TESTING CHEMICAL EMISSIONS FROM PRODUCTS AND MATERIALS

Simplifying product emission testing for ease of use by manufacturing industry

Dr Caroline Widdowson
Markes International, April 2011

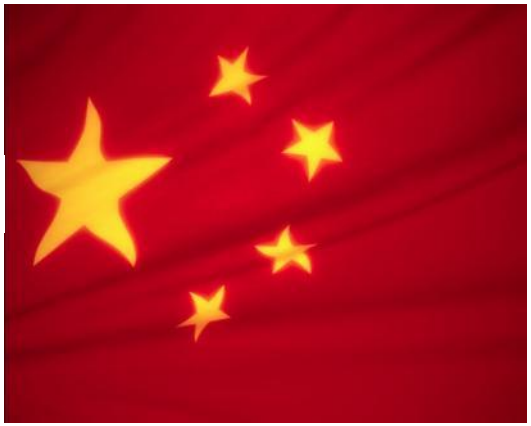
Emission testing by manufacturing industry is governed by regulations and market pressure...

Construction product regulations examples

New regulations for testing chemical emissions from construction products are getting stricter all over the world

Construction Product Directive/Regulation (CPD/CPR)

New US building codes



Chinese ‘REACH’

Construction product regulations and associated developments in Europe

Construction Product Regulation (CPR) 2011

Construction Product Regulation adopted in Feb 2011

- Implementation by 2013
- Requires '3rd party accreditation and Factory Production Control (**FPC)**

Process to harmonise target compounds and limit levels (LCIs)

- Prelim list due 2011, final list due 2012

Based on ISO 16000 series

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

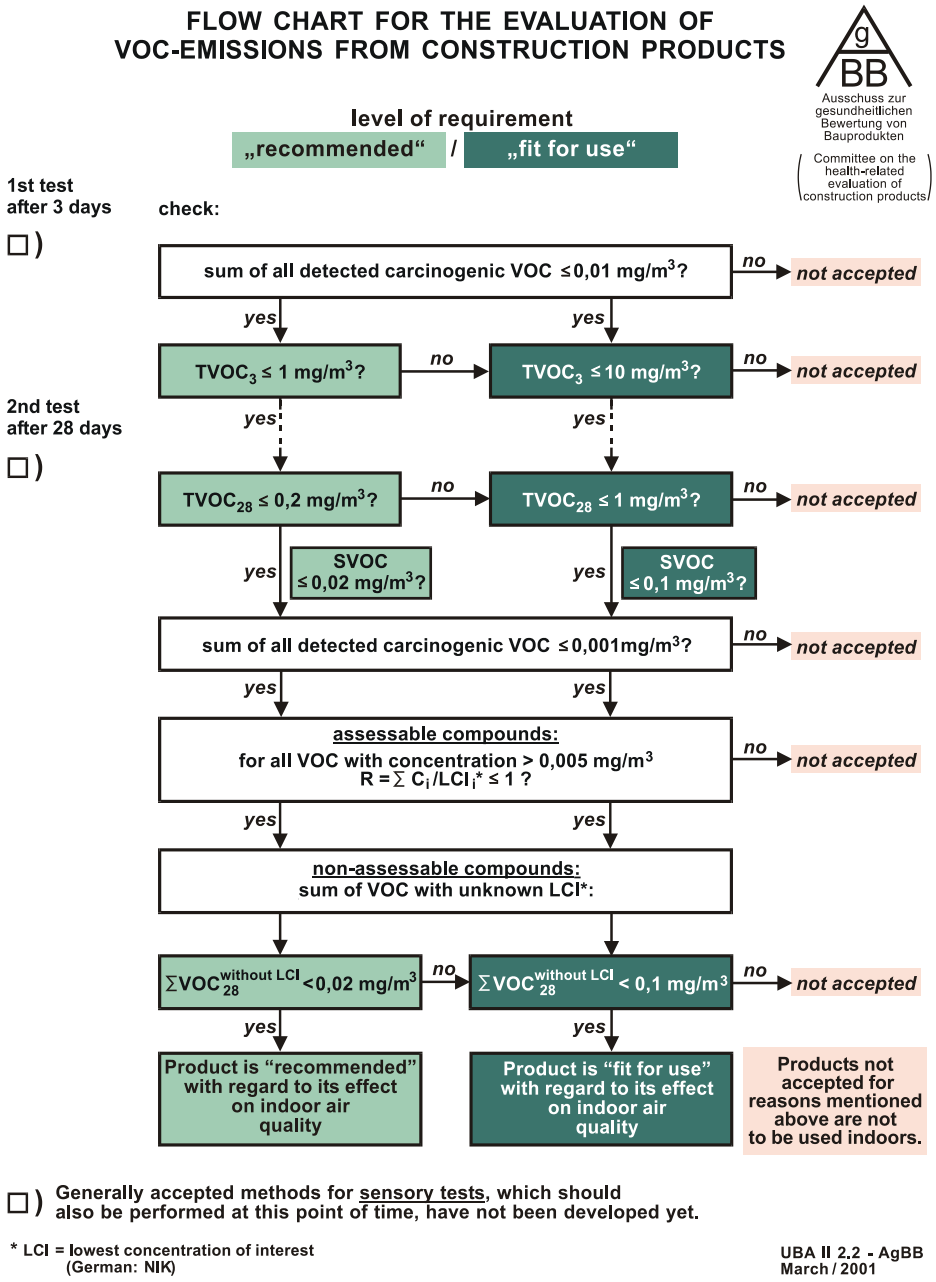
The 2005 German flooring regulation and AgBB scheme

Target compounds:

~160 toxic VOCs

~30 carcinogens

Emission data are converted to vapour concentrations in a reference room. Limit levels are quoted as ‘lowest concentrations of interest’ (LCIs)



