20NRM04 MetrIAQ

D3: Guideline for the preparation and analysis of gPRMs and gCRMs of indoor air pollutants stated in the EU-LCI list with relative uncertainties below 5 % ($k = 2$) and a shelf life of at least 1 year

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Summary

This is a guideline for the preparation and analysis of gaseous primary reference materials (gPRMs) and gaseous certified reference materials (gCRMs) developed in the European Metrology Programme for Innovation and Research (EMPIR) project Metrology for the determination of emissions of dangerous substances from building materials into indoor air (20NRM04 MetrIAQ). The gPRMs and gCRMs contain indoor air pollutants or volatile organic compounds (VOCs) stated in the EU-LCI list (n-hexane, methyl isobutyl ketone, toluene, butyl acetate, cyclohexanone, o-xylene, phenol, 1,3,5-trimethylbenzene). The aim of the project is to obtain reference materials with a relative expanded uncertainty below 5 % (k = 2) and a shelf life of at least 1 year. 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.

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1 Introduction

In industrialised countries more than 80% of the time is spent indoors. Products, such as building materials and furniture, emit volatile organic compounds (VOCs), which are therefore ubiquitous in indoor air [1-7]. Different VOC combinations may, under certain environmental and occupational conditions, result in reported sensory irritation and health complaints. A healthy indoor environment can be achieved by controlling the sources and by eliminating or limiting the release of harmful substances into the air. One way is to use materials proven to be low emitting. Meanwhile, a worldwide network of professional commercial and non-commercial laboratories performing emission tests for the evaluation of products for interior use has been established. Therefore, comparability and metrological traceability of test results must be ensured. A laboratory's proficiency can be proven by internal and external validation measures that both include the application of suitable reference materials. The emission test chamber procedure according to EN 16516 comprises several steps from sample preparation to sampling of test chamber air and chromatographic analysis [8]. Quality assurance and quality control (QA/QC) must therefore be ensured. Currently, there is a lack of suitable reference products containing components relevant for the health-related evaluation of building products.

The European Metrology Programme for Innovation and Research (EMPIR) project Metrology for the determination of emissions of dangerous substances from building materials into indoor air (20NRM04 MetrIAQ) aims to develop 1) gaseous primary reference materials (gPRM) and certification of gaseous (certified) reference materials (gCRM) and 2) emission reference materials (ERM).

This guideline describes the production, sampling, analysis, handling, storage and stability and uncertainty of gPRM and gCRM relevant for indoor air pollutants. The gPRM and gCRM described are gas-phase standards containing trace levels of VOCs in nitrogen or air. The selected VOCs (n-hexane, methyl isobutyl ketone, toluene, butyl acetate, cyclohexanone, o-xylene, phenol, 1,3,5-trimethylbenzene) are chosen based on the check standard described by EN 16516. The target expanded uncertainty is 5 % for the VOCs in the gPRM and gCRM. The gPRM and gCRM can be sampled into sorbent tubes to obtain gCRM for quality assurance and quality control. Static and dynamic gPRMs and gCRMs in sorbent tubes have been developed by the national metrology institute Van Swinden Laboratory (VSL) and gCRMs, dynamic and in sorbent tubes, have been developed by Vlaamse Instelling voor Technologisch Onderzoek N.V. (VITO) and VSL.

2 Materials

2.1 VOCs

The gPRM and gCRM are prepared from pure VOCs. The VOCs were selected based on the check material from paragraph 8.2.2.3 in EN16516 which describes the checks on analytical system performance [8]. The analytical performance can be

evaluated using a check material. The check material is a chromatographic test mix containing VOCs that are representative of the range of compounds of interest for indoor air quality. The EN 16516 check material contains at least *n*-hexane (CAS No. 110-54-3), Methyl Iso Butyl Ketone (MIBK, CAS No. 108-10-1), toluene (CAS No. 108-88-3), butyl acetate (CAS No. 123-86-4), cyclohexanone (CAS No. 110-82-7), o-xylene (CAS No. 95-47-6), phenol (CAS No. 143-74-8), 1,2,3-trimethylbenzene (1,2,3-TMB, 526-73-8) and *n*-hexadecane (CAS No. 544-76-3) [8]. The composition of the check material is adjusted, 1,2,3-trimethylbenzene is replaced by 1,3,5-trimethylbenzene (1,3,5-TMB, CAS No. 108-67-8) and *n*-hexadecane is not used (Table 1 and 2). It is difficult to purchase or obtain 1,2,3-TMB with a purity above 90 %. This has consequences for the reference material production and the measurements performed with the reference materials. If you do not take into account the purity of your starting materials you have a bias in the analytical measurement result. Furthermore, when using the analytical column (5 % phenyl / 95 % methyl polysiloxane capillary column) recommend by EN 16516 [8], 1,3,5-TMB coelutes with phenol. One of the impurities in 1,2,3-TMB is 1,3,5-TMB, so the phenol peak in your chromatogram would partly consist of 1,3,5-TMB which also gives a bias in the analytical measurement result. When you work with high purity starting materials this bias will be much smaller. The 1,3,5-TMB isomer can be purchased with high purity ≥ 98 %. VOC *n*-hexadecane is omitted from the gPRM and gCRM as this compound, with a boiling point of 287 °C and vapour pressure of 0.0025 kPa, cannot be produced as a gas mixture in a cylinder.

Table 1: VOCs used at VSL for production of the gPRM and gCRM

VOC	Supplier	Purity (%)
n-hexane	Fluke	99.90
MIBK	Sigma Aldrich	99.96
Toluene	TCI Europe	99.50
Butyl acetate	TCI Europe	99.00
Cyclohexanone	Fluke	99.60
o-Xylene	TCI Europe	99.00
Phenol	Sigma Aldrich	99.60
1,3,5-TMB	TCI Europe	99.50

Table 2: VOCs used at VITO for production of the gCRM

VOC	Supplier	Purity (%)
n-hexane	Thermo Scientific	99
MIBK	TCI Europe	99.5
Toluene	Honeywell Chemicals	99.9
Butyl acetate	Thermo Scientific	99.5
Cyclohexanone	Thermo Scientific	99

o-Xylene	Thermo Scientific	99
Phenol	Thermo Scientific	99.5
1,3,5-TMB	Thermo Scientific	99

2.2 Gases

2.2.1 Gases at VSL

For the static gPRM pure nitrogen (Air Products, 6.0) is used as matrix gas. The pure nitrogen has been checked for impurities in accordance with ISO 19229 [9].

For the preparation of the dynamic gPRM and gCRM, nitrogen and dry clean air are used. Nitrogen from the liquid nitrogen supply is additionally purified using an AeroNex inert gas purifier (Merck, NL) to remove water, CO_2, O_2, CO, volatile acids, bases and organics. Dry clean air is produced with a central pressurized air system (Umwelttechnik MCZ, Germany). The system purifies air through a series of filters for the removal of particles > 0.01 µm and oil vapor up to a level of ca. 5 nmol mol^{-1} and additional purification through a molecular sieve dryer and a catalytic purification unit.

2.3 Cylinders

The static gPRMs are produced in cylinders. The cylinders are 5 litre aluminium high pressure gas cylinders with a special passivation. During this project two types of passivations have been tested: 1) Spectra Seal and 2) Experis NO.

2.4 Sorbent tubes

The VOCs in the gPRM and gCRM can be sampled into sorbent materials in thermal desorption tubes. During this project two sorbent materials have been tested: 1) Tenax TA® (TTA) and 2) Materials Emissions/Soil Gas Monitoring (ME). The ME sorbent tube contains a triple bed sorbent materials with a weak, medium and strong sorbent material. Both sorbent materials are contained in SilcoNert® coated stainless steel tubes (Markes International, United Kingdom). The breakthrough and desorption efficiency of both sorbent tubes was determined (Annex 2).

3 Methods

3.1 Production gPRM

3.1.1 Static gas mixtures

Preparation of calibration gas mixtures in high pressure cylinders for the development of gPRMs is performed mostly by static gravimetry. By determination of the mass added for each component with a calibrated balance SI-traceable values for the amount fractions of the components in the gas mixture are calculated. This method is well covered in an international standard (ISO 6142-1

[10]). All cylinders used were flushed using nitrogen (6 x 15 bar and 2 hours vacuum). Then the cylinders were evacuated overnight using a high vacuum turbo pump ($p \approx 2$ x 10^{-7} mbar). Next a metrologically traceable solution with the VOCs (Table 1) was prepared, with a nominal fraction of 0.125 mol mol^{-1} for each VOC. Phenol, which is a solid at room temperature, dissolved immediately upon addition of the other VOCs. The VOC solution was then injected using a syringe into a cylinder, then vaporized and diluted with nitrogen, to obtain mother mixtures, with a nominal fraction of 10 µmol mol^{-1} for each VOC. Both the syringe and the cylinder were weighed before and after injection of the VOC solution to determine the exact mass transferred into the cylinder and calculate the amount-of-substance fractions of the VOCs [11].

The mother mixture was diluted with nitrogen in two steps to obtain the final mixtures. The mother mixture was diluted 10 times with nitrogen to obtain 2 mixtures, with a nominal fraction of 1 µmol mol^{-1} for each VOC. These 2 mixtures have been diluted 20 times with nitrogen to obtain 4 end mixtures, with a nominal fraction of 50 nmol mol^{-1} for each VOC, 2 mixtures in cylinders with the Spectra Seal treatment and 2 mixtures in cylinders with the Experis NO treatment. All gas mixture preparations were performed while heating the cylinder valves with a heat source set to approximately 60 °C. All cylinders were weighed before, after injection of the mother mixture and after injection of the nitrogen. After preparation, each mixture was homogenized for 2 hours. The composition of the gas mixtures was calculated according to ISO 6142-1 based on the weighing data obtained [11]. The composition and uncertainty of the gas mixtures prepared for this project can be found in Annex 1.1.

Analysis of all gPRMs after two weeks showed a decrease in phenol fraction of 80 % or more (Annex 3). Analysis after one month and thereafter showed no response for phenol (Annex 5). Based on these results it can be concluded it is not possible to make gas mixtures with phenol in high pressure cylinders.

