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Bundesanstalt für Materialforschung und -prüfung

EMISSION REFERENCE MATERIALS FOR INDOOR AIR MEASUREMENTS

C. Grimmer, A. Musyanovych, R. Strzelczyk, W. Horn, M. Richter

MetrIAQ
EMPIR EURAMET
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Background

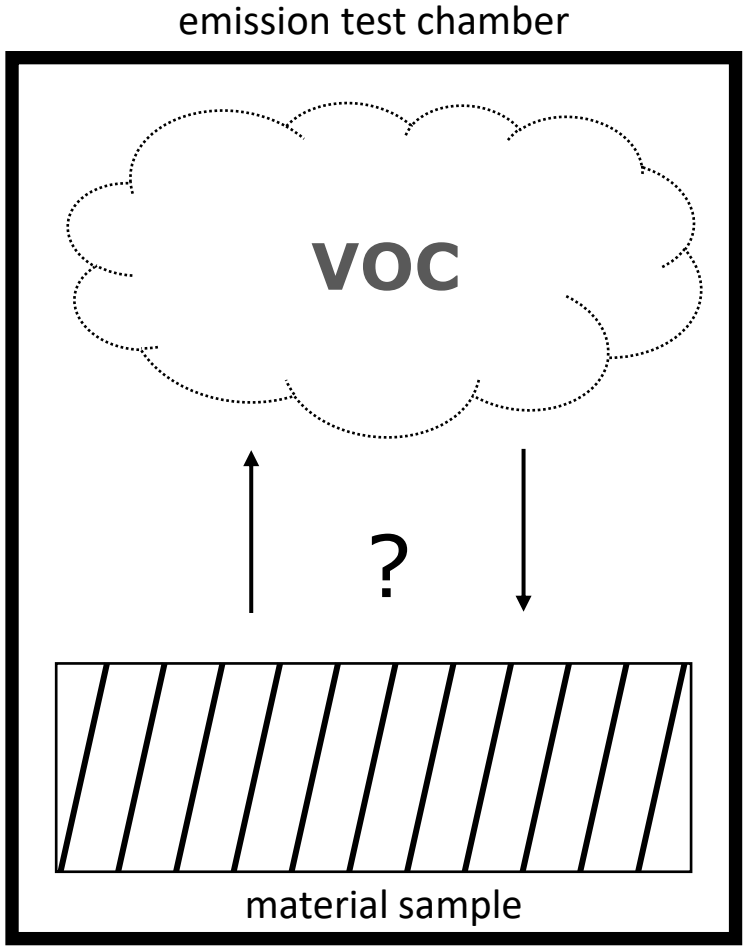
- Central European people spend 80–90% of time indoors
- Construction materials and other products used indoors are an important source for indoor air pollution, such as VOCs
- Health complaints reported
- Reduction of natural air exchange due to energy conservation

  ➢ EU Regulation No. 305/2011 - Construction Products Regulation (CPR) regulates, i.a., requirements for construction works as to hygiene, health and environment ***(BR No. 3)***






Emission test - Principle



Temperature (°C)

