Reliability of VOC emission chamber testing – progress and remaining challenges

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Abstract Chamber emission testing of volatile organic compounds (VOC) and formaldehyde is becoming more and more important for construction products, furniture and consumer products. Therefore, the question of reliability of such tests is crucial. A number of round robin tests and other comparative investigations were undertaken in order to document the variability of chamber emission testing. When using material with homogeneous emission properties it is possible today to achieve a repeatability of the analyses (after sampling from test chamber) of ± 10 %, a repeatability of the whole procedure within one laboratory of ± 20 %, and a variability of test results from different laboratories of ± 50 % (as RSD around average). Mainly, the differences are due to the analytical procedures. There are successful approaches to improve comparability of different laboratories, and it does not seem impossible any longer to obtain a variability of ± 30 %, but this has not yet been achieved.

Zuverlässigkeit von VOC-Emissionskammerprüfungen – Fortschritte und Herausforderungen

Zusammenfassung Prüfkammermessungen der Emissionen von flüchtigen organischen Verbindungen (VOC) und Formaldehyd aus Bauprodukten, Möbeln und Gebrauchsgegenständen gewinnen weltweit an Bedeutung. Dementsprechend wichtig ist die Zuverlässigkeit dieser Prüfungen. Eine Reihe von Ringversuchen und andere Vergleichsmessungen wurden durchgeführt, um die Wiederholbarkeit von Prüfkammermessungen zu dokumentieren. Bei Prüfmaterial mit homogenen Emissionseigenschaften ist es heute möglich, dass die Wiederholbarkeit der Analytik (nach Probenahme an der Prüfkammer) höchstens ± 10 % beträgt, die Wiederholbarkeit der gesamten Prüfung innerhalb eines Labors ± 20 % und die Vergleichbarkeit von Prüfergebnissen unterschiedlicher Prüflabors ± 50 % (jeweils als relative Standardabweichung um den Mittelwert). Die Hauptursachen für die Unterschiede zwischen Prüflaboratorien sind in der Analytik zu finden. Es gibt positive Erfahrungen, wie durch eine Optimierung der Prüfverfahren die Streuung der Ergebnisse reduziert werden konnte. Eine Vergleichbarkeit von ± 30 % erscheint nicht mehr unrealistisch, wurde aber noch nicht erreicht.

1 Introduction

Chamber emission testing is characterised by many specifications. Some of these are dealing with legal requirements such as the German DIBt approval system for floorings or Japanese restrictions of formaldehyde and VOC emissions from construction products and interior finishing. Most of the tests are required by quality labels such as German Blue Angel or Finnish M1 classification, industry labels such as EMICODE (adhesives), GUT and CRI (carpets), Floor Score (floorings), BIFMA (office furniture), CertiPUR and Eurolatex. Other tests are performed for complying with specifications issued by retailers and down-stream users such as car manufacturers.

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Complying with these specifications is important for manufacturing industry. This makes robustness (traceability, stability) and repeatability (variability) crucial for economy of users of emission test results.

Testing methods are described in EN ISO 16000, namely in Part 9 (chambers), Part 10 (cells), Part 11 (handling of test specimens), Part 6 (VOC sampling and analysis) and Part 3 (volatile aldehydes sampling and analysis) [1]. A number of ASTM and ANSI standards are also dealing with same issues, as well as the Japanese standard JIS A 1901. Additionally there are some product-specific testing standards, such as those for determination of formaldehyde from products with formaldehyde releasing binders.

None of these standards has undergone a systematic validation procedure yet. This is planned within the frame of present standardisation work within CEN Technical Committee 351 where the testing rules are about to be defined when emission testing will be taken up in future EN performance standards for CE labelling under European Construction Products Directive [2].

2 Methodology

A number of round robin tests have been organised where typically between 10 and 20 laboratories from all over Europe received equal cuts from the same test specimen and had to perform a complete emission chamber test. Results were collected and compared at a central laboratory. In some cases, correlations between laboratory parameters and test results where investigated. Some of these round robin tests were published, other ones were only presented in technical task forces – e. g. in meetings of the laboratories that are approved by German DIBt authority.

Only round robin tests that dealt with determination of VOC emissions in accordance with European testing protocols were included in this summary: A test specimen is made from the sample, placed in a stainless steel or glass emission test chamber, ventilated with clean air at 50 % relative humidity at 23 °C, and after some days air samples are taken from the test chamber outlet onto Tenax TA. Analysis is performed by thermal desorption of the air sampling tubes followed by gas chromatography and mass spectrometry (GC/MS).

The following round robin tests were taken into account: European VOCEM project with floorings and a paint [3], two GEV round robin tests with adhesives [4; 5], BAM round robin test with furniture parts [6], DIBt round robin test with two flooring materials [7], GUT round robin test with a textile flooring, Nordtest round robin test with a paint [8], a number of special studies.

