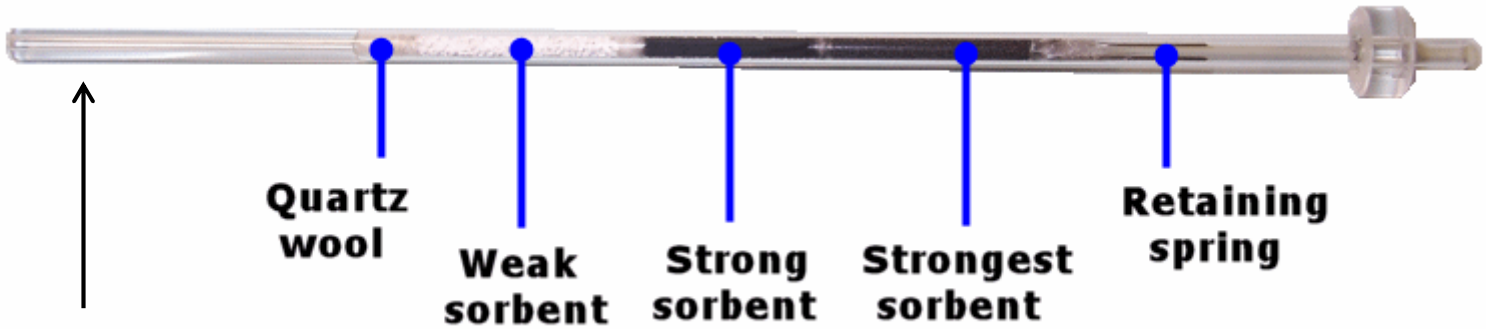


- Cold trap heated rapidly (**100°C/sec**) for sharp chromatographic peaks
- **Backflush** of cold trap for greater volatility range