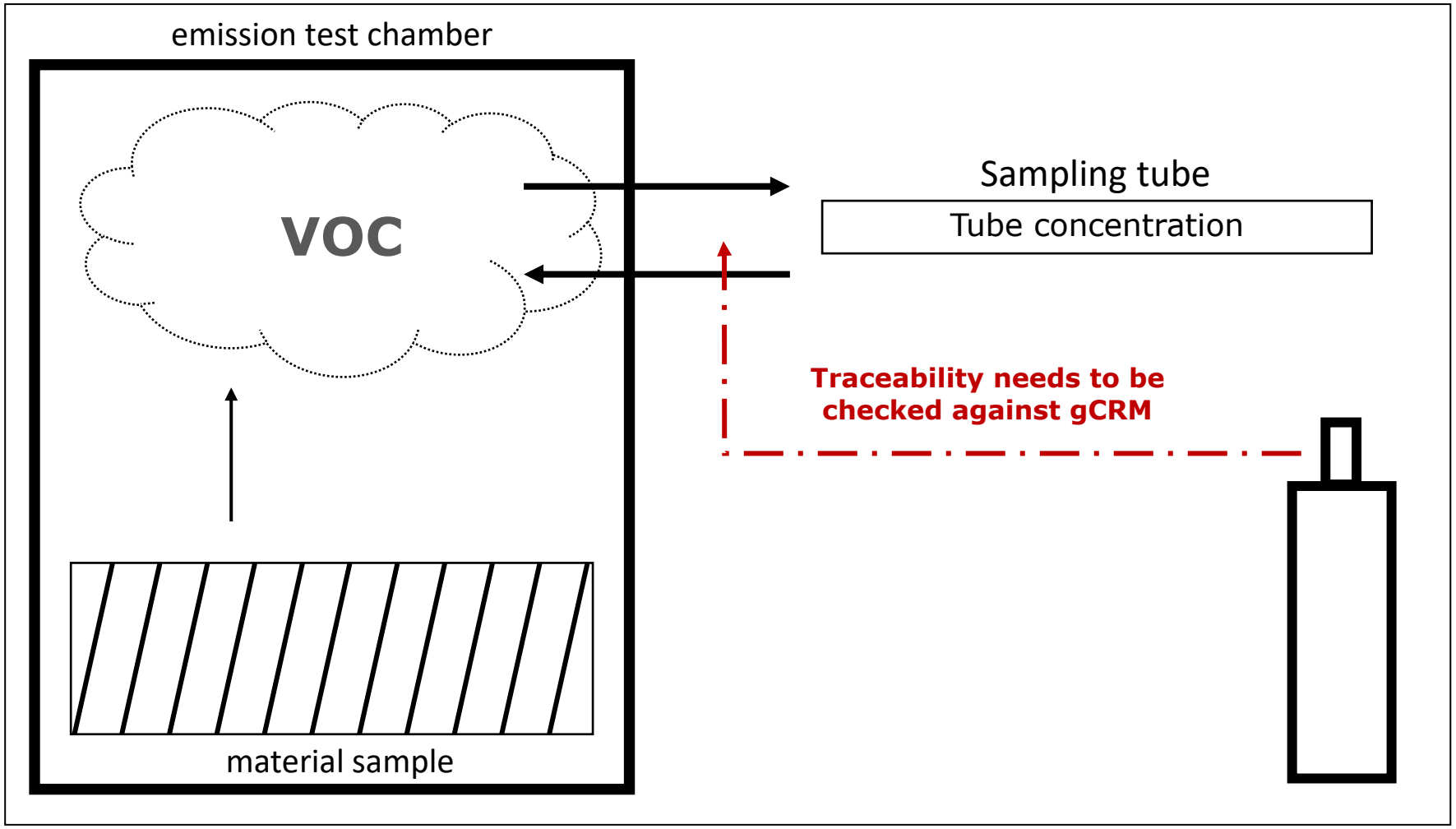
Rel. Humidity (RH [%])

Air exchange rate (AER [h^{-1}])

Great variety of VOC emissions

- **aliphatic hydrocarbons**
- **aromatic hydrocarbons**
- **aldehydes**
- **ketones**
- **aromatic alcohols**
- **glycols**
- **isothiazolinones**
- **siloxanes**
- **terpenes**
- **etc.**