2010 French regulation applies to construction and decorative products

- Implementation: all new products by Sept 2011 and for all products by Sept 2013.
- Products are not failed under the French scheme but are labelled A+, A, B or C. The class is assigned depending on the worst-performing compound of interest.
- France also operates the voluntary AFSSET scheme which includes nearly 200 target compounds and is very similar to AgBB
- *From 2012, construction products may only be sold in France if they show 28-day emission levels below 1 µg/m³ for trichloroethylene, benzene, DEHP and DBP tested with ISO 16000 and calculated for European reference room.*

Compounds of interest

formaldehyde

acetaldehyde

toluene

tetrachloroethylene

xylene

1,2,4-trimethylbenzene

1,4-dichlorobenzene

ethylbenzene

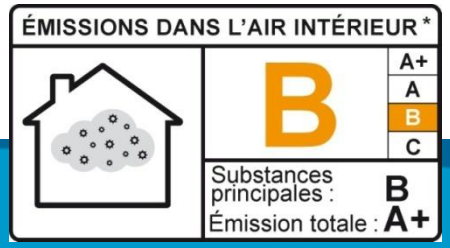
n-butyl acetate

2-butoxyethanol

styrene

TVOC

3 specified carcinogens



Construction product regulations and similar developments in the US

Primary legal instrument likely to be US building codes

- Vs 1.1 of Ca Spec 01350 fast becoming universal US protocol for emission testing.
  - Enshrined in: ANSI/ASHRAE 189.1, **IgCC** (2nd ed.), BIFMA M7 revision, etc.
  - Based on D5116 (chamber) & D6196 (TD-GCMS)
  - Similar to AgBB/AFSSET
- UL acquisition of AQS/GEI signals the growing importance of product emission testing in the US
- ASTM stds also available for emission screening:
  - D7706 Micro-scale chamber
  - D7143 FLEC
- NIST collaborating with lead European agencies to improve analytical QA for mat ems testing:
  - Check stds, PT schemes, CRMs.

Key Methods

ISO	ISO 16000-3	Indoor air – Part 3: Determination of formaldehyde and other carbonyl compounds – Active sampling method
ISO	ISO 16000-6	Indoor air – Part 6: Determination of VOCs in indoor & test chamber air by sampling on Tenax sorbent, TD-GC MS/FID
CEN/ISO	EN/ISO 16000-9	Indoor Air – Part 9: Emission test chamber method (Small)
CEN/ISO	EN/ISO 16000-10	Indoor Air – Part 10: Emission test cell method (FLEC)
CEN/ISO	EN/ISO 16000-11	Indoor Air – Part 11: Procedure for sampling and storage of samples and preparation of test specimens
ISO	ISO DIS 16000-23/24	Performance test for evaluating the reduction of formaldehyde (part 23) or VOC (pt 24) concentrations by sorptive building materials
ISO	ISO DIS 16000-25	Determination of the emission of semi-volatile organic compounds by building products - Micro-chamber method
California	Section 01350	Standard Method for testing & evaluation of VOC emissions from indoor sources using environmental chambers

Automotive methods/techniques

Direct desorption

Microchamber

Small chambers

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

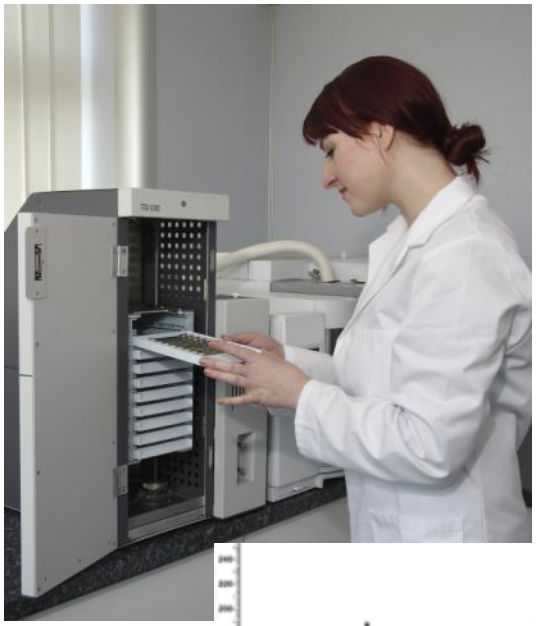
Step 2: Collect the vapours

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

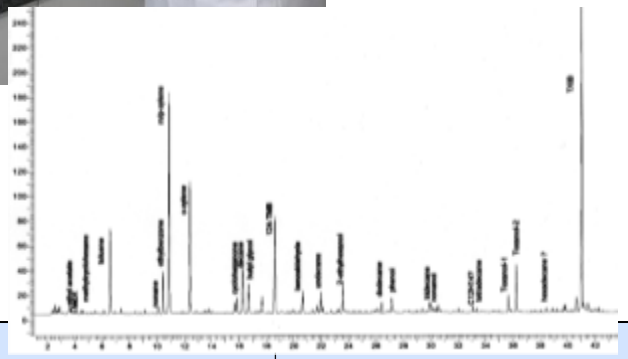
2 sorbent tubes in series + **2** tube sets in parallel = **4** tubes per measurement