3.1.2 VSL dynamic gas mixtures

Another route for the preparation of gPRMs is using a dynamic gas mixture preparation system working according to the continuous syringe injection method (ISO 6145-4) [12]. This method consists of a continuous accurate injection of VOC vapours into a complementary gas stream by means of a syringe. The dynamic system at VSL is developed for the preparation of dynamic gas mixtures of VOC in air at trace levels in the range between 10 nmol mol^{-1} and 1000 nmol mol^{-1}. A metrologically traceable solution of the VOCs was prepared. After preparation, the vial (4.5 mL volume) containing the solution is placed on an analytical balance (AT201, Mettler Toledo, Switzerland) operating in the range 0 g – 201 g and with 0.01 mg resolution. Through a septum in the cap of the vial, a capillary tube (deactivated fused silica column 100 µm, Agilent Technologies, United States) is immersed into the solution. The solution is forced through the capillary tube by a stream of nitrogen that is laterally introduced and finely controlled by a pressure controller (GE / Druck PACE5000). By regular weighing the vial with the solution

on the balance, a known accurate mass flow through the capillary in time is obtained. The weighing is performed automatically (Mettler Toledo Balance Link interface tool). The average mass flow (mg min^{-1}) for continuous injection of the solution is given by equation (1).

$$\overline{q_m} = \frac{\Delta m}{\Delta t} \tag{1}$$

where:
$\overline{q_m}$: Mass flow of the solution (mg min^{-1})
Δm: mass difference between start and end of the experiment (mg)
Δt: time difference between start and end of the experiment (min)

The solution flows through the capillary tube into a vaporiser (Elycra oven, Electrowarmte B.V, Netherlands). The vaporiser is heated at 125.0 ± 0.1 °C to ensure evaporation of the solution. A stream of nitrogen (0.2 – 2 L min^{-1}) helps complete vaporisation of the solution. The nitrogen flow is known and controlled by a Thermal Mass Flow Controller (MFC) (Bronkhorst, Netherlands). Subsequently, the vapours are further diluted with an accurately measured flow of dry clean air, controlled by a second MFC (Bronkhorst, Netherlands) operating in the range 2 – 20 L min^{-1}. This is the stage 1 gas mixture, this mixture is further diluted in a second stage (stage 2). This dilution is obtained using a glass venturi (Technoglass, Netherlands). A part of the stage 1 gas mixture is drawn into the venturi and diluted approximately 10 times with air to obtain the final VOC in air gas mixtures. The different nitrogen and air flows are calibrated with primary flow meters and corrected to standard conditions (101.315 kPa and 293.15 K). The obtained gas mixture flows through a glass system (Technoglass, Netherlands). The VOC mole fractions obtained with this dynamic system are computed from first principle (mass flow, gravimetry and volumetry in this instance [12]), thereby having the characteristics of a primary method of measurement [13-16]. The mole fraction can be calculated according to equation (2). An example of a dynamic gas mixture prepared can be found in Annex 1.2.

$$x_i = x_{i(S)} \frac{\overline{q_m}}{q_{v(n_2+air)}} \frac{q_{v(stage\,1)}}{q_{v(stage\,1)}+q_{v(air)}} \frac{V_m}{M_i} 1,000,000 \tag{2}$$

where:
x_i: Fraction of VOC i in the gas-phase standard (nmol mol^{-1})
$x_{i(S)}$: Mass fraction of VOC i in the solution (g g^{-1})
$q_{v(n_2+air)}$: Flow of nitrogen and air at standard conditions (L min^{-1})
$q_{v(stage1)}$: Flow from stage 1 gas mixture at standard conditions (L min^{-1})
$q_{v(air)}$: Flow of air added to the stage 1 gas mixture at standard conditions (L min^{-1})
V_m: Molar volume (24.0551 L mol^{-1}) at standard conditions
M_i: Molar mass VOC i (g mol^{-1})

3.2 Production gCRM

3.2.1 VSL sorbent tube sampling

At VSL gCRM are prepared via pumped sampling of known volumes from the static and dynamic gPRMs into sorbent tubes according to ISO 16017-1 [17]. This is obtained by means of a specially designed multi-sampling manifold, made up of 12 MFC (Bronkhorst, Netherlands) operating in sucking mode. Each MFC is connected to a 3-way valve. All valves are controlled with a timer, that allows them to switch simultaneously. The sampling flow (50 mL min^{-1}) is accurately calibrated and the sampling is carried out under controlled environmental conditions by taking care that the VOC safe sampling volumes are not exceeded. Transfer standards with accurately known masses between 10 ng and 1000 ng per VOC can be obtained. The mass sampled into the sorbent tubes can be calculated according to equation (3) for dynamic gPRM and equation (4) for static gPRM.

$$m_i = x_{i(S)} \frac{\overline{q_m}}{q_{v(n_2+air)}} \frac{q_{v(stage\,1)}}{q_{v(stage\,1)}+q_{v(air)}} q_{v(sample)}\, t\, 1{,}000{,}000 \tag{3}$$

where:
m_i: Mass VOC i sampled onto the sorbent tube (ng)
$q_{v(sample)}$: Pumped sampling flow at standard conditions (mL min^{-1})
t: Sampling time (min)

$$m_i = x_i \frac{M_i}{V_m} \frac{q_{v(sample)}\, t}{1{,}000} \tag{4}$$

The static gPRM was sampled from the cylinder. To ensure a controlled gas flow the cylinder was equipped with a reducer and an MFC. The 4 end mixtures in cylinders with a nominal fraction of 50 nmol mol^{-1} for each VOC and the dynamic gPRM were sampled directly.

The nominal mass sampled into the tubes was 125 ng per VOC, an example with exact masses can be found in Annex 1.3.

The sampled tubes were used to: 1) develop and validate the VSL analytical method (Annex 2), 2) compare the static and dynamic gas mixture preparation method at VSL (Annex 3) and 3) for the stability study of the gPRM (Annex 5).

3.2.2 VITO dynamic gas mixture preparation

The dynamic generation of gaseous VOCs at indoor air level concentrations (and at occupational hygiene levels) in a carrier gas throughout a glass distribution line is achieved by fluid injection through a capillary according to ISO 6145-4 [12]. The fluid, a metrologically traceable solution of the VOCs, is thermally heated, evaporated and injected dynamically into the carrier gas stream.

The main components of the capillary dosage unit are the capillary (glass or a deactivated fused silica column), a pressure reducer and a stainless-steel housing. A pressure difference between both ends of the capillary forces the liquid through it. At the upper end of the capillary, the fluid is flash-heated and evaporated. The

resulting vapour is dynamically injected into a primary flow of mass flow controlled nitrogen. This flow enters at the low pressure side of the capillary and transports the evaporated mixture to a Mass Flow Controller to take an aliquot and transfer it into the nitrogen carrier gas stream in the distribution line. The reservoir containing the liquid is placed on analytical balance which allows a continuous measurement of liquid consumption at any time during its injection process. Furthermore, the stability of the generated gas mixture is measured by an online GC-FID system equipped with an injection loop and total hydrocarbon analyser.

The technique of capillary dosage is theoretically based on Poiseuille's equation which allows the calculation of a laminar flow through a cylindrical tube with radius *r*. For a pressure difference *Δp* over a length *l* , the fluid flow is calculated according to equation (5).

$$Qv = \Delta p \Pi r^4 / 8Nl \tag{5}$$

where:

Δp: pressure drop across a cylindrical tube (N m^{-2})
R: internal tube radius (m)
L: the tube length (m)
N: the dynamic viscosity (kg ms^{-1})
Qv: the fluid flow (m³ s^{-1}).

Air concentrations (μg m^{-3}) are calculated using the weight loss of the mixture in the reservoir (μg min^{-1}) and the different mass flow controlled nitrogen flows (m³ min^{-1}), which are all calibrated with primary flow meters and corrected to standard conditions (101.315 kPa and 293.15 K). The total gas concentration of the mixture is recalculated to the individual VOCs by using the weight ratios of each VOC in the mixture.

3.2.3   VITO sorbent tubes sampling

The gCRMs at VITO are prepared via pumped sampling of known volumes of the gas mixture created by the capillary dosage in the glass distribution line. Based on the VSL infrastructure, a sampling manifold with 6 MFC (Bronkhorst, Netherlands) in sucking mode was developed. The MFCs are connected to a vacuum pump at the back side and equipped with a 3-way valve at the front side to be able to switch between lab air and the distribution line. For TTA tubes, sampling flows of 100 mL min^{-1} are used with a sampling period of 10 minutes. Each MFC is calibrated, and with knowledge of the sampling flow, the sampling duration, current environmental conditions (pressure and temperature) and the individual VOC concentrations in the sampled gas mixture the amounts of each VOC which is adsorbed into the TTA tube can be calculated.

3.3 Analysis method

3.3.1 VSL

The sorbent tubes/gCRMs are analysed using a Gas Chromatograph (GC) (Agilent technologies 7820A) coupled with a flame ionization detector (FID) and equipped with a thermal desorber (TD, TD650, Perkin Elmer) with a two stages desorption. In the first stage, the sorbent tube is heated, and the desorbed VOC components are transferred and concentrated into a cold trap cooled at -30 °C. The temperature used for the sorbent tube desorption is 250 °C for 5 min. In the second stage, the cold trap, packed with ME, is quickly heated so the compounds are released and sent to the gas chromatographic column where they are separated. The GC column is a DB-1, 30 m long, 0.32 mm internal diameter, 1.00 µm film thickness (Agilent). The initial GC oven temperature is 30 °C (hold 3 min). The oven temperature is then raised with two ramp rates: to 125 °C at 30 °C min^{-1} with a hold time of 3 minutes, to 225 °C at 30 °C min^{-1} (Figure 1). Results for validation of the method can be found in Annex 2.1.
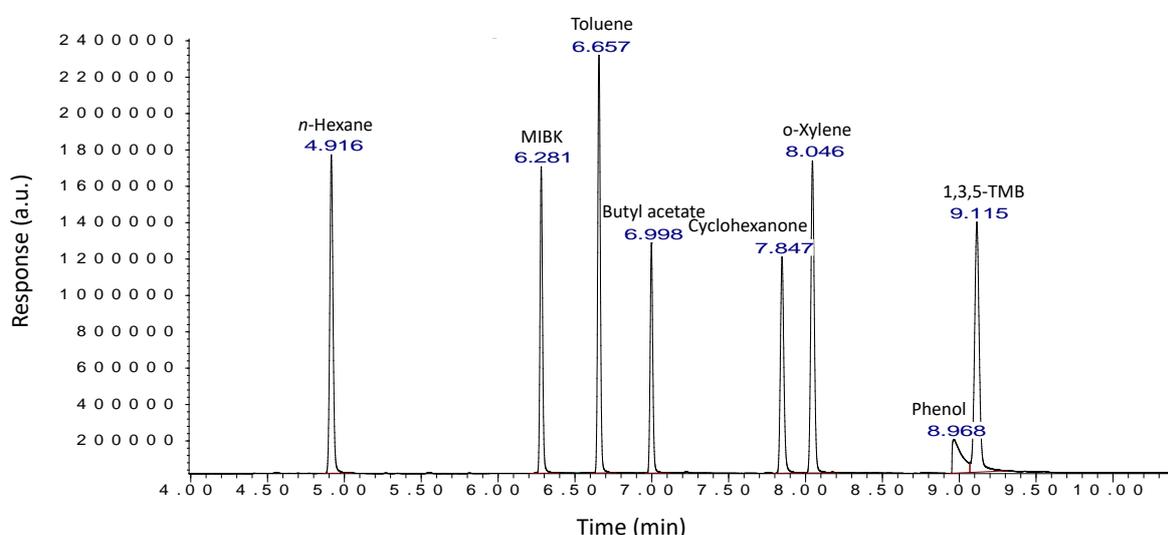
Figure 1: Chromatogram obtained with TD-GC-FID from a sorbent tube with a nominal mass of 125 ng for each VOC.

