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Metrological generation of SI-traceable gas-phase standards and reference materials for (semi-) volatile organic compounds

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Abstract

EN 16516 sets specifications for the determination of emissions into indoor air from construction products. Reliable, accurate and International System of Unit (SI)-traceable measurement results of the emissions are the key to consumer protection. Such measurement results can be obtained by using metrologically traceable reference materials. Gas-phase standards of volatile organic compounds (VOCs) in air can be prepared by a variety of dynamic methods according to the ISO 6145 series. However, these methods are not always applicable for semi-VOCs (SVOCs) due to their high boiling point and low vapour pressure. Therefore, a novel dynamic gas mixture generation system has been developed. With this system gas-phase standards with trace level VOCs and SVOCs in air can be prepared between 10 nmol mol^{-1} and $1000 \text{ nmol mol}^{-1}$. The VOCs and SVOCs in this study have normal boiling points ranging from $146 \text{ }^{\circ}\text{C}$ to $343 \text{ }^{\circ}\text{C}$. Metrologically traceable reference materials of the gas-phase standard were obtained by sampling of the VOC gas-phase standard into Tenax TA[®] sorbent material in SilcoNert[®] coated stainless steel tubes. Accurately known masses between 10 ng and 1000 ng per VOC were sampled. These reference materials were used to validate the dynamic system. Furthermore, the storage and stability periods of the VOCs in the reference materials were determined as these are crucial characteristics to obtain accurate and SI-traceable reference materials. In a round robin test (RRT), the reference materials were used with the aim of demonstrating the feasibility of providing SI-traceable standard reference values for SVOCs for interlaboratory comparison purposes. Based on the results from the validation, the storage and stability studies and the RRT, gas-phase standards and reference materials of VOCs and SVOCs with relative expanded uncertainties between 5% and 12% ($k = 2$) have been developed. These

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reference standards can be used as calibrants, reference materials or quality control materials for the analysis of VOC emissions.

Keywords: SVOC, dynamic calibration gas mixtures, metrology, sorbent tubes, thermal desorption, indoor air, reference materials

(Some figures may appear in colour only in the online journal)

1. Introduction

In industrialized countries, about 90% of the time is spent indoors [1]. Products, such as building materials and furniture, emit volatile organic compounds (VOCs), which are therefore ubiquitous in indoor air. VOCs, under certain environmental and occupational conditions, may result in reported sensory irritation and health complaints [2–5]. 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 (building) materials proven to be low emitting. In Europe, EU regulation No 305/2011/EU [6] sets basic requirements (BRs) on how construction works must be designed and built. BR 3 ‘hygiene, health and the environment’ states low emissions of toxic gases, VOCs, particles, etc from building materials. The relevant procedures for the determination of chemical emissions from materials used indoors in emission test chambers are described in the international standard series ISO 16000 [7–10] and are specified in the harmonized European testing standard EN 16516 [11]. Furthermore, the European Commission published a list of VOCs emitting from materials with their lowest concentration of interest, the EU-LCI values [12, 13].

Thermal desorption gas chromatography (TD-GC) is a technique that is widely used for measuring VOCs in indoor air [10, 11, 14]. EN 16516 sets requirements for the calibration and quality control of the TD-GC method for the assessment of VOCs from building materials [11]. ISO/IEC 17025-accredited laboratories are required to ensure their measurement results are traceable to the International System of Units (SIs). Nevertheless, it is a technique where calibrants, reference materials or quality control materials (on sorbent tubes) are largely unavailable and are made in-house in laboratories. Therefore, metrological traceability of measurement results to the SI is lacking or cannot be demonstrated. There is a need for external and independent inter-laboratory checks using reference values that are traceable to the SI as described here for performance verification purposes, such as the use of VOC gas-phase standards prepared by dynamic volumetric techniques according to the ISO 6145 series. Preparation methods for these gas-phase standards with VOCs in air are often based on the diffusion method (ISO 6145-8) [15–17]. This method is based on the constant diffusion of VOC vapours, when the pure VOC liquid is kept in a special cell at constant temperature. A stream of inert gas purges the cell, carrying with it the VOC vapours. By regular weighing of the cell in time, it is possible to determine the diffusion rate of each VOC with high accuracy. A further

dilution with a known flow of clean and dry air allows to obtain the desired VOC concentration. However, this method is not applicable for semi VOCs (SVOCs) due to their high boiling points and low vapour pressures. ISO 16000-6 and EN 16516 define VOC and SVOC classes [10, 11]. VOCs are compounds eluting between and including n-hexane and n-hexadecane on the gas chromatographic column specified as a 5% phenyl/95% methyl polysiloxane capillary column, while SVOCs elute between n-hexadecane and n-docosane [10, 11].

This paper demonstrates the development and validation of a novel system for the metrological preparation of dynamic SI-traceable gas-phase standards with relevant VOCs and SVOCs in indoor air. VOCs from various groups of compounds have been selected for the validation such as hydrocarbons, phthalates and several VOCs with low LCI values as stated in the EU-LCI list [12]. Sorbent tubes, containing suitable sorbent materials, can be sampled with known volumes of these VOC and SVOC gas-phase standards to obtain accurate SI-traceable reference materials which can be used as calibration and/or quality control materials. These reference materials are key to establish the traceability chain for the measurement data of emissions of dangerous substances from building materials into indoor air. The reference material has the closest metrological traceability to the SI and is prepared according to primary methods (e.g. gravimetry and volumetry).

For the validation of the reference material preparation, sorbent tubes were directly spiked with a liquid VOC solution using a syringe [18]. This method is applicable for SVOCs and often performed in house by calibration and test laboratories. However, preparing the reference materials via a dynamic gas-phase standard has the advantages that (a) it simulates real air sampling conditions, (b) the gas-phase standard can directly be sampled into a measurement system for calibration purpose and (c) series of sorbent tubes can be sampled homogeneously.

This paper also shows the outcome of the studies identifying the ideal storage conditions and the stability of the sorbent tubes with Tenax TA[®] as sorbent material.