Cold Trap

Flow during trap desorption

Flow during focusing / sampling onto trap

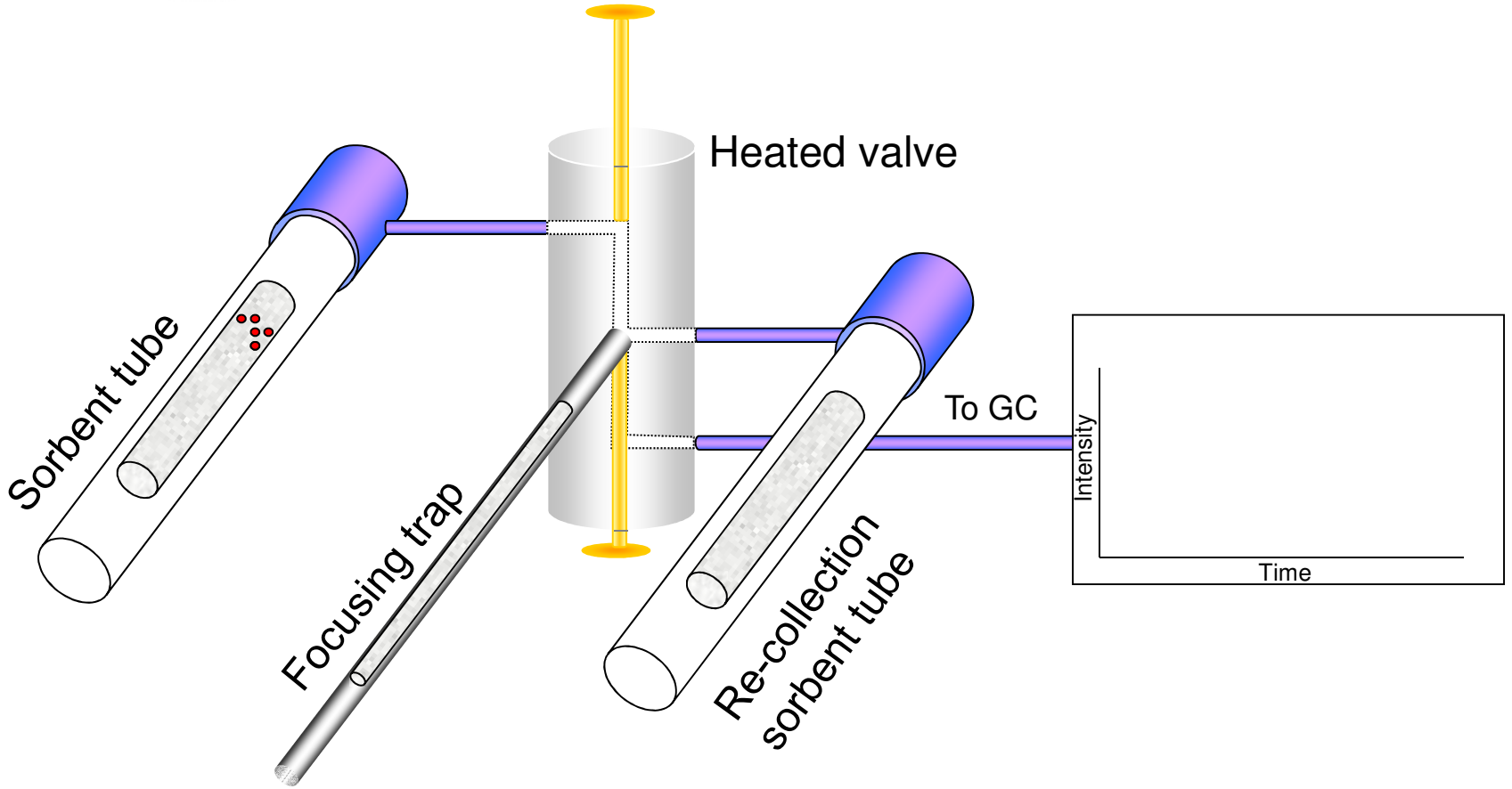


Restricted narrow bore inlet / outlet end of trap

- Narrow design allows splitless injection
- Use sorbent(s) to suit specific application

2-stage desorption using ‘universal’ TD valve:

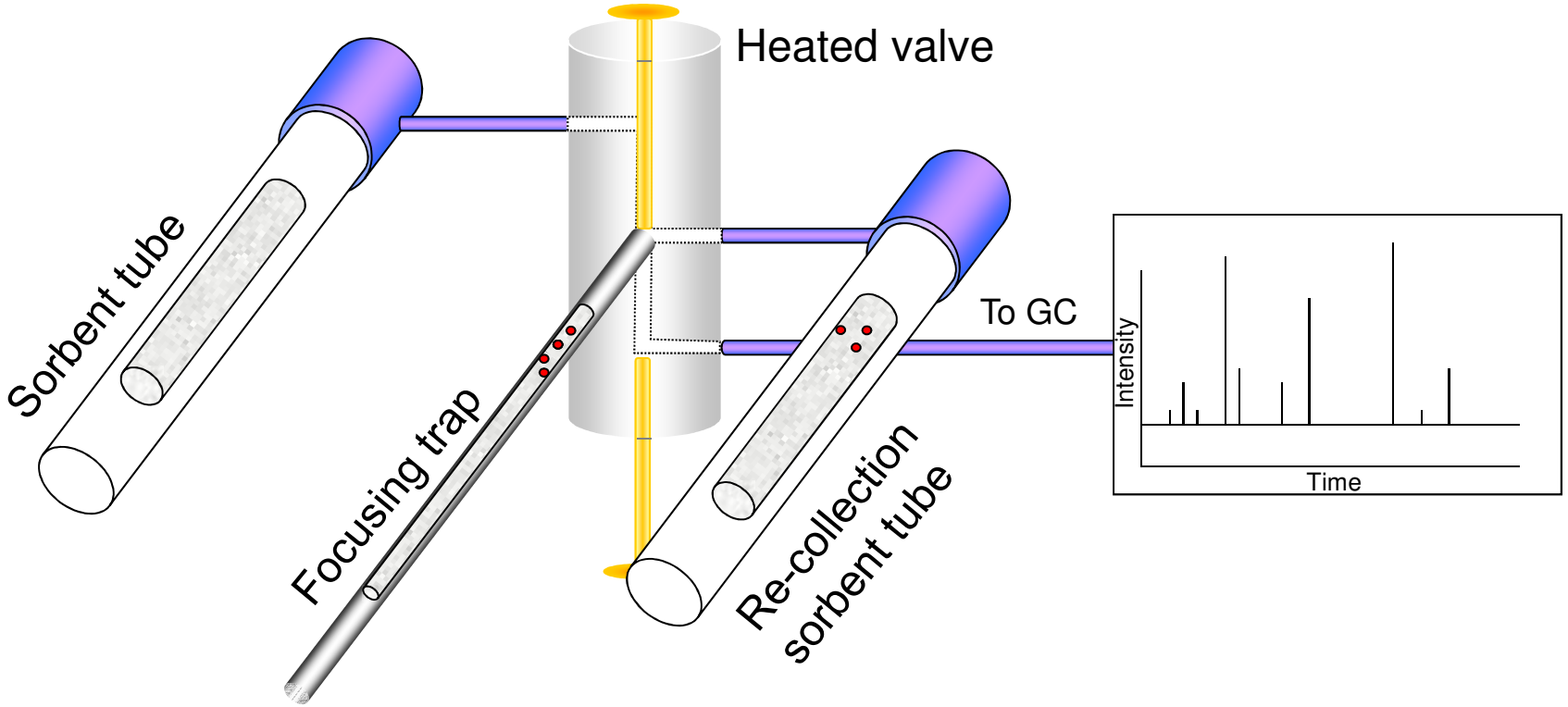
Stage 1: Primary (tube) desorption with optional (inlet) split