3.3.2 VITO

At VITO, the TTA sorbent tubes are analysed with a GC-MS instrument. The tubes are loaded into the TD-100 autosampler (Markes) where they are desorbed at 300 °C for 10 minutes. The released VOCs are transferred to a GPH cold trap (general purpose hydrophobic, Markes) where the compounds are trapped at 10°C. After this, the cold trap is quickly heated up to 300°C for 5 minutes and the VOCs are transferred to the GC (Trace GC Ultra, Thermo Scientific) column (Rxi-5 Sil MS, 60 m, 0.25 mm ID, d_f = 1.0 µm; Restek) where they are separated. The initial oven temperature is 50°C (hold 5 min), then raised with 9 °C/min up to 275 °C (hold 2 min) leading to a chromatogram of 32 minutes. The VOCs are detected and

quantified using an MS (DSQ II, Thermo Scientific) with a seven point external calibration curve.

4 Uncertainty VSL gPRM and gCRM

The uncertainty of the VSL dynamic and static gPRM and gCRM is determined using the law of propagation of uncertainty of the Guide to the expression of Uncertainty in Measurement (GUM) [19].

The VOCs in the dynamic gPRM have a relative expanded uncertainty of 5 % (Table A4.1, Annex 4).

Uncertainty sources that need to be considered for the static gPRM are:

- Uncertainty for the preparation of the gPRM and sampling into sorbent tubes for the analysis (u_{prep}, Annex 4). The standard uncertainty of the VOC fractions in the static gas mixtures are calculated according to ISO 6142-1 [10] giving a relative standard uncertainty of 0.015 %. Sampling of the static gas mixture into sorbent tubes gives a relative standard uncertainty of 0.5 % (Table A4.3, Annex 4).
- Calibration of the measurement method with the dynamic gas mixtures sampled into tubes (u_{cal}, Annex 4). Sampling of VOCs from the dynamic gas mixtures give a relative standard uncertainty of 2.5 % (Table A4.2, Annex 4).
- Measurement uncertainty for the verification (u_{meas}, Annex 2.1). When using the ME sorbent tubes relative standard uncertainties between 1.1 % and 10 % are assigned based on the VOC (Table A2.1, Annex 2).

As both the dynamic and static gPRMs are analysed by sampling the gas mixtures into 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.

Based on these uncertainty sources the uncertainties of the amount fractions of the components in the static gPRM and gCRM have been calculated according to the GUM [19] (Table 3 and Table A4.3, Annex 4).

Table 3: Relative expanded uncertainty (U) for the mass sampled into ME sorbent tubes for each VOC from a static gas mixture ($k = 2$).

VOC	u_{prep} (%)	u_{cal} (%)	u_{meas} (%)	u (%)	U (%)
n-hexane	0.5	2.5	1.2	2.8	6
MIBK	0.5	2.5	1.1	2.8	6
Toluene	0.5	2.5	1.2	2.8	6
Butyl acetate	0.5	2.5	1.6	3.0	6
Cyclohexanone	0.5	2.5	2.5	3.6	7
o-Xylene	0.5	2.5	1.1	2.8	6
Phenol	0.5	2.5	10	10	20
1,3,5-TMB	0.5	2.5	1.5	3.0	6

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

5 Handling, storage and stability of the reference materials

5.1 Handling, storage and stability of the static gPRM

The high-pressure cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous material. Do not use the cylinder in case the pressure of the gas mixture is below 1 MPa. The gPRMs can be used to validate and/or calibrate analytical methods and equipment. Further instructions regarding the handling of calibration gases can be found in ISO 16664:2017 [18].

The stability of the static gPRMs has been studied over a period of one year. The results can be found in Annex 5. The study showed that it is not possible to prepare gas mixtures in high pressure cylinders with phenol. Based on the slope of the interpolation function it can be concluded that save from cyclohexanone in cylinders with a Spectra Seal treatment all VOCs are stable over a period of 1 year. However, based on the deviation of one or more measurements from the gravimetric value it can be concluded that instability was found for all the VOCs in both cylinder types, save from n-hexane in cylinders with a Spectra Seal treatment. The instability based on the deviation could be caused by initial loss of the VOC during preparation or due to absorption to the cylinder wall. Thereafter the VOC gas mixture is stable in cylinders. During the remainder of the project stability of the mixtures will be further investigated to give a final conclusion in deliverable D6 "Report on the preparation and measurement uncertainty of ERMs, gPRMs and gCRMs". Furthermore, the stability of the gas mixture in cylinders with a different treatment is currently tested.

5.2 Handling, storage and stability gCRM in sorbent tubes

The gCRM in sorbent tubes can be stored capped with stainless steel caps at room temperature for a period of 28 days. The long-term stability is still under investigation for a period of 1 year (Annex 6).

6 Conclusion

The MetrIAQ project consortium prepared gPRMs and gCRMs with the selected VOCs. Preparation of static gas mixtures with phenol was not possible, during or after preparation phenol decomposes, precipitates as a solid and/or absorbs to the

cylinder wall. Fortunately, it is possible to prepare dynamic gas mixtures with phenol.

After preparation of the static and dynamic gPRMs both gas mixtures can be sampled into sorbent tubes to obtain gCRMs. The ME sorbent tubes give the best analytical results. When using TTA sorbent tubes keep in mind the save sampling volume of *n*-hexane.

The sorbent tubes can be used to calibrate a GC for the determination of these VOC in indoor air. 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 gPRM has been determined, and relative expanded uncertainties of 5 % have been obtained for gPRMs prepared dynamically. Static gPRMs, in cylinders, have relative expanded uncertainties between 6 % - 20 %. As both the static and dynamic gPRMs are analysed by sampling the gas mixtures into sorbent tubes to obtain the gCRM the uncertainty of the gPRM and gCRM are the same.

The stability of the static gPRM has been determined over a period of 1 year. Instability is found for all the VOCs over a period of 1 year within the expanded uncertainty in both cylinder types tested, save from n-hexane in cylinders with a Spectra Seal treatment. Further research is performed during the remainder of the MetrIAQ project to improve the stability of the static gPRMs.

Annex 1 Results gPRM and gCRM production

A1.1 Static gas mixtures

All the static gas mixtures, mother mixture, dilutions and end mixtures, were prepared in March and April 2022 (Table A1.1).

Table A1.1: The final gravimetric VOC composition of the static gPRMs prepared expressed in amount fractions

Mixture	VOC solution	Mother mixture	Dilution 1	Dilution 2
Number	LM0130	VSL361175	VSL114005	VSL114043
Cylinder type	Glass vial	Experis NO	Experis NO	Experis NO
Fraction (standard uncertainty (k = 1))				
	cmol mol^{-1}	µmol mol^{-1}	µmol mol^{-1}	µmol mol^{-1}
n-hexane	11.7431 (0.0007)	9.3367 (0.0012)	0.93217 (0.00012)	0.93373 (0.00012)
MIBK	12.7124 (0.0008)	10.107 (0.0013)	1.0091 (0.00013)	1.0108 (0.00013)
Toluene	12.6018 (0.0009)	10.019 (0.0013)	1.0003 (0.00013)	1.0020 (0.00013)
Butyl acetate	12.7571 (0.0007)	10.143 (0.0013)	1.0127 (0.00013)	1.0143 (0.00013)
Cyclohexanone	12.6121 (0.0007)	10.028 (0.0013)	1.0011 (0.00013)	1.0028 (0.00013)
o-Xylene	12.7876 (0.0009)	10.167 (0.0013)	1.0151 (0.00013)	1.0168 (0.00013)
Phenol	12.4069 (0.0007)	9.8644 (0.0012)	0.98486 (0.00012)	0.98650 (0.00013)
1,3,5-TMB	12.3480 (0.0008)	9.8176 (0.0012)	0.98019 (0.00012)	0.98182 (0.00013)
Mixture	End mixture 1	End mixture 2	End mixture 3	End mixture 4
Number	VSL114044	VSL114045	VSL187546	VSL187555
Cylinder type	Experis NO	Experis NO	Spectra Seal	Spectra Seal
Fraction (standard uncertainty (k = 2))				
	nmol mol^{-1}	nmol mol^{-1}	nmol mol^{-1}	nmol mol^{-1}
n-hexane	46.308 (0.006)	46.813 (0.006)	46.569 (0.006)	46.627 (0.006)
MIBK	50.131 (0.007)	50.677 (0.007)	50.412 (0.007)	50.476 (0.007)
Toluene	49.694 (0.007)	50.236 (0.007)	49.974 (0.007)	50.036 (0.007)
Butyl acetate	50.307 (0.006)	50.855 (0.006)	50.590 (0.007)	50.653 (0.006)
Cyclohexanone	49.735 (0.006)	50.277 (0.006)	50.015 (0.007)	50.077 (0.006)
o-Xylene	50.427 (0.007)	50.976 (0.007)	50.710 (0.007)	50.774 (0.007)
Phenol	48.926 (0.006)	49.459 (0.006)	49.201 (0.006)	49.262 (0.006)
1,3,5-TMB	48.694 (0.006)	49.224 (0.006)	48.967 (0.007)	49.029 (0.006)

A1.2 VSL dynamic gas mixtures

For preparation of the dynamic gas mixture a fresh VOC solution was prepared (Table A1.2.). The VOC solution was forced through the capillary with a mass flow of 1.335 mg min^{-1}. After evaporation in the vaporiser the vapours are mixed with a total flow (nitrogen and air) of 11.804 L min^{-1} to obtain the stage 1 gas mixture. From the stage 1 gas mixture 0.100 L min^{-1} is taken by the venturi and mixed with 9.728 L min^{-1} to obtain the final gas mixture with a nominal fraction of 43.1 nmol mol^{-1} for each VOC (Table A1.2).