Emission test - Principle



Sampling on

- **Desorption tubes**
- **DNPH cartridges**
- **etc.**

followed by chromatographic analysis

gCRM partially available

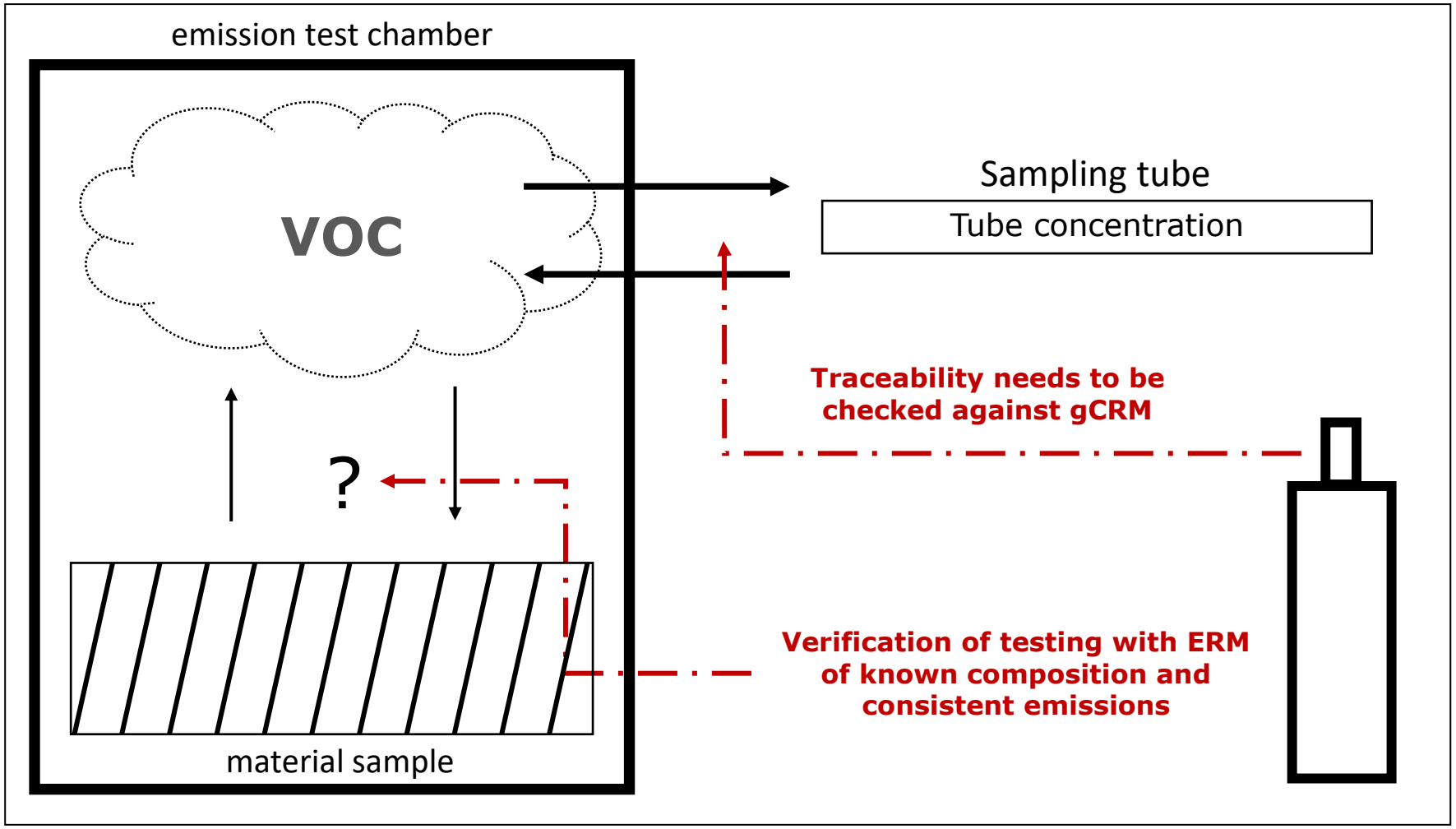
but

still needed for

- **higher boiling VOCs**
- **VOCs on EU-LCI list**

gPRM needed for certification of commercial VOC test gas mixtures

Emission test - Principle



gCRM partially available

<u>but</u>

still needed for

- **higher boiling VOCs**
- **VOCs on EU-LCI list**

gPRM needed for certification of commercial VOC test gas mixtures

No suitable ERM with predictable emission rates available

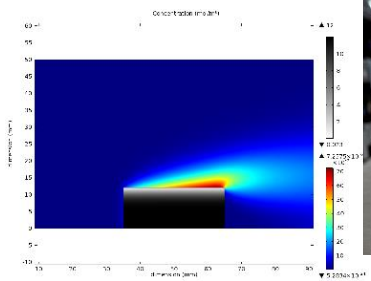
MetrIAQ Objectives

1. Development of an emission reference material (ERM) that releases (assessment) relevant compounds with a temporarily stable emission profile (decrease < 10% over at least 14 days)

2. Development of a numerical model to calculate the emission profile as well as the uncertainty

3. Development of gaseous primary as well as certified reference materials (gPRM/gCRM) with (assessment) relevant compounds

4. Internal and external validation of the developed reference products



Emission test chamber method (EN 16516)

8.4.2 External references

Notified and accredited laboratories shall verify performance of the whole method by comparing against external references and by following the quality control requirements of ISO 16000-3, ISO 16000-6, EN ISO 16000-9 and EN ISO 16000-11.