Analysis of the key factors that may contribute to differences between different laboratories has to take into account the major elements of emission testing:

- transportation of the sample to the testing laboratory,
- unpacking, preparation of a test specimen,
- ventilation of the test specimen in the emission test chamber,

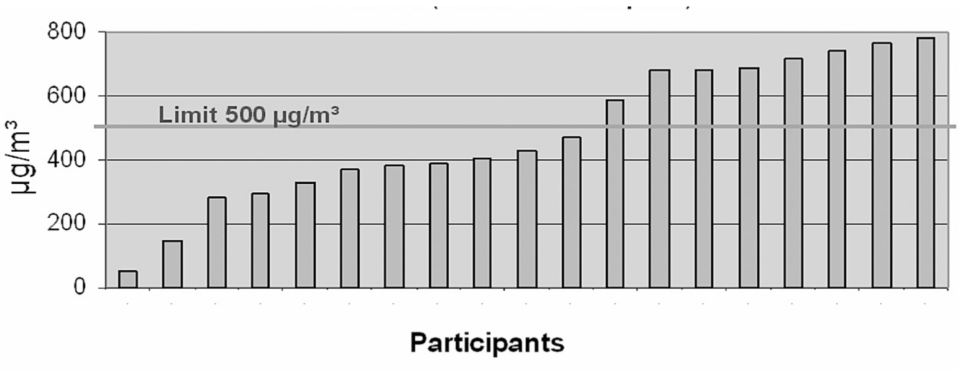

Figure 1. Round robin test results with a test adhesive – Total VOC (1 lab did not report a TVOC) [4].

- wall material of the test chamber (adsorption effects),
- test chamber climate (temperature, humidity, air velocity),
- date and technique of air sampling from test chamber outlet,
- analytical equipment,
- analytical procedures,
- identification of emitted substances,
- calibration and quantification.

3 Results

Several round robin tests with some 20 participants all ended similarly. They showed a variability of ± 50 % (RSD), with factor 1 : 10 or 1 : 15 between highest and lowest result, see e. g. **Figure 1**. The last round robin tests for German DIBt showed an improvement after the participating laboratories had been through an extensive process of technical exchange and agreements on harmonising their procedures, resulting in more detailed specifications in the German testing protocol [7]. A combination of the conclusions from the included round robin tests and from additional investigations is presented in the following. These conclusions are meant to contribute to present standardisation work within CEN/TC 351 on emissions from construction products.

3.1 Sampling, packaging and sample transport

The sample should be taken in such a way that emission properties are representative for the whole production. Typically this would mean to take an average sample from production or from stock, not from the beginning of a manufacturing series. If sampling from stock is performed, the shortest realistic storage time should be realised to avoid an underestimation of emissions. Sample size should be larger if the product is known to show inhomogeneous emissions over the surface.

Packaging should be airtight for avoiding contamination from outside during transport. For solids, typical packaging is effected first twice with aluminium foil and then with polyethylene foil. For liquids, commercial cans or laboratory bottles are appropriate. Extreme temperatures during transport may change the emission profile of the product and should be avoided – if necessary by thermal insulation packaging. When organising a round robin test, homogeneity across the product and stability over time of the product emissions shall be monitored.

3.2 Preparation of a test specimen from the sample

Opening of packaging and preparation of a test specimen from the sample shall occur in clean environment to avoid contamination by solvents used in the laboratory. The size of the test specimen is defined by the loading factor (the ratio between surface and chamber volume) required in the respective testing protocol. Some of these allow a simultaneous change (normally: increase) of loading factor and ventilation. For substances with significant volatility this does not seem to change the emission properties significantly for solid products, while a higher air velocity over the surface and over the chamber walls may lead to higher emission results for less volatile compounds with a boiling point above some 200 °C, and it may change the film building process and, thus, influence the emission behaviour over time for liquids.

For solid samples, emissions from back and edges may differ significantly from top surface emissions. If in reality only top surface is in contact with indoor air, e. g. for floorings, then back and edges shall be covered air-tight for achieving representative results. A seal box as defined in the Japanese standard JIS A 1901 or aluminium foil along with aluminium tape can be appropriate tools, while just wrapping with aluminium foil showed to be insufficient in case of high emissions from the covered parts of the material.

Liquids are applied on glass or metal in a manner that is reflecting typical use. But in reality, many liquids are applied on porous and non-inert substrates which changes emissions decay over time significantly. Anyhow, application on inert and non-porous substrate gives much better reproducibility of emissions and is preferred for this reason by most testing protocols. Depending on type of product, the amount of liquid applied may have only minor effect (for thick coating by viscous products) or significant effect (for thin coating by liquid products). This is depending on the impact on emissions of the surface film formed by the liquid within the first day(s). Minor effect is observed if emissions no longer are controlled by evaporation but by diffusion through that film [9].