Table A1.2: The mass fraction of the VOCs in the VOC solution and the dynamic gas mixture

VOC	Fraction VOC solution (u (k =1)) (g/g)	Fraction gas mixture (U (k = 2)) (nmol mol^{-1})
n-hexane	0.1251 (0.0013)	50.5 (2.5)
MIBK	0.1261 (0.0013)	43.8 (2.2)

Toluene	0.1244 (0.0012)	47.0 (2.4)
Butyl acetate	0.1257 (0.0013)	37.7 (1.9)
Cyclohexanone	0.1219 (0.0012)	43.3 (2.2)
o-Xylene	0.1271 (0.0013)	41.7 (2.1)
Phenol	0.1260 (0.0013)	46.6 (2.3)
1,3,5-TMB	0.1288 (0.0013)	34.4 (1.7)

A1.3 VSL sorbent tube sampling

Sorbent tubes were sampled with the static end mixtures and the dynamic gas mixture. The nominal mass sampled into the tubes was 125 ng per VOC (Table A1.3).

Table A1.3: The VOC mass sampled into the sorbent tubes including the sampling flow rate and sampling time for the dynamic gas mixture and the 4 static end mixtures.

Cylinders	Dynamic gas mixture	VSL114044	VSL114045	VSL187546	VSL187555
$q_{v(sample)}$ (mL min^{-1})	50.17	50.16	50.16	50.16	50.16
t (min)	14.0	12.0	12.0	12.0	12.0
Mass (U (k = 2)) (ng)					
n-hexane	127 (6)	99.9 (1.0)	100.9 (1.0)	100.4 (1.0)	100.5 (1.0)
MIBK	128 (6)	125.6 (1.3)	127.0 (1.3)	126.3 (1.3)	126.5 (1.3)
Toluene	127 (6)	114.6 (1.1)	115.8 (1.2)	115.2 (1.2)	115.4 (1.2)
Butyl acetate	128 (6)	146.2 (1.5)	147.8 (1.5)	147.0 (1.5)	147.2 (1.5)
Cyclohexanone	124 (6)	122.1 (1.2)	123.5 (1.2)	122.8 (1.2)	123.0 (1.2)
o-Xylene	129 (6)	134.0 (1.3)	135.4 (1.4)	134.7 (1.3)	134.9 (1.3)
Phenol	128 (6)	146.4 (1.5)	116.5 (1.2)	115.9 (1.2)	116.0 (1.2)
1,3,5-TMB	121 (6)	115.2 (1.2)	148.0 (1.5)	147.3 (1.5)	147.5 (1.5)

Annex 2: Validation analysis method

A2.1 Validation VSL method

For the validation of the analysis method, 24 TTA and 24 ME tubes were sampled from the dynamic gas mixture. The tubes have been analysed in a period of two weeks on 8 different days. Each day 4 TTA and 4 ME tubes have been analysed. Based on the results the repeatability standard deviation (sr, expressed as coefficient of variation in %) and reproducibility standard deviation (sR, expressed as coefficient of variation in %) were calculated according to ISO 5725-2:2019 using one-way analysis of variance (ANOVA) [20]. The repeatability of the method is the closeness of the agreement between the results of successive individual measurements for each VOC in the sorbent tubes.

The reproducibility for each VOC is the closeness of the agreement between the results obtained on three different days in a two week period (Table A2.1).

Table A2.1: The results of the repeatability standard deviation (sr, expressed as coefficient of variation in %) and reproducibility standard deviation (sR, expressed as coefficient of variation in %) for each VOC. Based on the sr and sR results relative expanded measurements uncertainties can be assigned for each VOC using the different sorbent tubes ($k = 2$).

VOC	TTA sorbent tubes		U (%)	ME sorbent tubes		U (%)
	sr (%)	sR (%)		sr (%)	sR (%)	
n-hexane	1.7	2.6	5	0.6	1.2	2.4
MIBK	1.0	1.3	2.6	0.7	1.1	2.2
Toluene	0.6	1.2	2.4	0.7	1.2	2.4
Butyl acetate	2.0	2.2	4	1.5	1.6	3.2
Cyclohexanone	3.4	3.5	7	2.5	2.5	5
o-Xylene	0.6	1.3	2.6	0.6	1.1	2.2
Phenol	11	15	30	6	10	20
1,3,5-TMB	1.2	1.9	4	0.5	1.5	3.0

A2.1.1 Breakthrough test sorbent tubes

Breakthrough of the VOCs during sampling can occur especially for very volatile VOCs. To determine the breakthrough, two sorbent tubes were placed in series during the sampling of the dynamic gas mixture. On the first tube the VOCs should be adsorbed and the second tube should be empty unless breakthrough occurs. This experiment was performed with 2 x 6 TTA and 2 x 6 ME sorbent tubes. After sampling all tubes were analysed with TD-GC-FID.

When VOCs were detected on the second tube, the relative breakthrough was calculated according to equation 2.1.

$$BT = \frac{A_{tube(2)}}{A_{tube(1)} + A_{tube(2)}}$$ (2.1)

Were:
BT: Relative breakthrough (%)
$A_{tube(x)}$: Peak area (a.u.)

The results show breakthrough only for *n*-hexane on the TTA tubes. A breakthrough of 1.9 % was detected with a standard deviation of 1.6 %. Save from *n*-hexane no other VOC peaks were found during the analysis of the second TTA sorbent tubes and no VOC peaks were found during analysis of the second ME sorbent tubes.

A2.1.2 Desorption efficiency test sorbent tubes

To determine the desorption efficiency, sorbent tubes sampled with VOC were analysed with TD-GC-FID. Directly after analysis, the tubes were analysed for a second time to determine if desorption during the first analysis was complete. This experiment was performed with 6 TTA and 6 ME sorbent tubes.

The relative desorption efficiency was calculated according to equation 2.2.

$$DE = 1 - \frac{A_{analysis(2)}}{A_{analysis(1)} + A_{analysis(2)}}$$ (2.2)

were:
DE: Relative desorption efficiency (%)
A_i: Peak area (a.u.)

The results show full desorption of the tubes with the TD-method we developed. No VOC peaks were found during the second analysis of both the TTA and ME sorbent tubes.

A2.1.3 Conclusion

The analytical method developed is suitable for the analysis of the VOC gas mixtures. The method has a measurement uncertainty < 5 % for the VOCs save from cyclohexanone with has a measurement uncertainty of 7 % when using TTA sorbent tubes and 5 % when using ME sorbent tubes and the measurement uncertainty for phenol is 30 % when using TTA sorbent tubes and 20 % ME sorbent tubes. When using TTA tubes also the 1.9 % breakthrough of hexane needs to be taken into account. Therefore, at VSL we continue to use the ME sorbent tubes for future measurements.

A2.2 Validation VITO method

For the validation of the analysis method, 20 TTA tubes are spiked with a methanolic solution of the compounds. The tubes have been analysed in a period of two weeks on 3 different days, and a fourth day several months later. Each day, 5 TTA tubes have been analysed.

Based on the results the measurement uncertainties were calculated according to ISO 20988:2007 (with reference to the GUM document, Guide to the expression of uncertainty in measurement) considering the bias, the repeatability and the reproducibility of the method.

Table A2.2: The results of expanded measurements uncertainties for each VOC using the TTA tubes (k = 2).

VOC	U (%)
n-hexane	14
MIBK	6
Toluene	6
Butyl acetate	8
Cyclohexanone	10
o-Xylene	7
Phenol	7
1,3,5-TMB	5

To determine the desorption efficiency sorbent tubes sampled with VOC were analysed with TD-GC-MS. Directly after analysis the tubes were analysed for a second time to determine if desorption during the first analysis was complete. This experiment was performed with 10 TTA sorbent tubes.

No VOC peaks higher than a blank tube value (for some VOCs) were found during the second analysis of the TTA tubes.

The results show full desorption of the tubes with the developed TD-method.

Annex 3: Comparison VSL static and dynamic gPRMs

For the verification of the mixture preparation, the static and dynamic gPRMs were compared with each other. Both gas mixtures were sampled into ME tubes. Using the dynamic gas mixture, 6 tubes were sampled and from each of the 4 static end mixtures 4 tubes were sampled. The tubes were sampled 10 or 11 days after preparation of the static gas mixtures. All tubes were analysed directly after sampling with TD-GC-FID. The dynamic gas mixture was used to calibrate the TD-GC-FID and based on the calibration the mass sampled for each VOC from the static end mixtures was calculated according to equation 3.1. The relative deviation for each VOC was determined according to equation 3.2 (Table A3.1 and Figure A3.1).

$$m_{i(verification)} = \frac{m_{i(dynamic)} \, A_{i(static)}}{A_{i(dynamic)}} \qquad (3.1)$$

Where:

$m_{i(verification)}$: mass of VOC i sampled into the sorbent tube from the static gPRM based on the verification (ng)

$m_{i(dynamic)}$: mass of VOC i sampled into the sorbent tube from the dynamic gPRM (ng)

$A_{i(static)}$: peak area of VOC i from the static gPRM

$A_{i(dynamic)}$: peak area of VOC i from the dynamic gPRM

$$D_{rel} = \frac{m_{i(verification)} - m_{i(cylinder)}}{m_{i(cylinder)}}$$

$$(3.2)$$

Where:

D_{rel}: Relative deviation (%)

Table A3.1: Relative deviation between the dynamic and static gPRMs with 50 nmol mol^{-1} fractions of the VOCs.