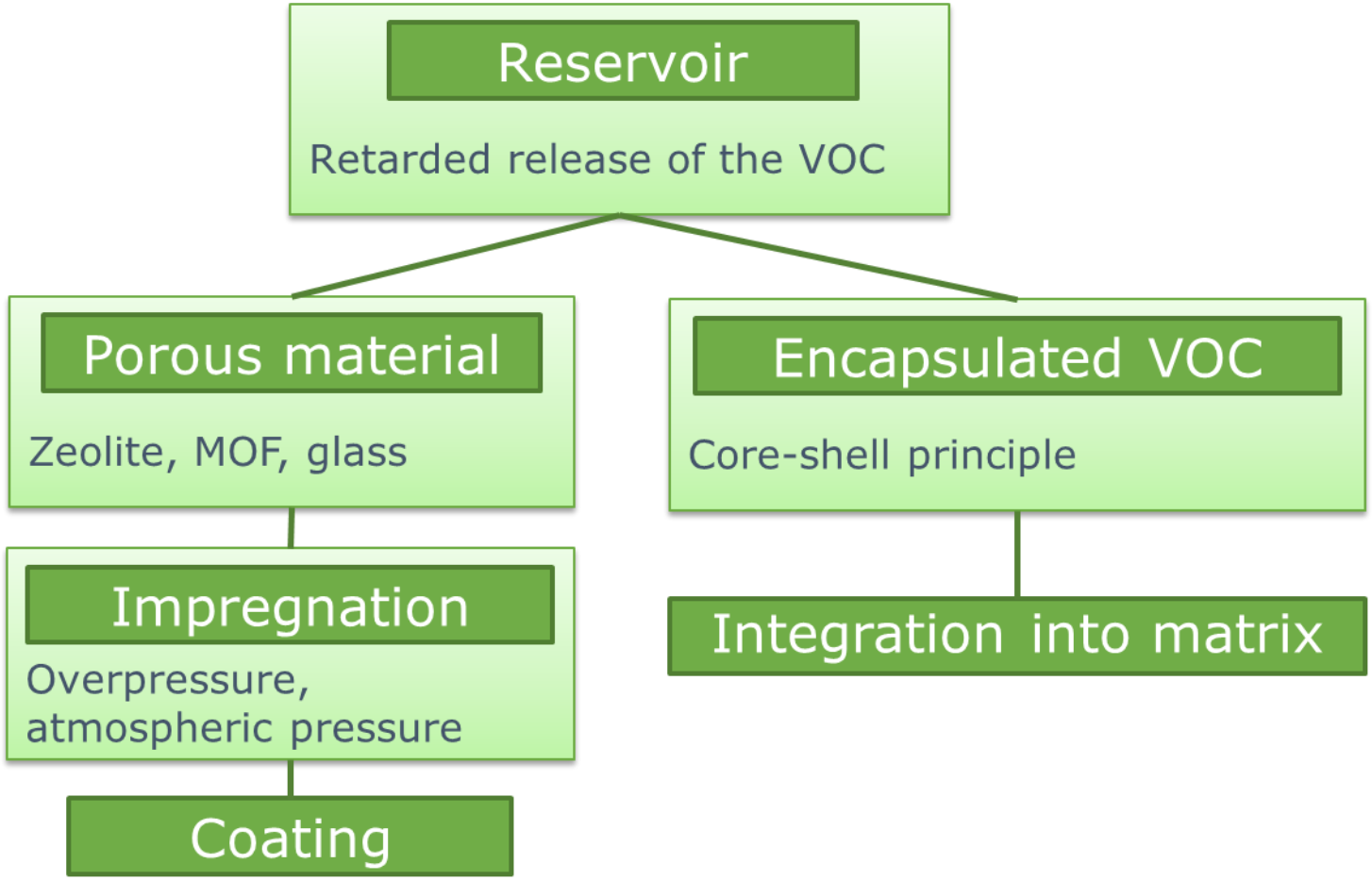
NOTE Use of external reference materials spiked with VOCs with known emission rate, and with known emission decay profiles, are a useful tool for evaluating the performance of the whole procedure against primary standards, provided the quality of the reference materials is known. Alternatively, the recovery tests described in EN ISO 16000-9 can be used to determine test chamber sink effects.

Participation in round robin tests and relevant independent analytical proficiency testing schemes is useful for comparing performance against a group of laboratories and is strongly recommended.

- Project goal to combine both:

ERM with known VOC composition and stable compounds release

ERM with temporally constant emission rate



- Combination of reservoir materials loaded with VOC
- Modularity allows customised product preparation
- Avoidance of colligative effects