The development of the dynamic system was carried out in the European funded projects ENV01 MACPoll and ENV56 KEY-VOCs, under the European Metrology Research Programme (EMRP), and 20NRM04 MetrIAQ, under the European Metrology Programme for Innovation and Research (EMPIR) where Van Swinden Laboratory (VSL) and Bundesanstalt für Materialforschung und—prüfung (BAM) jointly worked at developing a measurement infrastructure for SVOCs. These efforts have paved the way to further collaborate in the 2018 round robin test (RRT) with the aim of demonstrating the feasibility of providing SI-traceable reference values for SVOCs for interlaboratory comparison purposes.

Table 1. VOCs used during the validation.

VOC	Abbreviation	CAS nr.	Boiling point (°C)	Molecular weight (g mol ⁻¹)	Supplier (purity (%))	Experiments
Styrene	—	100-42-5	146	104.2	TCI Europe N.V. (99.9)	RRT
Benzyl alcohol	BA	100-51-6	204	108.1	Sigma Aldrich (99.9)	Validation
Naphthalene	—	91-20-3	218	128.2	Sigma Aldrich (100)	Storage and stability study, RRT
Dodecamethylcyclohexasiloxane	D6	540-97-6	245	444.9	TCI Europe N.V. (99.7)	Validation, storage and stability study
Butylated hydroxytoluene	BHT	128-37-0	265	220.4	Sigma Aldrich (100)	Validation, storage and stability study, RRT
n-decane	C10	124-18-5	174	142.3	Sigma Aldrich (99.7)	Validation, storage and stability study, RRT
n-hexadecane	C16	544-76-3	287	226.4	Fluka (99.9)	Storage and stability study
n-octadecane	C18	593-45-3	317	254.5	Sigma Aldrich (99.1)	Validation, storage and stability study
n-eicosane	C20	112-95-8	343	282.6	Sigma Aldrich (98.9)	Storage and stability study, RRT
Dimethyl phthalate	DMP	131-11-3	282	194.2	Sigma Aldrich (99.4)	RRT
Diethyl phthalate	DEP	84-66-2	296	222.2	Sigma Aldrich (99.8)	Validation
Dibutyl phthalate	DBP	84-74-2	340	278.3	Sigma Aldrich (99.9)	Storage and stability study
Methanol	—	67-56-1	65	32.0	Fluka (99.9)	For dilution

2. Methods and materials

2.1. Process

The reference materials were produced by starting with preparation of a VOC liquid solution, with selected VOCs (section 2.2.1). The solution was evaporated and diluted with clean dry air to obtain a gas-phase standard using the dynamic system (section 2.4). The gas-phase standard was sampled into sorbent tubes to obtain the reference material (section 2.5). For the validation of the process again a VOC liquid solution is prepared (section 2.2.1). The mass fraction of the VOCs in this solution is approximately 200 times smaller. This was achieved by dilution with methanol. The diluted solution was directly spiked into sorbent tubes (section 2.7). All sorbent tubes were analysed using TD-GC with a flame ionization detector (FID) (section 2.8).

2.2. Chemicals

2.2.1. VOCs. For the validation of the reference materials, the storage and stability study and RRT a set of pure VOCs and SVOCs was used with boiling points ranging from 146 °C to 343 °C (table 1).

From one or more of the VOCs a metrologically traceable liquid solution was prepared in an organic solvent, typically methanol. The composition of these solutions were determined from the preparation data. The solid VOCs (Naphthalene, BHT, C18 and C20) dissolve in the other VOCs like Styrene and the solvent methanol. Furthermore methanol was added to dilute the VOC solution to the desired mass fraction. The solution was prepared gravimetrically with a calibrated analytical balance (AT201, Mettler Toledo,

Table 2. Sorbent tubes (Markes International, United Kingdom).

Sorbent material	Tube material	Experiments
TTA	Stainless steel (SS)	Storage and stability study
TTA	SilcoNert [®] coated SS	Validation, storage and stability study and round robin test

Switzerland). The calculation composition is metrologically traceable.

2.2.2. Gases. For the preparation of the gas-phase standards, nitrogen and dry clean air are used. Nitrogen from the liquid nitrogen supply was additionally purified using an AeroNex inert gas purifier (Merck, NL) to remove water, CO₂, O₂, CO, volatile acids, bases and organics. Dry clean air was 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 vapour up to a level of ca. 5 nmol mol⁻¹ and additional purification through a molecular sieve dryer and a catalytic purification unit.

The purity of air and nitrogen used is checked regularly and are suitable for use in gas-phase standard preparation if the level of VOCs is less than 1 nmol mol⁻¹.

2.3. Sorbent tubes

For the work presented in this paper, Tenax TA[®] (TTA) (60/80 mesh) was used as sorbent material. The sorbent material was contained in two different tube types (table 2).

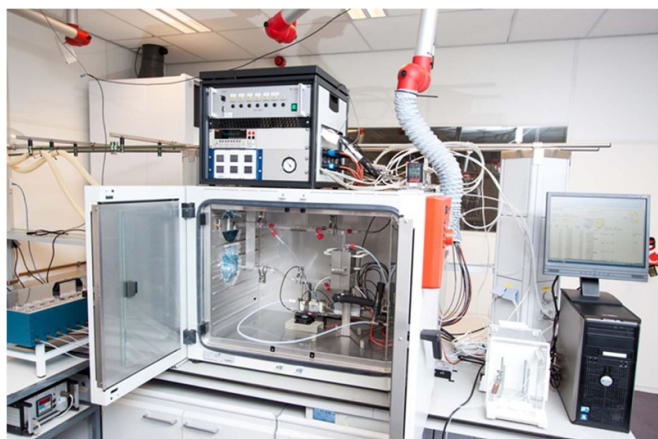


Figure 1. Picture of the dynamic system in the laboratory of VSL in Delft, the Netherlands.

