Testing chemical emission from materials and products

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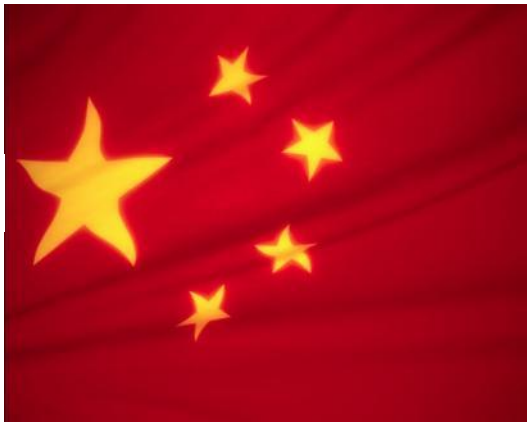
Emission testing by manufacturing industry is governed by regulations and market pressure...

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

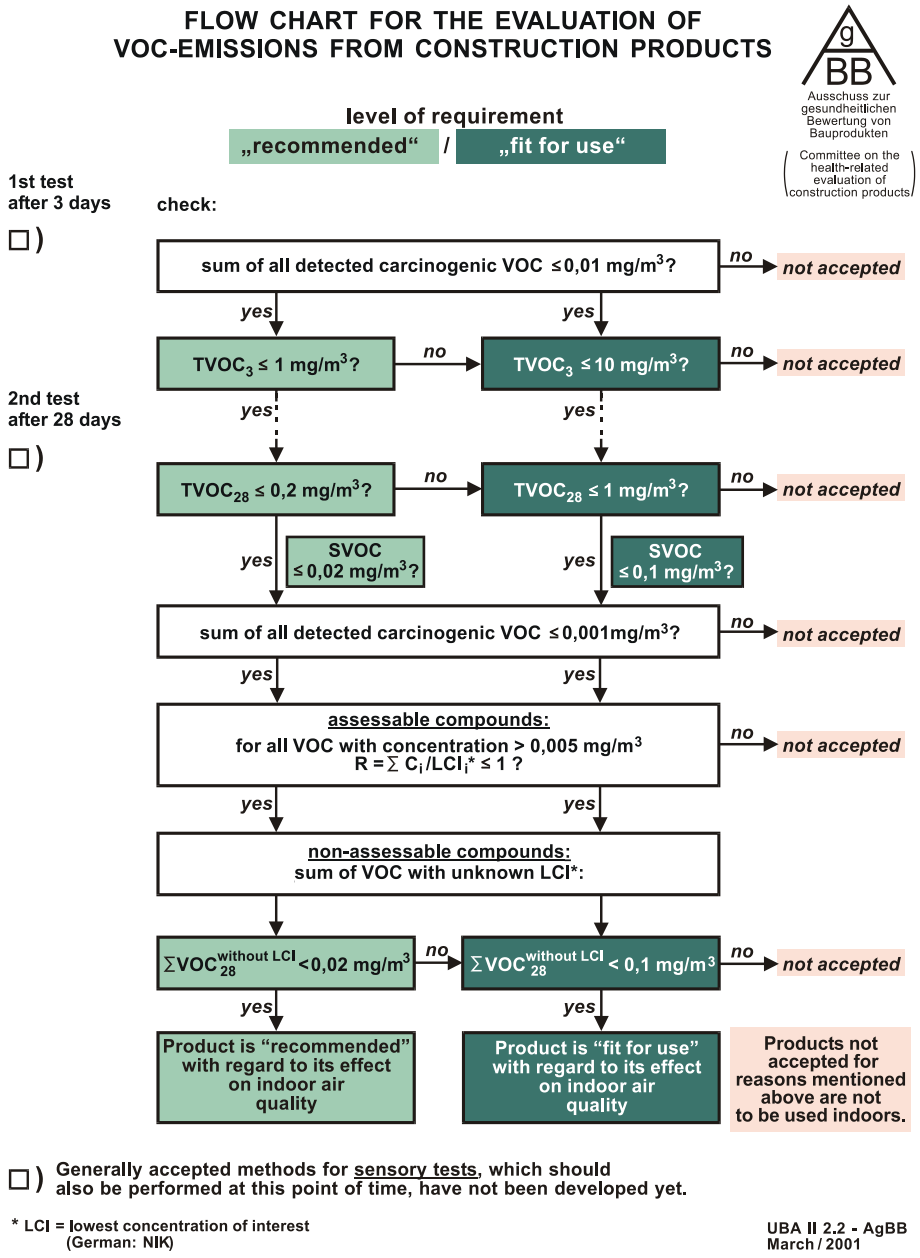
The 2005 German flooring regulation and AgBB scheme

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

CMR emissions
From 1. Jan 2010, only construction products **may be sold in France** if they show **28 days emission** of CMR substances **trichloroethylene, benzene, DEHP and DBP** below 1 µg/m³ each, tested with ISO 16000 and calculated for European reference room.

Compulsory VOC emissions labelling - now published
Another French regulation (Decree) was published on 25 March 2011 regarding a **mandatory labelling** of **construction products installed indoors, floor and wall coverings, paints and lacquers** with their emission classes based on emission testing.

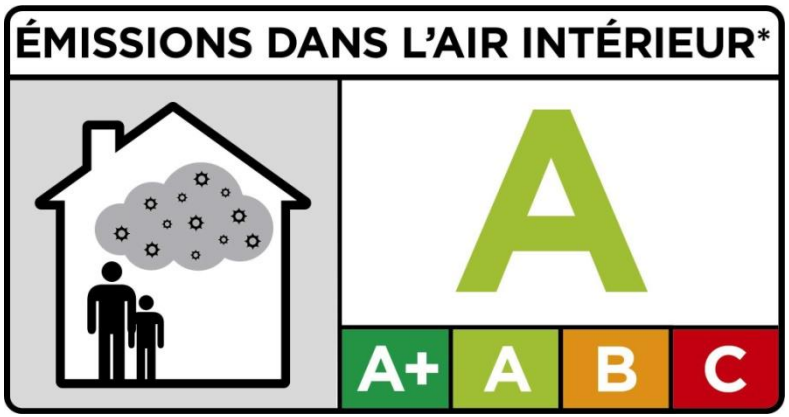
From 1. Jan. 2012, any covered product placed on the market has to be labelled with emission classes based on their emissions after 28 days, tested with ISO 16000 and calculated for European reference room, as for the two other French regulations.

Products that are in French market before that date need to be labelled from September 2013 on.

2010 French regulation applies to construction and decorative products

Classes	C	B	A	A+
Formaldehyde	>120	<120	<60	<10
Acetaldehyde	>400	<400	<300	<200
Toluene	>600	<600	<450	<300
Tetrachloroethylene	>500	<500	<350	<250
Xylene	>400	<400	<300	<200
1,2,4-Trimethylbenzene	>2000	<2000	<1500	<1000
1,4-Dichlorobenzene	>120	<120	<90	<60
Ethylbenzene	>1500	<1500	<1000	<750
n-Butylacetate	>10000	<10000	<7500	<4800
2-Butoxyethanol	>2000	<2000	<1500	<1000
Styrene	>500	<500	<350	<250
TVOC	>2000	<2000	<1500	<1000

Limit thresholds of exposure concentration $\mu g.m^3$ measured after 28 days re ISO 16000 series



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.