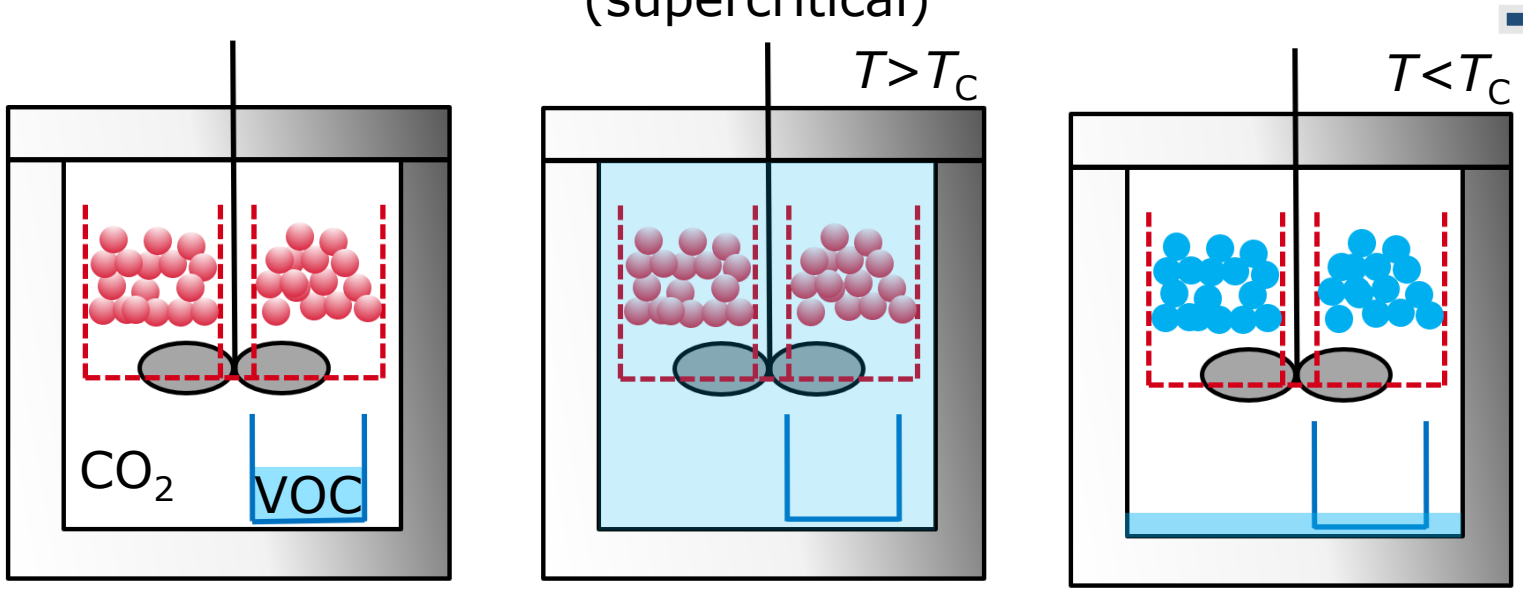
Approach 1: Impregnation of porous materials

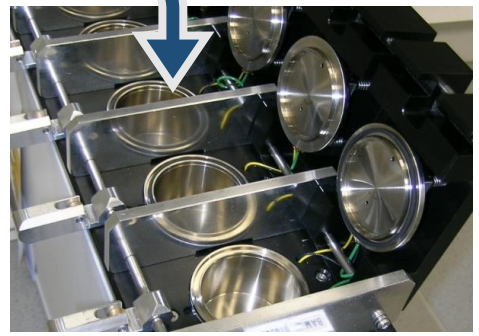
Preparation

Impregnation (supercritical)

Pressure release

Transfer into chamber





- Regular sampling on thermodesorption tubes
- Analysis by TD-GC-MS
- Stability of emission for at least 14 days