2.4. Dynamic system

For the gas-phase standard preparation, VSL developed a unique dynamic system, working according to the continuous syringe injection method (ISO 6145-4:2004) [19]. This method consists of a continuous accurate injection of VOC vapours into a complementary gas stream by means of a syringe. The dynamic system was developed especially for the preparation of dynamic gas-phase standard of VOCs and SVOCs at trace levels in air in the range between 10 nmol mol^{-1} and $1000 \text{ nmol mol}^{-1}$. To be able to vaporise SVOCs, the dynamic system was built inside an oven and makes use of a solution of one or more VOCs in an organic solvent with a metrologically traceable composition (see section 2.2.1), typically methanol (figure 1).

A solution in a vial (10 ml vol) was placed on a calibrated analytical balance (AT201, Mettler Toledo, Switzerland) operating in the range 0–201 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) was 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 weighing at regular time intervals, the vial with the solution on the balance, a known accurate mass flow through the capillary was obtained. The weighing is performed automatically every 60 s (Mettler Toledo Balance Link interface tool). The mass flow (mg min^{-1}) for continuous injection of the solution is given by equation (1):

$$\bar{q}_m = \frac{\Delta m}{\Delta t} \quad (1)$$

where:

\bar{q}_m : mass flow rate of the solution (mg min^{-1})

Δm : mass difference between start and end of the experiment (mg)

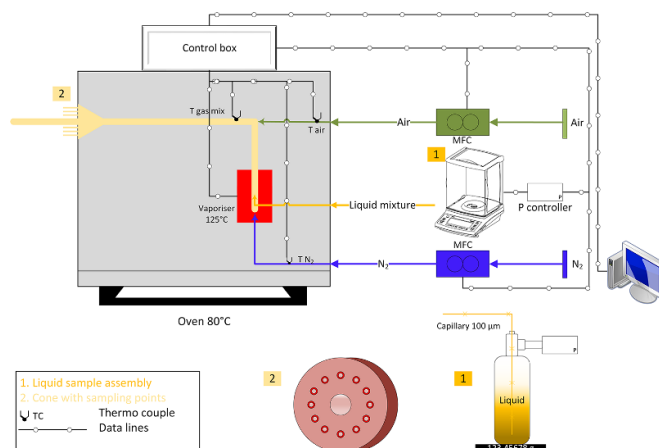


Figure 2. Schematic representation of the dynamic system.

Δt : time difference between start and end of the experiment (min).

The mass flow rate is left to stabilize for 30–60 min. The mass flow rate is stable when the relative standard deviation of the difference between two weighings over a period of 30 min is smaller than 2.2%. Then the experiment can start and usually last at least 15 min up to several hours depending on how long the obtained gas-phase standard was needed to sample tubes. Also during the experiment the relative standard deviation of the difference between two weighings must be smaller than 2.2%.

The solution flows through the capillary tube into a vaporiser (Elycra oven, Electrowarmte B.V, Netherlands). The vaporiser is heated at $125.0 \pm 0.1 \text{ }^\circ\text{C}$ to ensure evaporation of the solution. A stream of nitrogen (2 l min^{-1}) helps complete vaporisation of the solution. The nitrogen flow was 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 $2\text{--}20 \text{ l min}^{-1}$. The total flow of the VOC in air gas-phase standard was determined with primary flow meters and corrected to standard conditions (101.315 kPa and 293.15 K). The obtained gas-phase standard flows through a glass system (Technoglass, Netherlands) (figure 2).

The vaporiser and the glass system are placed inside an oven (Binder incubator, Binder GmbH, Germany). The temperature in the oven was kept at $80.0 \pm 1.0 \text{ }^\circ\text{C}$ to prevent condensation of the SVOCs in the gas-phase standard. The two MFCs are situated outside the oven and the gas flowing from the MFC into the oven was heated at $80.0 \pm 1.0 \text{ }^\circ\text{C}$. The glass system exits the oven through the left wall of the oven via a glass cone with 12 sampling points (figure 2). The gas-phase standard not sampled will flow out of the oven through a scrubber into the vent.

The VOC amount fractions obtained with this dynamic system are computed from first principles (mass flow rate, gravimetry and volumetry in this instance [19]), thereby having the characteristics of a primary method of measurement [20–23].



Figure 3. Sampling manifold with valves and MFCs.

The VOC amount fraction can be calculated according to equation (2):

$$x_i = w_{i(S)} \frac{\bar{q}_m}{q_{v(N_2+air)}} \frac{V_m}{M_i} 10^6 \quad (2)$$

where:

x_i : amount fraction of VOC i in the gas-phase standard (nmol mol^{-1})

$w_{i(S)}$: 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})

V_m : molar volume ($24.0551 \text{ l mol}^{-1}$) at standard conditions

M_i : molar mass of VOC i (g mol^{-1}).

2.5. Sorbent tube sampling

Reference materials were prepared via pumped sampling of known volumes of the gas-phase standard into sorbent tubes according to ISO 16017-1 [24]. This preparation is done using a specially designed multi-sampling manifold, made up of 12 MFCs (Bronkhorst, Netherlands) operating in sucking mode. Each MFC is connected to a three-way valve. All valves are controlled with a timer, that allows them to switch simultaneously (figure 3). The sampling flow rate (50 ml min^{-1}) was accurately calibrated and the sampling was carried out under controlled environmental conditions and taking care that the VOCs safe sampling volumes are not exceeded. After sampling the sorbent tubes were flushed with zero air (500 ml) to remove the methanol solvent. Reference materials with accurately known masses between 10 ng and 1000 ng per VOC can be obtained.

The VOC mass sampled into the sorbent tubes was calculated according to equation (3):

$$m_i = w_{i(S)} \frac{\bar{q}_m}{q_{v(N_2+air)}} q_{v(sample)} t_{(sample)} 10^3 \quad (3)$$

where:

m_i : mass VOC i sampled onto the sorbent tube (ng)

$q_{v(sample)}$: pumped sampling flow at standard conditions (ml min^{-1})

$t_{(sample)}$: sampling time (min).

