Publishable Summary for 20NRM04 MetrIAQ
Metrology for the determination of emissions of dangerous substances from building materials into indoor air

Overview

Given that European citizens spend more than 80 % of their time indoors, it is vital to have a healthy indoor environment. To achieve this, the release of harmful substances from building materials, such as paints, flooring, and from other products used indoors, such as furniture, into the air must be minimised. Reliable, accurate, traceable measurements of the emissions are paramount to reach high level consumer protection. The overall aim of the project is to develop traceable measurement of emissions of volatile organic compounds (VOC) from such materials, by providing well-defined emission reference materials (ERM) and certified reference gas standards (gCRM), in accordance with the emission test chamber procedure described in EN 16516. The project results will support the efforts to minimise the use of building products, that emit dangerous substances, thereby ensuring improved indoor air quality.

Need

EU regulation No 305/2011/EU (Construction Products Regulation, CPR) codifies that emissions from building products must be controlled in order to meet the formulated basic requirements (BR) for construction works. This takes place either on the manufacturer side or in test laboratories accredited under ISO/IEC 17025. EN 16516 describes a mandatory test procedure for the determination of VOC emissions from construction materials in environmental test chambers whose results are used for the Declaration of Performance (DoP) demanded by the CPR demonstrating conformity with the BR. Furthermore, the test chambers results will be used for the mandatory health-related evaluation of these products, once a harmonised evaluation concept defining emission classes is available in Europe. Comparability between measurement results is fundamentally important, as such, EN 16516 demands verification of the performance of the whole method by comparing against external references and the participation in round robin tests (RRT). For this purpose, both ERM and gCRM are urgently needed.

In recent times, studies related to the development of reference materials for emission test chamber measurements have focused mainly on investigating one or two VOCs (i.e. toluene and formaldehyde). However, the findings from these studies often do not consider long-term stability over a time period > 100 hours, in contrast to the standard testing time of 28 days. In previous RRT performed with commercial materials, the relative standard deviations of reproducibility between labs varied from 46 % to 300 %. In addition, a common factor with such approaches is a decreasing emission profile, thus making it difficult to predict the emission rate, which is essential for an external reference. All of these issues highlight the need for ERMs with reproducible and homogenous emission properties. The ERMs should also be supplemented with a suitable numerical model describing the mass transport inside the material which would enable the prediction of the VOC release and allow accurate performance verification of test chambers.

Suitable ERMs, that emit a known amount of a compound are currently not available, although a first approach of an artificial one on lacquer basis was made in the former EMRP project ENV01 MACPoll. However, shortcomings in its long-term stability and reproducibility between the batches have been identified and require further development. In addition, in view of the great variety of dangerous substances occurring in indoor air, the lack of availability of a gCRM hinders progress in this area.

Objectives

The overall goal of this project is to provide reference materials to improve the traceable measurement and characterisation of emissions of VOCs from materials for interior use according to EN 16516 and to provide CEN/TC 351/WG 2 and other standardisation committees related to materials emissions testing with validation data for future revision of their standards. The specific objectives are:

1. To develop an emission reference material (ERM) that contains and releases relevant compounds typically emitted by construction products within the range of the EU-LCI list with a constant emission profile that decreases by less than 10 % over at least 14 days, in order to improve the quality assurance and quality control (QA/QC) of the emission test chamber method as described in EN 16516.
2. To develop gaseous certified reference materials (gCRM) of indoor air pollutants for compounds selected from key groups that are relevant for the health-related evaluation of building products as stated in the EU-LCI-list, such as aldehydes, unsaturated aldehydes, cyclic dimethylsiloxanes and glycol compounds.
3. To validate the newly developed ERM and gCRM by investigating the short- and long-term stability, reproducibility, and uncertainty in an inter-laboratory comparison, thereby demonstrating the benefits of the reference materials for the test procedure described in EN 16516.
4. To develop a suitable numerical model for simulating the transport processes inside the ERM and the compound release into test chamber air enabling the prediction of the emissions for each of the selected target VOC. The model should support the customised generation of the ERM. All relevant process parameters affecting the release of the compounds from the material will be determined.
5. To contribute to the standards development work of the technical committees CEN/TC351 WG2 and ISO/TC146 SC6 to ensure that the outputs of the project are aligned with their needs, communicated promptly to those developing the standards and to those who will use them (e.g., test chamber operators and gas standards manufacturers), and in a form that can be incorporated into the standards at the earliest opportunity.