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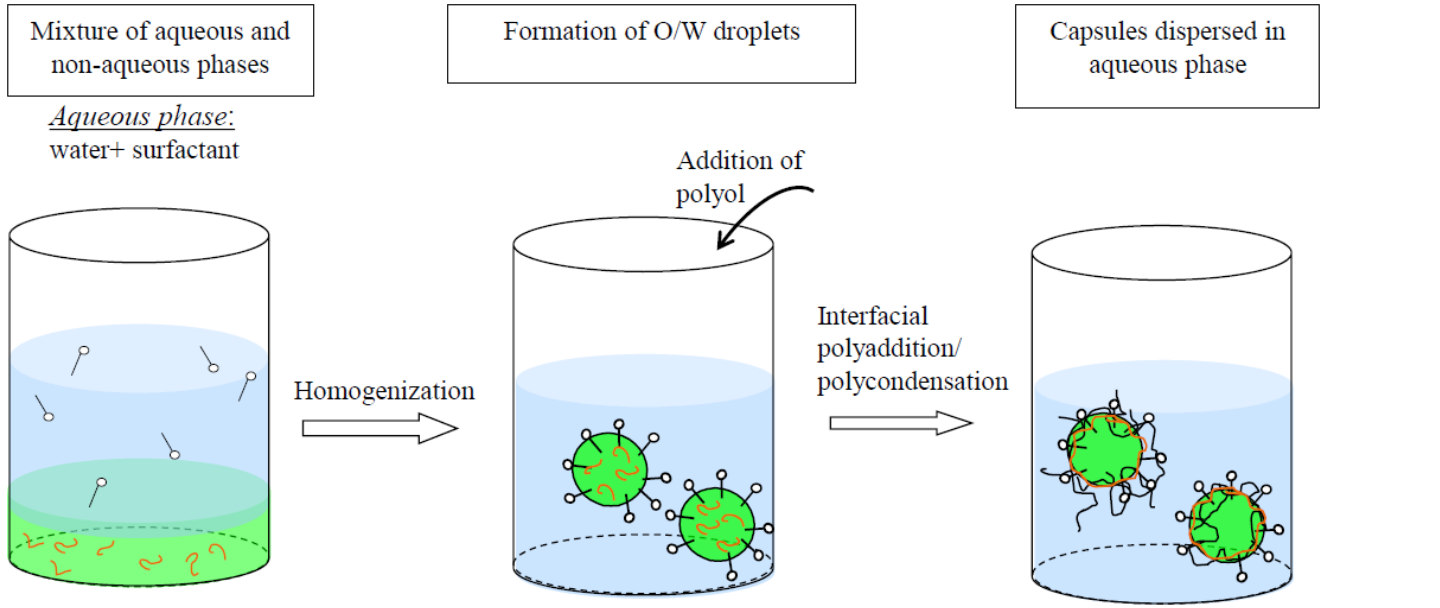
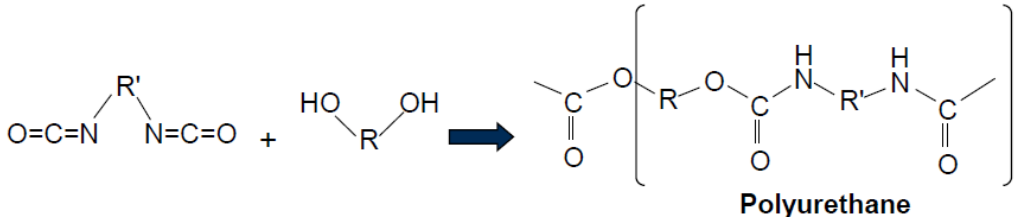
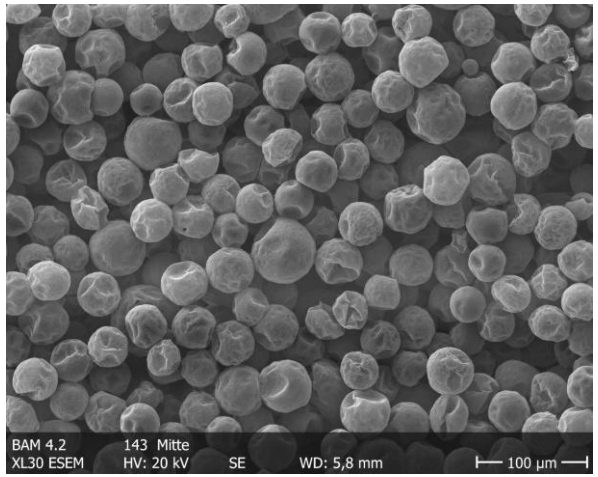
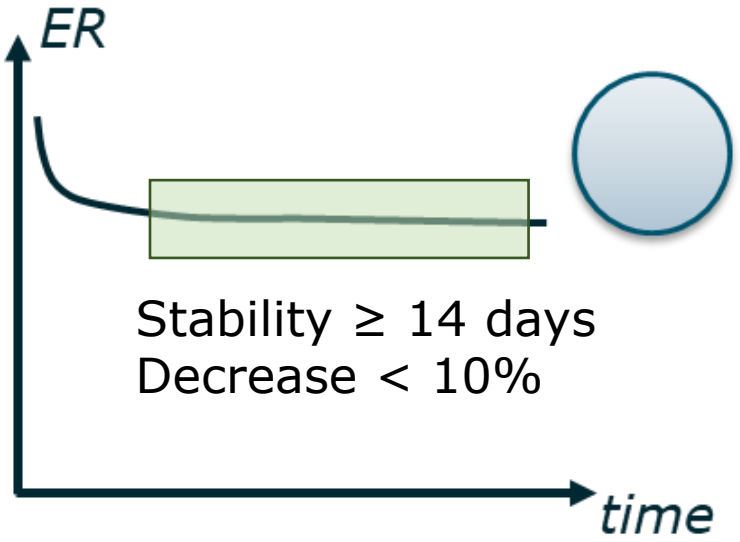
Approach 2: Encapsulation of VOC