- Heated TD valve is inert and low volume: Allows quantitative recovery of high & low volatility compounds and reactive species
- The heated valve also isolates the TD system allowing: leak testing, backflush trap desorption, purge to vent, sample overlap, *etc.*

2-stage desorption using ‘universal’ TD valve:

Stage 2: Secondary (trap) desorption with optional (outlet) split



- Repeat analysis of re-collected samples makes it easy to validate analyte recovery through the TD flow path
- A change to the overall VOC profile indicates any bias

Complexity of reference method is not practical to set up within the manufacturing industry

Secondary emission screening methods
Micro-Chamber/Thermal Extractor™(µ-CTE™)*

- Simpler/quicker emission screening for in-house industrial applications: routine QC, R&D, *etc.*
- Dynamic Headspace
- **Surface-only** or **bulk** emissions can be assessed
- **4 or 6 samples/hour**
- Sorbent tubes or DNPH cartridges

Standardization of micro-chamber methods

ASTM D7706-11: Standard practice for rapid screening of VOC emissions from products using micro-scale chambers.

ISO 12219-3: Interior air of road vehicles – Part 3: Screening method for the determination of the emissions of volatile organic compounds from vehicle interior parts and materials – Micro-scale chamber method

VDI 2083-17: Reinraumtechnik – Reinraum- und reinheitstauglichkeit von werkstoffen (Cleanrooms – Cleanroom cleanliness and suitability of materials).

ASTM D7859 - 13e1 - Standard Practice for Spraying, Sampling, Packaging, and Test Specimen Preparation of Spray Polyurethane Foam (SPF) Insulation for Testing of Emissions Using Environmental Chambers

ASTM WK40293 - New Standard Estimating Chemical Emissions from Spray Polyurethane Foam (SPF) Insulation Using Micro-Scale Environmental Test Chambers

EN 16402 (Draft) Paint and varnishes - Assessment of emissions of substances from coatings into indoor air - Sampling, conditioning and testing

CEN/TS 16516-2013: Construction Products - Assessment of release of dangerous substances

ISO 16000-25: Determination of the emission of semi-volatile organic compounds by building products – Microchamber method.

These are all screening methods

ASTM D7706-11 Standard practice for rapid screening of VOC emissions from products using micro-scale chambers.