2.6. Uncertainty of the masses of VOCs in the reference materials

To determine the uncertainty of the VOC mass sampled on the sorbent tubes, the uncertainty sources due to the generation of the gas-phase standard must be taken into consideration, supplemented by the uncertainty sources due to the pumped sampling of these gas-phase standards into the sorbent tubes [19, 24]. The standard uncertainty associated with the sampled mass, calculated based on equation (3), was determined using the law of propagation of uncertainty of the Guide to the expression of Uncertainty in Measurement (GUM) [25].

The standard uncertainty associated with the mass fraction ($w_{C10(S)}$) was obtained by propagating the uncertainties from the gravimetric preparation as described in section 2.1.1. The standard uncertainty of the mass flow rate of the solution is equal to the standard deviation of the 1 min averages as described in section 2.4. The standard uncertainty associated with the average flow rate of the gases ($q_{v(N_2+air)}$) and the sampling flow rate ($q_{v(sample)}$) was obtained based on calibration of the MFC with the VSL primary flow meters. The standard uncertainty associated with the sampling time ($t_{(sample)}$) is based on the calibration of the timer by the VSL time department.

The uncertainty budget belonging to 52.1 ng of C10 is shown in table 3. The expanded uncertainty in this case is 2.6 ng ($k = 2$), which is equal to a relative expanded uncertainty of 5%. The uncertainty applies to all VOCs sampled with masses ranging from 10 to 1000 ng.

These uncertainty budgets were validated during the validation, storage and stability studies and the RRT. Based on the results of the validation, the final uncertainty has been determined in section 3.4.

2.7. Liquid spiking sorbent tubes

For the validation of the dynamic system and for the storage and stability studies, a batch of reference materials was prepared by liquid spiking from a liquid solution, with one or more VOCs in methanol, into sorbent tubes (table 1). A known volume of the solution, between 10 μl and 50 μl , was carefully injected onto the TTA sorbent material in the sorbent tubes by means of a micro-syringe (VICI A-2 series 100 μl syringe, Switzerland). By weighing the sorbent tube before and after injection of the solution, the mass of the VOCs on the sorbent tube was determined. After injection the sorbent tubes were flushed with zero air (500 ml) to remove the methanol solvent. The relative expanded uncertainty of the VOC mass spiked into the sorbent tubes is 5%.

Table 3. Uncertainty budget for 52.1 ng C10 reference material, calculated from equation (3) using the GUM.

Measurement	Value	Standard uncertainty	Sensitivity	Uncertainty contribution
$w_{C10(S)}$	$3.92 \times 10^{-4} \text{ g g}^{-1}$	$3.92 \times 10^{-6} \text{ g g}^{-1}$	$1.33 \times 10^5 \text{ g}$	0.521 ng
$\overline{q_m}$	$1.89 \times 10^6 \text{ ng min}^{-1}$	$4.15 \times 10^4 \text{ ng min}^{-1}$	$27.6 \times 10^{-5} \text{ min}$	1.15 ng
$q_{V(N_2+air)}$	$10.652 \text{ l min}^{-1}$	$0.0294 \text{ l min}^{-1}$	$4.89 \text{ ng min l}^{-1}$	0.144 ng
$q_{V(sample)}$	$50.07 \times 10^{-3} \text{ l min}^{-1}$	$0.202 \times 10^{-3} \text{ l min}^{-1}$	$1.04 \times 10^3 \text{ ng min l}^{-1}$	0.210 ng
$t_{(sample)}$	15.000 min	0.015 min	$3.47 \times 10^{-3} \text{ ng min}^{-1}$	0.0521 ng
m_{C10}	52.1 ng	1.3 ng	—	—

2.8. GC analysis

The sorbent tubes were analysed using gas chromatography (GC) (Autosystem XL, Perkin Elmer) coupled with a FID and equipped with a thermal desorber (ATD350, Perkin Elmer) with a two-stage desorption. In the first stage, the sorbent tube is heated, and the desorbed VOCs are transferred and concentrated into a cold trap cooled at -30°C . The temperature used for the sorbent tube desorption was 300°C for 10 min. In the second stage, the cold trap, packed with TTA, is quickly heated so the VOCs are backflushed into the gas chromatographic column where they are separated. The GC column is a Rxi 5Sil MS, 60 m long, 0.25 mm internal diameter, 0.25 μm film thickness (Restek). The initial GC oven temperature was 40°C (hold 5.5 min). The oven temperature was then raised with three ramp rates: to 100°C at 5°C min^{-1} with a hold time of 4 min, to 160°C at $10^\circ\text{C min}^{-1}$ and then to 300°C at $10^\circ\text{C min}^{-1}$ with a hold time of 3 min.

3. Results and discussion

3.1. Validation

For the preparation of gas-phase standard with VOCs in air several solutions of the selected VOCs (table 1) were prepared and diluted with different amounts of methanol (BA, D6, BHT, C10, C18 and DEP). For the validation, solutions were prepared with nominal VOC mass fractions of 0.024 g g^{-1} and 0.0088 g g^{-1} . Each solution was forced through the capillary with a mass flow between 1.5 mg min^{-1} and 2.2 mg min^{-1} . After evaporation in the vaporiser the vapours were mixed with a total flow (nitrogen and air) between 27 and 8.5 l min^{-1} . During the validation four different variations of the settings were used to test the dynamic system (table 4).

These settings resulted in preparing four gas-phase standards with an average composition of 20 nmol mol^{-1} for each VOC in air ($\pm 10\%$ tolerance). The amount fraction was calculated according to equation (2).

For the validation SilcoNert[®] coated SS sorbent tubes were sampled with the VOC gas-phase standard. The MFCs in the sampling manifold have been calibrated before use with the VSL primary mass flow meters for a pumped sampling flow of 50 ml min^{-1} . The sorbent tubes were sampled for 16 min leading to a mass of $\sim 120 \text{ ng}$ per VOC per sorbent tube ($\pm 10\%$

tolerance) calculated according to equation (3). During the validation the sorbent tubes were analysed directly after sampling.