Stability ≥ 14 days
Decrease < 10%

Fraunhofer IMM

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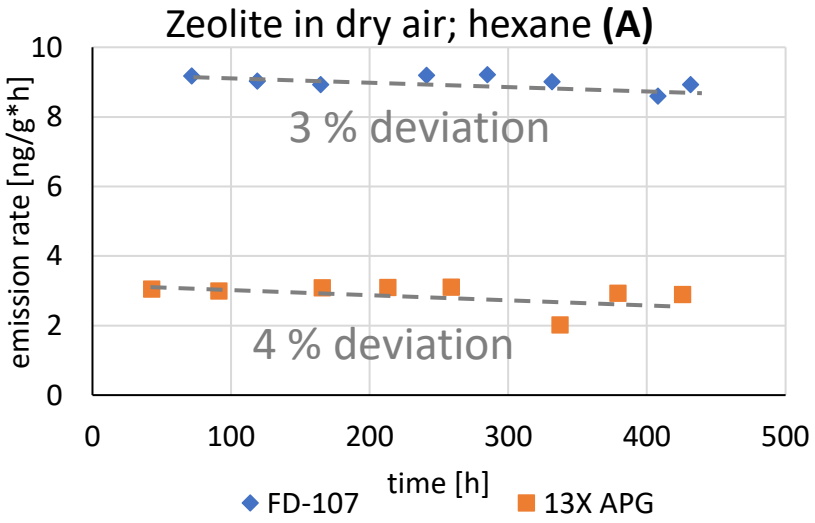
VOCs relevant for Indoor Air Quality

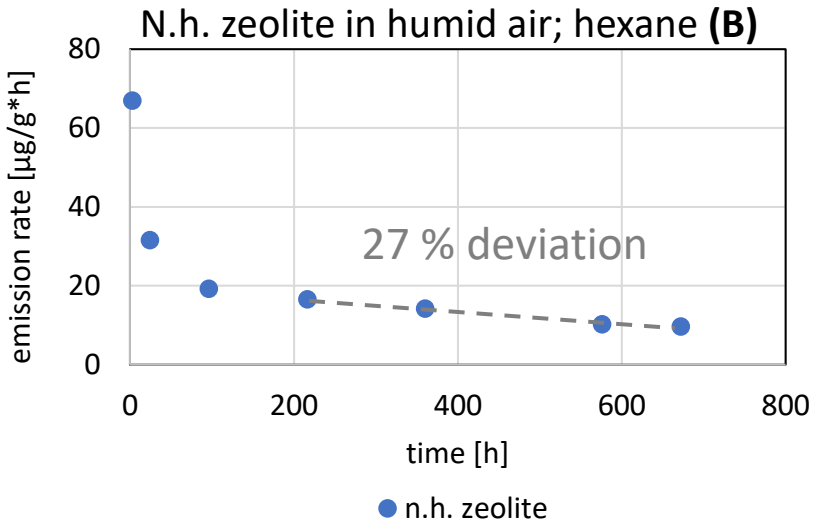
Name	capsules	impregnation
n-hexane	X	X
n-hexadecane	X	X
butyl glycol		X
propylene glycol		X
limonene	X	X
2-ethyl-1-hexanol		X
toluene	X	X
benzene		X
octylisothiazolinone		X
decamethylcyclo-pentasiloxane (D5)		X
methylisobutylketone		X

List based on standards, literature, experience and consultation with EU-LCI WG, stakeholder group

Results: Emission Reference Material (ERM)

Porous materials





- „Standard zeolites“ (hygroscopic)
- Very high stability
- Only in dry air – no emission in humid air!

- Non-hygroscopic (n.h.) zeolites work well in humid air
- Less stable over time

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Results: Emission Reference Material (ERM)

