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CEN TC 351 WG2:

VOC emissions testing standard

Basics, results and findings of method robustness validation (and repeatability)

Based on the report as discussed and approved with some changes and amendments by CEN TC 351 WG2 (documents N173 and N174)

Principles of draft standard

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- **Basis: ISO 16000 standards, but with additional specifications**
  - Default approach: 3 days + 28 days test in test chamber.
  - Shorter test duration possible under certain conditions.
  - FLEC cell accepted only as secondary method, not as reference.
- **Testing conditions:**
  - 23 ± 1 °C temperature;
  - 45 - 55 % relative humidity of supply air;
  - 1/2 air change per hour;
  - Loading factor as in EU Reference Room;
  - Smallest test chamber = 20 liters;
  - Deviation of ventilation and loading factor allowed in narrow intervals
    - Then recalculation to the reference parameters;
  - Parallel test for CPD and formaldehyde E1 in one run – possible under certain conditions
  - Liquid products: Conditioning period in separate chamber / container can be specified by product TC, if appropriate.

Validation project – introduction

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- **Validation of draft CEN harmonized VOC testing norm**
  - Document TC351 WG2 N129 was the basis (revised version = N176).
- **Robustness validation of test method**
  - Variation of single testing parameters, one by one;
  - Compare area specific emission rate with the assumption that changing each specific parameter should not change test result when expressed as area specific emission rate;
  - Step 1: Analysis of existing and published knowledge and data;
  - Step 2: Fill remaining gaps with experimental data;
  - Conclude whether present specification is okay, or needs more precision;
  - Then modify draft standard in light of these findings.
- **Round Robin Tests**
  - Have several products tested by larger number of testing laboratories, including testing of one product several times in one testing lab;
  - Compare mean value, distribution, variation.

Validation project – review of existing data

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- **Robustness validation**
  - Step 1: Analysis of existing and published knowledge and data
  - Report: CEN TC351 WG2 N 154

Validation experiments – work plan

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- **Robustness validation**
  - Work plan for filling remaining gaps in existing data; 5 months time.
  - Report: CEN TC351 WG2 N 157
    - **Homogeneity testing** (4 – 6 samples per material)
    - **Temperature** (19°C – 27 °C)
    - **Humidity of supply air** (45% – 55% RH)
    - **Chamber size** (0,02 m³, 0,119 m³, 1 m³, 3,2 m³)
    - **Loading factor** (0,3 m²/m³, 0,7 m²/m³, 1,5 m²/m³)
    - **Ventilation rate** (0,3 ach, 0,7 ach, 1,5 ach)
    - **Loading factor and ventilation rate** (parallel change of both)
    - **Techniques for sealing back and edges** (foil, tape, seal box, frame)
    - **Reference material for toluene emissions** (VT / NIST)
    - **Benzene artifact generation** while sampling air on Tenax TA tubes
  - Data are in report CEN TC351 WG2 N 173.
  - Interpretation is in report CEN TC351 WG2 N 174.
  - Additional findings were made regarding
    - **Age of sample**
    - **Analytical determination** (hexanal, and the VVOC n-pentane)

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Validation experiments Results

Validation experiments – results

- **Sample representative and not representative**
  - Samples were selected in such a manner that
    - they were assumed to be representative for different emissions mechanisms:
    - they were expected to show relatively high emissions; low emissions would not allow to compare.
  - Samples do not represent emissions of the product group they belong to.
- **Sample selection**
  - Resilient flooring: Linoleum from stock, higher emissions expected
  - Vinyl flooring: With recycled vinyl in back from stock
  - Porous product: PS insulation foam, fresh from production
  - Wooden flooring: Parquet from stock
  - Wood-based panel: Particle board from stock
  - Mineral insulation: Glass wool, fresh from production
  - Liquid product: Low emitting water-based formulation, spiked with a number of target VOCs

Validation experiments – results

- **Homogeneity of samples**
  - Samples were acquired from leading manufacturers.
  - Tests of 4-6 samples at BAM with small chamber, Microchamber, or test cell.
  - Results:
    - Variation of emissions within the test samples between less than 10% and some 20%;
    - Only wooden flooring showed higher variation – only because one out of six test results was much higher than the other test results.
- **Conclusions for draft VOC testing standard**
  - Include an informative note saying that typical inhomogeneity of a products needs to be taken into account
    - for deciding on minimum size of test specimen;
    - when evaluating test results.

