Primary reference materials for quality assurance and quality control measures in material emissions testing

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Introduction

Considering that European citizens spend over 80% of their time indoors, it is vital to have a healthy indoor environment. A worldwide network of professional commercial and non-commercial laboratories performing emission tests for the evaluation of products for interior use has been established. Currently, there is a lack of suitable reference products containing components relevant for the assessment of dangerous substance released from construction products into indoor air.

Most commercial gas standards of indoor-relevant compounds are not certified due to a lack of primary reference materials to which the MetrIAQ project aims to contribute. The EU-funded EMPIR project 20NRM04 MetrIAQ aims to develop gaseous primary reference materials (gPRM). The gPRM under development is a gas-phase standard in a high-pressure cylinder containing trace levels of volatile organic compounds (VOCs) in nitrogen. Dynamic standard gas mixtures of the VOCs in air are prepared as an independent method to support the validation of the gPRM.

Preparing gPRMs, Dynamic Standard Gas Mixtures and gCRMs

Set up

The VOCs in the gas mixture were selected from the list of VOCs of the quality control standard specified in EN 16516: n-hexane, methyl isobutyl ketone, toluene, butyl acetate, cyclohexanone, o-xylene, phenol, 1,3,5-trimethylbenzene with a target uncertainty of 5%. The gPRM can be sampled onto sorbent tubes to obtain transfer standards in the form of gaseous certified reference materials (gCRM).

gPRMs (ISO 6142-1)

Static gas mixtures are prepared by injection of a liquid VOC mixture into a high-pressure cylinder. Two dilutions were required to achieve a mixture of 50 nmol mol^{-1} of each VOC in nitrogen. Two types of cylinder treatment were tested.

Liquid VOC mixture 12 cmol mol^{-1} → Mother mixture in N_2 10 µmol mol^{-1} → Dilution 1 1 µmol mol^{-1} → Dilution 2 50 nmol mol^{-1}

Dynamic Standard Gas Mixtures (ISO 6145-4)

The method is based on the delivery of a constant mass flow of the liquid VOC mixture through a capillary. The constant mass flow is obtained by applying a constant pressure to the liquid VOC mixture, thereby forcing it through the capillary. Two dilution stages were required to achieve a mixture of 50 nmol mol^{-1} of each VOC in air.

Liquid VOC mixture 0.12 g g^{-1} → Stage 1: evaporation VOC mixture add 11.8 L min^{-1} air → Stage 2: dilute 0.1 L min^{-1} of stage 1 with 9.7 L min^{-1} air → Final gas mixture 50 nmol mol^{-1}

Sorbent Tube Sampling (ISO 16017-1)

gCRM are prepared via pumped sampling of known volumes from the gPRMs and the dynamic standard gas mixtures onto sorbent tubes (Materials Emissions/Soil Gas Monitoring, Markes International, UK). The sampled tubes were used to develop and validate the analytical method (TD-GC-FID), compare the gPRMs and dynamic standard gas mixture preparation, and for the stability study of the gPRMs.

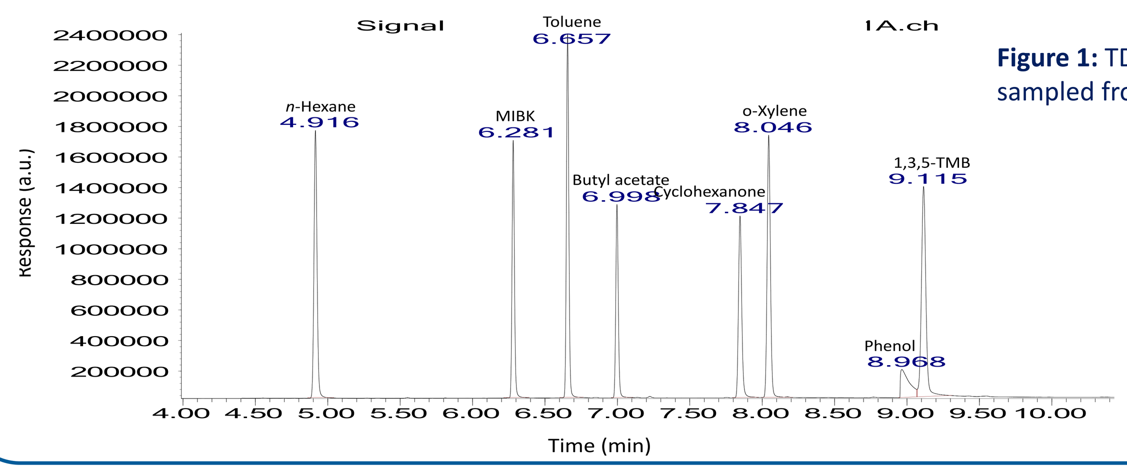
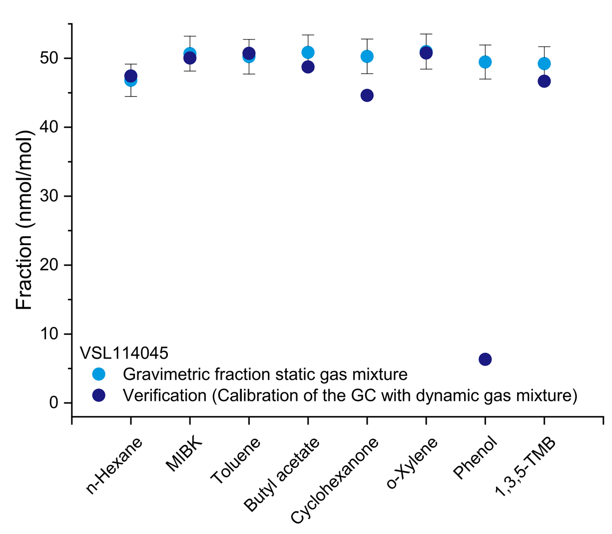