Cylinders	VSL114044	VSL114045	VSL187546	VSL187555
D_{rel} (%)				
n-hexane	1.9	1.3	1.5	1.6
MIBK	-0.35	-1.3	-4	-1.1
Toluene	1.4	1.0	0.8	1.2
Butyl acetate	-1.8	-4	-8	-2.3
Cyclohexanone	-6	-11	-22	-10
o-Xylene	-0.12	-0.4	-0.9	-0.16
Phenol	-90	-87	-95	-84
1,3,5-TMB	-5	-5	-7	-4
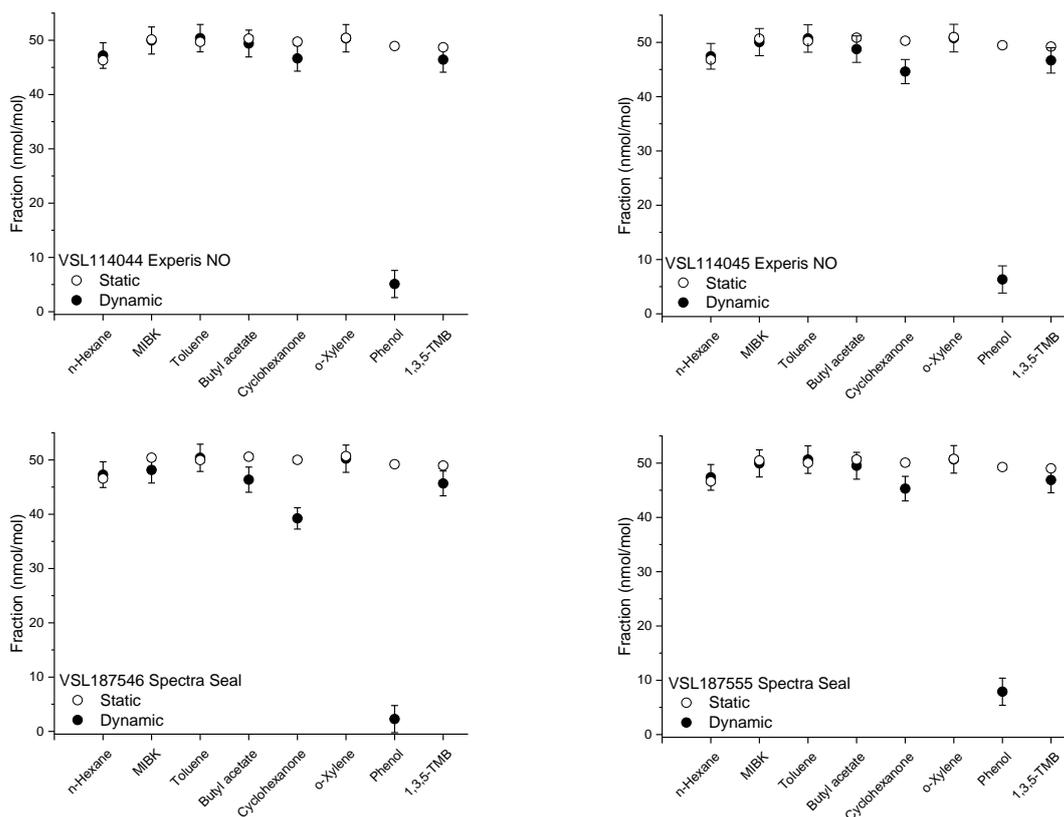
Figure A3.1: Graphic representation of the results from the comparison between the dynamic and static gPRMs. The relative expanded uncertainty of the dynamic gas mixture preparation and sampling into sorbent tubes is 5 % ($k = 2$). The uncertainty for sampling the static gas mixtures into sorbent tubes is 1 % ($k = 2$), the uncertainty bars for the static gPRMs are not visible because they are too small.

For n-Hexane, MIBK, Toluene, Butyl acetate, o-xylene and 1,3,5-TMB, the composition of the dynamic and the static gPRM is comparable. For cyclohexanone, an average deviation of -8 % in the Experis NO cylinders was determined and in the Spectra Seal an average deviation of -16 %. This deviation could be obtained due to condensation during the preparation of the static gas mixtures or due to instability. The stability study of the gas mixtures performed will show if the fraction of cyclohexanone shows instability (Annex 5). The deviation for phenol is larger than 80 % for all four cylinders. Phenol is a solid with high boiling point and low vapour pressure (182 °C and 0.03 kPa). During or after preparation phenol can decompose, precipitate as a solid and/or absorb to the cylinder wall. In theory it should be possible to prepare gas mixtures in cylinders with phenol, as could be shown with the preparation of gas mixtures containing liquids such as decamethylcyclopentasiloxane (siloxane D5) which has a higher boiling point and lower vapour pressure (210 °C and 0.04 kPa) [21, 22].

A stability study was performed to determine the stability of the components in the cylinders (Annex 5).

Annex 4: Uncertainty calculations

Table A4.1: Uncertainty budget for 50.5 nmol mol^{-1} n-Hexane in dynamic gPRM, calculated from equation (2) according to the GUM [19]. The expanded uncertainty in this case is 2.4 nmol mol^{-1} (k = 2), which is equal to a relative expanded uncertainty of 5 %.

Measurand	Value	Distribution	Standard uncertainty	Sensitivity	Uncertainty contribution
$x_{n-Hexane(S)}$	0.1250 g g^{-1}	Normal	0.0013 g g^{-1}	4.04 10^2	5.05 10^{-1} nmol mol^{-1}
$\overline{q_m}$	1.33 10^6 ng min^{-1}	Normal	2.67 10^4 ng min^{-1}	3.79 10^{-5}	1.01 nmol mol^{-1}
$q_{v(n_2+air)}$	11.804 L min^{-1}	Normal	0.058 L min^{-1}	-4.28 ng	0.247 nmol mol^{-1}
$q_{v(stage\,1)}$	0.1002 L min^{-1}	Normal	0.004 L min^{-1}	5.04 10^2	2.04 10^{-1} nmol mol^{-1}
$q_{v(stage\,1)} + q_{v(air)}$	7.828 L min^{-1}	Normal	0.26 L min^{-1}	-6.45	-1.68 10^{-1} nmol mol^{-1}
V_m	24.055 L mol^{-1}	Rectangular	0.024 L mol^{-1}	2.10	5.05 10^{-2} nmol mol^{-1}
M_i	86.175 g mol^{-1}	Normal	0.004 g mol^{-1}	-5.86 10^{-1}	-2.13 10^{-3} nmol mol^{-1}
$m_{n-Hexane}$	**50.5 nmol mol^{-1}**	**Normal**	**1.2 nmol mol^{-1}**		

Table A4.2: Uncertainty budget for 127 ng n-Hexane sampled into a sorbent tube from the dynamic gPRM (u_{cal}), calculated from equation (3) according to the GUM [19]. The expanded uncertainty in this case is 6 ng (k = 2), which is equal to a relative expanded uncertainty of 5 %.

Measurand	Value	Distribution	Standard uncertainty	Sensitivity	Uncertainty contribution
$x_{n-Hexane(S)}$	0.1250 g g^{-1}	Normal	0.0013 g g^{-1}	1.02 10^3	1.27 ng
$\overline{q_m}$	1.33 10^6 ng min^{-1}	Normal	2.67 10^4 ng min^{-1}	9.53 10^{-5}	2.54 ng
$q_{v(n_2+air)}$	11.804 L min^{-1}	Normal	0.058 L min^{-1}	-1.08 10^1	-6.22 10^{-1} ng
$q_{v(stage\,1)}$	0.1002 L min^{-1}	Normal	0.004 L min^{-1}	1.27 10^3	5.13 10^{-1} ng
$q_{v(stage\,1)} + q_{v(air)}$	7.828 L min^{-1}	Normal	0.26 L min^{-1}	-1.62 10^1	-4.22 10^{-1} ng
$q_{v(sample)}$	0.05017 L min^{-1}	Normal	0.00023 L min^{-1}	2.53 10^3	5.90 10^{-1} ng
T	14.000 min	Normal	0.015 min	9.08	1.36 10^{-1} ng
$m_{n-Hexane}$	**127 ng**	**Normal**	**3.0 ng**		

Table A4.3: Uncertainty budget for 99.9 ng n-Hexane sampled into a sorbent tube from a static gPRM (u_{prep}), calculated from equation (4) according to the GUM [19]. The expanded uncertainty in this case is 1.0 ng (k = 2), which is equal to a relative expanded uncertainty of 1.0 %.

Measurand	Value	Distribution	Standard uncertainty	Sensitivity	Uncertainty contribution
$x_{n-Hexane}$	46.308 nmol mol^{-1}	Normal	0.0070 nmol mol^{-1}	2.16	1.51 10^{-2} ng
V_m	24.055 L mol^{-1}	Rectangular	0.024 L mol^{-1}	-4.15	-9.99 10^{-2} ng
M_i	86.175 g mol^{-1}	Normal	0.004 g mol^{-1}	1.16	4.21 10^{-3} ng
$q_{v(sample)}$	0.05016 L min^{-1}	Normal	0.00023 L min^{-1}	1.99 10^3	4.63 10^{-1} ng

T	12.000 min	Normal	0.015 min	8.32	1.25×10^{-1} ng
$m_{n-Hexane}$	**99.9 ng**	**Normal**	**0.5 ng**		

Table A4.4: Uncertainty of n-Hexane in a static gPRM according to the GUM [19]. The relative expanded uncertainty in this case is 6 % (k = 2). Three uncertainty sources are taking into account 1) sampling of the sorbent tube from the static gPRM (u_{prep}, Table A4.3), 2) uncertainty of the calibration standards (u_{cal}, Table A4.2), in this case the dynamic gPRM sampled into sorbent tubes and 3) the measurement uncertainty (u_{meas}, Table A2.1).

Measurand	Value	Distribution	Relative standard uncertainty (%)	Sensitivity
u_{prep}	99.9 ng	Normal	0.5	1
u_{cal}	99.9 ng	Normal	2.5	1
u_{meas}	99.9 ng	Normal	1.2	1
$u_{n-Hexane}$	**99.9 ng**	**Normal**	**2.8**	

Annex 5: Results stability study static gPRM

An important property of reference materials is the stability period. In case of the static 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, the 4 static gPRMs were prepared at t = 0 in high pressure cylinders with two different treatments (Section A1.1 end mixtures). After preparation, the gPRMs were sampled into sorbent tubes at t = 2 weeks, 2 months, 3 months, 7 months, 9 months and 13 months (Section 3.2.1). After sampling, the tubes were analysed using TD-GC-FID. The GC was calibrated with tubes sampled from a dynamic gPRM (Section 3.1.2). The dynamic gPRM was prepared at the same time as the sorbent tubes were sampled from the static gPRMs. From each gPRM 4 tubes were sampled and the peak areas were averaged. Based on the average peak area the actual mass on the tube sampled with the static gPRM was calculated (Equation (A5.1),Table A5.1). Using the sampling time and sampling flow the mole fraction of the VOC in the cylinder at the time of sampling has been calculated backward according to Equation (4).

$$m(gPRM)_i = \frac{m(cal)_i \; \overline{A(gPRM)_i}}{\overline{A(cal)_i}}$$

Eq. (A5.1)

Were:

$m(gPRM)_i$: calculated mass of VOC i in the static gPRM(ng)
$\overline{A(gPRM)_i}$: average peak area of VOC i for the static gPRM
$\overline{A(cal)_i}$: average peak area of VOC i for the calibration

Table A5.1: Results $m(gPRM)_i$ for the 4 gPRMs at the different times, in days, after preparation of the gas mixture.