Two series of 12 sorbent tubes were sampled from each of the four gas-phase standard prepared. Each variation (table 4) has been repeated on three different days, except for variation 4 which has been repeated twice, to obtain VOC in air gas-phase standards and to prepare samples in sorbent tubes. In total 264 samples in sorbent tubes have been prepared. Directly after sampling all the samples have been analysed. The GC was calibrated with six liquid spiked sorbent tubes with the same nominal mass per VOC ($\pm 10\%$ tolerance). The mass in the samples taken from the VOC in air gas-phase standards was therefore determined according to one-point calibration as described in ISO 12963:2017 [26]. To compare all the samples coming from the four gas-phase standard variations on the three different days, a normalisation of the mass was applied, that set the mass of each VOC in the sampled sorbent tubes and spiked sorbent tubes to exactly 120 ng, to make data processing easier. The verification of the VOC mass sampled onto the sorbent tubes was calculated according to equation (4). The factor ($f_{(x)}$) was calculated according to equation (5):

$$m_{i(GC)} = \frac{(A_{i(sample)} f_{(sample)}) m_{nor}}{(A_{i(spike)} f_{(spike)})} \quad (4)$$

where:

- $m_{i(GC)}$: verification mass VOC i in the sorbent tube (ng)
- $A_{i(sample)}$: peak area VOC i sampled onto the sorbent tube
- $A_{i(spike)}$: peak area VOC i spiked onto the sorbent tube
- m_{nor} : normalised mass (ng)
- $f_{(sample)}$: factor to convert to the normalised mass
- $f_{(spike)}$: factor to convert to the normalised spiked mass

$$f_{(x)} = \frac{m_{nor}}{m_i} \quad (5)$$

The repeatability standard deviation ($s(r)$) and reproducibility standard deviation ($s(R)$) of the samples, covering four variations of gas-phase standard repeated in three different days, were calculated using analysis of variance (ANOVA) according to ISO 5725-2:2019 [27]. The standard deviations were calculated using the calculated verification mass of the VOC in the sorbent tube from the 264 samples.

Table 4. Variations of the settings used to obtain dynamic VOC gas-phase standards in air using the dynamic system.

Settings	Variation			
	1	2	3	4
Average VOC mass fraction solution (g g^{-1})	0.024	0.024	0.0088	0.0088
Mass flow through the capillary (mg min^{-1})	1.7	1.5	1.7	2.2
Total flow (N_2 and air) (l min^{-1})	27.0	24.8	8.5	8.5

Table 5. Repeatability standard deviation ($s(r)$), reproducibility standard deviation ($s(R)$), average mass and relative difference compared to the reference mass of 120 ng.

VOC	$s(r)$ (%)	$s(R)$ (%)	$m_{i(\text{GC})}$ (ng)	D_i (%)
BA	3.3	5.0	115	-4.2
D6	2.1	2.9	117	-2.5
BHT	1.6	2.0	115	-4.2
C10	1.5	2.0	117	-2.5
C18	3.8	5.5	112	-6.7
DEP	4.9	5.9	110	-8.3

The relative difference (D_i) between the measured mass and the normalised sampled mass (at 120 ng) was calculated with equation (6) (table 5):

$$D_i = \frac{m_{i(\text{GC})} - m_{\text{nor}}}{m_{\text{nor}}} \quad (6)$$

where:

D_i : relative difference (%)

$m_{i(\text{GC})}$: verification mass VOC i in the sorbent tube (ng).

The GC column used for the analysis did not allow sharp peak shape for BA and this resulted in a high $s(r)$ and $s(R)$. The VOCs C18 and DEP also show rather high $s(r)$ and $s(R)$. In general, the relative difference of the measured mass versus the reference sampled mass (D_i) for of BA, D6 is in the same order of magnitude as $s(R)$. However, for BHT, C10, C18 and DEP, D_i is larger than $s(R)$. The negative values for D_i indicate loss of the VOCs during the preparation or analysis. Losses could be caused by respectively condensation effects or not complete desorption for these high boiling VOCs. For BA, D6, BHT and C10, $s(R)$ and D_i are smaller or equal to the relative expanded uncertainty of 5% originally calculated for the reference materials (par. 2.5). For C18 and DEP these values are significantly higher.

3.2. Storage and stability study

To obtain accurate and SI-traceable reference materials, storage and stability are crucial characteristics. The storage and stability of reference materials with selected VOCs (Naphthalene, D6, BHT, C10, C16, C18, C20 and DBP (table 1)) into the two different sorbent tubes (a) uncoated SS tubes and (b) SilcoNert® coated SS tubes, have been tested (table 2).

For sampling of the sorbent tubes, a VOC gas-phase standard is obtained with the dynamic system. The solution

Table 6. Storage and stability analysis scheme.

Time	Storage temperatures ($^{\circ}\text{C}$)
Immediate	N/A
2 weeks	40
1 month	-20 and 20
3 months	-20 and 20
6 months	-20 and 20

prepared had nominal VOC mass fractions of 0.0013 g g^{-1} . The mass flow of the solution through the capillary was 1.82 mg min^{-1} and mixed with a total flow of 22.40 l min^{-1} to obtain a gas-phase standard containing on average 12 nmol mol^{-1} of each VOC in air. The VOC gas-phase standard has been sampled into the sorbent tubes with a pumped sampling flow of $49.99 \text{ ml min}^{-1}$ for 10 min. The resulting mass was nominally 50 ng per VOC per sorbent tube.