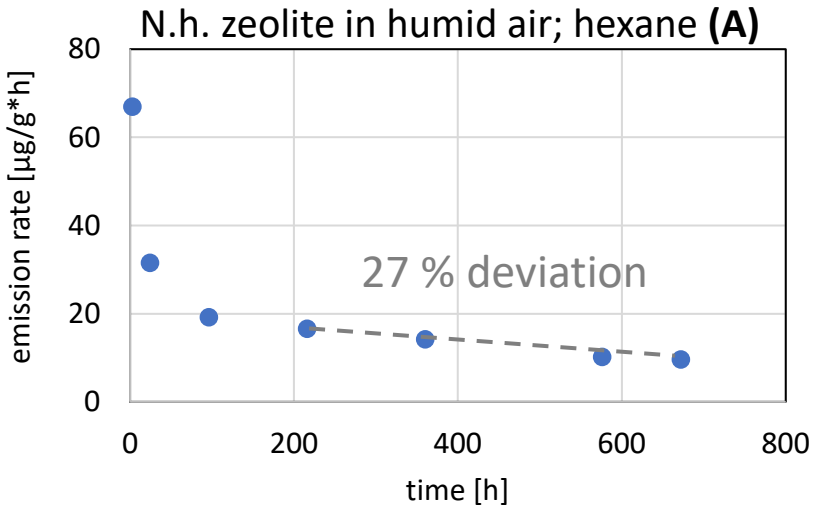
Porous materials

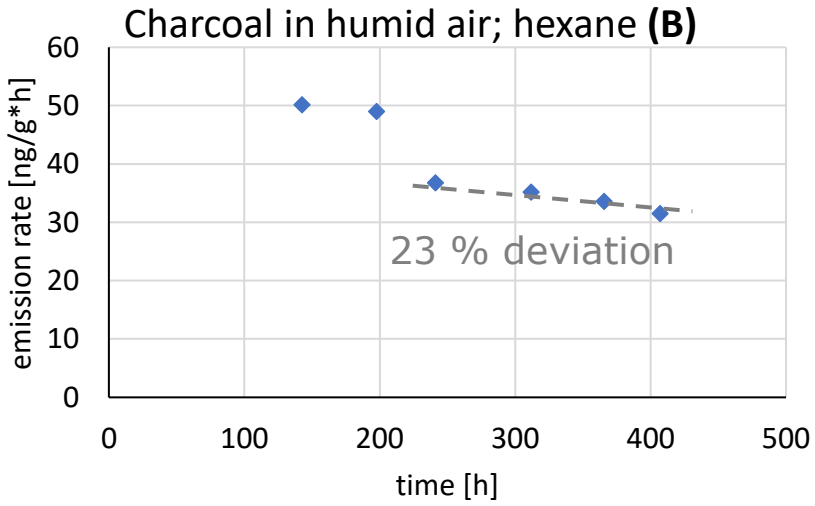
- Testing of different materials and material properties:
  - Zeolites
  - n.h. zeolites
  - Carbons
  - MOF & aerogel
- VOCs tested so far: *n*-hexane, toluene, 2-ethyl-1-hexanol and limonene

Material	Pore volume [cm^3/g]	Pore size [nm]	Surface [m^2/g]	
FD-107	0.217	0.86	610	Zeolite
13X APG	0.245	0.8	686	
3A EPG	-	-	15	
n.h. BEA	-	0.7	> 500	
n.h. MFI	-	0.6	> 300	
A8x30	1.538 (total)	-	1250	Charcoal
MC14x35	1.909 (total)	-	1200	
40_4	-	-	1250	
45_4	-	-	1000	
47_4	-	-	900	
Merck	-	1-25	-	
ZIF-8	0.663	1.16	1947	MOF
Aerogel	-	-	-	Aerogel

Results: Emission Reference Material (ERM)

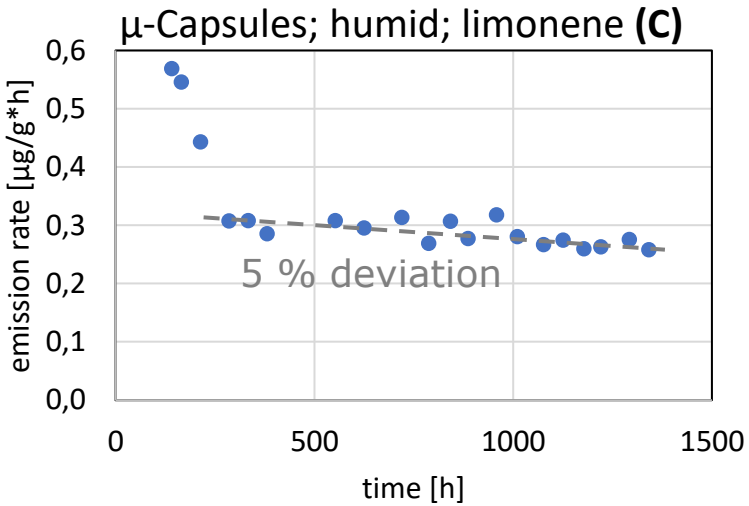
Porous materials





- Optimisation of impregnation parameters (*T*, *p*, *t*)
- Testing different materials (pore sizes, surface areas, polarity etc.)

Encapsulated VOCs



- Optimisation of capsule parameters (pore size, wall thickness, cross linking)
- VOC (limonene) encapsuled by polyurea or polyurethane

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Summary

1. Novel emission reference materials (µ-capsules) for QA/QC measures fulfil the requirements of test standards using emission test chambers
   - Partly long ageing time before profile has stabilised (~ 10 days)

2. Impregnation of porous materials is simple but emission stability not yet good enough
   - Different parameters were tested (surface area, porosity, polarity, *T*, *p*, *t*)
   - Key parameter to improve stability not yet found

3. Numerical model to get deeper understanding of the processes of mass transfer from the material into the test chamber air under development

4. Internal and external validation of prototype materials

Thanks for your attention

MetrIAQ
https://metriaq.eu

Dr Matthias Richter (Coordinator)
Bundesanstalt für Materialforschung und –prüfung (BAM)
+49 30 8104-4132
matthias.richter@bam.de

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