Many products in reality are covered by other products, e. g. insulation material by walls, wall material by wall coverings, cement floor and adhesives by floorings, etc. It could be shown that this leads to clear reduction of emissions in case of non-permeable covering material and much less or even no reduction in other cases [10; 11]. Testing with simulation of covering layer makes emission processes more complicated which increases sources of non-repeatability. Present discussion therefore is going for testing products without coverage even if they are covered always in reality, but possibly apply correction factors to the results: Factor 1 (no reduction) for no covering and for permeable covering, factor 0.5 for semi-permeable covering, and factor 0.1 for impermeable covering.

3.3 Test chamber material and operation

No clear difference was seen for use of stainless steel or glass chamber walls, while Plexiglas showed loss of emissions by adsorption effects or even by diffusion through chamber walls in some cases [12].

3.4 Air sampling from test chamber

When following the prescriptions given in the respective standards, sampling air flow and sampling air volume did not show any impact on the results. Use of backup tubes just is important for monitoring any breakthrough in case of unexpected high emissions. Double determination is essential for monitoring any sampling errors. Typically, results from double determination with the same sample performed in the same laboratory can show a repeatability of ± 10 % (RSD).

3.5 Analysis and identification of emissions

Analyses of the emissions after sampling from the test chamber showed to be the most critical issue in most round robin tests. Only a good separation of chromatographic signals from the emitted compounds allows clear identification. The identity of the VOCs determines the correct assignment of limit values, and the correct application of calibration factors for quantification e. g. poor separation of gas chromatographic (GC) signals may deteriorate differentiation between saturated aliphatic hydrocarbons (with high DIBt limit values) and unsaturated olefinic hydrocarbons (falling into the group of VOC without specific DIBt limit values, thus with very sharp restrictions in Germany). Identification quality may thus decide on acceptance of a product.

The respective ISO Standards are leaving quite some freedom on how the laboratories may perform the analysis. This allows flexibility but increases non-variability. Laboratories working for DIBt emission testing have undergone a process of improvement of testing procedure details, resulting in an improvement of variability in latest round robin test [7]. Main conclusions for reduction of variability are listed below.

- Separation performance of gas chromatography in use should be defined by either setting minimum separation requirements for a VOC test mixture, or minimum requirements regarding GC column length and GC temperature programme.
- Minimum requirements for use of analytical standards are essential for good MS identification. DIBt requires that analytical standards shall be available and in use for all VOC with specific LCI limits.
- Different GC columns still are in use for GC analysis. Since the definition of what a VOC is relies on the retention times on a non-polar GC column, no other columns should be applied for analysis.

More stringent definition of the testing protocol will allow significant reduction of differences between testing laboratories. Anyhow, it seems to be common understanding that no better variability than ± 30 % (RSD) can be achieved. The reason is that in some cases the chromatogram is difficult to interpret. This is not an issue of good or bad analysis, but of specific interpretation of, where the border between two signal peaks and the signal baseline is set, see **Figures 2** and **3**.

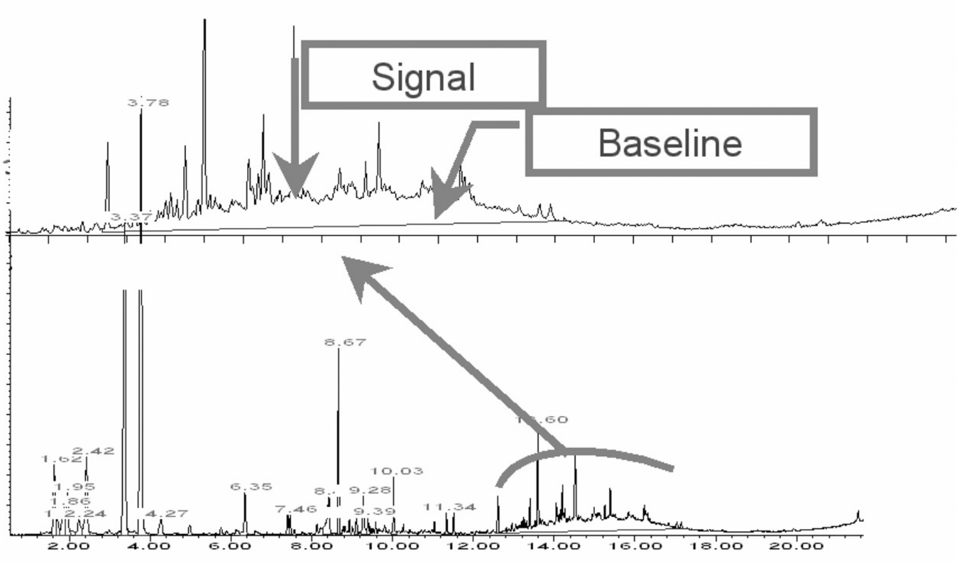

Figure 2. Example 1 for difficult decision on how to interpret a gas chromatogram.