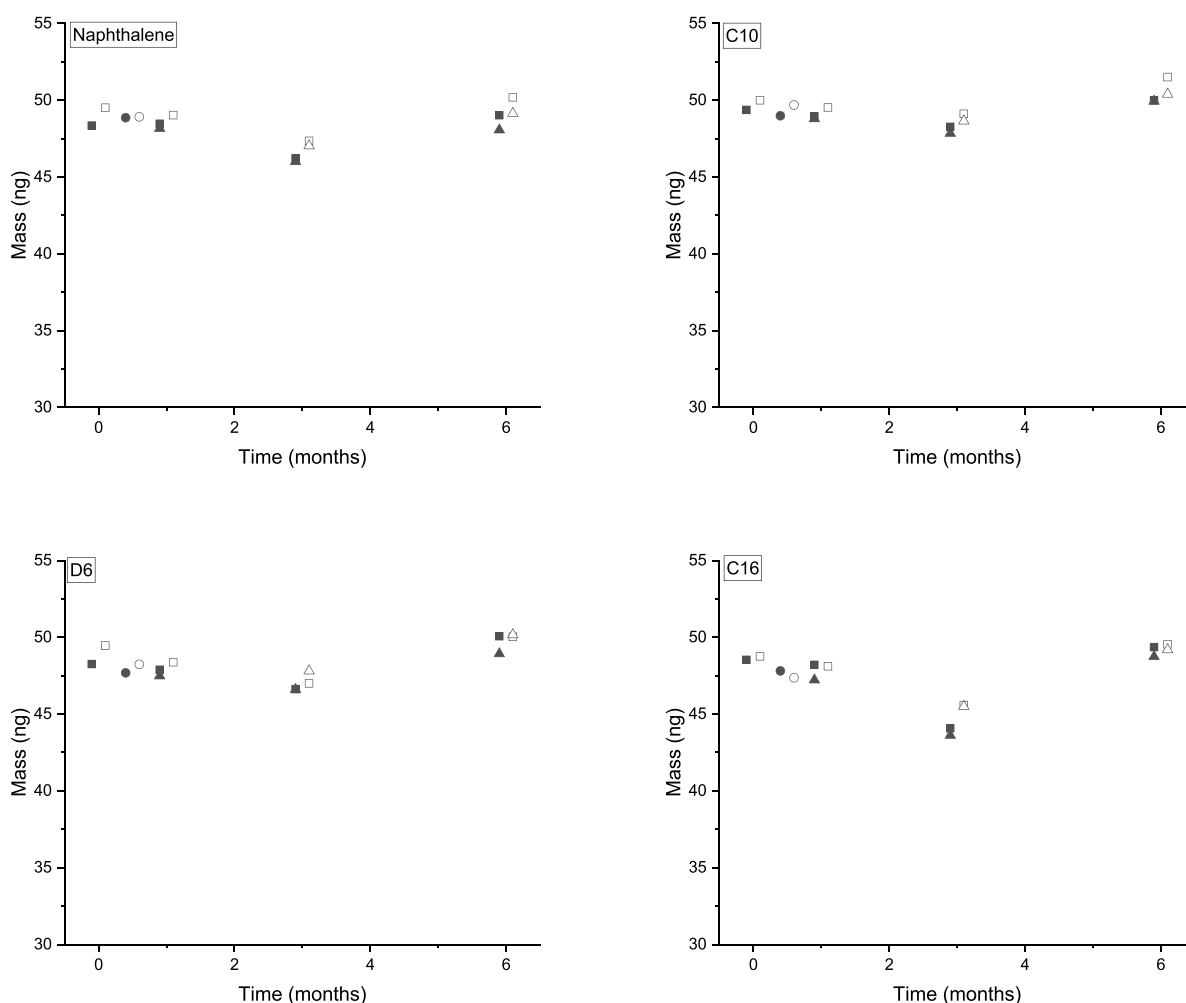
All the sorbent tubes, uncoated SS and SilcoNert® coated SS tubes, used for the storage and stability study have been sampled during six sampling series. To determine the stability of the VOCs on the sorbent tube part of the tubes have been analysed immediately after sampling, after 2 weeks, 1 month, 3 months and 6 months (table 6). To determine the most suitable storage conditions, three batches of the sampled sorbent tubes have been stored at -20°C , 20°C and 40°C (table 6). To simulate transport of the sorbent tubes to other laboratories 1 batch of sorbent tubes was stored at 40°C for two weeks. During the analysis immediately after sampling 6 uncoated SS and 6 SilcoNert® coated SS tubes were analysed. For the other data points 3 or 4 sorbent tubes from each storage temperature were analysed. The average peak area was used for the evaluation.

The GC was calibrated with liquid spiked sorbent tubes with the same nominal mass per VOC ($\pm 10\%$ tolerance). The mass on the sorbent tubes sampled with the VOC in air gas-phase standard was determined in the same way as the validation step. To compare all the measurement results, a normalised mass was used, that set the mass of each VOC in the sampled sorbent tubes and spiked sorbent tubes to exactly 50 ng. The verification of the VOC mass sampled into the sorbent tubes was calculated according to equations (4) and (5) using 50 ng for m_{nor} .

Compared to the spiked sorbent tubes the measurements carried out immediately after preparation show small to significant negative relative differences (D_i) (table 7). The relative differences are calculated according to equation (6).

Table 7. Repeatability standard deviation $s(r)$ and relative difference (D_i) of the VOC measured mass compared to the reference mass of 50 ng (immediately after preparation).

VOC	Uncoated sorbent tubes		SilcoNert [®] coated sorbent tubes	
	$s(r)$	D_i (%)	$s(r)$	D_i (%)
Naphthalene	2.1	-3.3	0.8	-1.0
D6	1.0	-3.5	1.0	-1.1
BHT	6	-7	1.7	-1.5
C10	1.0	-1.3	1.0	0.0
C16	3.1	-2.9	0.9	-2.5
C18	5	-5	1.8	-4
C20	8	-11	4	-12
DBP	9	-10	6	-12

**Figure 4.** Stability and storage study measurements of standards with ~ 50 ng per VOC per sorbent tube. ■ TTA in uncoated SS tubes stored at room temperature (20°C), ● TTA in uncoated SS tubes stored at 40°C , ▲ TTA in uncoated SS tubes stored in the freezer (-20°C), □ TTA in SilcoNert[®] coated SS tubes stored at room temperature (20°C), ○ TTA in SilcoNert[®] coated SS tubes stored at 40°C , △ TTA in SilcoNert[®] coated SS tubes stored in the freezer (-20°C).

The difference in $s(r)$ and D_i , between the uncoated SS tubes and the SilcoNert[®] coated SS tubes, are within the calculated relative expanded uncertainty of 5%.