Progress beyond the state of the art

Within the preceding EMRP project ENV01 MACPoll an important approach towards a candidate ERM was made with a lacquer material that was added with a selection of VOCs. However, production reproducibility was only shown within the batch of the lacquer material and the emission profile for this decreased rapidly after its application. Furthermore, colligative effects of the added VOCs in terms of miscibility, volatilisation or chemical reactions during curing were reported.

This project will develop a material with retarded compound release leading to a temporarily constant emission profile or at least a significantly decelerated one. It will contain at least 4 VOCs, that are typically emitted from building materials and relevant for the health-related evaluation, e.g. furfural, 2-ethyl-1-hexanol, D5 siloxane or methyl isothiazolinone. Based on data obtained by material characterisation regarding all parameters that have an impact on the compound release, a numerical model will be developed enabling the calculation of the emission profile for any VOC introduced. Current results have shown that it is feasible to reach temporally constant emission profiles with the chosen approaches of porous materials, such as zeolites, impregnated with selected VOCs as well as encapsulated VOCs. Stability for more than 14 days could currently be shown for *n*-hexane, *n*-heptane, toluene, limonene and *alpha*-pinene.

The availability of Primary Reference Materials in gaseous form (gPRM) and gCRM will be improved. Test gases provided by manufacturers today that contain compounds as stated in the EU-LCI list are mostly not certified and traceability to SI units is rarely demonstrated. The gPRMs and gCRMs developed in this project will establish the traceability chain for the measurement data of emissions of dangerous substances from building materials into indoor air. The project has progressed in terms of the successful preparation of a gPRM in a gas cylinder containing the substances of the ‘check standard’ as defined by EN 16516, which is currently under validation. Furthermore, the gas standards generation line for the preparation of the gCRM in adsorbent tubes was successfully put into operation. Their short-term stability (28 days) under varying environmental conditions is currently under investigation.

By validation of relevant metrological parameters of the ERM, gPRM and gCRM and their use as reference materials for the verification of the performance of the test method EN 16516 in an inter-laboratory comparison (ILC), detailed data on the total measurement uncertainty involving all parts of the method will be provided for the first time. The ILC is envisaged for October 2023.

Results

Development of an ERM with consistent emissions for QA/QC of the EN 16516 emission test chamber method (Objective 1)

From the target compounds list involving relevant compounds of the chemical groups of alkanes, glycols, aldehydes, terpenes, alcohols, aromatic hydrocarbons, isothiazolinones, and cyclic dimethylsiloxanes reservoir materials serving as temporally constant emission source were produced. For that, in one approach, more than 100 samples of polymeric microcapsules loaded with single VOCs (*n*-hexane, *n*-heptane, toluene, limonene, *alpha*-pinene) were synthesized to optimize the process in terms of shell composition, morphology, capsule stability, and encapsulation efficiency. The capsules were obtained through polyaddition/polycondensation interface reaction in direct (oil-in-water) emulsion.

In a parallel approach, reservoirs made from porous materials (zeolites, MOFs, nanoporous carbons) that are impregnated with the VOCs from the target list – currently *n*-hexane, *n*-heptane, toluene – in a high-pressure process were produced. Optimisation of the impregnation with *n*-heptane in zeolite showed a retarded emission profile with ≤ 5 % decrease over 14 days in an emission test chamber operated with dry air. The uptake of water was observed to be problematic for regular zeolites. Tests with non-hygroscopic materials (modified zeolites, carbons, etc.) proved their applicability in humid air, whereby the performance is still below the target (~ 25 % decrease of emission profile over 14 days).

Measurements of both types indicate eligibility for stabilisation of the emission profile. The project consortium is continuing to work on the optimisation of the process parameters, particularly to the material's performance under humid air conditions. Once the target stability has been demonstrated, ways are sought to combine the reservoir materials into a multi-component material that can be safely delivered to the end user.

Development of gaseous certified reference materials of indoor air pollutants relevant for the health-related evaluation of building materials as stated in the EU-LCI list (Objective 2)

The compounds that have been selected for gPRM and gCRM are those demanded by EN 16516 in the so-called check standard, except for hexadecane that cannot be used in gas cylinders due to its low volatility. Instead of 1,2,3-trimethylbenzene as prescribed by the test standard, the consortium in consultation with the stakeholder advisory board has selected 1,3,5-trimethylbenzene. The former is only available in poor purity, which cannot be used in a reference material. In addition to that, a gPRM for formaldehyde will be developed.