Figure 1: TD-GC-FID chromatogram from a TD tube sampled from the dynamic standard gas mixture.

Verification



Analysis of the gPRMs, using dynamic standard gas mixtures to calibrate the TD-GC-FID, showed comparable results for most VOCs expect for cyclohexanone and phenol.

During or after preparation of the gPRM phenol decomposes, precipitates as a solid and/or absorbs to the cylinder wall.

Figure 2: Graphical representation of the results from the verification of the gPRMs, using dynamic standard gas mixtures to calibrate the TD-GC-FID.

Uncertainty

Uncertainty sources:

- Preparation and sampling of the gPRM onto sorbent tubes → 1% (k = 2)
- Calibration of the GC using dynamic standard gas mixtures sampled onto sorbent tubes → 5% (k = 2)

VOC	U_{meas} (%)	U (%)
n-hexane	2.4	6
MIBK	2.2	6
Toluene	2.4	6
Butyl acetate	3.2	6
Cyclohexanone	5	7
o-Xylene	2.2	6
Phenol	20	20
1,3,5-TMB	3.0	6

Table 1: Overview of the measurement uncertainty (U_{meas} (k = 2)) and the combined relative expanded uncertainties (U) for the VOCs in the gPRMs (k = 2).

The objective in the MetrIAQ project is to obtain gPRMs with a relative expanded uncertainty smaller than 5%. The dynamic standard gas mixtures have a relative expanded uncertainty of 5%. For the gPRM the relative expanded uncertainty ranges from 6% – 20%, for these gas mixtures the objective has not been reached.

Stability

An important property of reference materials is the stability period. In the case of the gPRM this is the period during which the composition of the gas mixture in a cylinder is stable. To determine the stability of the VOCs in this study 4 gPRMs were prepared at t = 0 in high pressure cylinders with two different treatments.

After preparation, the gPRMs were sampled onto sorbent tubes at t = 2 weeks, 2 months, 3 months, 7 months, 9 months and 13 months and analysed using TD-GC-FID. The GC was calibrated with tubes sampled from freshly prepared dynamic standard gas mixtures.

