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.

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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. Porous materials, such as zeolites, metal organic frameworks (MOF) and activated charcoal were impregnated with the target compounds under overpressure conditions. In another approach VOC were incapsulated (core-shell principle). Particularly, the latter approach proved to be suitable to obtain constant emission profiles, although an aging time of ~10 days is currently required to reach this stable phase. Zeolites with a homogeneous porosity are also promising but sensitive towards air humidity. Hydrophobic materials are available and currently tested.

Based on data obtained by material characterisation regarding all parameters that have an impact on the compound release, a numerical model is under development enabling the calculation of the emission profile for the VOC introduced. As the reference material will be used in emission test chambers, temperature, pressure and air velocity above the surface are the main parameters to be investigated. Based on that, in a first step, a simplified mathematical model based on the mass balances of the test chamber and the emission reference materials (ERM) have been implemented. With this, the controlling phenomena inside the test chamber were identified and now used for a Finite Element Model (FEM) to characterise the material performance.

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. In this project, high quality gPRM and gCRM are developed containing the components of the so-called check standard defined in EN 16516. 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 gPRM and gCRM are already validated. When they are generated dynamically, uncertainties below 5 % can be reached. The gPRM prepared in a gas cylinder is subject of further investigation, as it came up that phenol is not stable and the uncertainties of most of the other compounds are greater than the targeted 5 %. The prototype ERM are currently undergoing the internal validation. For all three reference product types the next validation step is an inter-laboratory comparison with ten participants from the stakeholder community. This is to demonstrate their usability as reference materials for the verification of the performance of the test method EN 16516 and to obtain data on the total measurement uncertainty involving all parts of the method will be provided for the first time.

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 in a size range of 15 and 50 µm 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 and permeability, 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 and 2-ethyl-1-hexanol – 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, with the exception of 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 have 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 is under development.

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, both ways of gPRM generation (static and dynamic) were internally validated and their uncertainty determined (Objective 3). It came up that preparation of static gas mixtures with phenol was not possible, but, fortunately, by use of dynamic generation methods. Furthermore, the stability of

the compounds with the exception of n-hexane in the chosen gas cylinder types was not satisfying and is subject of further improvement. The gPRM shall 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. The internal validation of the ERM started in the past reporting period. Final results will be available by April 2024. An inter-laboratory comparison with 10 external participants takes place in January 2024

Static gPRMs have been prepared in high pressure cylinders by gravimetry. It appeared impossible to prepare static gPRMs with phenol, due to the high boiling point and low vapour pressure of the VOC. For the other VOCs in the static PRM a relative expanded uncertainty between 6 % and 20 % has been determined. The stability of the VOCs in the static gPRM has been determined and save from n-hexane the VOCs show instability. Further research is currently performed to improve the stability. The gPRM obtained with dynamic methods has an uncertainty of 5 % and can be used to obtain a reference material containing phenol. Both the static and dynamic gPRMs can be sampled into sorbent tubes to obtain gCRMs. The VOCs sampled into sorbent tubes are stable for a period of 28 days. The uncertainty of the gPRM and gCRM are the same, 5 % when sampled from the dynamic gPRM and between 6 % and 20 % when sampled from the static gPRM.

A comprehensive report on this work has been published (DOI: https://doi.org/10.5281/zenodo.8189413).

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

Experiments have been carried out 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 mathematical model based on the mass balances of the test chamber and the emission reference materials (ERM) have been implemented over two case studies (preliminary prototypes) to verify the Biot number of experiments. 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.

In the next step, measurements with prototype versions of the ERM were carried out under varying chamber parameters and are still ongoing. With the input from these experiments, the material performance will be characterised with the help of Finite Element Modelling (FEM).

Impact

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 was interested to use the gPRM gas mixture developed in Objective 2 for own analytical purposes. In turn, the data obtained can be used for the validation work. On 18 October 2023, a stakeholder workshop entitled *Metrology for Indoor Air Quality* will take place at the premises of project partner VITO in Mol, Belgium. Besides information on the project outcome, it will be shown how the gCRMs are prepared, handled, and analysed. The participants will be given the opportunity to sample their own tubes with their own equipment for own purposes. Shortly after the workshop, the first part of the inter-laboratory comparisons (gCRMs) on the reference products will take place. 10 participants including stakeholders have already registered. Part 2 (ERMs) will start in January 2024. The registration process is still ongoing.

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"
- 21st International Metrology Congress (CIM) (7-10 March 2023, Lyon, France): oral presentation on "Metrological sound reference products for quality assurance and quality control measures in material emissions testing"
- 18th Healthy Buildings 2023 Europe Conference (11-14 June 2023, Aachen, Germany): poster presentation on "Reference products for quality assurance and quality control measures in material emissions testing"

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, CEN/TC421 Emission safety of combustible air fresheners, and CEN/TC 437 Electronic cigarettes and air liquids.

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, as well as in September 2023 ISO/TC 146 SC 6/WG 3 was informed about the activities of the project. The feedback was very positive, particularly with regard to future exploitation routes after completion of the project. As meetings in other addressed committees, i.e. CEN/TC 421 and CEN/TC 437, did not take place, the respective chairpersons were actively contacted and informed in May 2023.

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, Türkiye 3. VSL, Netherlands	External Funded Partners: 4. Eurofins, Denmark 5. FhG, Germany 6. POLITO, Italy 7. VITO, Belgium 8. ZAG, Slovenia	Unfunded Partners: -