Chronic Reference Exposure Level (REL)s

OEHHA
Office of Environmental Health Hazard Assessment

Table 4-1 Target CREL VOCs and their maximum allowable concentrations

No.	Compound Name	CAS No.	Allowable Conc.[a] ($\mu g/m^3$)
1	Acetaldehyde	75-07-0	70
2	Benzene	71-43-2	30
3	Carbon disulfide	75-15-0	400
4	Carbon tetrachloride	56-23-5	20
5	Chlorobenzene	108-90-7	500
6	Chloroform	67-66-3	150
7	Dichlorobenzene (1,4-)	106-46-7	400
8	Dichloroethylene (1,1)	75-35-4	35
9	Dimethylformamide (N,N-)	68-12-2	40
10	Dioxane (1,4-)	123-91-1	1,500
11	Epichlorohydrin	106-89-8	1.5
12	Ethylbenzene	100-41-4	1,000
13	Ethylene glycol	107-21-1	200
14	Ethylene glycol monoethyl ether	110-80-5	35
15	Ethylene glycol monoethyl ether acetate	111-15-9	150
16	Ethylene glycol monomethyl ether	109-86-4	30
17	Ethylene glycol monomethyl ether acetate	110-49-6	45
18	Formaldehyde	50-00-0	16.5[b]
19	Hexane (n-)	110-54-3	3,500
20	Isophorone	78-59-1	1,000
21	Isopropanol	67-63-0	3,500
22	Methyl chloroform	71-55-6	500
23	Methylene chloride	75-09-2	200
24	Methyl *t*-butyl ether	1634-04-4	4,000
25	Naphthalene	91-20-3	4.5
26	Phenol	108-95-2	100
27	Propylene glycol monomethyl ether	107-98-2	3,500
28	Styrene	100-42-5	450
29	Tetrachloroethylene	127-18-4	17.5
30	Toluene	108-88-3	150
31	Trichloroethylene	79-01-6	300
32	Vinyl acetate	108-05-4	100
33-35	Xylenes, technical mixture (m-, o-, p-xylene combined)	108-38-3, 95-47-6, 106-42-3	350

a) Refer to http://www.oehha.ca.gov/air/chronic_rels/AllChrels.html. All maximum allowable concentrations are one-half the corresponding CREL adopted by Cal/EPA OEHHA with the exception of formaldehyde. For any future changes in the CREL list by OEHHA, values in Table 4.1 shall continue to apply until these changes are published in the Standard Method.

b) Formaldehyde has a CREL of 9 $\mu g/m^3$ (December 2008); guidance value established by this Standard Method at 16.5 $\mu g/m^3$ before Dec 31st, 2011 and at 9 $\mu g/m^3$ starting from Jan 1st, 2012. See Section 4.3.2.

Reference methods for testing chemical emissions from products

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

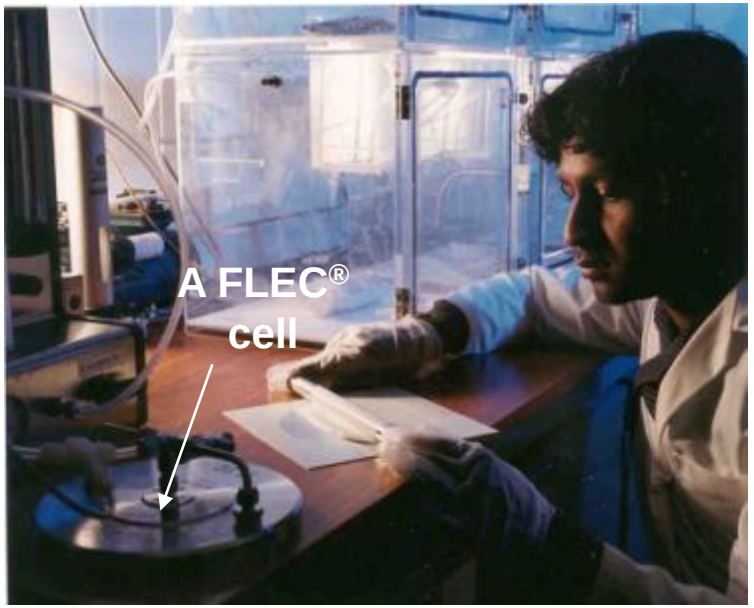
1. Place the material in a test chamber or cell.