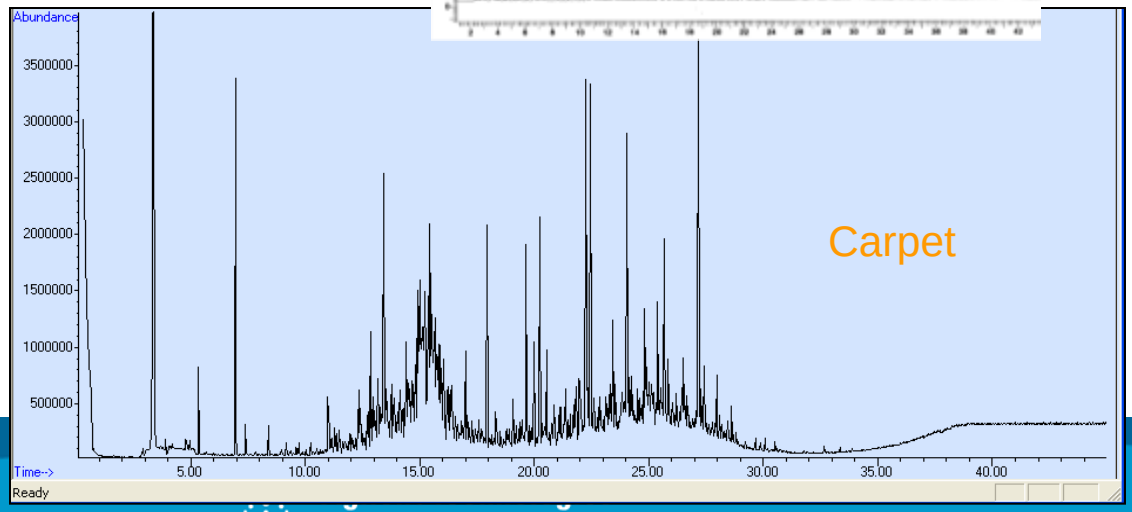
+ blanks

Steps 3 & 4: Sample and data analysis



- **TD-GC/MS/FID:** Markes versatile TD 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



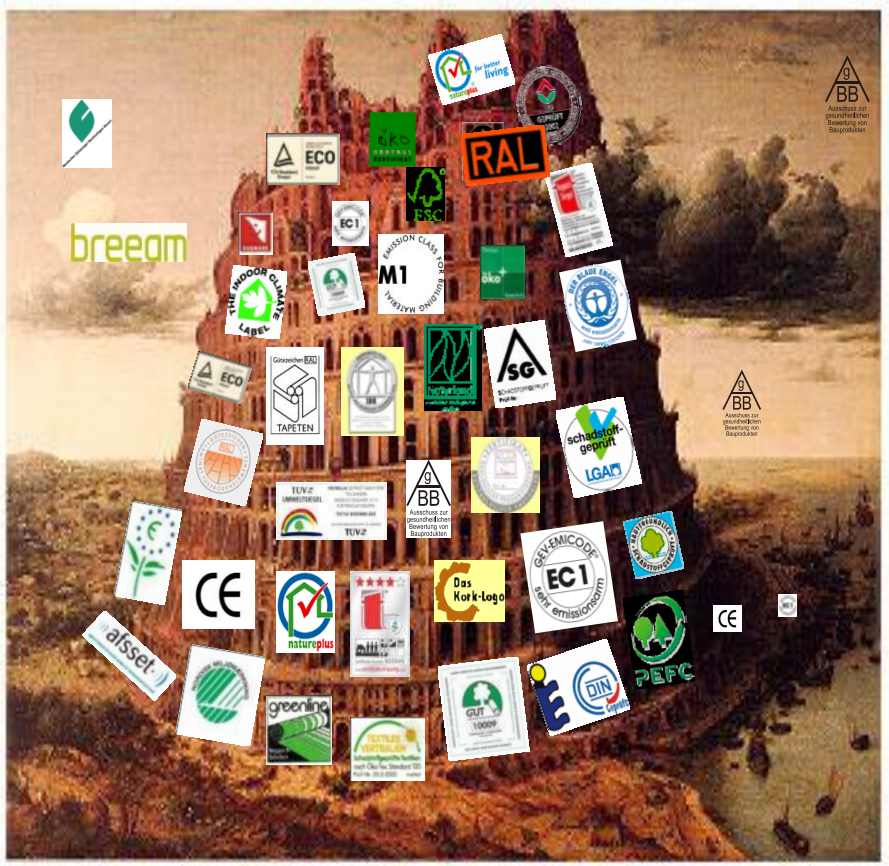


Certification/labelling

In Europe alone there are currently >20 different labels, each requiring a different but similar test protocol

New regulations aim to replace all these different labelling schemes with one *e.g.*

- CE mark in Europe
- IgCC or UL in USA



After CE marking the best voluntary schemes, e.g. the German Blue Angel, might survive as optional additional labels (gold stars!)

Certification/labelling

California Department of Public Health CDPH

CE

CARB Rule
Your resource for California ATCM Compliance

VOC emission testing

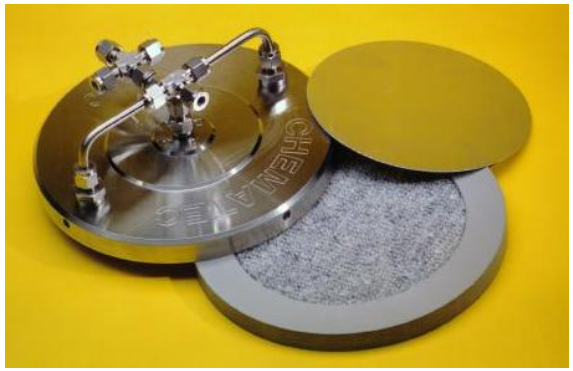
Accredited Lab

Factory product control

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

FLEC methods
ISO 16000-10, D7143

- The Field and Laboratory Emission Cell (FLEC) is an easy-to-use device for the certification of indoor products/materials according to their VOC emission levels (EN ISO 16000-10, ASTM D7143).