- **Surface-only** or **bulk** emissions testing
- **4 or 6 samples/hour**
- Sorbent tubes ((S)VOC) or DNPH cartridges (H_2CO)

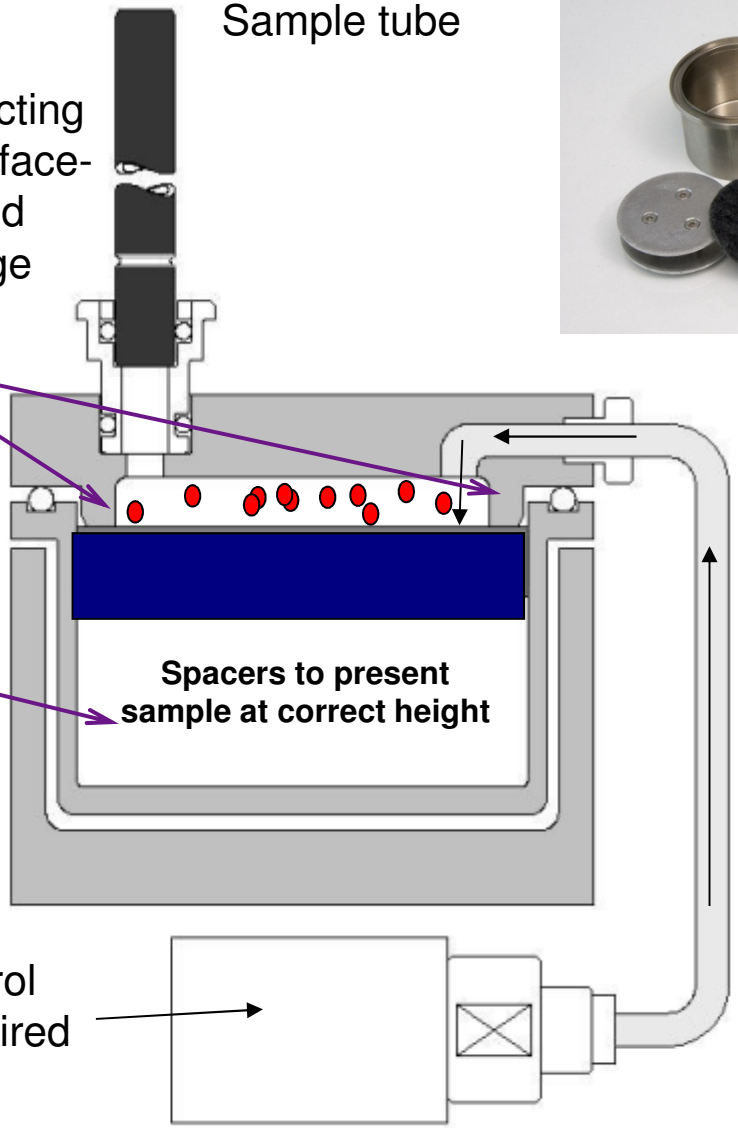
Test Parameter	**VOCs**	**Formaldehyde**
Equilibration time range (min)	20–40	20–40
Chamber temperature (°C)	40	40
Inlet gas flow rate range (ml/min)	50	250
Gas sampling time (min)	10	60

*** UK patent application 0501928.6**

Surface emissions

Sample tube

Heated lid: The collar projecting from lid defines area for surface-only emission testing and minimises ingress of edge emissions



Heated air stream

Proprietary flow control device – no pump required

Micro-chamber data has been shown to correlate with results from long term tests using ordinary chambers

Using the microchamber for bulk emissions (content testing)