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

Photo: Eurofins Environment A/S

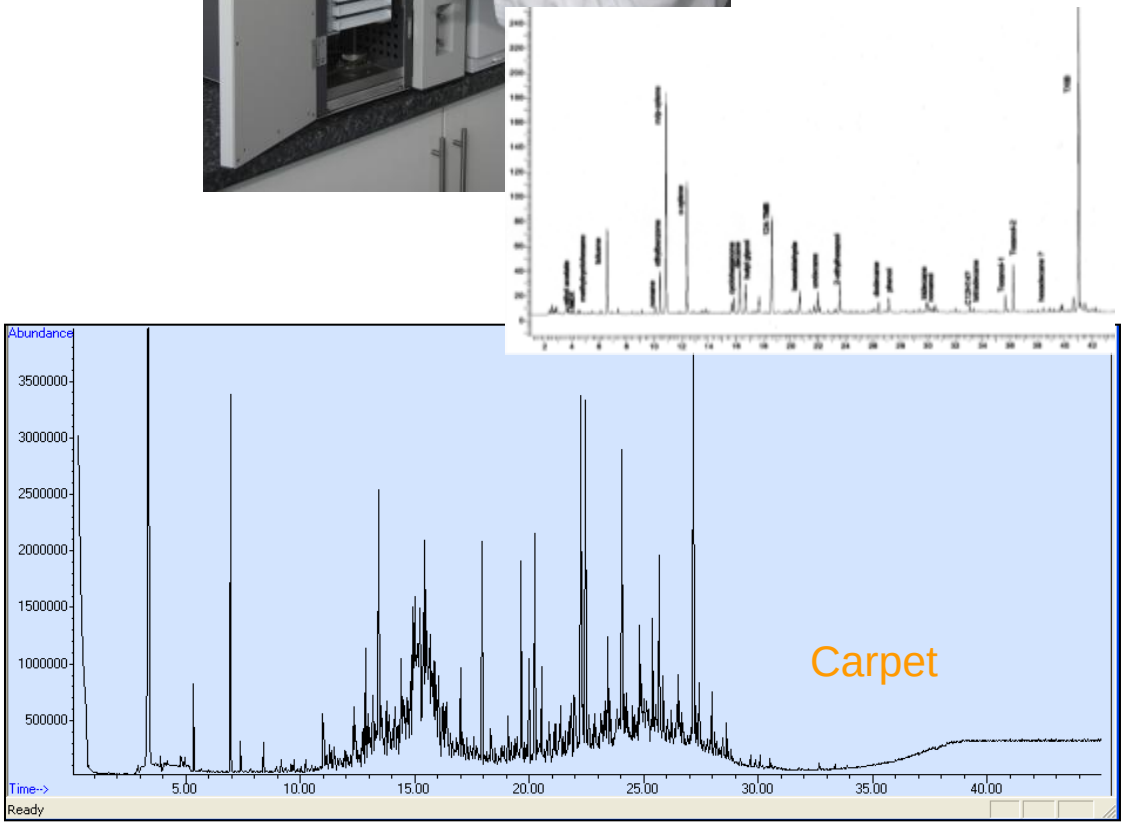
Step 2: Collect the vapours

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

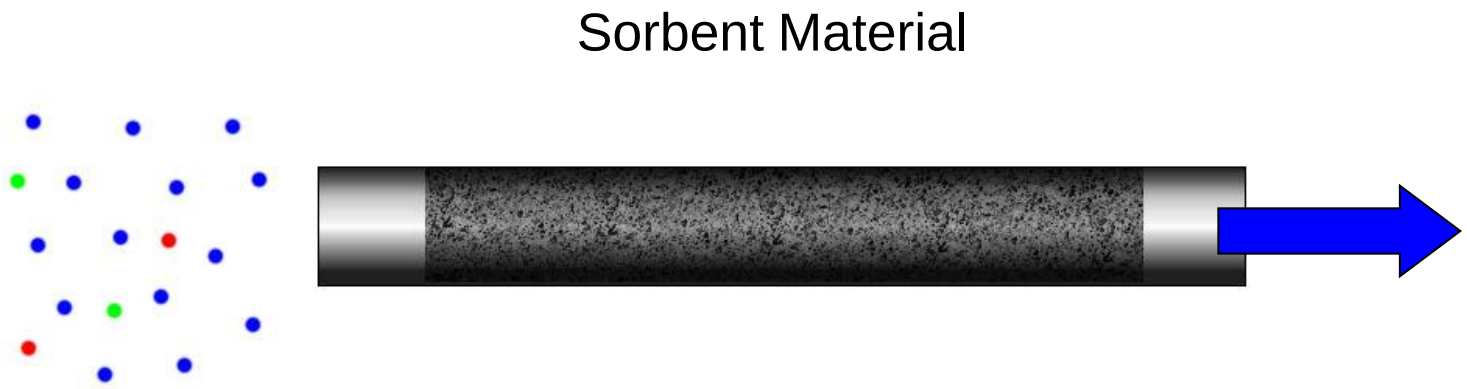
2 sorbent tubes in series + **2** tube sets in parallel = **4** tubes per measurement + blanks

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



What is Thermal Desorption?

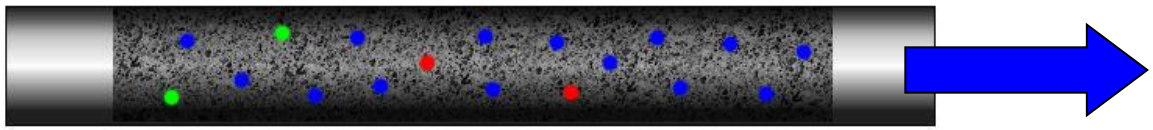


Sample Matrix

e.g. Chamber or micro-chamber air

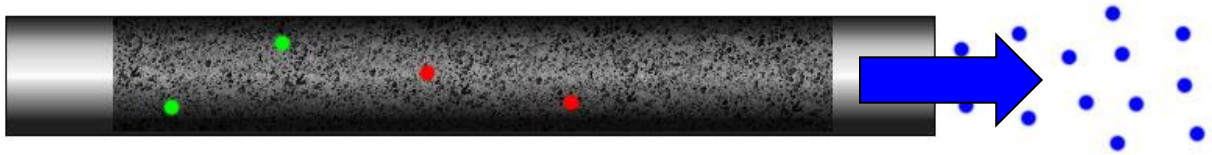
What is Thermal Desorption?

