Chemical release from products and materials:

Correlation and validation of (S)VOC sampling and analysis techniques

Caroline Widdowson
Markes International, Nov 2011
Generally speaking, it is no longer tenable for a manufacturer not to know what dangerous chemicals could be emitted by one of their products in normal use. This is to make sure products can’t pose a risk to consumers.

Fundamentally, this is what’s driving many of the new regulatory initiatives relating to product emission testing and certification.
Example regulations controlling chemical emissions from products and materials

Construction (and decorative) product sectors

New US protocols, regs and building codes

Construction Product Directive/Regulation (CPD/CPR)

Examples:
IgCC, LEED 2012 & CARB formaldehyde rule

German and French National Regs

Committee for Health Evaluation of Building Products
Example regulations controlling chemical emissions from products and materials

General...

Intentional and unintentional release of chemicals from ‘articles’

California: Assembly Bill 1879

Hazardous chemicals from consumer articles...

EC REACH

Chinese ‘REACH’
Other drivers can be equally strong

Commercial / competitive pressure

Quality control

Retailers

Purchasing power

New guidelines for selecting product standards and ecolabels for ‘greening’ (US) federal procurement
Construction product regulations and associated developments in Europe

• Construction Product Regulation adopted in April 2011. Supercedes the CPD.
  – Implementation by 2013
  – Requires 3rd party accreditation and Factory Production Control (FPC)
• Process to harmonise target compounds and limit levels (LCIs)
  – Prelim list due end 2011, final list due 2012
• Test methods based on ISO 16000 series

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)

FLOW CHART FOR THE EVALUATION OF VOC-EMISSIONS FROM CONSTRUCTION PRODUCTS

1st test after 3 days

- yes
  - sum of all detected carcinogenic VOC ≤ 0.01 mg/m²?
    - yes
      - TVOC_{3} ≤ 1 mg/m²?
        - yes
          - not accepted
        - no
          - TVOC_{3} ≤ 10 mg/m²?
            - no
              - not accepted
    - no
      - TVOC_{28} ≤ 0.2 mg/m²?
        - yes
          - SVOC ≤ 0.02 mg/m²?
            - yes
              - SVOC ≤ 0.1 mg/m²?
                - yes
                  - sum of all detected carcinogenic VOC ≤ 0.001 mg/m²?
                    - yes
                      - not accepted
                    - no
                      - not accepted
                - no
                  - not accepted
            - no
              - not accepted
      - no
        - not accepted

2nd test after 28 days

- yes
  - TVOC_{28} ≤ 1 mg/m²?
    - yes
      - assessable compounds:
        - for all VOC with concentration > 0.005 mg/m³
          - R = \sum C_{i}/LCI_{i} ≤ 1?
            - yes
              - not accepted
            - no
              - not accepted
        - non-assessable compounds:
          - sum of VOC with unknown LCI:
            - no
              - not accepted
            - yes
              - Product is “recommended” with regard to its effect on indoor air quality

- no
  - Product is “fit for use” with regard to its effect on indoor air quality
  - Products not accepted for reasons mentioned above are not to be used indoors.

Generally accepted methods for sensory tests, which should also be performed at this point of time, have not been developed yet.

* LCI = lowest concentration of interest
  (German: NIK)
### 2010 French regulation applies to construction and decorative products

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

- Limit thresholds of concentration (μg.m⁻³) measured after 28 days using ISO 16000 stds and calculated using model room.
- France also has the voluntary AFSSET scheme which includes nearly 200 target compounds and is very similar to AgBB.
Construction product regulations and similar developments in the US

- Vs 1.1 of Ca Spec 01350 fast becoming universal US protocol for emission testing.
  - Enshrined in: ANSI/ASHRAE 189.1, IgCC (2nd ed.), revision of BIFMA M7, etc.
  - Based on D5116 (chamber) & D6196 (TD-GCMS)
  - Similar to AgBB/AFSSET
  - Strong requirement for ongoing quality control/conformity assessment (e.g. CARB H₂CO Rule).