Bulk Emissions

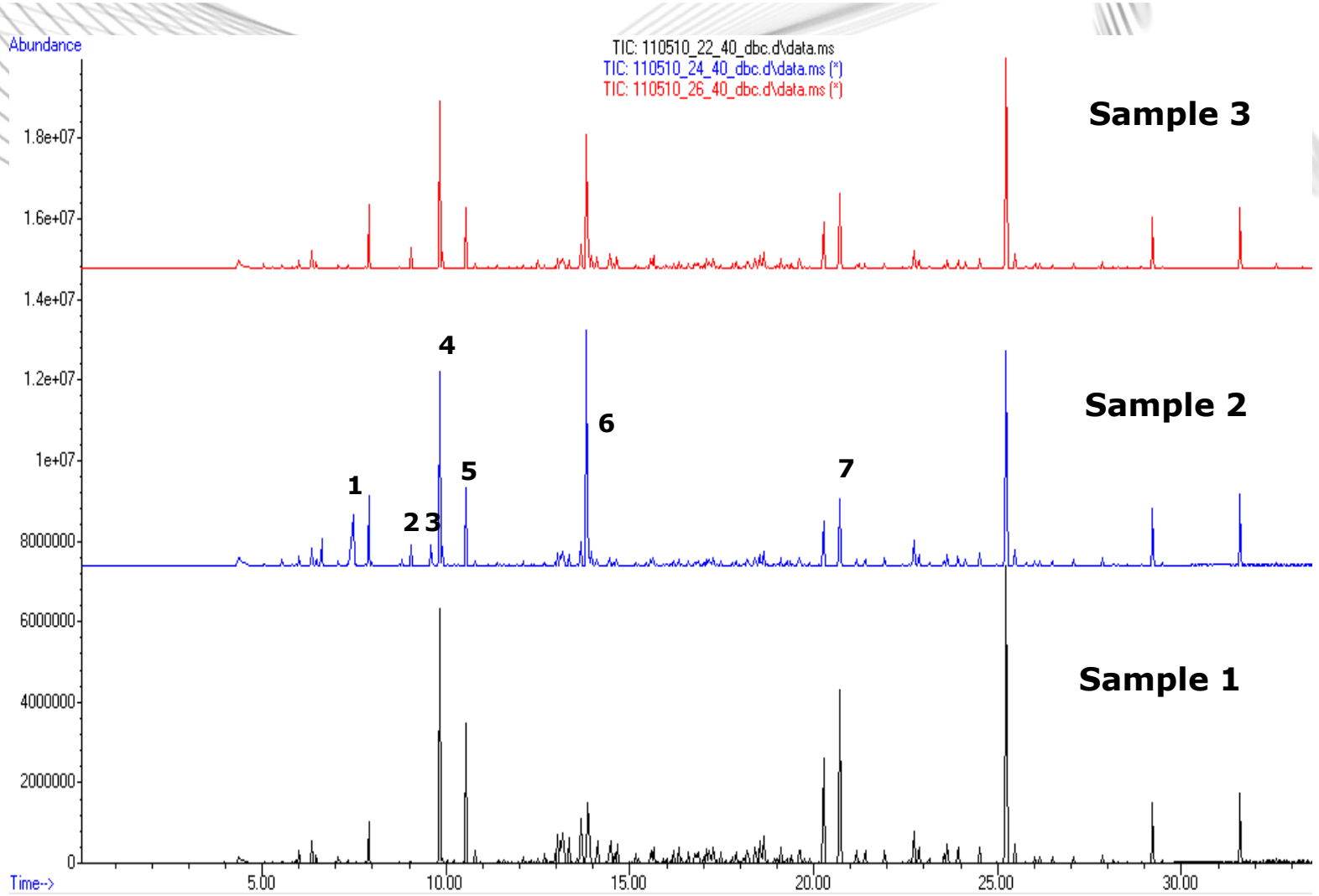
- Ambient/elevated temperature
- Dynamic Headspace
- Homogenous sample