VSL114044						
Time (days)	11	40	97	208	267	391
n-Hexane	47.18	45.59	49.14	46.94	46.68	45.97
MIBK	49.96	47.57	46.67	49.30	49.04	48.98
Toluene	50.37	48.04	47.99	50.03	49.53	49.08
Butyl acetate	49.39	45.94	45.08	47.44	48.12	48.86
Cyclohexanone	46.64	43.82	40.71	42.66	47.72	47.93
o-Xylene	50.37	48.36	47.59	50.19	49.89	49.52
Phenol	5.11	0.00	0.00	0.00	0.00	0.00
1,3,5-TMB	46.43	43.49	42.10	46.07	44.70	46.37
VSL114045						
Time (days)	10	39	96	207	266	390
n-Hexane	47.43	45.76	46.86	47.43	47.12	46.40
MIBK	50.04	48.32	44.75	50.22	49.58	49.06
Toluene	50.71	48.27	45.74	50.60	50.03	49.55
Butyl acetate	48.74	48.13	43.86	49.27	48.84	48.04
Cyclohexanone	44.62	48.60	41.47	47.25	48.39	46.55
o-Xylene	50.78	48.73	45.34	50.70	50.41	49.99
Phenol	6.34	0.00	0.00	0.00	0.00	0.00
1,3,5-TMB	46.67	46.07	40.32	46.45	45.24	43.67

VSL187546

Time (days)	11	40	97	267	391	
n-Hexane	47.29	46.19	48.51	46.66	46.20	
MIBK	48.15	45.98	44.48	46.71	46.35	
Toluene	50.39	48.19	47.37	49.27	49.15	
Butyl acetate	46.37	44.21	43.03	44.16	43.11	
Cyclohexanone	39.23	36.46	32.29	34.08	30.84	
o-Xylene	50.23	48.40	46.27	49.67	49.17	
Phenol	2.27	0.00	0.00	0.00	0.00	
1,3,5-TMB	45.67	42.88	40.41	43.46	42.78	

VSL187555

Time (days)	10	39	96	266	390	
n-Hexane	47.37	45.40	44.09	46.74	46.17	
MIBK	49.94	47.29	41.28	48.92	48.57	
Toluene	50.64	47.67	42.69	49.47	49.29	
Butyl acetate	49.51	46.37	40.74	48.08	47.22	
Cyclohexanone	45.29	43.84	35.61	46.26	44.02	
o-Xylene	50.69	48.36	42.33	50.17	49.66	
Phenol	7.89	0.00	0.00	0.00	0.00	
1,3,5-TMB	46.88	43.54	37.72	44.77	48.47	

The stability of the gPRMs was evaluated using ordinary least squares regression using a straight line as decay model. This model entertains only first-order effects (i.e., a small change over time of the amount fraction of the component of interest [23,24]). The results of the stability study measurements were fitted as a function of time. The gas mixture was considered stable if the absolute value of the slope was smaller than two times its associated standard uncertainty. Then, it was evaluated whether the analytical results lied within the interval given by the amount fraction obtained from gravimetric gas mixture preparation and the combined uncertainty from preparation and the stability study measurements. If this test was passed, the gas mixture could be value-assigned based on the approach described in ISO 6142-1 [**Fout! Verwijzingsbron niet gevonden.**] (Table A5.2 Figure A5.1 – A5.4). All calculations were performed in R.

Table A5.2: Results of the stability study from the 4 static gPRMs in nmol mol^{-1}. a[0] and a[1] denote the intercept and slope of the straight line, respectively. The mean of the stability study results is denoted by mu, and this result was used to calculate the loss (difference between mu and the value obtained from gravimetry). Stable (a[1]) indicates if the VOCs in the static gPRMs are stable based on the slope of the measurement points. Stable (deviation) indicates if the VOCs are stable in the static gPRMs based on the deviation between the calculated fraction based on measurement results (Table A5.1) and the gravimetric fraction (Table A1.1). If the deviation of one or more measurements is larger than the expanded uncertainty the VOCs are considered not to be stable in the static gPRM.

	a[0]	u(a[0])	a[1]	u(a[1])	mu	u(mu)	loss	u(loss)	Stable (a[1])	Stable (deviation)
VSL114044										
n-Hexane	47.33	0.88	-0.0024	0.0041	46.92	0.51	1.02	1.57	True	False
MIBK	48.25	0.87	0.0020	0.0041	48.59	0.50	-1.88	1.64	True	False
Toluene	49.03	0.73	0.0008	0.0034	49.17	0.41	-0.66	1.58	True	True
Butyl acetate	46.78	1.16	0.0041	0.0054	47.47	0.69	-3.52	1.90	True	False

Cyclohexanone	43.29	1.92	0.0096	0.0089	44.91	1.21	-6.44	2.62	True	False
o-Xylene	48.98	0.78	0.0020	0.0036	49.32	0.45	-1.45	1.60	True	False
Phenol	2.12	1.30	-0.0075	0.0060	0.85	0.85	-46.80	5.21	True	False
1,3,5-TMB	44.08	1.21	0.0046	0.0056	44.86	0.72	-4.61	1.88	True	False
VSL114045										
n-Hexane	46.84	0.48	0.0000	0.0022	46.83	0.27	0.02	1.40	True	True
MIBK	48.12	1.45	0.0032	0.0068	48.66	0.83	-2.56	2.02	True	False
Toluene	48.61	1.34	0.0032	0.0063	49.15	0.77	-1.63	1.95	True	False
Butyl acetate	47.34	1.43	0.0028	0.0067	47.81	0.81	-3.52	2.09	True	False
Cyclohexanone	45.18	1.89	0.0057	0.0088	46.15	1.10	-5.09	2.60	True	False
o-Xylene	48.63	1.47	0.0041	0.0068	49.32	0.85	-2.34	2.04	True	False
Phenol	2.62	1.61	-0.0093	0.0075	1.06	1.06	-46.83	5.35	True	False
1,3,5-TMB	45.18	1.75	-0.0026	0.0082	44.74	0.99	-4.05	2.28	True	False
VSL187546										
n-Hexane	47.37	0.68	-0.0025	0.0031	46.97	0.43	0.80	1.48	True	True
MIBK	46.44	1.02	-0.0006	0.0047	46.33	0.59	-3.97	1.73	True	False
Toluene	48.79	0.88	0.0005	0.0041	48.87	0.51	-1.19	1.66	True	True
Butyl acetate	44.95	0.85	-0.0048	0.0039	44.17	0.60	-5.64	1.74	True	False
Cyclohexanone	37.17	1.61	-0.0161	0.0074	34.58	1.49	-12.85	2.41	False	False
o-Xylene	48.49	1.17	0.0016	0.0054	48.75	0.69	-2.22	1.83	True	False
Phenol	0.98	0.67	-0.0032	0.0031	0.45	0.45	-48.22	5.12	True	False
1,3,5-TMB	43.38	1.43	-0.0021	0.0066	43.04	0.84	-5.59	2.03	True	False
VSL187555										
n-Hexane	45.79	0.97	0.0010	0.0045	45.95	0.57	-0.84	1.63	True	True
MIBK	46.51	2.59	0.0043	0.0120	47.20	1.54	-3.97	2.95	True	False
Toluene	47.29	2.35	0.0041	0.0109	47.95	1.40	-2.74	2.74	True	False
Butyl acetate	45.98	2.57	0.0025	0.0119	46.38	1.50	-4.67	2.98	True	False
Cyclohexanone	42.08	3.19	0.0058	0.0147	43.01	1.90	-7.99	3.65	False	False
o-Xylene	47.44	2.55	0.0050	0.0118	48.24	1.53	-3.33	2.92	True	False
Phenol	3.38	2.32	-0.0112	0.0107	1.58	1.58	-45.88	5.59	True	False
1,3,5-TMB	42.55	2.88	0.0108	0.0133	44.28	1.85	-6.48	3.22	True	False

Two methods have been used to determine if the VOCs are stable in the static gPRMs, 1) if the slope (a[1]) of the interpolation function, based on stability measurements, was smaller than two times its associated standard uncertainty the stability measurements show a horizontal trend and no instability and 2) looking at the deviation between the measured amount fraction and the gravimetric amount fraction of the VOCs in the static gPRMs. The VOCs are not stable in the static gPRM if the deviation of one or more stability measurements is larger than the expanded uncertainty (Table 3). The results for phenol were not processed, as it was evident from visual inspection of the data that the mixtures were unstable with respect to the amount fraction of this component.