- UL acquisition of AQS/GEI signals the growing importance of product emission testing in the US

- Latest draft edition of LEED (2012) is moving to emissions rather than content testing for paint, coatings, adhesives, etc

- Key BIFMA furniture standards are being revised

- US EPA ‘Design for the Environment (DfE)’ labels recently announced for cleaning products
# Chronic Reference Exposure Levels (CREL)

Taken from the CDPH/EHLB standard method (01350) Version 1.1 (02/10)

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound Name</th>
<th>CAS No.</th>
<th>Allowable Conc. (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetaldehyde</td>
<td>75-07-0</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>71-43-2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>Carbon disulfide</td>
<td>75-15-0</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>Carbon tetrachloride</td>
<td>56-23-5</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Chlorobenzene</td>
<td>108-90-7</td>
<td>500</td>
</tr>
<tr>
<td>6</td>
<td>Chloroform</td>
<td>67-66-3</td>
<td>150</td>
</tr>
<tr>
<td>7</td>
<td>Dichlorobenzene (1,4-)</td>
<td>106-46-7</td>
<td>400</td>
</tr>
<tr>
<td>8</td>
<td>Dichloroethylene (1,1)</td>
<td>75-35-4</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>Dimethyldiformamide (N,N-)</td>
<td>68-12-2</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>Dioxane (1,4-)</td>
<td>123-91-1</td>
<td>1,500</td>
</tr>
<tr>
<td>11</td>
<td>Epichlorohydrin</td>
<td>106-89-8</td>
<td>1,5</td>
</tr>
<tr>
<td>12</td>
<td>Ethylbenzene</td>
<td>100-41-4</td>
<td>1,000</td>
</tr>
<tr>
<td>13</td>
<td>Ethylene glycol</td>
<td>107-21-1</td>
<td>200</td>
</tr>
<tr>
<td>14</td>
<td>Ethylene glycol monoethyl ether</td>
<td>110-80-5</td>
<td>35</td>
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<tr>
<td>15</td>
<td>Ethylene glycol monoethyl ether acetate</td>
<td>111-15-9</td>
<td>150</td>
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<tr>
<td>16</td>
<td>Ethylene glycol monomethyl ether</td>
<td>109-86-4</td>
<td>30</td>
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<td>17</td>
<td>Ethylene glycol monomethyl ether acetate</td>
<td>110-49-6</td>
<td>45</td>
</tr>
<tr>
<td>18</td>
<td>Formaldehyde</td>
<td>50-00-0</td>
<td>16.5 b</td>
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<tr>
<td>19</td>
<td>Hexane (n-)</td>
<td>110-54-3</td>
<td>3,500</td>
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<td>20</td>
<td>Isophorone</td>
<td>78-59-1</td>
<td>1,000</td>
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<tr>
<td>21</td>
<td>Isopropanol</td>
<td>67-63-0</td>
<td>3,500</td>
</tr>
<tr>
<td>22</td>
<td>Methyl chloroform</td>
<td>71-55-6</td>
<td>500</td>
</tr>
<tr>
<td>23</td>
<td>Methylene chloride</td>
<td>75-09-2</td>
<td>200</td>
</tr>
<tr>
<td>24</td>
<td>Methyl t-butyl ether</td>
<td>1634-04-4</td>
<td>4,000</td>
</tr>
<tr>
<td>25</td>
<td>Naphthalene</td>
<td>91-20-3</td>
<td>4.5</td>
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<td>26</td>
<td>Phenol</td>
<td>108-95-2</td>
<td>100</td>
</tr>
<tr>
<td>27</td>
<td>Propylene glycol monomethyl ether</td>
<td>107-98-2</td>
<td>3,500</td>
</tr>
<tr>
<td>28</td>
<td>Styrene</td>
<td>100-42-5</td>
<td>450</td>
</tr>
<tr>
<td>29</td>
<td>Tetrachloroethylene</td>
<td>127-18-4</td>
<td>17.5</td>
</tr>
<tr>
<td>30</td>
<td>Toluene</td>
<td>108-88-3</td>
<td>150</td>
</tr>
<tr>
<td>31</td>
<td>Trichloroethylene</td>
<td>79-01-6</td>
<td>300</td>
</tr>
<tr>
<td>32</td>
<td>Vinyl acetate</td>
<td>108-05-4</td>
<td>100</td>
</tr>
<tr>
<td>33-35</td>
<td>Xylenes, technical mixture (m-, o-, p-xylene combined)</td>
<td>108-38-3, 95-47-6, 106-42-3</td>
<td>350</td>
</tr>
</tbody>
</table>
Measuring the release of chemical from materials