The mass of all VOCs, except BHT, is stable in the 6 month stability period on both the uncoated and SilcoNert[®] coated tubes (figure 4). BHT is only stable on the SilcoNert[®] coated

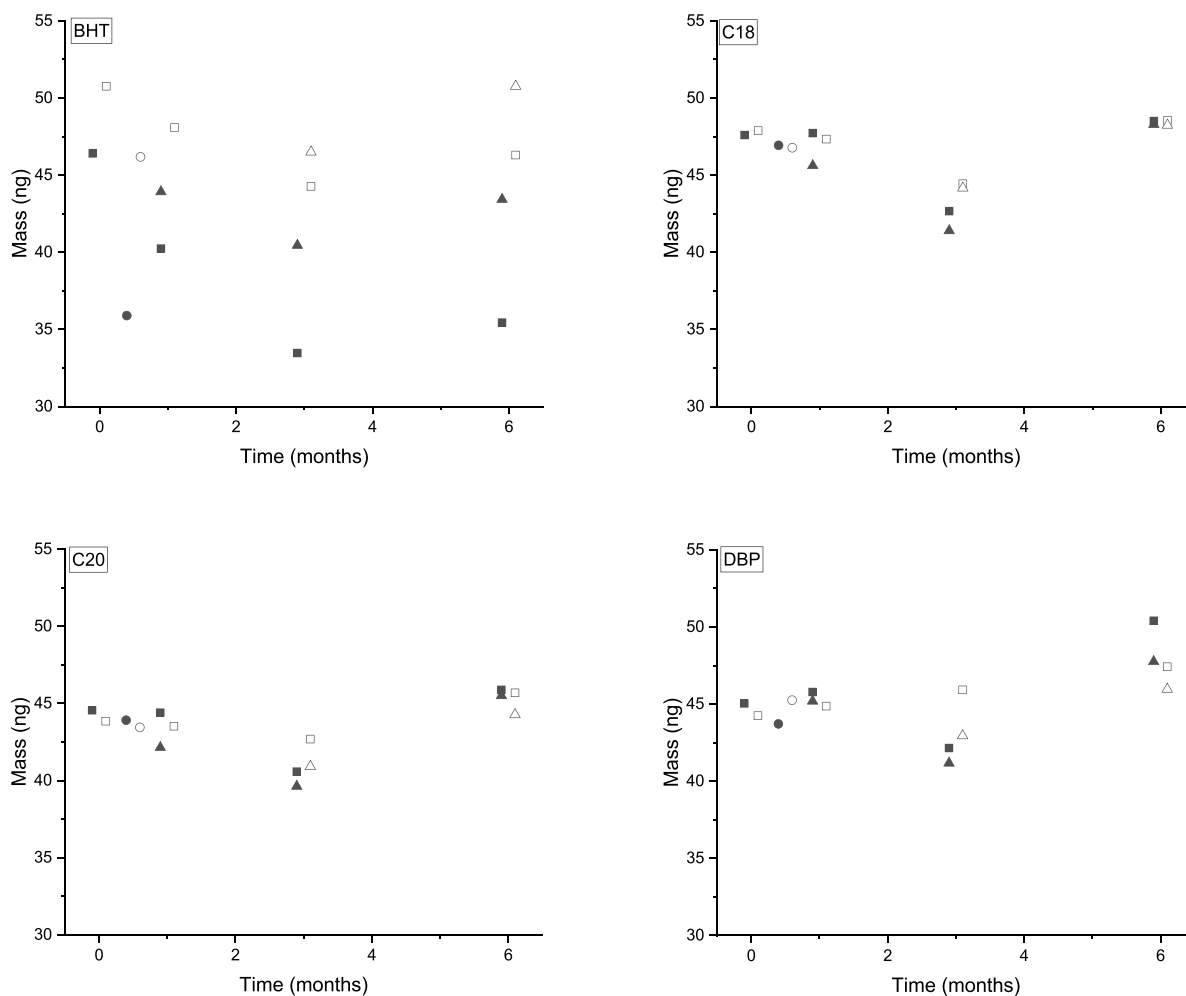


Figure 4. (Continued.)

tubes. Except for BHT on uncoated SS tubes, storage at 40 °C for a short period does not influence the stability of the standard. Only for BHT a difference between storage at room temperature (20 °C) and in the freezer (−20 °C) is seen, storage in the freezer shows improved stability of the standards. An increased recovery is shown for naphthalene, D6, BHT and C10 when using SilcoNert® coated SS tubes instead of uncoated SS tubes.

The reference materials with VOCs in TTA sorbent materials in SilcoNert® coated SS tubes are stable for 6 months and should be stored in the freezer in case BHT is one of the VOCs.

3.3. Round robin test (RRT)

Biennially, a RRT for emission test chamber measurements is organised by BAM. Goal is the evaluation of the measurement performance of emission testing institutes by means of identical samples (homogeneous reference materials) that are loaded into environmental emission chambers followed by the identification and quantification of emitting VOCs or SVOCs as well as odour evaluation [28].

In the 2018 RRT, with more than 50 participating testing institutes, an additional sample was included with the aim of evaluating the performance of analysis by TD-GC with mass selective detector (TD-GC/MS). For this purpose, standards, in the form of reference materials on sorbent tubes, were prepared by VSL. The TTA sorbent tubes were sampled with accurate masses of six VOCs from a gas-phase standard obtained with the dynamic system.

A 29 out of the 50 participants of the BAM RRT have participated in the performance evaluation of the analysis by TD-GC/MS. The participants provided cleaned sorbent tubes with TTA as sorbent material; three for sampling with the VOC in air gas-phase standard and one as shipping blank.

A solution with the selected VOCs (styrene, naphthalene, BHT, C10, C20 and DMP (table 1)) was prepared with a nominal VOC mass fraction of 0.0029 g g^{−1}. The solution was forced through the capillary with a mass flow of 1.89 mg min^{−1}. By adding a total flow of 10.652 l min^{−1} a gas-phase standard with an average amount fraction of 12 nmol mol^{−1} of each VOC in air was obtained.