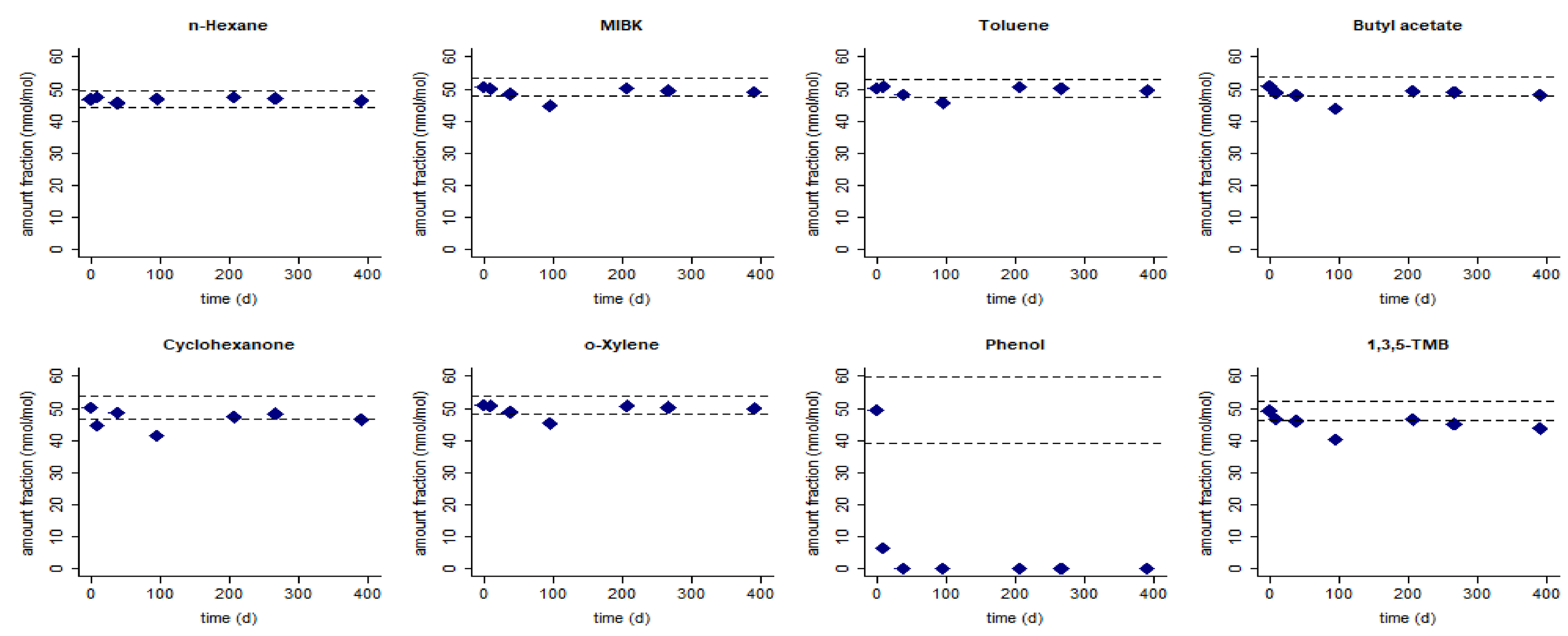


Figure 3: Graphical representation of the stability results for the VOCs in the gPRM. First point in the graph is the gravimetric amount fraction (nmol mol^{-1}). The other points are the calculated amount fractions based on the measurements. The doted lines indicate the expanded uncertainty determined for the VOC in the gPRM.

VOC	Treatment 1		Treatment 2	
	Initial loss	Long Term Instability	Initial loss	Long Term Instability
n-Hexane	Yes	No	No	No
MIBK	Yes	No	Yes	No
Toluene	Yes	No	Yes	No
Butyl acetate	Yes	No	Yes	No
Cyclohexanone	Yes	No	Yes	Yes
o-Xylene	Yes	No	Yes	No
1,3,5-TMB	Yes	No	Yes	No

Table 2: Stability results for the VOCs in gPRMs comparing the two cylinder treatments used.

Conclusions

After preparation, of the gPRMs and dynamic standard gas mixtures, both gas mixtures can be sampled onto sorbent tubes to obtain gCRMs. It is not possible to prepare gas mixtures with phenol in high pressure cylinders. Fortunately, it is possible to prepare dynamic standard gas mixtures with phenol.

The sorbent tubes can be used to calibrate a GC for the determination of these VOC in indoor air. Another project partner (VITO) determined the VOCs in the tubes/gCRMs are stable for a period of 28 days and can be stored at room temperature.

The uncertainty budget for the reference materials have been determined. For dynamically prepared standard gas mixtures a relative expanded uncertainty of 5% has been obtained. For gPRMs, gas mixtures in cylinders, relative expanded uncertainties are between 6% - 20%. As both the static and dynamic standard gas mixtures are analysed by sampling the gas mixtures onto sorbent tubes to obtain the gCRM the uncertainty of the gPRM and gCRM are the same. Sampling of the sorbent tubes does not increase the uncertainty as the uncertainty contribution is small.

The stability of the gPRM has been determined over a period of 1 year. Initial loss is found for all the VOCs, except for n-hexane in cylinder treatment 2. After the initial loss, the fraction of the VOCs is stable over a period of 1 year within the expanded uncertainty in both cylinder types tested, except for cyclohexanone in cylinder treatment 2.

Future Perspectives

During the remainder of the MetrIAQ project another cylinder treatment will be tested to improve the stability of the gPRMs.

Currently, an interlaboratory comparison (ILC) is ongoing to determine the capabilities of project partners and stakeholders for the analysis of these VOCs from TD tubes.

Based on the ongoing stability study and ILC the uncertainty budgets will be improved including a contribution for the initial loss.

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Full report