- Chronic reference exposure levels (CRELs)
- Toxic air contaminants (TACs)
- Carcinogens, mutagens and reprotoxins (CMRs)
- Occupational exposure limits (OELs)
Reference methods for testing chemical emissions from products
Ca01350 based on ASTM stds in the US ISO 16000-series methods

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 23°C under a flow of clean air at 50% relative humidity

* 28 °C in Japan, 25 °C in Korea
Step 2: Collect the vapours

Vapour sampling: 3 & 28 days or at 10 to 14 days (US) (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**: Versatile TD technology is designed to allow analysis of volatile, semi-volatile AND reactive species in a single run.
- **HPLC**: is used for formaldehyde and carbonyls
- **TD-GC/MS**: emission profiles can be very complex. New software programmes can automate & enhance data processing
Complexity and duration of reference methods are impractical 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 differs from conventional chambers because it is open on one side.

• This open side is placed onto planar materials such that the sample surface effectively becomes one wall of the emission cell (sample holders are available for compressible materials).
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 secondary / 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 (H₂CO)

<table>
<thead>
<tr>
<th>Test Parameter</th>
<th>VOCs</th>
<th>Formaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibration time range (min)</td>
<td>20–40</td>
<td>20–40</td>
</tr>
<tr>
<td>Chamber temperature (°C)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Inlet gas flow rate range (ml/min)</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>Gas sampling time (min)</td>
<td>10</td>
<td>60</td>
</tr>
</tbody>
</table>

* 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
Automotive sampling Methods

External - Certification
VOC emission profiles under ‘real-use’ conditions are best obtained using test chambers or cells with sorbent tube sampling and TD-GC(-MS) analysis.

Internal QC - Prevention
Direct thermal desorption/thermal extraction of materials - Measures VOC content as an indication of emission potential
ISO 12219-1 Whole vehicle test chamber - Specification and method for the determination method for the determination of volatile organic compounds in car interiors

ISO 12219-2 Determination of the emissions of volatile organic compounds from car trim components – Bag (Screening method)

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

ISO 12219-4 Determination of the emissions of volatile organic compounds from car trim components – Small chamber method
**ISO 12219-3** Determination of the emissions of volatile organic compounds from car trim components – **Micro-chamber method**

- **Surface-only** or **bulk** emissions testing
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</tr>
<tr>
<td>Chamber temperature (°C)</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Inlet gas flow rate range (ml/min)</td>
<td>50</td>
<td>250</td>
</tr>
<tr>
<td>Gas sampling time (min)</td>
<td>15</td>
<td>2-4 hrs</td>
</tr>
</tbody>
</table>
Direct desorption - content testing (VDA 278)

- Homogeneous samples
- Small section of material placed inside of empty sorbent tube and content thermally extracted
- Desorbing for 30 minutes at 90 °C - VOCs up to n-C\textsubscript{20} followed by 60 minutes at 120 °C - SVOCs n-C\textsubscript{16} to n-C\textsubscript{32}
Microchamber

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

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

Spacers to present sample at correct height.

Proprietary flow control device – no pump required.