FLEC methods
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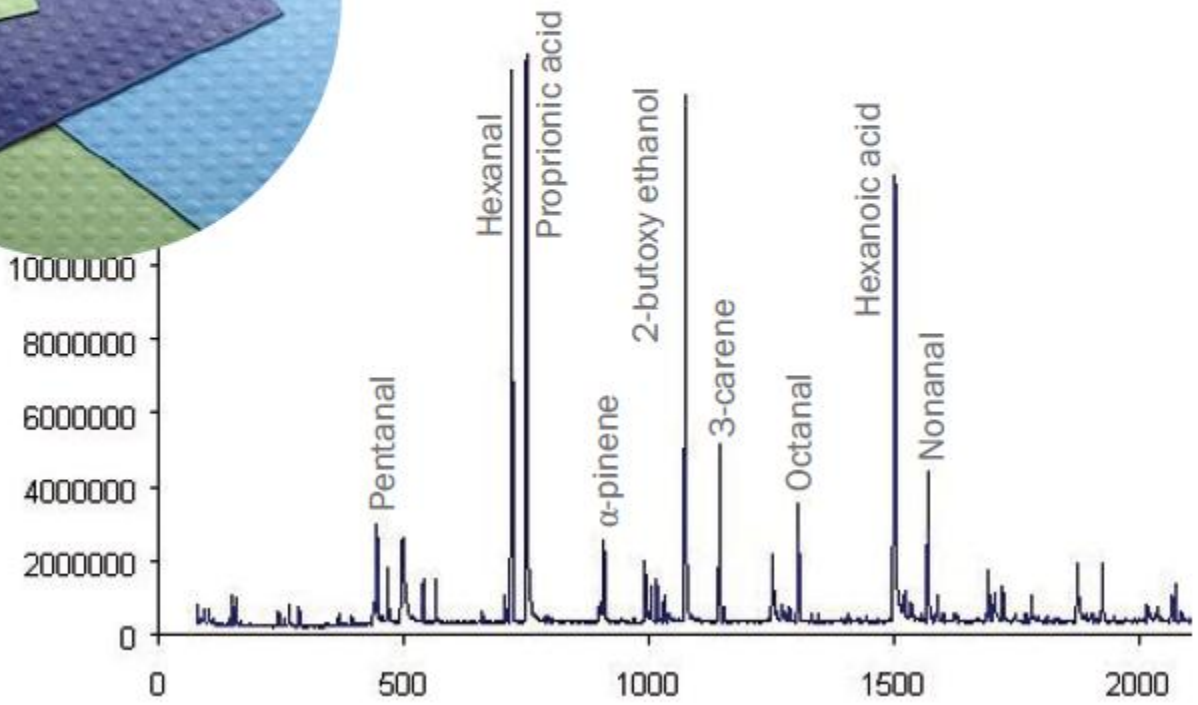


Typical analytical conditions:

- Sample area: 177 cm^2
- Test time: Equilibration 24 hrs (certification), 1–2 hrs (routine)
- Vapour sampling: 15–30 mins using a Tenax TA or Quartz/Tenax TA/Carbopack X tube
- TD System: UNITY 2 or TD-100
- Trap: U-T9TNX-2S (Tenax) or U-T12ME-2S (Material emissions)
- Analysis: GC/MS

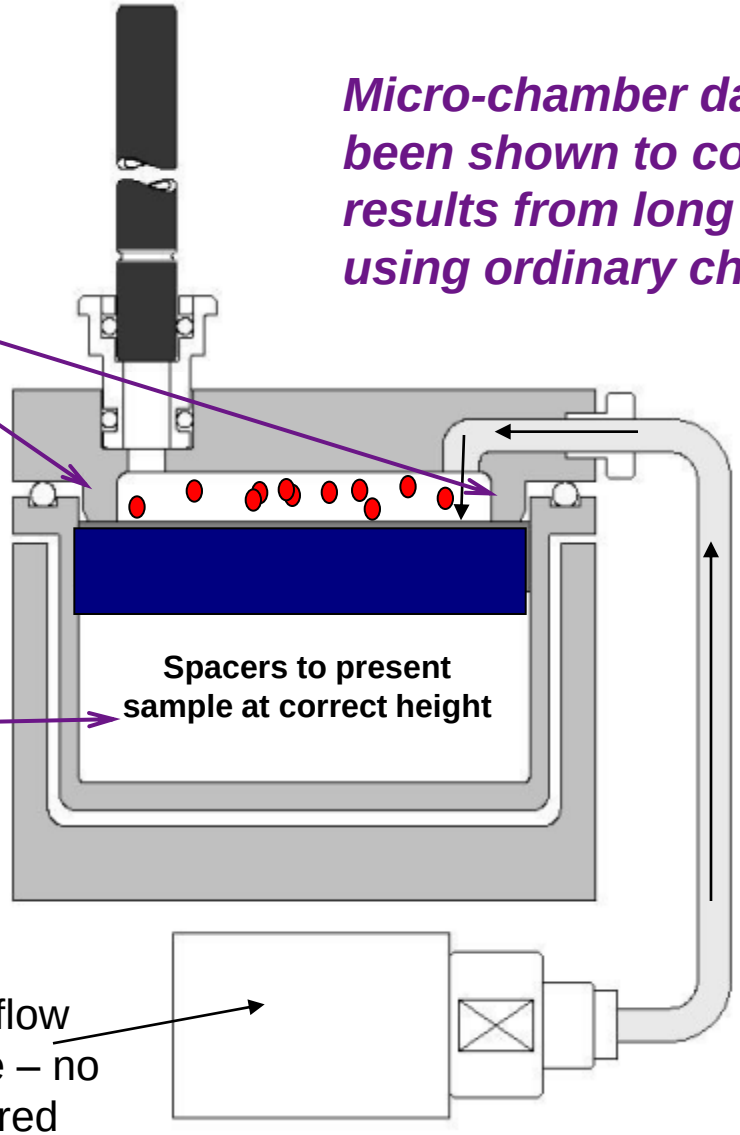
Secondary emission screening methods Micro-Chamber/Thermal Extractor™(μ-CTE™)*

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

µ-CTE: Tubes are attached to all micro-chambers in parallel. 4 or 6 samples can be processed in 1 hr