In conclusion, based on the slope, save from cyclohexanone in gPRMs VSL187546 and VSL187555 all VOCs in the static gPRMs are stable. These are the gas mixtures in cylinders with a Spectra Seal treatment. Based on the deviation the VOCs are not stable save from n-hexane in the Spectra Seal cylinders. Nevertheless, a few static gPRMs also show stability for toluene, VSL114044 shows stable results for toluene, VSL114045 for n-hexane, VSL187546 for n-hexane and toluene and VSL187555 for n-hexane.

n-Hexane

MIBK

Toluene

Butyl acetate

Cyclohexanone

o-Xylene

Phenol

1,3,5-TMB
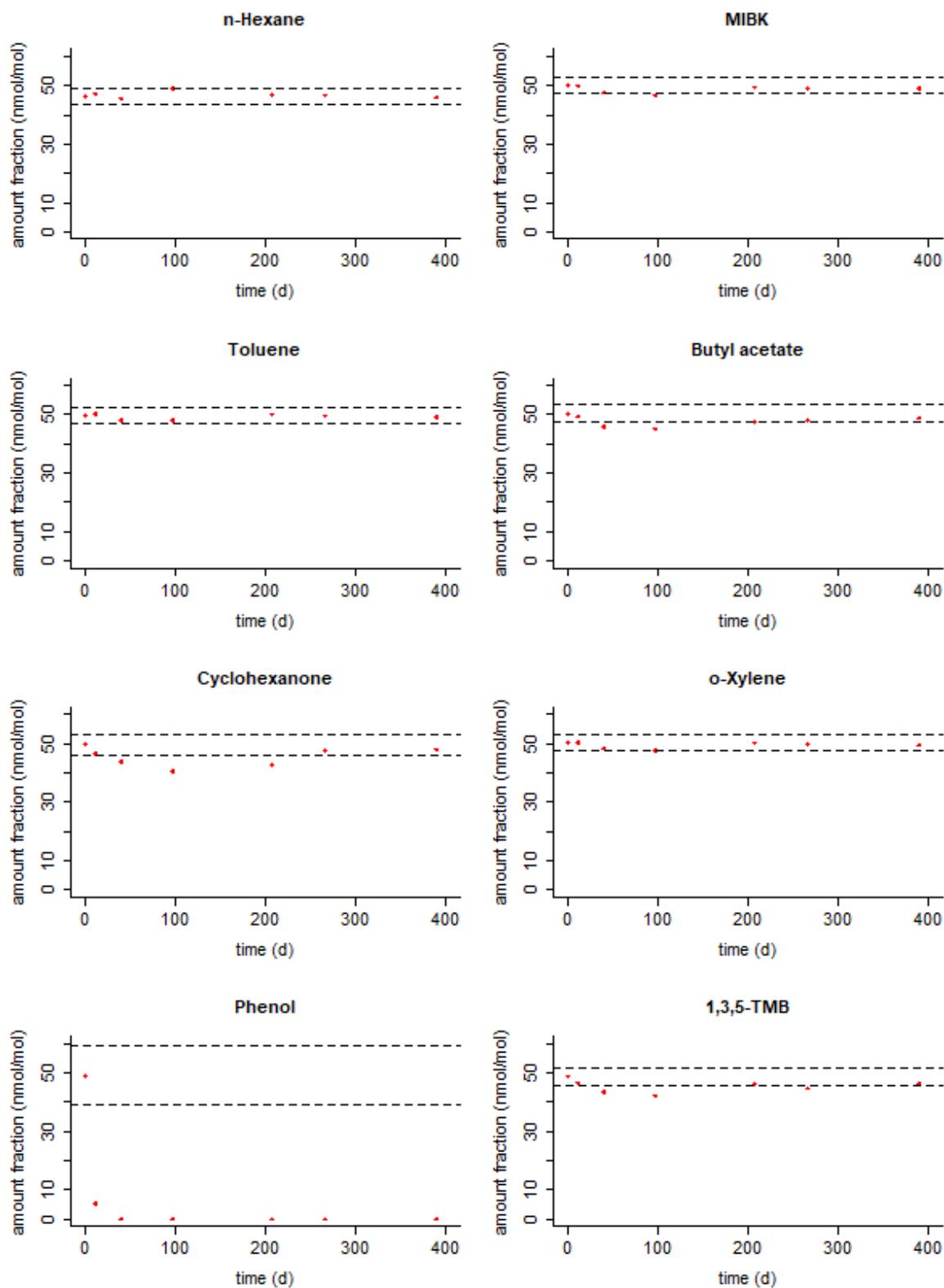
Figure A5.1: Graphic presentation of the stability results for the VOCs in static gPRM VSL114044. First point in the graph is the gravimetric amount fraction. The other points are the calculated amount fractions based on the measurements. The dotted lines indicate the expanded uncertainty determined for the VOC in the static gPRM.
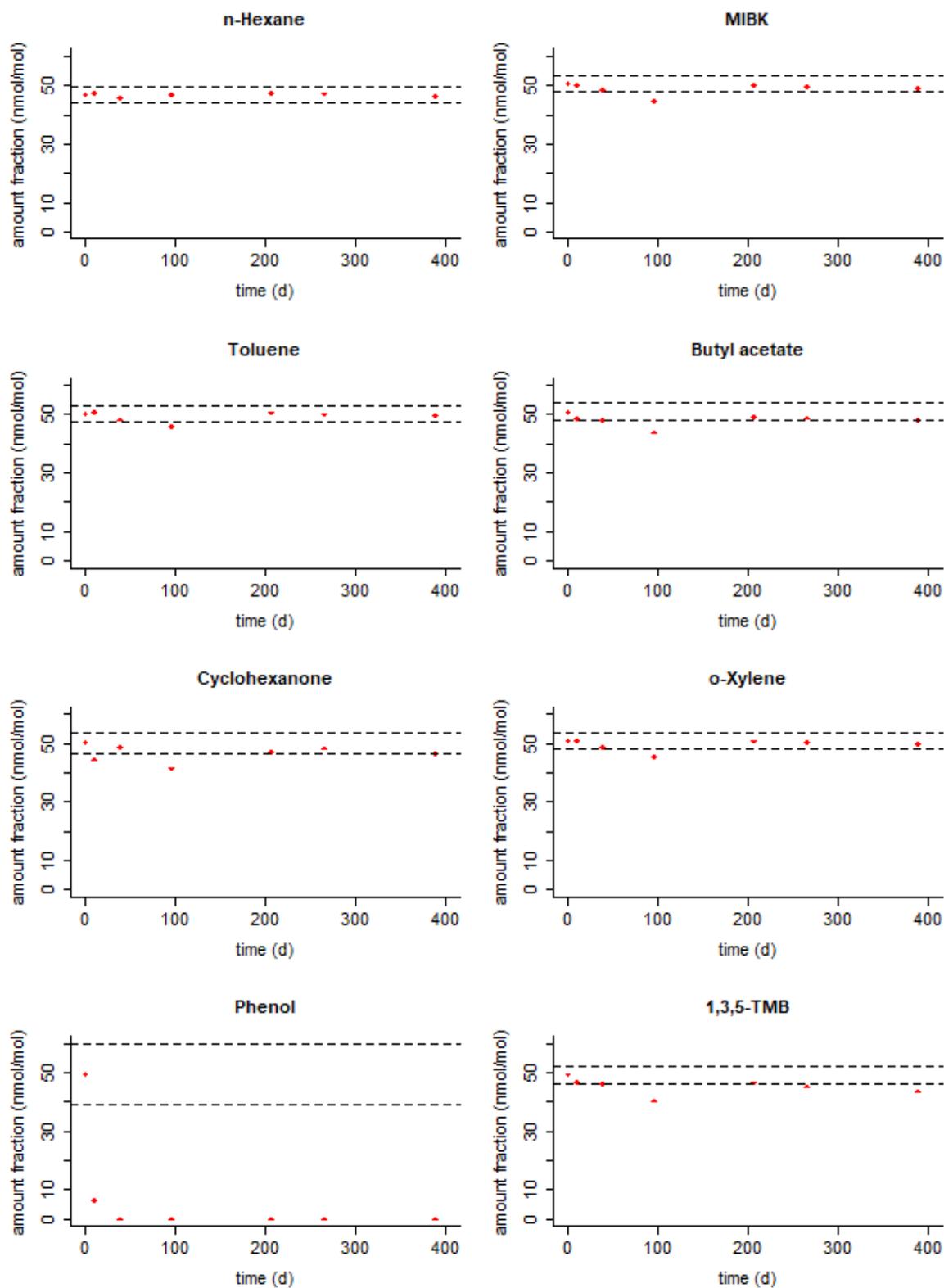
Figure A5.2: Graphic presentation of the stability results for the VOCs in static gPRM VSL114045. First point in the graph is the gravimetric amount fraction. The other points are the calculated amount fractions based on the measurements. The dotted lines indicate the expanded uncertainty determined for the VOC in the static gPRM.
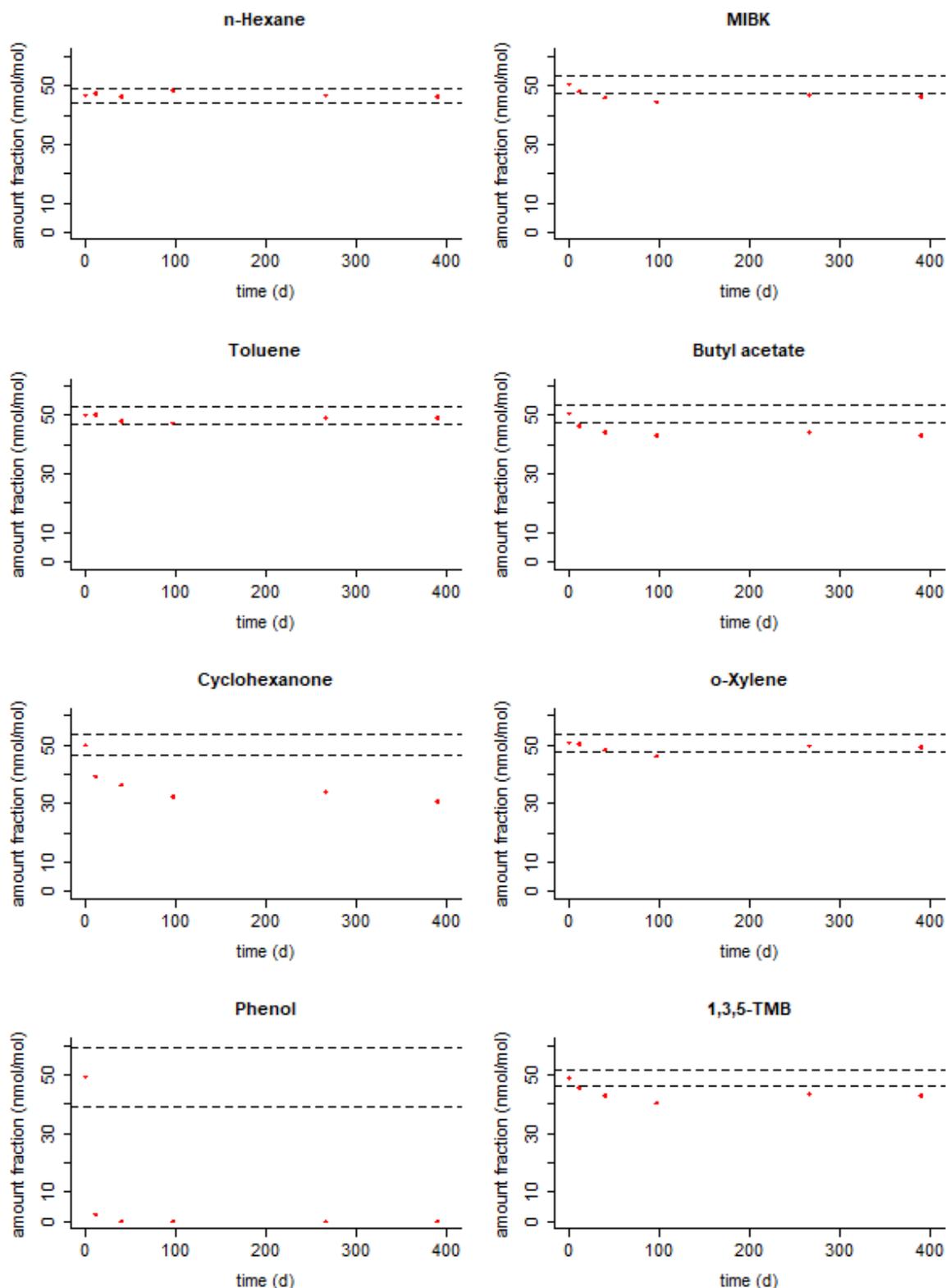
Figure A5.3: Graphic presentation of the stability results for the VOCs in static gPRM VSL187546. First point in the graph is the gravimetric amount fraction. The other points are the calculated amount fractions based on the measurements. The dotted lines indicate the expanded uncertainty determined for the VOC in the static gPRM.
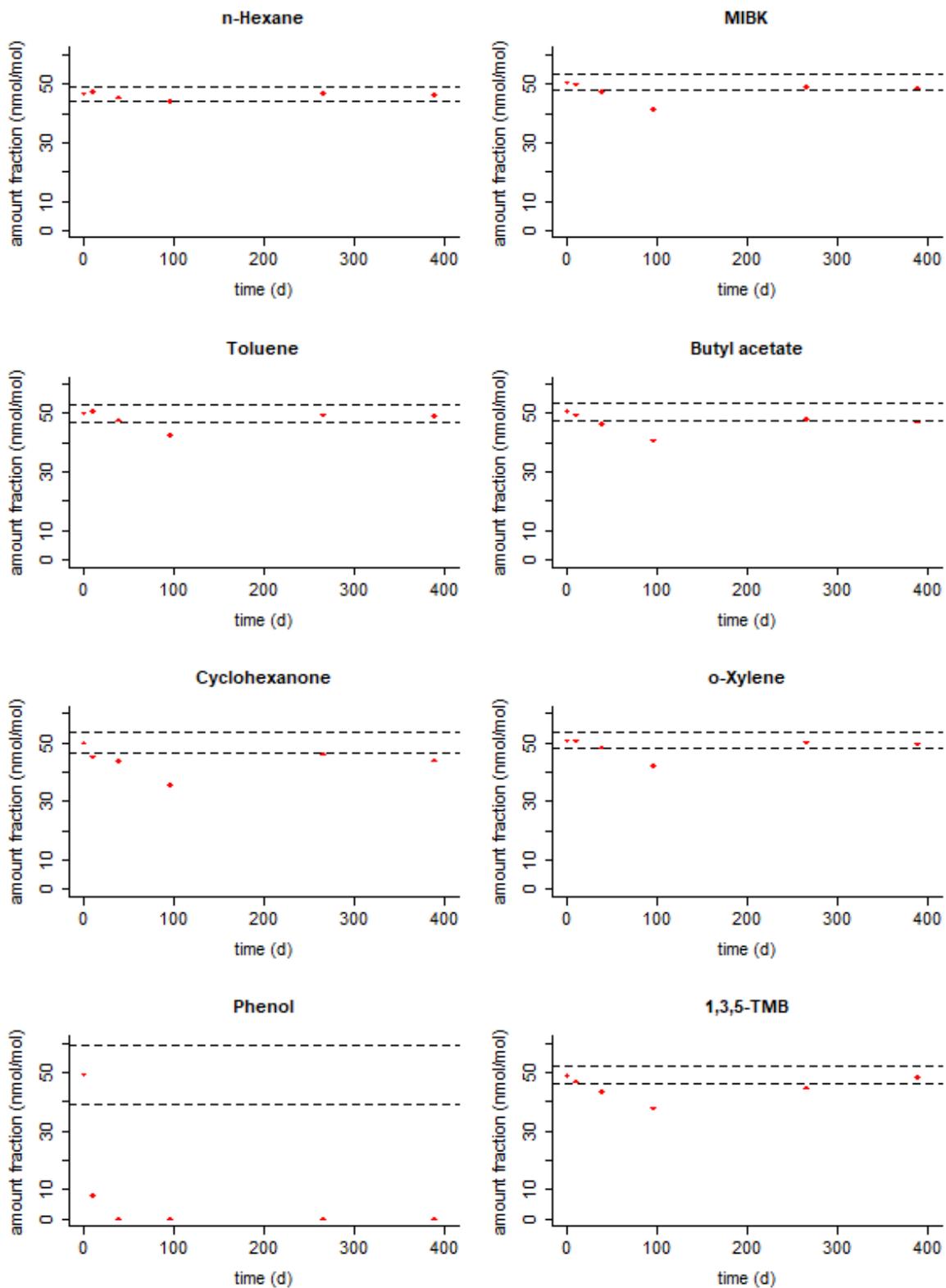
Figure A5.4: Graphic presentation of the stability results for the VOCs in static gPRM VSL187555. First point in the graph is the gravimetric amount fraction. The other points are the calculated amount fractions based on the measurements. The dotted lines indicate the expanded uncertainty determined for the VOC in the static gPRM.