Flooring Material: Determining formulation to ensure compliance with regulations

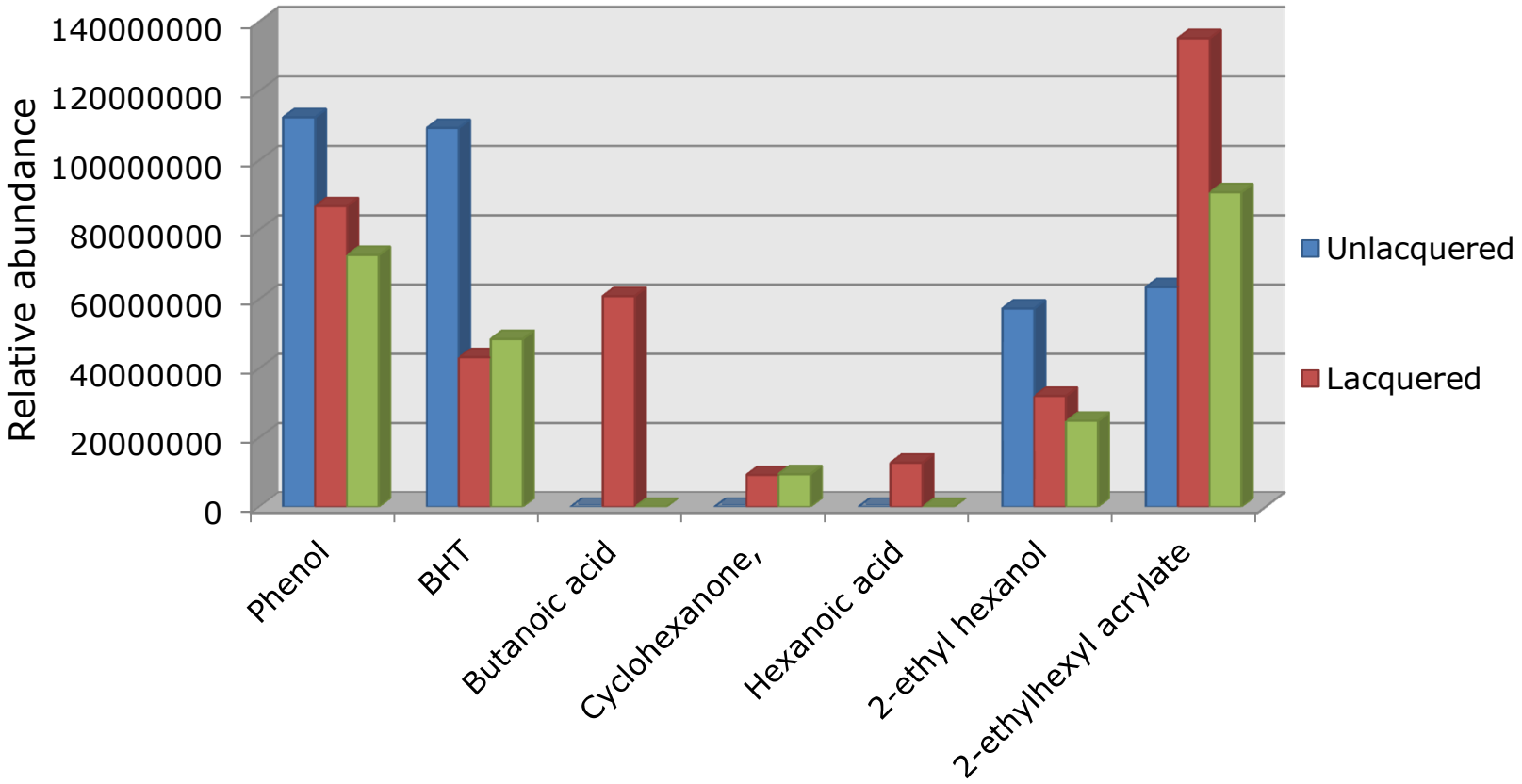
Of particular interest are the relative levels of butanoic acid, cyclohexanone, hexanoic acid, phenol, 2-ethyl hexanol, 2-ethylhexyl acrylate an BHT (butylated hydroxtoluene) emitted by each sample, indicative of differing product formulations.

1 2 3

Sample	Formulation	Lacquer	Extra heat cycle	Info
1	A	No Lacquer	N	Liquid coated UV cured
2	A	Lacquer A	N	Liquid coated UV cured + Lacquer A
3	A	Lacquer A	Y	Liquid coated UV cured + Lacquer A + heat cycle