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

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



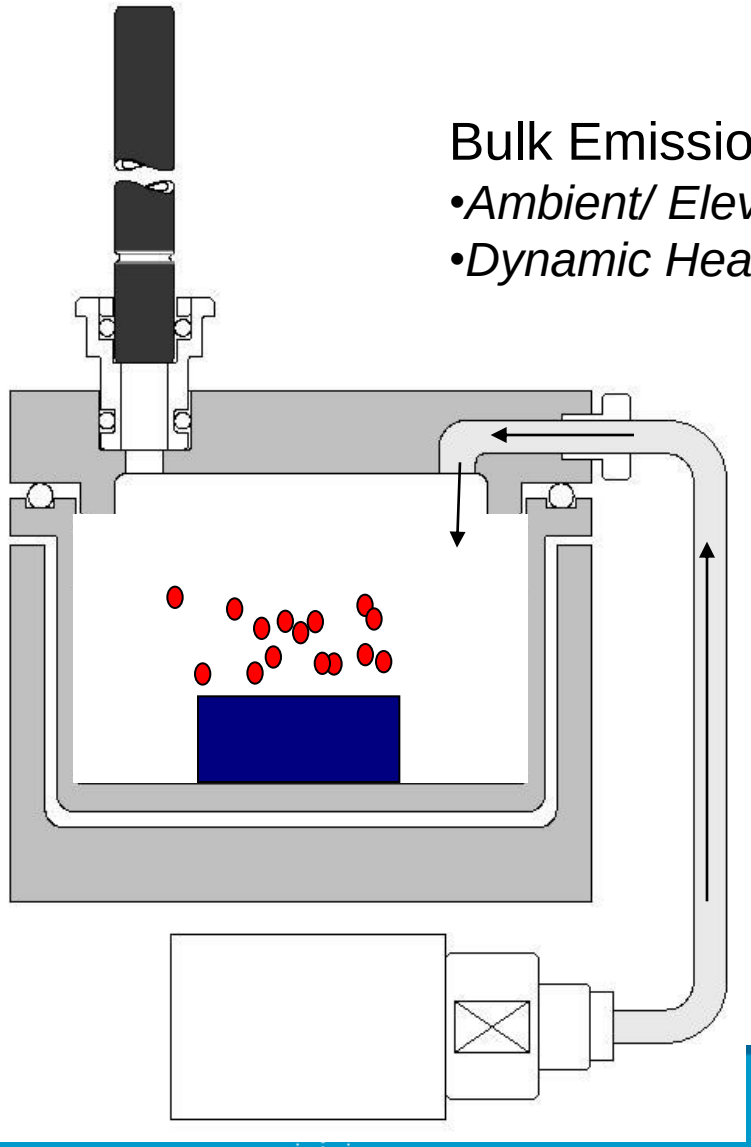
µ-CTE: Tubes are attached to all micro-chambers in parallel. 4 or 6 samples can be processed in 1 hr

1. Set temp. and flow

2. Insert sample
   - Building Material
   - Liquid
   - Soil sample etc.

3. Collect compounds

4. Analyse
   using TD GC/MS
   (ISO 16000-6)



Bulk Emissions
- *Ambient/ Elevated temperature*
- *Dynamic Headspace*

Standardisation of micro-chamber methods

ISO 12219-3 for car trim and 16000-25 for SVOCs in construction products

ASTM D7706 for construction and other products used indoors

CEN TC351 – as secondary/indirect method and/or for content testing for construction products

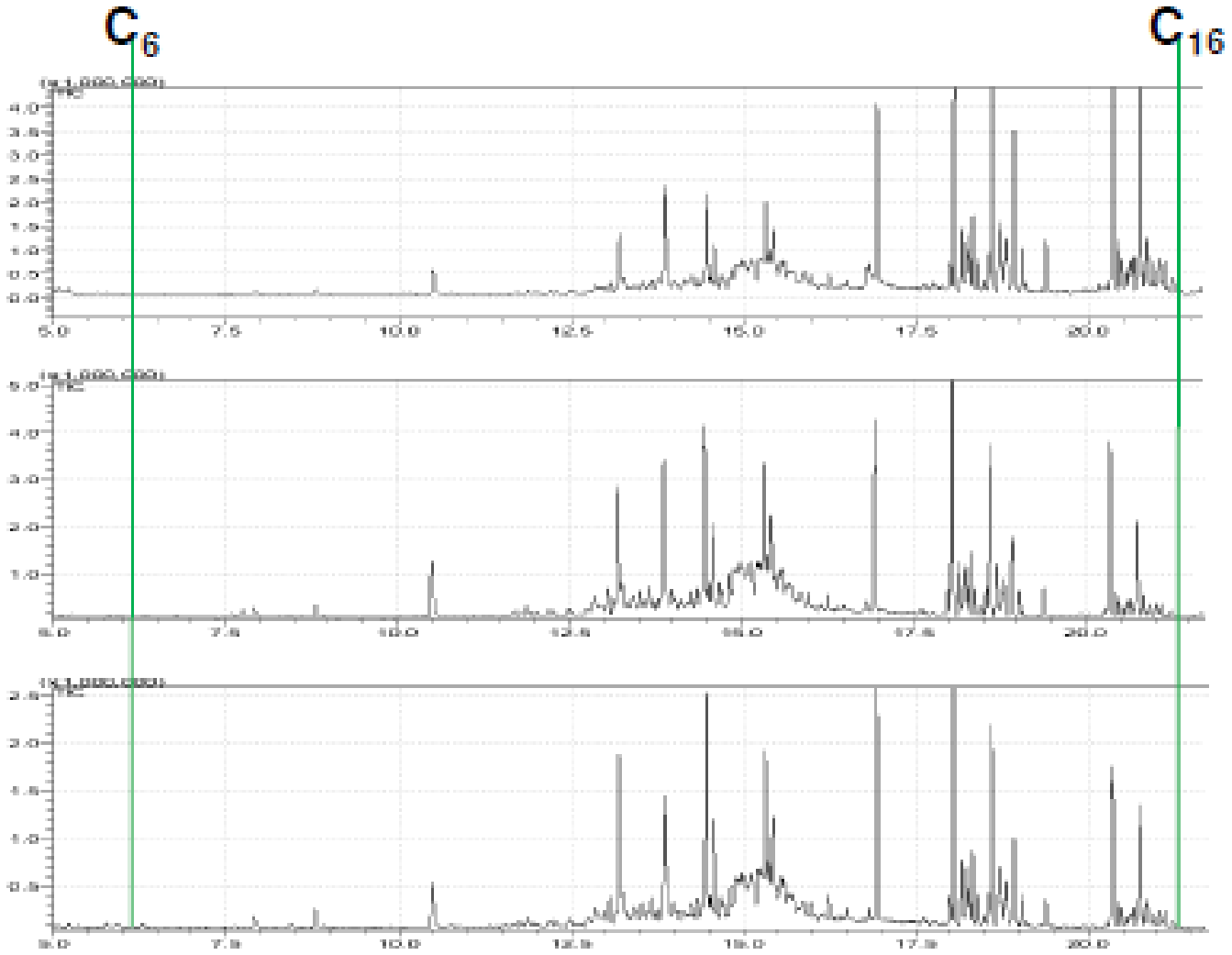
VDI 2083 for cleanroom construction materials and possible follow on ISO std