Validation experiments – results

- **Testing temperature**
  - Tests at 19°C, 23°C, 27°C with constant absolute humidity.
  - 6 materials:
    - Glass wool, wood-based panel, wooden flooring; all releasing formaldehyde by hydrolysis of binder with humidity from air;
    - Resilient flooring, porous product (foam), liquid product.
  - Results:
    - Both increase, decrease, and no change of emission rate with higher T.
    - Formaldehyde:
      - No significant change of emission rate with wood-based panel;
      - Some increase of emission rate observed with glass wool and with wooden flooring.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed.
    - Maintain range ± 1°C as in present draft.
  - Only editorial improvements.

Validation experiments – results

- **Relative humidity of supply air**
  - Tests at 45%, 50%, 55% RH of supply air with constant temperature.
  - 6 materials.
  - Results:
    - Both increase, decrease, and no change of emission rate with higher RH, but less strong impact than variation of temperature.
    - Formaldehyde:
      - No significant change of emission rate with wood-based panel;
      - Some increase observed with glass wool and wooden flooring.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed.
    - Maintain range ± 5% RH in supply air as in present draft.
    - Overlapping range of testing parameters with EN 717-1 (RH = 45-48%) allows using one test for both standards for formaldehyde.
    - Recent work of WKI (WG2 document N167) showed how formaldehyde results can be re-calculated between EN 717-1 and this standard.
  - Only editorial improvements.

Validation experiments – results

- **Testing chambers with different sizes**
  - Tests in chambers of 0,02 m³, 0,119 m³, 1 m³, 3,2 m³.
  - 2 materials (porous, liquid), 1 solid reference material.
  - Results:
    - No clear trend; therefore all 4 chambers are regarded equivalent.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed.
    - Maintain present specification (test chamber volume minimum 20 liters)
      - Set such minimum size mainly for ensuring sufficient size of test specimen for partly leveling out product inhomogeneity.

Validation experiments – results

- **Loading factor and ventilation**
  - Tests with 0,3/0,7/1,5 m²/m³ and 0,3/0,7/1,5 air change per hour (ach).
  - Tests with constant ventilation, constant loading, and proportional changes of both.
  - 3 materials (resilient flooring, porous product, liquid product).
  - Results:
    - Solid products: No change of emission rate with changed parameters;
    - Liquid products: No clear trend, except
      - Texanol, butyldiglycol: increase of emissions with higher loading
      - DEP: Decrease of emissions with higher ventilation.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed; only editorial improvement.
    - Maintain present specifications that allow testing in one run
      - for this standard,
      - for EN 717-1, and for US standards (ASTM, ANSI, CDPH), all with different ventilation rate and loading factor;
    - by finding the overlap range of loading and ventilation for testing.

Validation experiments – results

- **Techniques for sealing back and edges**
  - Tests of products with emissions from top surface expected to be different from emissions from edges and back:
    - Wooden flooring
    - Vinyl flooring with recycled content in back
  - Tests without sealing and with different sealing techniques.
  - Some, but low, emissions from aluminum tape when glued on a plate.
  - Best sealing techniques were:
    - Back to back storage of plates, edges covered with aluminum tape
    - Tight coverage of edges and back with aluminum foil
    - Seal box as specified in JIS A 1901
    - Inclusion of a joint in test specimen of parquet: No difference
    - Less efficient:
      - Tray, fixing on a plate with tape (both in CDPH Section 1350)
- **Conclusions for draft VOC testing standard**
  - Add specifications on determination of blank value of the aluminum tape.
  - Add specifications on best sealing techniques.