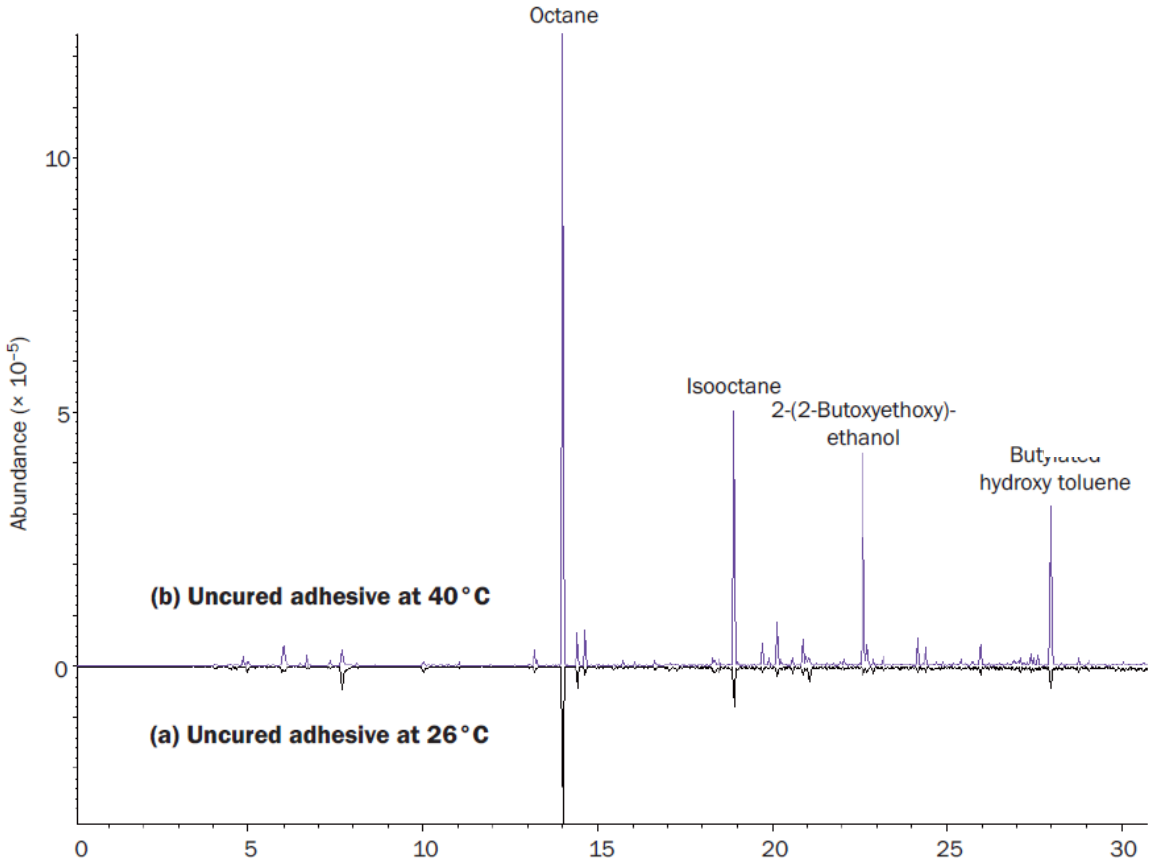
Chromatograms of all three flooring samples.
1) Butanoic acid, 2) Cyclohexanone, 3)Hexanoic acid, 4) Phenol, 5) 2-ethyl hexanol, 6) 2-ethylhexyl acrylate, 7) BHT



Sample	Formulation	Lacquer	Extra heat cycle	Info
1	A	No Lacquer	N	Liquid coated UV cured
2	A	Lacquer A	N	Liquid coated UV cured + Lacquer A
3	A	Lacquer A	Y	Liquid coated UV cured + Lacquer A + heat cycle

Example of Adhesive Screening

Comparison of VOC profiles of the uncured adhesive at 26 °C and 40 °C. Emissions were sampled using the Micro-Chamber/Thermal Extractor onto sorbent tubes packed with Tenax TA, and analysed by TD–GC/MS.



What's in the Air you Breath…….Part 2: Vehicle Interior Air Quality

New Car Smell Could Be Dangerous

abc GOOD MORNING AMERICA

Sept. 27, 2005

Some people can't get enough of that new car smell, but studies show the odor can be bad for your health.

CNN Living

Politics | Justice | Entertainment | Tech | Health | Living | Travel | Opinion | iReport | Mor

Don't inhale that new car smell

The Telegraph

HOME | NEWS | WORLD | SPORT | FINANCE | COMMENT | BLOGS | CULTURE | TRAVEL

USA | US Election 2012 | Asia | China | Europe | Middle East | Australasia | Africa | South A

Afghanistan | Pakistan | India | North Korea | South Korea | Japan | Kazakhstan

HOME » NEWS » WORLD NEWS » ASIA » JAPAN

Enjoying the smell of a new car 'is like glue-sniffing'

WebEx – 24th April
3pm CET