Heated air stream.
Controlling edge effects from surface emissions

Injection molded resin

Injection molded resin with coating no edge control

Resin with coating: mCTE lid edge control

Prof. Mangoo Kim, Kangwon, National University, Korea. (2010)
Presentation to ISO TC146 SC6 WG13 (Document # N0087)
Using the microchamber for bulk emissions (content testing)

Bulk Emissions
- Ambient/elevated temperature
- Dynamic Headspace
- Homogenous sample

Heated air stream

Proprietary flow control device – no pump required
Micro-Chamber/Thermal Extractor: Testing chemicals released by children’s plastic toys

1. Toluene
2. Ethyl benzene
3. p-xylene
4. o-xylene
5. Cyclohexanone
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: 40°C
- 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
Project P2/00/05 – Horizontal Evaluation Method for the Implementation of the CPD – HEMICPD

“It was demonstrated that it is possible with alternative methods (µ-chamber and FLEC) to achieve a qualitative and quantitative correlation with the reference method.”
Qualitative comparison of results obtained (after 3 days) for a highly emissive PVC floor covering using various techniques

Quantitative comparison between the FLEC cell and the reference test chamber for two different floor coverings tested after 3 days.
Comparison of individual emissions from a sample of PVC floor covering tested after 3 days with the FLEC and µ-CTE procedures.
HEMICPD Conclusions

“Firstly, it has been shown that the microchamber data were reproducible for all four tested materials (PVC floor covering, linoleum, wall-to-wall carpet and insulation material). As already reported this sampling instrument is really convenient and is less reliant on the expertise of the user.

This project has also shown that the μ-CTE gives semi-quantitative results with a pretty good correlation compared to those obtained using with the FLEC, making the Micro-Chamber Thermal Extractor a suitable tool for screening materials in order to have an idea of the concentration range for emitted VOCs.”

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.
Validating TD-GC/MS analytical performance for material emission testing – aid to correlation

- **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
  - During routine maintenance visits
  - As a routine in-house check
  - For troubleshooting
  - By accredited 3rd party auditors

**Proposed compound list:**
- n-hexane
- Toluene
- Methyl isobutyl ketone
- Butyl acetate
- Hexanal
- Phenol
- Cyclohexanone
- Trimethylbenzene,1,2,3
- 4-Phenylcyclohexene
- Butylated hydroxytoluene
- n-hexadecane

*Check std developed by Markes in conjunction with international experts*
Chromatography – Gas loaded tubes
New WASP proficiency testing scheme for material emission testing laboratories

• Starting April 2012
• Contact proficiency.testing@hsl.gov.uk

Workplace Analysis Scheme for Proficiency (WASP)

• Proficiency testing (PT) scheme established in 1988 by the UK Health and Safety Laboratory to assess the performance of analytical laboratories undertaking analysis of air samples
• Test samples shipped to laboratories every 3 months (4 test cycles per annum)

Current WASP VOC PT schemes

• started 1991 for laboratories undertaking workplace/ambient air analysis
• currently ~ 100 participating laboratories from 15 countries
• 82 test cycles completed to date
• ~ 5000 VOC test samples prepared per annum
• ~ 1500 formaldehyde test samples prepared per annum
Material Emission Proficiency Testing Scheme

Planned MET Proficiency Test sample
• Up to 13 (S)VOC components on Tenax (flexible)
• Proposed loading range 50-300 ng per component (flexible)

PT sorbent tube loading system
• VOC standard atmosphere generated using procedures set out in ISO 6145-4
• 30 tubes loaded simultaneously
• Computer controlled with adaptive feedback
• 10% of tubes analysed for homogeneity assessment via ISO 17025 accredited method
• Measured batch to batch loading repeatability typically < 1.5%

PT scheme overview
• Laboratory performance to be statistically assessed using z-score approach as outlined in ISO 13528
• 2 rounds per annum starting in April 2012
• Trial round to test scheme starting November 2011
Is it all bad news for manufacturers??

• Industry is already being affected
  • No use hiding head in sand!!

• It is better to seize the initiative
  • Regulatory changes are creating new markets for low-emission products. Why wouldn’t a company want to position itself to take advantage of this?
  • The new regulations will be a barrier to cheap imports – EU products and imports will need the same labels

• Practical emission screening options are available for industry and will benefit R&D as well as compliance
  • Uptake will be limited by company size and resources
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