GUT (and possible follow on ISO standard)

ASTM working group for spray polyurethane foam

These are all secondary / screening methods

Correlation: can µ-CTE data be used to predict longer term reference test results?

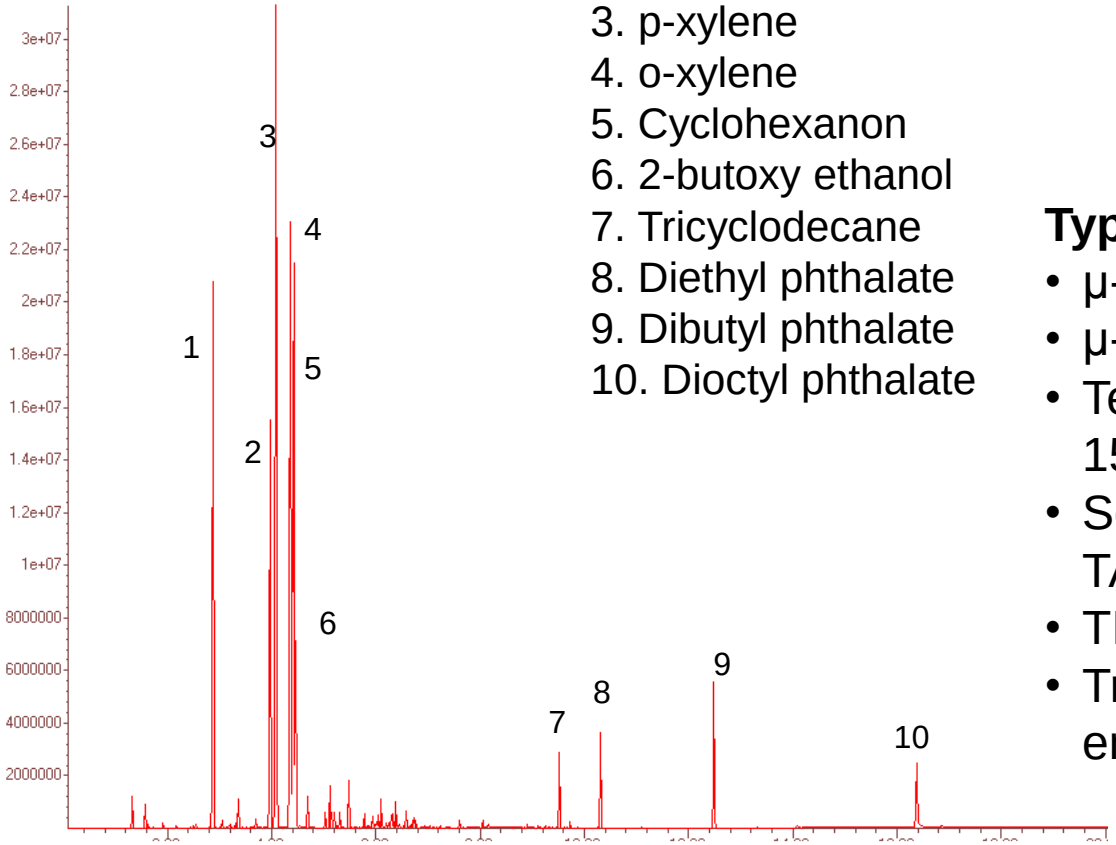


Small chamber - Days

Tedlar bag- Hours

Microchamber- Minutes

Micro-Chamber/Thermal Extractor: Testing chemicals released by children's plastic toys