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

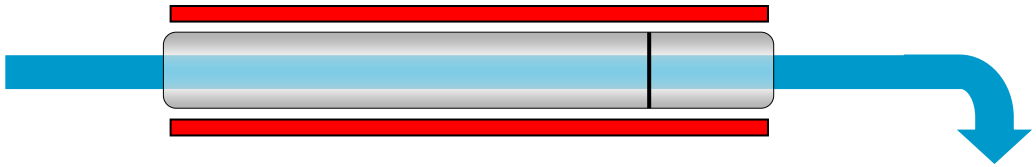
2 Stage Thermal Desorption

PROBLEM: Compounds are released SLOWLY from the sorbent tube

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

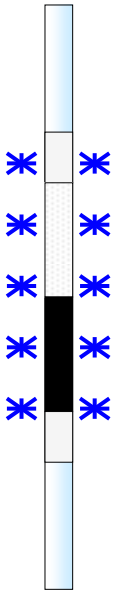
2 Stage Thermal Desorption

SOLUTION: Use a narrow secondary trap



STAGE 1

Transfer compounds from tube to secondary trap

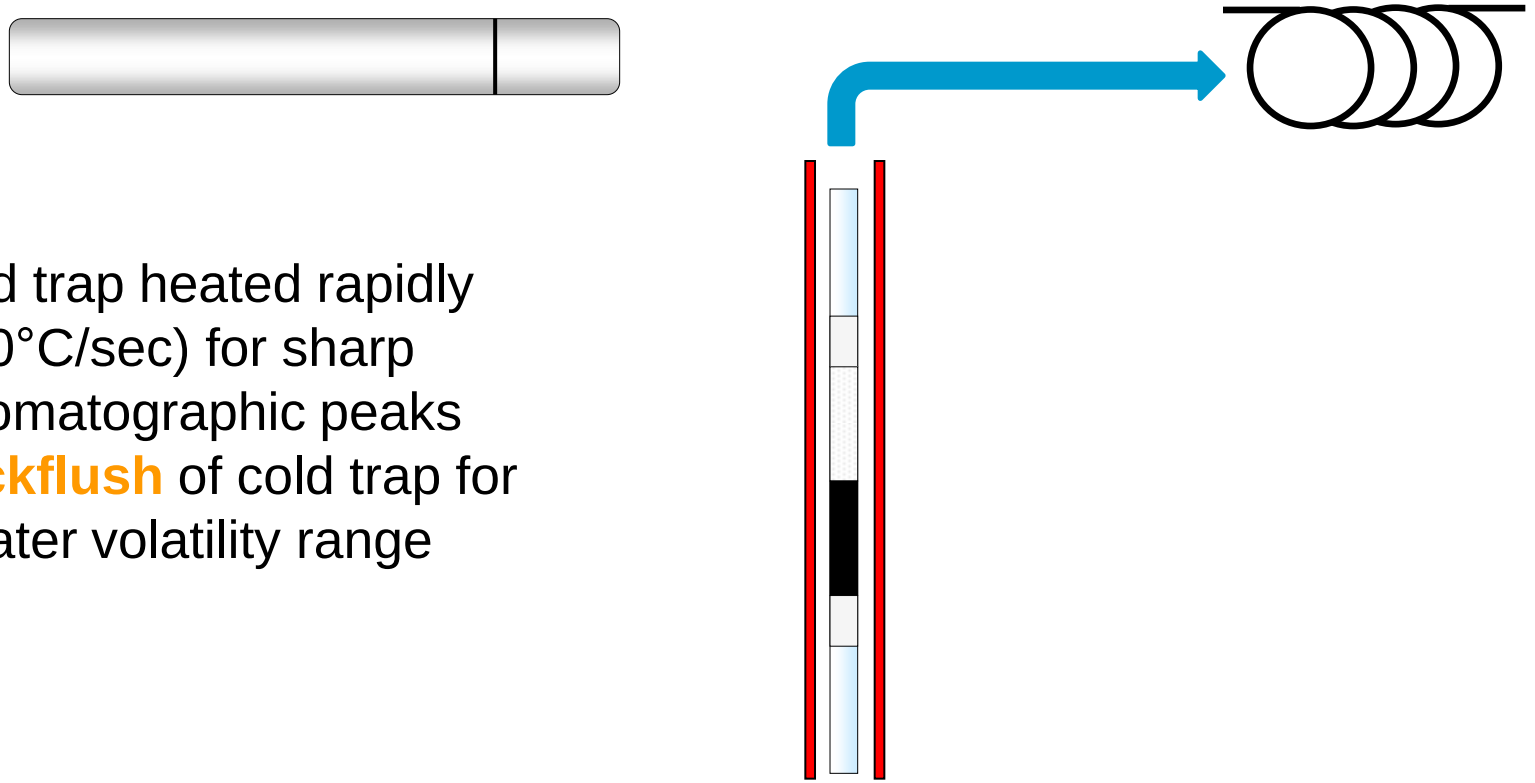


Electrically cooled narrow bore cold trap

2 Stage Thermal Desorption

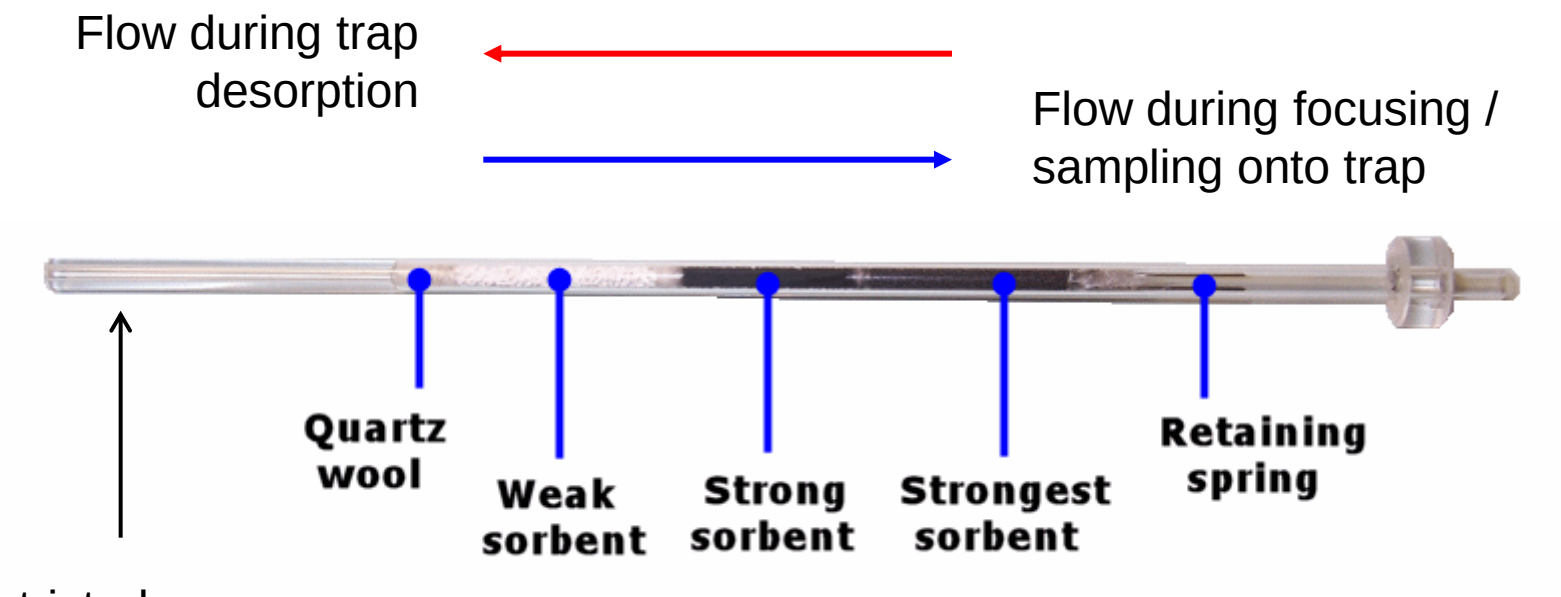
STAGE 2

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



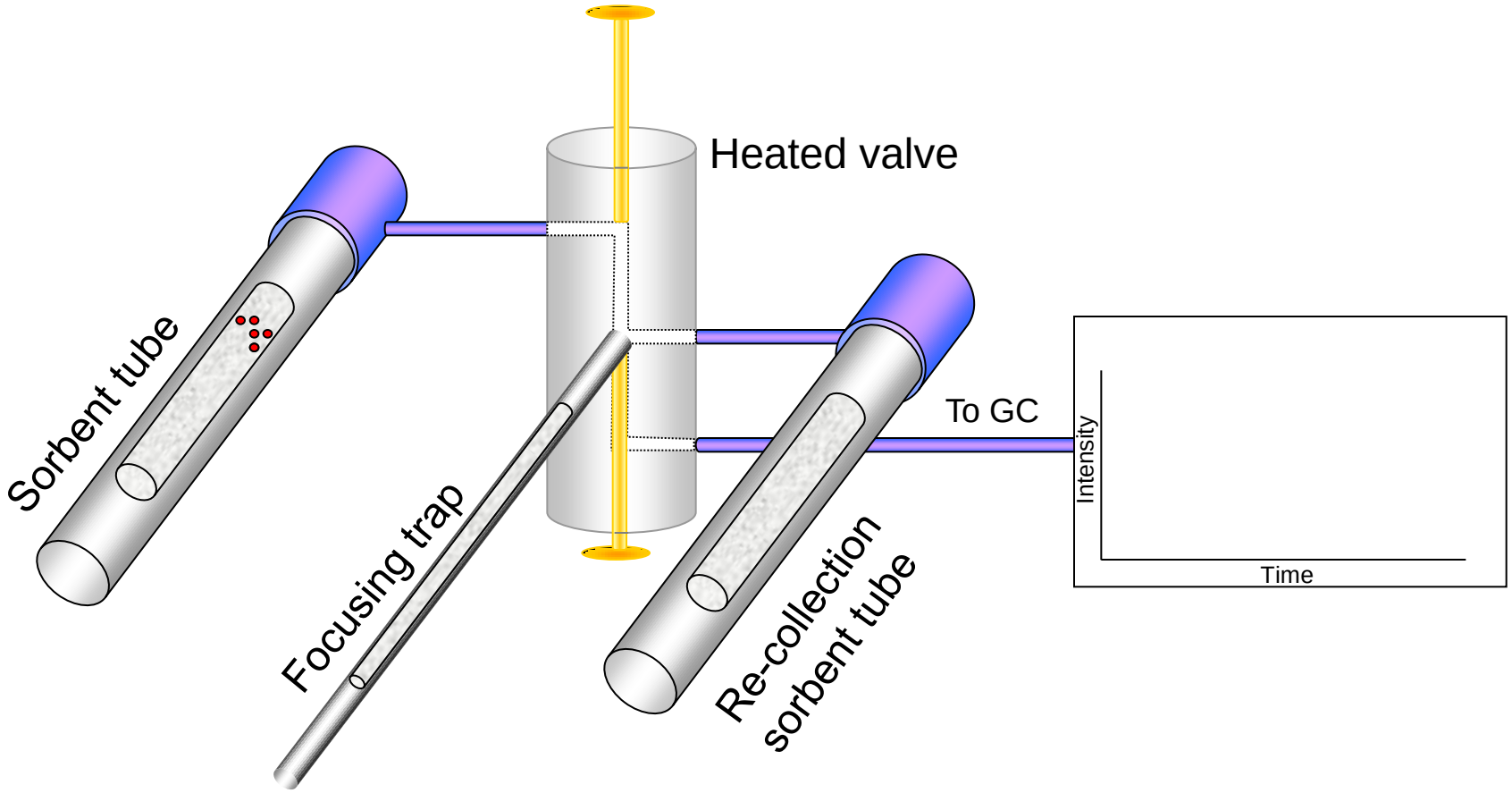
Narrow design allows splitless injection