Two types of cylinders with inert inner surfaces for the preparation of the gPRM and two types of adsorbents for the gCRM (Tenax® TA and multi-bed) have been selected. Dynamic methods have been set up to generate a gas mixture of the selected components in air according to ISO 6145-4. Sorbent tubes have been sampled to obtain the gCRMs and the short-term stability test of 28 days could be successfully finished.

In the past reporting period of the project, the gPRM end mixture in the low ppm level was prepared from mother mixtures with single components according to ISO 6142-1 and is currently validated. An uncertainty of 5 % is targeted at a shelf life of 1 year. The gPRM will finally be used for the validation of the gCRMs.

Validation of the newly developed ERM, gPRM and gCRM (Objective 3)

In this objective the reference products undergo internal and external validation involving an inter-laboratory comparison with the stakeholder community. Experimental approaches for the internal validation of the ERM have been set up, so that the validation can take place in the following months of the project. The comparison exercise is envisaged for October 2023. The call for participation will be launched in April 2023 via the project website, the LinkedIn 'VOC Measurements' group or directly via email to stakeholders who have already expressed interest.

The long-term stability study for the gPRM is currently ongoing and will last 12 months. Final data will be available in May 2023. In parallel, the long-term stability study for the gCRM on sorbent tubes has been started and is also ongoing.

Development of a suitable numerical model to predict the compound release out of the ERM (Objective 4)

Experiments have been started to identify the transport controlling steps in the ERM. At first, work has been performed in an empty emission test chamber to investigate the reproducibility and spatial distribution of the main parameters which are expected to impact the emission rate of the ERM, such as temperature, pressure, and fan velocity. Based on that, a simplified model of emission was developed taking into consideration lumped parameters to account for the internal (ERM) and external (chamber) transport. Characterization experiments were designed based on the influence quantities of the simplified model with the scope of identifying the controlling phenomena inside of the chamber.

For the next step, measurements with interim versions of the ERM will be carried out under varying chamber parameters. With the input from these experiments, the material performance will be characterised with the help of Finite Element Modelling (FEM).

Impact

The project is now at its mid-term. To maximise the impact of the project and ensure a wide dissemination of the knowledge generated, a website was created, which is permanently updated. A Stakeholder Advisory Board (SAB) with currently 21 members was set up containing representatives from the EU-LCI working group, indoor emission testing laboratories, labelling schemes, manufacturers of construction products, regulators, and standardisation bodies. News is furthermore posted in the LinkedIn group “VOC measurements”. Any activities undertaken so far are summarised below.

Impact on industrial and other user communities

The relevant industrial user communities will already be involved in the validation of the ERMs and gCRMs developed in this project. After validation, these communities will be able to uptake the project outputs for: (i) providing reliable emission testing data with a properly estimated uncertainty; (ii) complying to the QA/QC measures required by the relevant testing standards (EN 16402, EN 16516, EN 16738, ISO 12219 series, ISO 16000 series); (iii) organising RRT to monitor the proficiency of test laboratories; and (iv) calibration of analytical instruments. Moreover, emissions from building materials and wooden showcases in museums or galleries or from cultural heritage artwork itself can affect indoor air quality. The comparable and accurate measurement of VOCs released from artworks is a critical point for conservation and monitoring of artwork state.

The project engages with industrial and end user communities through the set-up of its Stakeholder Advisory Board (SAB). The SAB met already twice (16 February 2022 and 08 December 2022) and discussed the project results. Apart from that, the project benefits from the active support of the single SAB members that provide advice or sample material for test purposes.

A research institute is interested to use the gPRM gas mixture developed in Objective 2 in its current state for own analytical purposes. In turn, the data obtained can be used for the validation work.

Impact on the metrology and scientific communities

NMIs/DIs will be able to produce the ERMs developed and validated during the project and have access to ERMs that emit a larger number of substances thereby extending their portfolio of reference materials. This in turn will provide the stakeholders from testing institutes, labelling schemes, and industry with guidelines for using the ERMs to ensure uniform use and the best possible performance. Specifically, BAM and FhG intend to commercialise the ERM and make it available to stakeholders. In addition, BAM will use the ERMs to organise an internationally recognised RRT for the emission test chamber method according to EN 16516 and ISO 16000-9. Further to this, VSL intends to develop new calibration services on the project’s development of dynamic and static reference materials.