Annex 6: Results storage and short-term stability study sorbent tubes

To check the possible influence of storage temperature and the way of packaging on the stability of sampled TTA tubes, VITO sampled a total of 48 tubes on the 25th of October 2022 in a concentration range of 70-160 μg/m³ (corresponding to the same amounts in ng when sampling 1 litre). During the course of 1 month these tubes were analysed at certain intervals: immediately after sampling, and then 3, 9, 13, 20 and 28 days after sampling.

Twenty-one tubes were stored under regular conditions: in a black plastic box in the lab at room temperature. Six of them were analysed immediately after sampling, and then 3 at each remaining analysis day.

Nine tubes were stored in the freezer (-18°C), nine tubes were stored in the fridge (6°C) and nine tubes were stored at lab temperature, but in a transparent plastic package. These tubes were analysed per 3 on day 3, 13 and 28.

The results are summarized in Table A6.1 and shown visually in Figure A6.1.

Table A6.1: The results of the short term stability study (reg = regular, RSD a.v. = RSD analytical validation)

Concentrations in μg/m³	d0 reg	d3 reg	d3 plastic	d3 fridge	d3 freezer	d9 reg	d13 reg	d13 plastic	d13 fridge	d13 freezer	d20 reg	d28 reg	d28 plastic	d28 fridge	d28 freezer	average	RSD (%)	RSD a.v. (%)
hexane	125	111	108	103	111	117	122	121	117	132	113	116	121	118	119	**117**	6%	5%
MIBK	115	120	119	117	117	117	117	118	116	120	116	120	120	118	119	**118**	1%	2%
toluene	110	114	114	115	113	115	110	113	109	114	113	113	115	115	109	**113**	2%	2%
butyl acetate	74	73	73	76	74	72	72	74	73	76	74	72	73	73	71	**73**	2%	2%
o-xylene	137	140	136	137	135	139	135	135	137	140	137	137	138	138	136	**137**	1%	3%
cyclohexanone	89	93	94	92	91	92	90	90	90	92	91	93	93	91	92	**92**	2%	4%
phenol	50	56	57	56	53	54	57	60	53	56	55	55	62	55	51	**55**	5%	3%
1,3,5-TMB	120	123	120	122	117	119	121	119	121	121	116	119	116	120	121	**120**	2%	2%
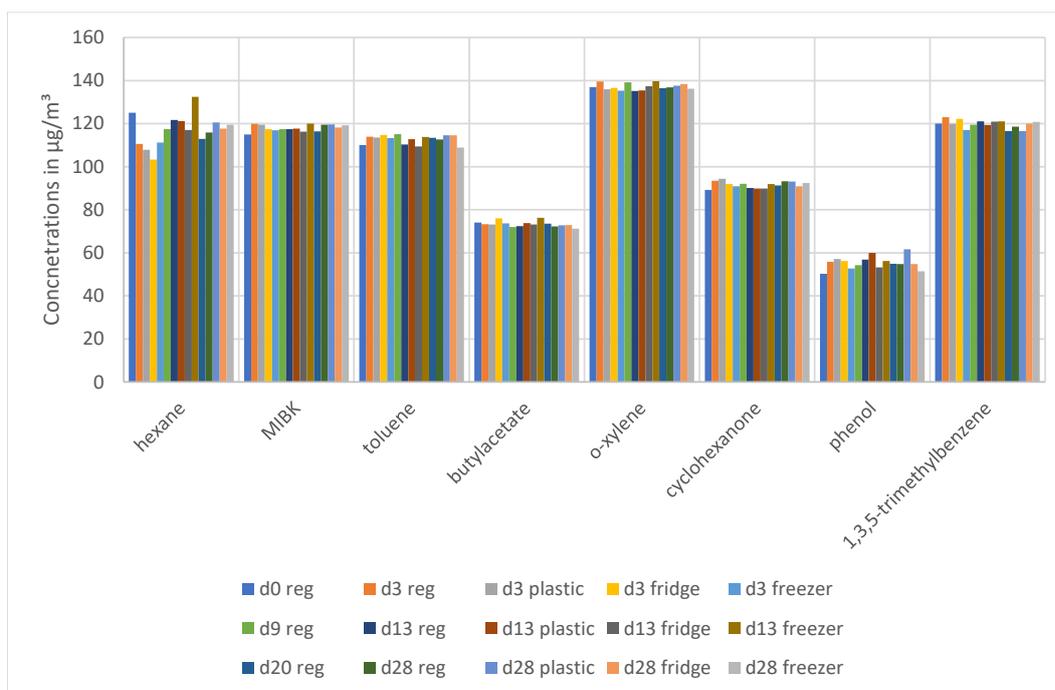
Figure A6.1: Graphic representation results short term stability study

By comparing the relative standard deviations (repeatability) throughout the whole experimental set (so including the regulars, and the tested analytical days and storage conditions) with the repeatability of the spiked tubes during the analytical validation process (RSD a.v. Table A6.1) we can conclude that the tested possible effects (storage time and storage place/temperature) have no influence on the analytical result for all the compounds.

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