Use sorbent(s) to suit specific application

15 standard traps + custom packed traps available from Markes

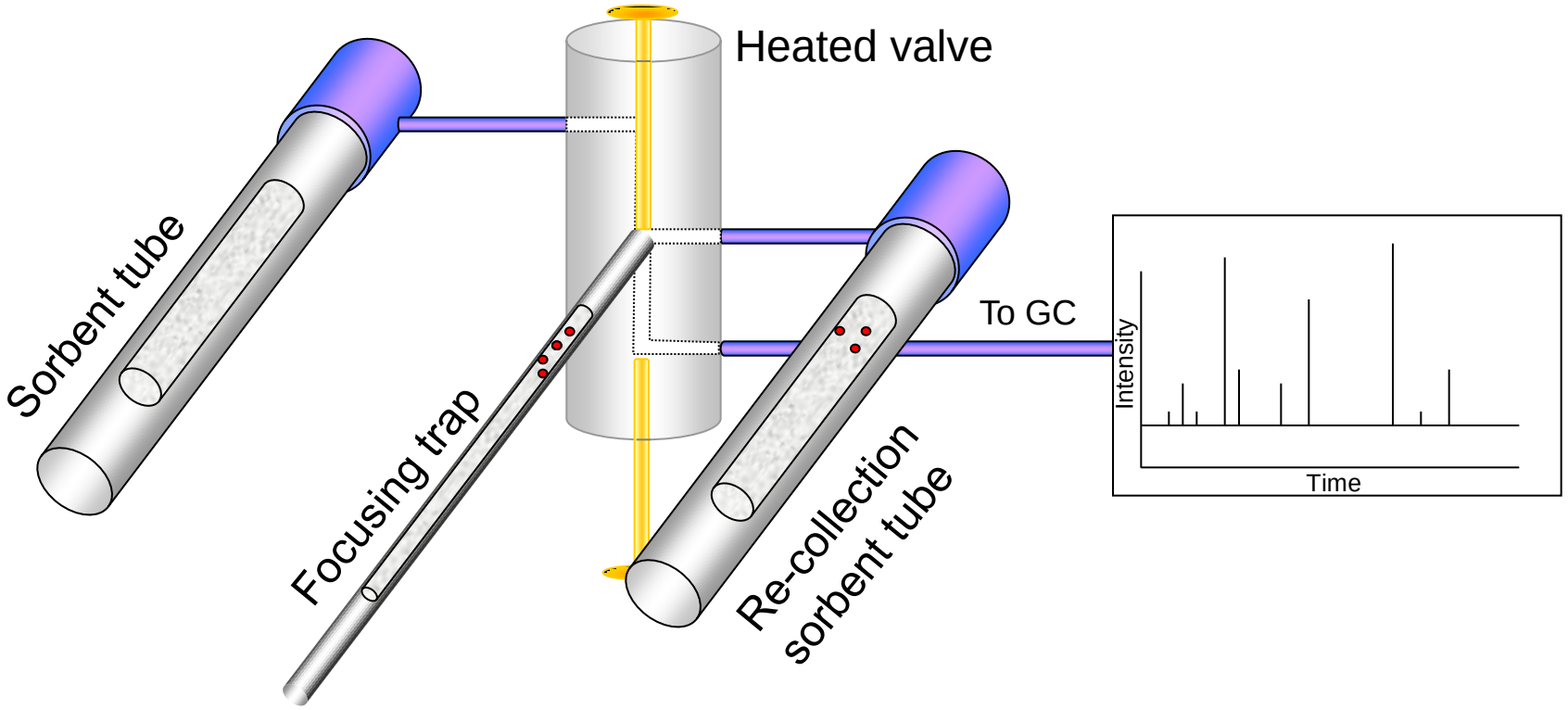
2-stage desorption using ‘universal’ TD valve:

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



2-stage desorption using ‘universal’ TD valve:

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

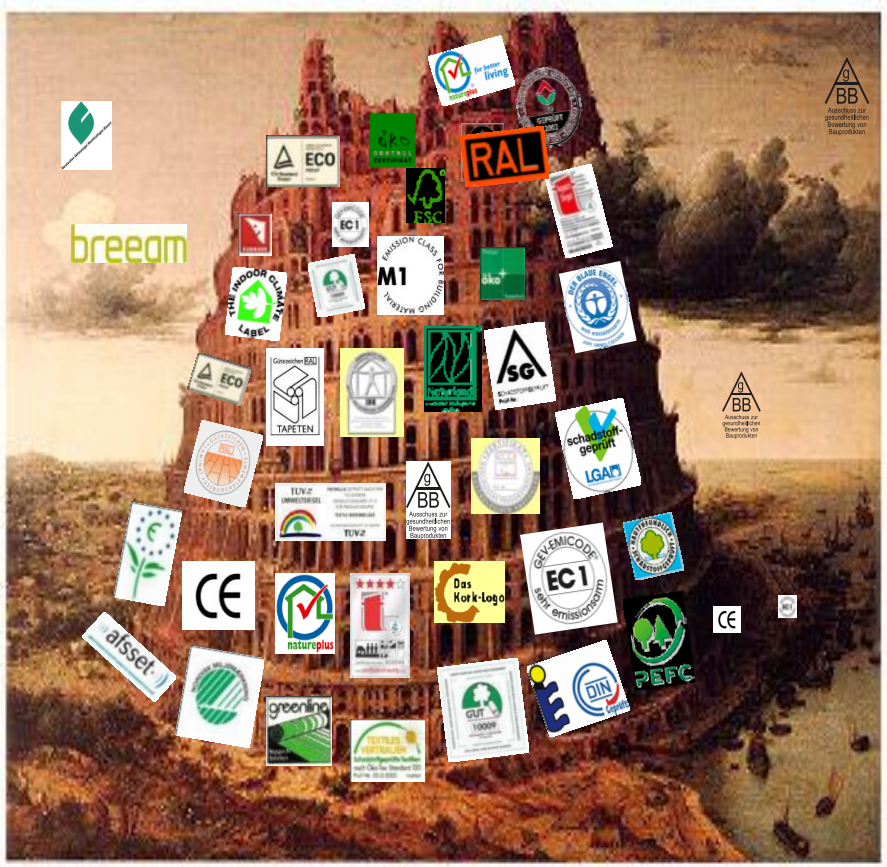


Certification/labelling

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

Who will be affected:
Leading manufacturers of flooring …

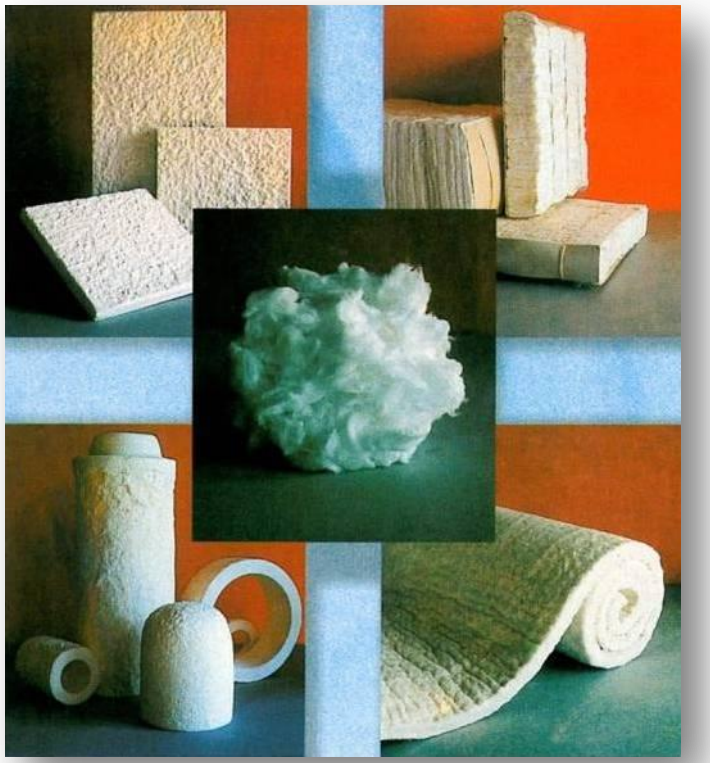
Who will be affected:
Leading manufacturers of…