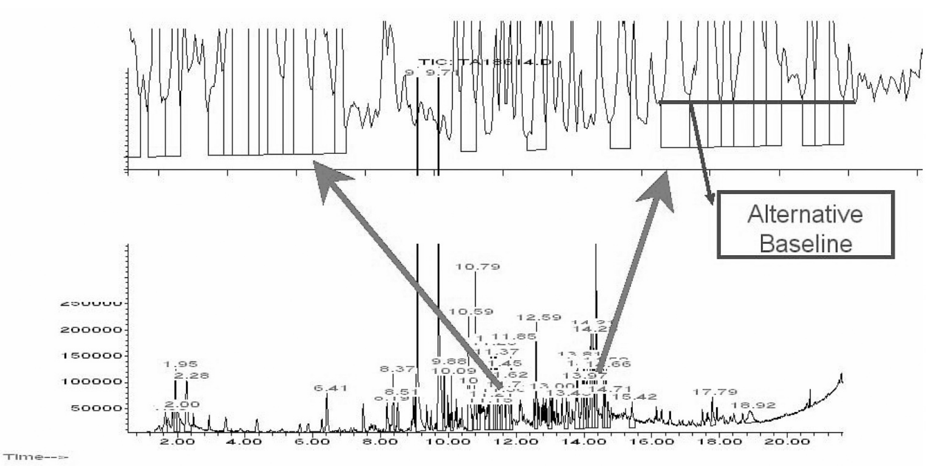

Figure 3. Example 2 for difficult decision on how to interpret a gas chromatogram.

3.6 Calibration, quantification, calculation

Quantification quality may determine acceptance of a product. Application of correct calibration factors does not only need good identification, but also use of good and traceable calibration standards. **Figure 4** shows the impact of identification and of the use of a specific or a non-specific calibration standard, on the test results for ethylene glycol in a round robin test with an adhesive. In that case, correct identification and specific calibration resulted in low concentrations – the high results were calculated as toluene equi-

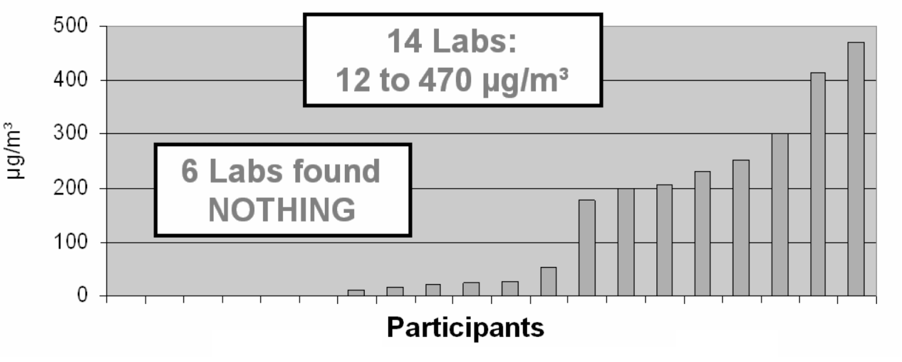

Figure 4. Round robin test results with a test adhesive – Ethylene glycol.

valent, as prescribed for absence of an appropriate calibration solution.

Regarding quality and age of calibration standards, a round robin test with textile floorings resulted in the finding that caprolactam calibration standards may be sensitive to ageing, leading to deterioration of calibration factor. Another issue is the linearity of calibration function. Outside the linearity interval, more calibration dilutions are needed for precise quantification.

Use of either a toluene equivalent calibration (as the default solution) or of a specific calibration (in case of clear identification) will result in very different quantitative results. Sum parameters such as TVOC (Total VOC) will be influenced by all above decisions taken in the laboratory.

4 Interpretation and outlook

Inhomogeneity of emission rate over surface will be a limiting factor for testing repeatability for many materials that cannot be overruled by improvement of analytical procedures. Nevertheless, variability of emission test results from different laboratories still can be reduced. Most helpful is a more stringent definition of the parameters defining identification and quantification during analyses of the air samples taken from the test chamber outlet. Most work on more precise definitions has been realised by German DIBt, leading to some improvements regarding variability of test results.

But the impact of other factors on the emission test result has not yet been clarified in an unambiguous manner. Robustness of the test result against variations of

- temperature and relative humidity in the test chamber,
- air velocity over the emitting surface,
- air velocity over the test chamber walls,
- impact of permeability of upper layer on reduction of emissions from lower layer in an aggregate construction,

still need to be investigated in order to find out how a better control of these factors may improve repeatability and variability. The current standardisation work in CEN/TC 351 on emissions from construction products is intending to take up these issues.

Literature

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