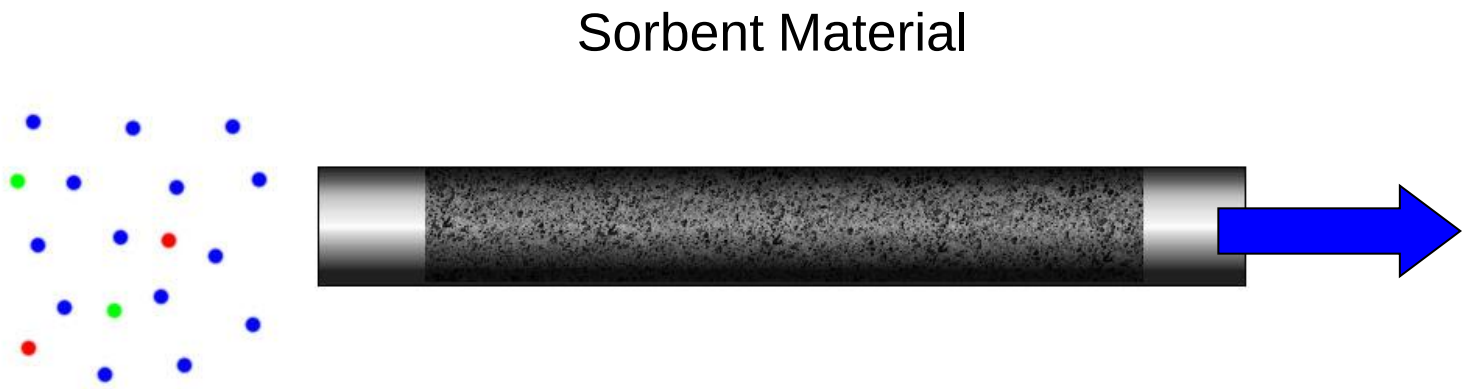


1. Toluene
2. Ethyl benzene
3. p-xylene
4. o-xylene
5. Cyclohexanon
6. 2-butoxy ethanol
7. Tricyclodecane
8. Diethyl phthalate
9. Dibutyl phthalate
10. Dioctyl phthalate

Typical analytical conditions:

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

What is Thermal Desorption?

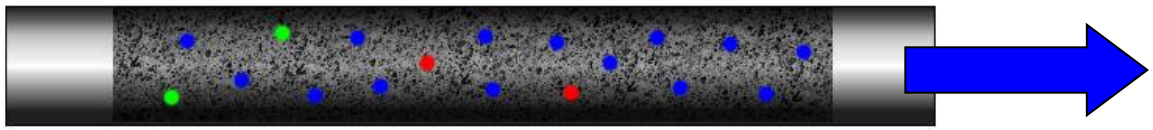


Sample Matrix

e.g. Chamber or micro-chamber air

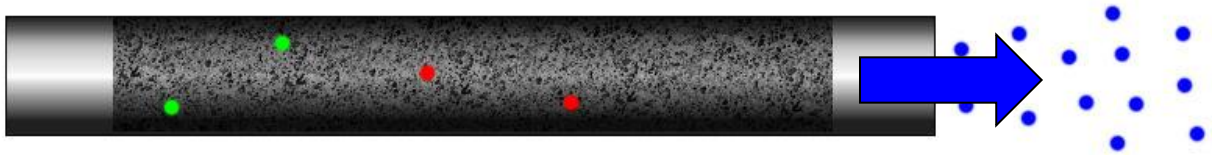
What is Thermal Desorption?

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

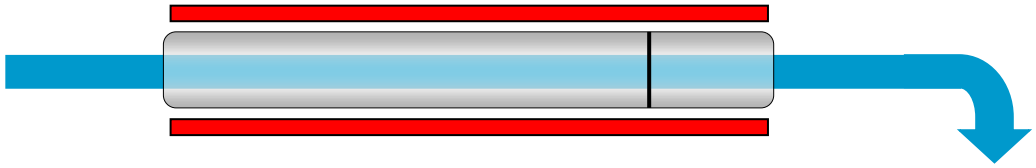
2 Stage Thermal Desorption

PROBLEM: Compounds are released SLOWLY from the sorbent tube

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

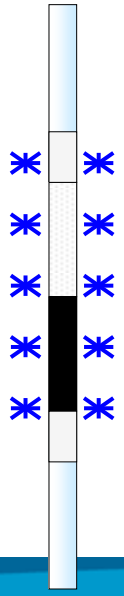
2 Stage Thermal Desorption

SOLUTION: Use a narrow secondary trap



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

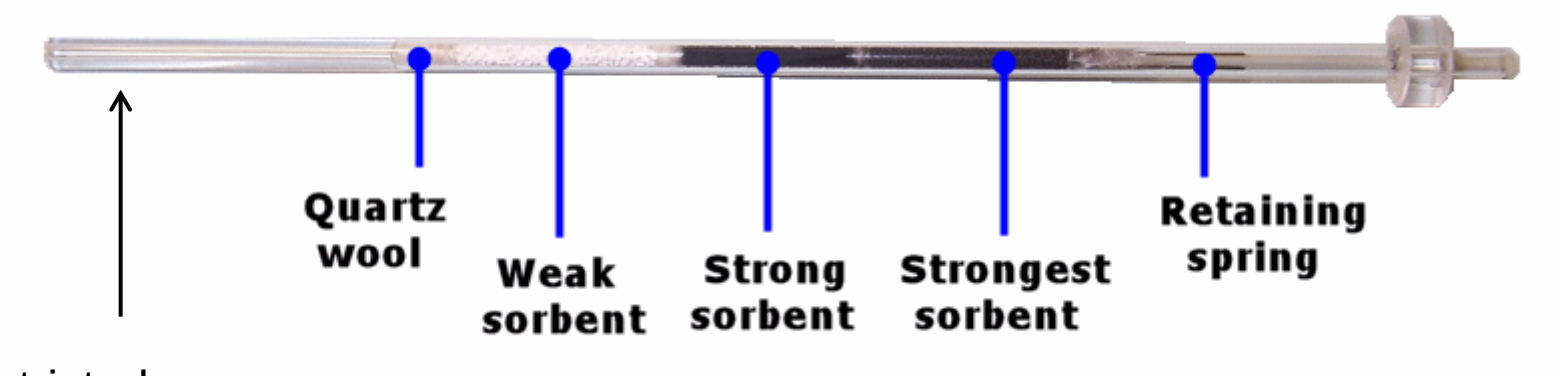
Cold trap heated rapidly (100 C/sec) for sharp chromatographic peaks

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

15 standard traps + custom packed traps available from Markes

What can TD-GC/MS do?