Validation experiments – results

- **Reference material for method validation**
  - Film is spiked with toluene.
  - Transport in dry ice, storage in deep freezer.
  - Decay of emissions in test chamber is predicted by model.
  - Best prediction was reported after 2 and 3 days in test chamber.
  - Results:
    - Most test results between 80% and 120% after 2 days;
    - More variation after 3 days.
  - This or similar reference material can be used
    - for checking the whole testing procedure, not only single elements;
    - e.g. after installing new test chambers, or as occasional routine check of overall performance.
  - Comparisons in round-robin tests are another tool for check of performance
- **Conclusions for draft VOC testing standard**
  - Add a clause on possible use of reference material and of participation in round-robin tests.

Other proposals and observations

- **Determination of VOC and TVOC (1)**
  - Different GC separation columns will include different range of VOC, giving different results for the sum parameter TVOC.
  - This contributes to differences between laboratories.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed.
    - This was solved in present draft standard by requiring use of a precisely defined slightly polar GC column.

Other proposals and observations

- **Determination of VOC and TVOC (2)**
  - Different calibration of VOC give different results.
    - Substance specific calibration vs. calculation as "toluene equivalent".
  - Different detectors give different results for TVOC.
  - This contributes to differences between laboratories.
  - This should be harmonized by no longer allowing different ways of calibration and quantification.
- **Conclusions for draft VOC testing standard**
  - Specify one specific calibration method for individual VOCs.
  - Delete the FID option for TVOC determination.

Other proposals and observations

- **Issue: Pre-conditioning of wet-applied samples**
  - During initial high VOC concentrations some VOCs will adsorb on walls and then may increase test result after 28 days by re-desorption of VOCs from stainless steel test chamber walls.
  - This is far from realistic conditions because gypsum, cement and wood on walls will adsorb VOCs and water much faster and release them much less and much later than stainless steel wall.
  - This is worse if high initial water concentrations contribute by
    - dissolution of VOCs in condensed water;
    - condensation of water on test chamber walls;
    - condensation of water in air sampling tubes.
  - Pre-conditioning outside test chamber before start of test can solve this.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed, only editorial precisions.
    - Specify quality of pre-conditioning environment, e.g. it must be separate from environment, but also allow some more flexibility.

Other proposals and observations

- **Issue: Storage in test chamber until date of test**
  - Equilibrium between test specimen surface, test chamber air, and test chamber walls will be disturbed if sample is taken out of test chamber during testing period.
  - Low vapor pressure VOCs and SVOCs are most sensitive to this effect.
  - Especially results after 28 days will be different with and without such intermediate storage outside test chamber.
  - This will impair comparability of test results.
- **Conclusions for draft VOC testing standard**
  - No major change was proposed.

Outlook

- **Repeatability and reproducibility depend strongly on:**
  - Inhomogeneity of the tested product.
  - Chemical characteristics of the identified VOCs.
  - Height of emissions when testing;
    - both traces of VOC emissions and very high emissions are more difficult to analyze.
    - Emissions mechanisms and emissions decay over time of the tested product.
  - Storage duration of test sample before testing, especially in the case of the porous product.
  - The selected VOCs for analysis.

Outlook

- **Conclusions for within-lab repeatability validation**
  - Robustness validation delivered data on repeatability within the same lab under the same conditions (annex 2 of document CEN TC351 WG2 N 174)
    - Number of chamber tests: 36.
    - Number of involved products: 6.
    - Number of involved testing laboratories: 9.
    - Number of repeatability data (= number of VOCs analyses): 171.
      - 56 data with duplicate, 115 data with triplicate determination.
  - Repeatability = average deviation from mean, as % of the mean value.
    - Median = 50% of values below 13%.
    - 75% of values below 26%.
    - 95% of values below 54%.
    - Standard deviation: 18%; expanded uncertainty: 35%
- **Conclusions for draft VOC testing standard**
  - Add a clause on repeatability of VOC emission testing within one lab.
  - Note that repeatability studies always include material inhomogeneity and cannot be better.

Outlook

- **Conclusions for reproducibility (or better comparability) validation**
  - Round-robin tests have been organized by BAM recently *with very similar methodology* for
    - Sealant (pasty product)
    - Varnish (liquid product)
    - Wooden plate (running in early 2012) (solid product)
  - These could deliver much information and can speed up next step in validation as this information may not need repetition.
- **Proposals:**
  - Use the results of these studies for repeatability and comparability validation of the draft standard.

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