The partners in this consortium are actively involved in the CCQM Gas Analysis Working Group (GAWG) and in EURAMET Metrology in Chemistry Technical Committee (TC-MC) and the outputs from this project will be presented to them. The successful development of gPRMs and gCRMs will support the organisation of future Key Comparisons organised by the CCQM GAWG and EURAMET TC-MC and will allow new calibration and

measurement capability claims in the field of indoor air and VOC analysis. The gained know-how can be used by the scientific community and by other reference material providers for the preparation of similar calibration standards.

Research results achieved during the project will be submitted for publication in high impact peer-reviewed scientific journals. A workshop and online webinars on the preparation of traceable and accurate gCRMs and ERMs will be held, to which representatives of industry (both manufacturers and users), academic, standardisation and users will be invited. Young academics will be promoted by integrating the project's approaches in designing functional materials in the master course "Architecture" held at POLITO.

Project results were presented at the following occasions:

- 36th European Colloid & Interface Society Conference (4-9 September 2022, Crete, Greece): poster presentation on "Polymeric Capsules with VOCs for Controlled Emission"
- 10th International Symposium on modern principles of air monitoring and biomonitoring (Airmon) (7-10 November 2022, Bristol, United Kingdom): oral presentation on "Constant emitting reference material for material emissions test procedures"

Impact on relevant standards

The project will provide impact for all standards describing procedures for the determination of chemical emissions from materials for interior use and requiring the use of emission test chambers, such as EN 16516, EN 16402, EN 16738, ISO 16000 series, ISO 12219 series. They all have similar QA/QC requirements in common and recommend the use of external references. With the validation data acquired in this project the total uncertainty of measurement results obtained with the test chamber method will be determined and delivered in form of reporting documents to the respective standardisation committees for use in upcoming revision work.

Through interaction with ISO/TC158 "Gas Analysis" data on the performance characteristic of gas generators can be used to improve documentary standards such as those on dynamic methods for preparation of calibration gas mixtures (e.g., ISO 6142-1, ISO 6145-4 and ISO 6145-8). Further to this the project intends to provide input to the standardisation committees ISO/TC61 SC11 Products, ISO/TC146 SC6 Indoor air and CEN/TC421 Emission safety of combustible air fresheners.

In June 2021, June and October 2022, the project informed CEN/TC 351/WG 2 on the project's progress at its regular meetings. In April and September 2022, ISO/TC 146 SC 6/WG 3 was informed about the activities of the project.

Longer-term economic, social and environmental impacts

The project hopes to support the longer-term market position of European manufacturers of low-emitting products through the availability of better reference materials and hence increased reliability of testing. Once, the declaration of emission data for CE marking is mandatory, more reliable testing will also increase consumer confidence in the product and the manufacturer, and thus increase sales. A similar effect on voluntary evaluation schemes that help consumers make decisions when choosing low-emitting products is also expected. Moreover, an improved comparability in emissions tests strengthens customers' trust in these labels, promotes fair competition between manufacturers, and safeguards the European common market in building future products.

The improvement of the metrological infrastructure in the field of materials emissions testing supports the long- term European harmonisation of the health-based evaluation of indoor emissions from construction products regulated by the CPR. This will support a higher level of consumer protection and should improve the health and well-being of the citizens. Furthermore, the results of this project might give additional impetus to those European member states that still are in the early stages of implementing an infrastructure for emissions testing, such as Slovenia.

- Press release "BAM develops reference material for better indoor air", published on 4 November 2021
- Publication in professional press: "Bessere Luft in Innenräumen" (in German), published in ReinRaumTechnik, Vol. 24, January 2022

List of publications

de Krom, I., Heikens, D., Horn, W., Wilke, O., Richter, M., and Baldan, A., Metrological generation of SI-traceable gas-phase standards and reference materials for (semi-) volatile organic compounds, *Measurement Science and Technology* 34(3) (2023) 035018. https://doi.org/10.1088/1361-6501/aca704

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	01 June 2021, 36 months	
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Chief Stakeholder Organisation: GEV – Association for the Control of Emissions in Products for Flooring Installation, Adhesives and Building Materials	Chief Stakeholder Contact: Klaus Winkels	
Internal Funded Partners: 1. BAM, Germany 2. TUBITAK, Turkey 3. VSL, Netherlands	External Funded Partners: 4. Eurofins, Denmark 5. FhG, Germany 6. POLITO, Italy 7. VITO, Belgium 8. ZAG, Slovenia	Unfunded Partners: -
RMG: -		