Who will be affected:
Leading manufacturers of…

Wood and wood based products

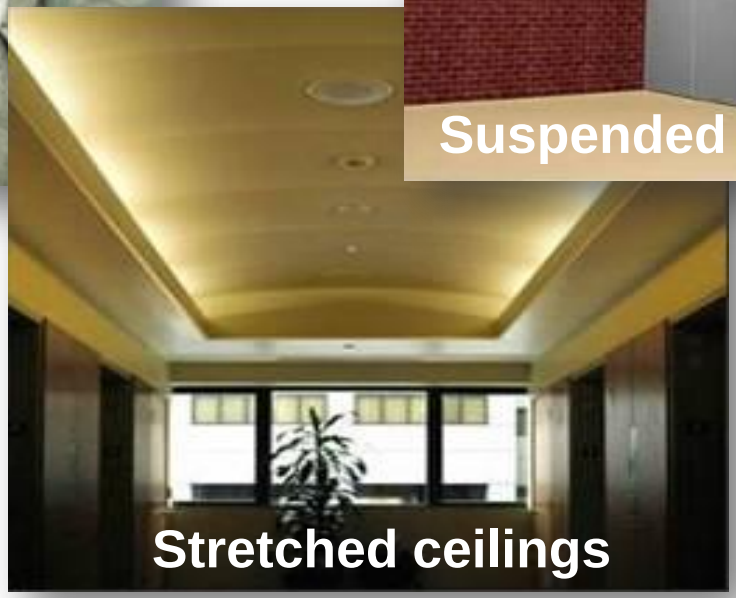
Who will be affected:
Leading manufacturers of…

Structural plastics and foams



Insulation materials
(thermal & sound)

Who will be affected:
Leading manufacturers of…



Who will be affected:
Leading manufacturers of…

Paints & varnishes

Adhesives & sealants

Who will be affected:
Leading manufacturers of…

Grout

Door & window frames

Binders

Waterproofing materials

And all their suppliers…

Other example references include…

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

Micro-Chamber/Thermal Extractor™(µ-CTE™)

	MCTE250I
No° Chambers	4
Max Temp (°C)	250
Chamber volume	114cm^3
Flow range	10-500mL/min
Toggle valves	No
Inert coated	Yes

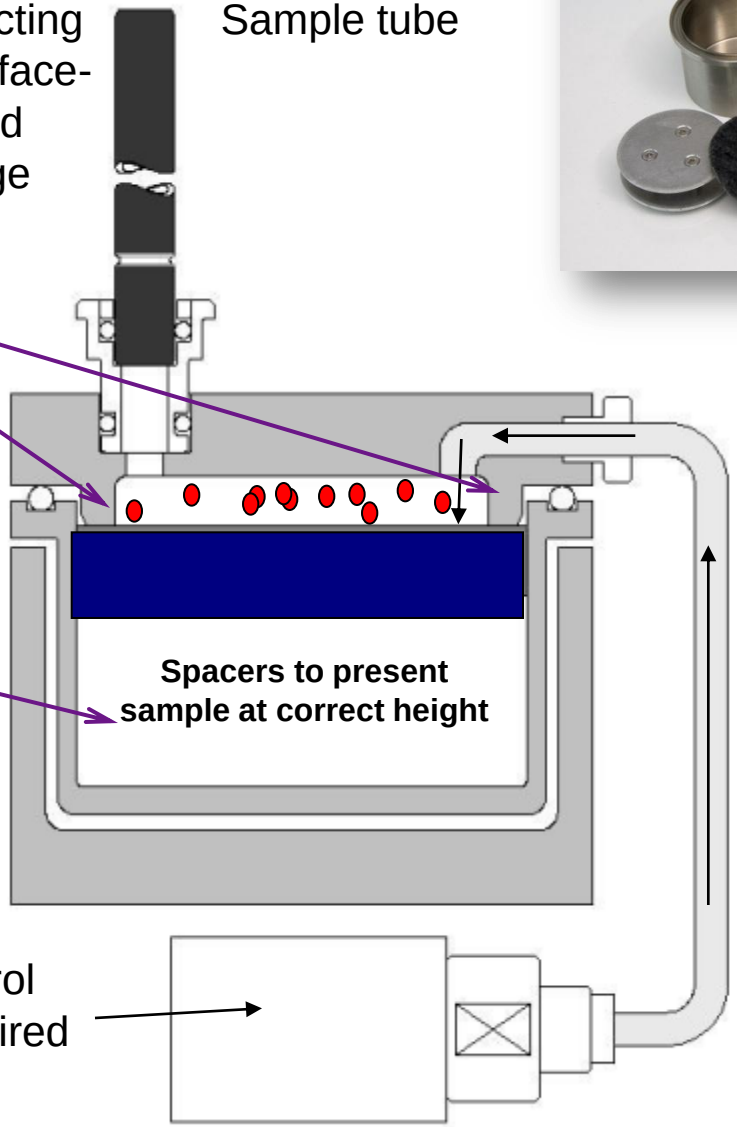
Secondary emission screening methods Micro-Chamber/Thermal Extractor™(µ-CTE™)*

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

Surface emissions

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

Sample tube



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

Standardisation of micro-chamber methods

ASTM D7706 for construction and other products used indoors

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

CEN TC351 – as secondary/indirect method for surface/content testing of construction products

VDI 2083-17 for CleanRoom construction materials and possible follow on ISO std

GUT flooring screening method (and possible follow on ISO standard)

ASTM working group for spray polyurethane foam

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 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**

Suggested Initial Conditions for Routine Use of the Micro-Scale Chamber for Measuring Emissions of VOCs and Formaldehyde Initial test conditions for routine use of micro-scale chamber

Using the microchamber for bulk emissions (content testing)

Bulk Emissions

- Ambient/elevated temperature
- Dynamic Headspace
- Homogenous sample

Micro-chamber correlation with reference methods

- Absolute correlation has been demonstrated but is not the usually the main objective. Relative correlation is normally more important
- Answers obtained from micro-chambers within minutes of production need to be reliable indicators of product performance in longer term reference tests.
- Key references relating to the correlation of micro-chamber data with small chamber / FLEC methods include:

1. T. Salthammer, et al: J. of Analytical and Bioanalytical Chemistry, 387, 5, 1907-1919, (2007).
2. PARD Report: Correlation between the VDA 276 test and microchamber testing. 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. M. Lor, E. Goelen, et al: HEMICPD Report, Published by the Belgian Science Policy Reference D/2010/1191/12 (2010)

Regulation & Market Pressure in similar application fields

Similar opportunities in other markets include:

Car interior trim components

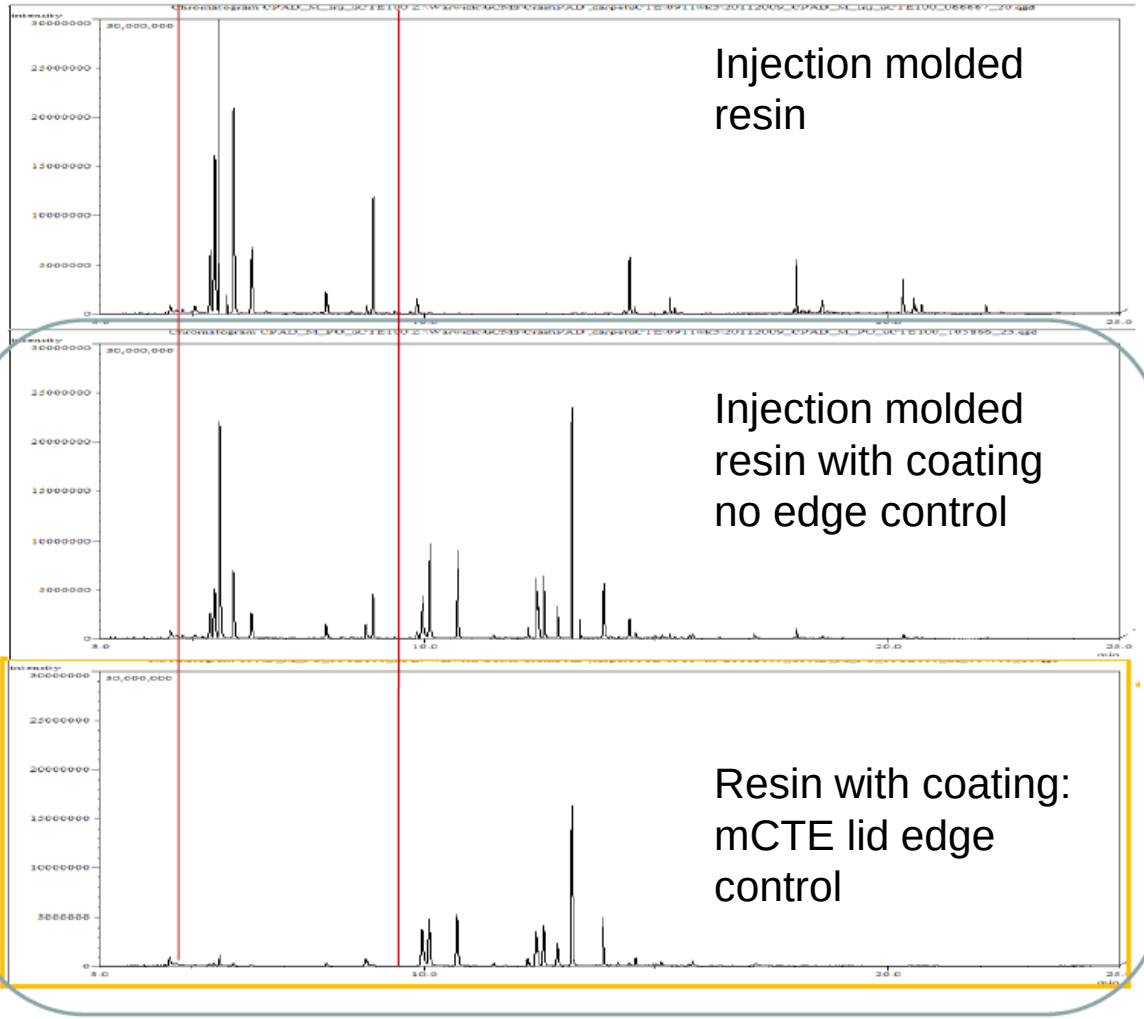
ISO 12219-3 Determination of the emissions of volatile organic compounds from car trim components – Micro-chamber method

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

*** UK patent application 0501928.6**

Test Parameter	**VOCs**	**Formaldehyde**
Equilibration time range (min)	20–40	20–40
Chamber temperature (°C)	65	65
Inlet gas flow rate range (ml/min)	50	250
Gas sampling time (min)	15	2-4 hrs

Controlling edge effects from surface emissions

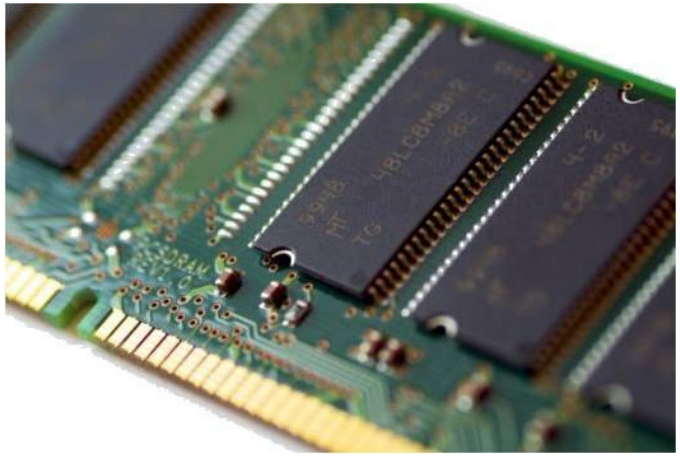


Prof. Mangoo Kim, Kangwon, National University, Korea.(2010) Presentation to ISO TC146 SC6 WG13 (Document # N0087)

Similarly effected markets include:

Electronic computer components

Various proprietary ‘Dynamic headspace’ (DHS) tests using micro-chambers with TD-GC/MS (Seagate, Western Digital, *etc.*)



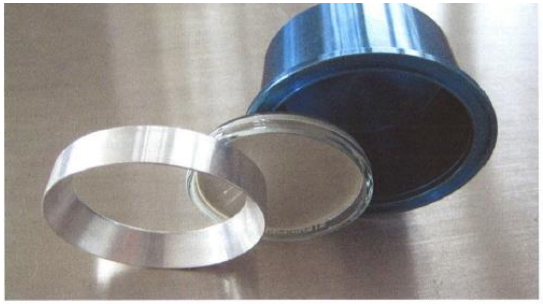
Similarly effected markets include:

Cleanroom components

VDI 2083/17 purity & suitability of cleanroom construction materials using Micro-chamber (Also proposed ISO std)

VDI2083-17 Suitable tool for selecting Cleanroom-suitable materials

- An easy-to-use calculation model gives an estimation of the expected TVOC level regarding the relevant materials.
- The comprehensive database www.ipa-csm.com enables Cleanroom planners and operators a deep insight into the VOC-emission behaviour of tested materials.

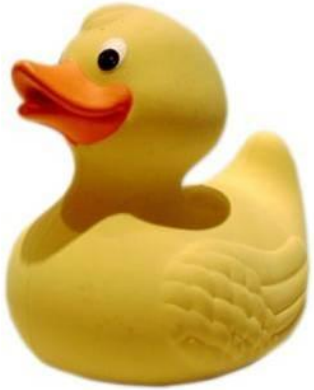


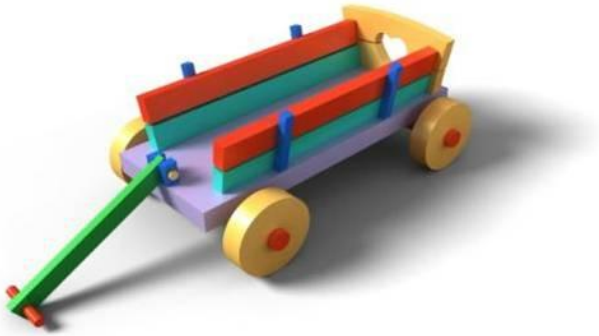
Test Parameter	**VOCs**
Equilibration time range (days)	30
Chamber temperature (°C)	25
Inlet gas flow rate range (ml/min)	100
Gas sampling time (min)	60

Similarly effected markets include:

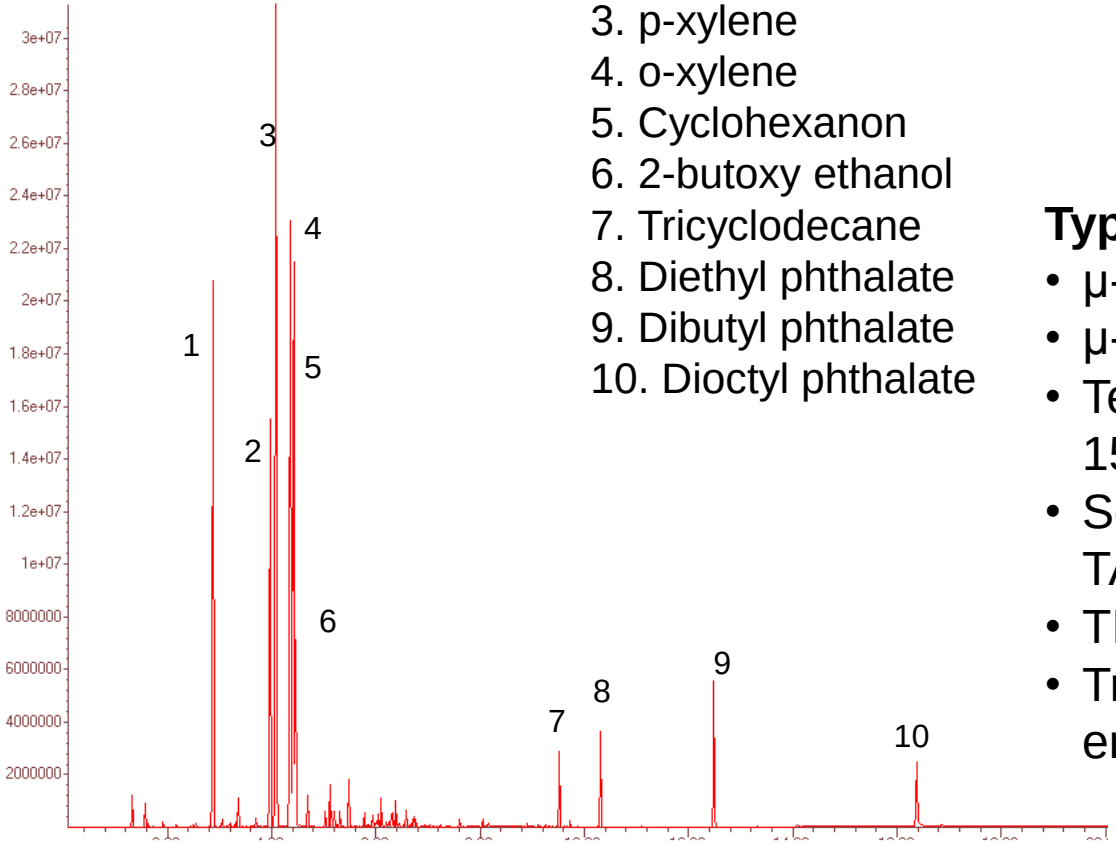
Toys

BS EN 71-11: Organic chemical compounds – Methods of analysis including thermal extraction with TD-GC/MS





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/Carbograph 5
- TD system: TD-100
- Trap: U-T12ME-2S Material emissions

Similarly effected markets include:

Furniture

ANSI/BIFMA M7.1-2007 Standard Test Method For determining VOC Emissions From Office Furniture Systems, Components and Seating using small chambers with TD-GC/MS

ANSI/BIFMA X7.1-2007 Standard for Formaldehyde and TVOC Emissions of Low-Emitting Office Furniture Systems and Seating. Method as above

Similarly effected markets include:

Cleaning products

Methods expected to follow same procedures as construction products, toys, etc.

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

Proposed compound list:

n-hexane

toluene

methyl isobutyl ketone

butyl acetate

phenol

cyclohexanone

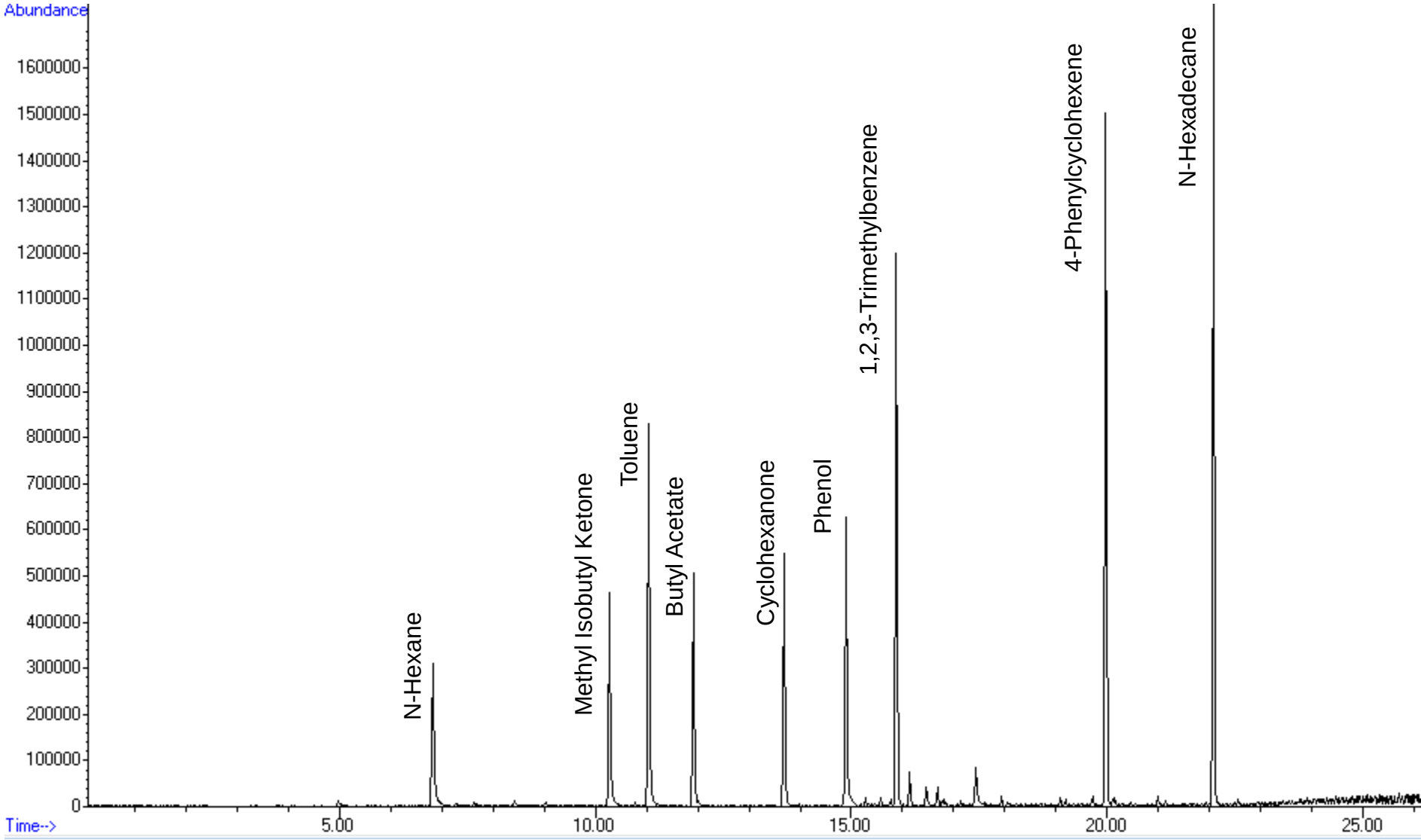
trimethylbenzene,1,2,3

4-phenylcyclohexene

n-hexadecane

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

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

What makes us the preferred solution for material emission testing?

Sampling → Thermal desorption → GC/MS → Data analysis

µ-CTE

FLEC

Tubes

Cryogen-free

Universal: C_2 to C_{40} + reactive compounds

Repeat analysis

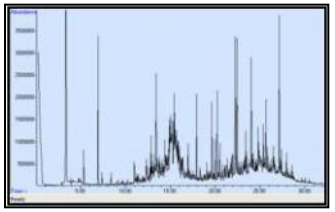
100 tubes

TubeTAG: enhanced QA of tubes

GC/MS

Complete system support

Check standard



Data processing software

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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