Any volatile or semi-volatile organic compounds which meet the following criteria:

- ≤ n-C_{40}, bpt ≤525 C
- Can be easily gas chromatographed
- The sorbent or matrix containing the compounds is compatible with the high temperatures required

Unsuitable compounds

- Inorganic compounds
- Most permanent gases – *exceptions include* N_2O, SF_6 & CS_2
- Compounds with volatility > n-C_{40}
- Compounds which don't work well with GC (including formaldehyde)
- Methane

Emissions testing equipment - Summary

Manual

Automated

Validating TD-GC/MS analytical performance for material emission testing

Check standard* for monitoring system performance; peak shape, peak ratios, carryover, etc.

Proposed compounds cover relevant analyte volatility and polarity range

Can be applied e.g.:

- At system installation
- As a routine in-house check
- For troubleshooting
- By accredited 3rd party auditors

** Check std developed by Markes in conjunction with international experts*

Proposed compound list:

n-hexane

toluene

methyl isobutyl ketone

butyl acetate

hexanal

phenol

cyclohexanone

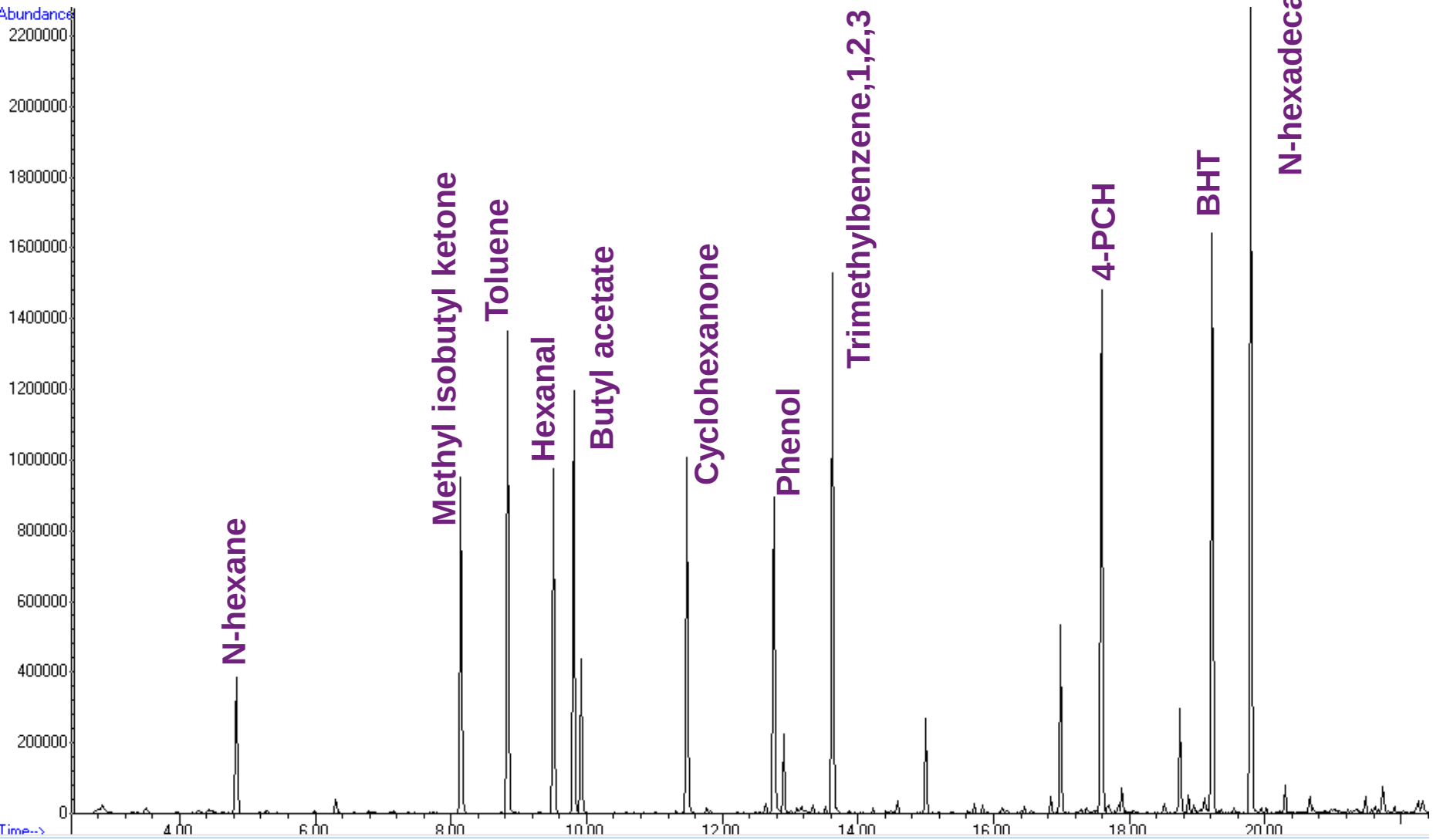
trimethylbenzene,1.2.3

4-phenylcyclohexe

butylated hydroxyt

n-hexadecane

Material emission check standard



Certified reference material

- Polymer film is loaded with a representative volatile organic compound (currently focusing on toluene) through a diffusion process.

- What makes this prototype reference material “unique” is that its emission rate can be measured in a traditional chamber test, as well as independently verified using material/chemical properties and a fundamental mass transfer model.

Photo: Eurofins Environment A/S

Applications in accredited test labs

New regulations require product emissions tests by accredited third party labs.

Billable services will include:

1. Certification of products using reference methods
2. Auditing the quality control measures used by industry
3. Emissions screening service for small companies *e.g.* for QC or R&D

Increased in-house testing by manufacturers will generate additional auditing revenue for accredited test houses

Product emission testing is an business opportunity for manufacturers

As well as aiding regulatory compliance, in-house product emission testing helps manufacturers to:

- Test the quality of raw materials
- Compare emissions profiles across a range (red *vs.* blue finish)
- Pre-screen products before expensive 3rd party emission tests
- Compare products with competitive materials
- Develop new, low-emission, higher-value materials in R&D and…
- **Differentiate low emission products from cheap competitors**

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