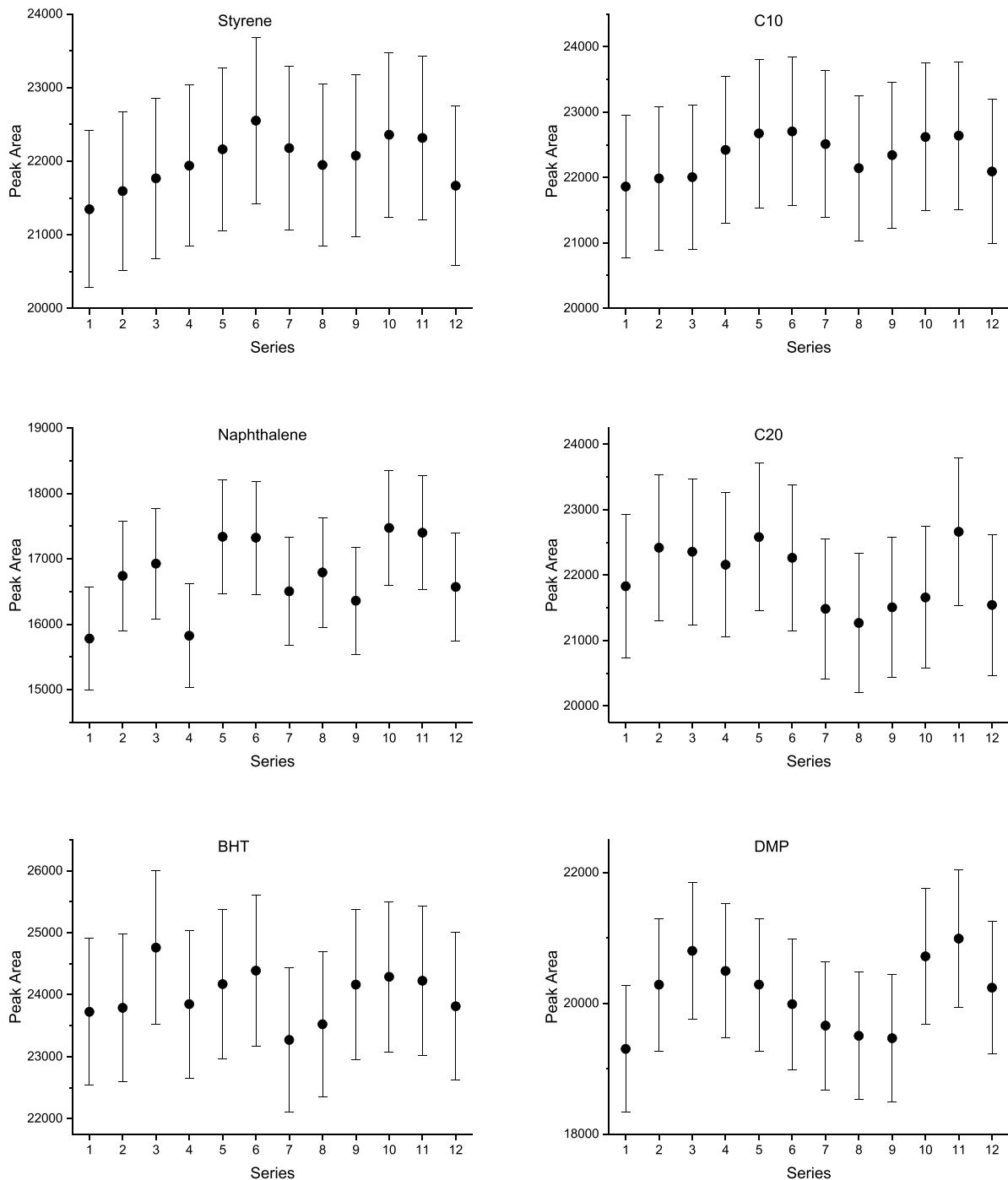


Figure 5. The peak areas obtained for each VOC from the 12 sampling series. The error bars indicate the expanded uncertainty of 5% ($k = 2$).

The sorbent tubes were sampled identically in 12 series. Each series contained eight sorbent tubes from different participants and four tubes from VSL (table 2) with TTA in SilcoNert[®] coated SS tubes. A sampling flow of $50.07 \text{ ml min}^{-1}$ was used to sample the sorbent tubes for 15 min. The average mass was 63 ng per VOC per sorbent tube.

Homogeneity of the sampling between the 12 series is crucial to obtain accurate reference materials for the RRT. After

sampling the VSL tubes have been used to determine the homogeneity through TD-GC analysis.

3.3.1. Homogeneity study. From each sampling series one VSL sorbent tube has been analysed to determine the homogeneity for each VOC in the 12 sampling series. The homogeneity has been determined by means of the GC-response (peak area) (figure 5).

Table 8. Relative difference (D_i) between the calculated mean mass of the RRT participants reported results ($\overline{m}_{i(\text{part})}$) and VSL sampled VOC mass (m_i).

VOC	m_i (U ($k = 2$)))	$m_{i(\text{part})}$ (std)	D_i (%)
Styrene	53.9 (2.7)	52 (7)	-4
Naphthalene	59.0 (3.0)	58 (9)	-1.7
BHT	57.9 (2.9)	51 (13)	-14
C10	52.1 (2.6)	53 (8)	1.7
C20	64.0 (3.2)	61 (12)	-5
DMP	93 (5)	90 (15)	-3.3

The difference between the peak areas is smaller than the relative expanded uncertainty of 5% for all the VOCs. Therefore the 12 sampling series are considered homogeneous.

3.3.2. Results RRT. After preparation and the homogeneity study, the reference materials were sent back to the participants. The participants were requested to analyse them immediately after reception. Alternatively, the sorbent tubes should have been stored in the freezer at -20°C until analysis.

To facilitate the calibration of the analytical equipment, the names of the VOCs contained in the reference materials were disclosed in advance. Participants were furthermore informed on the range of the VOCs sampled masses in the reference materials (i.e. 50–100 ng).

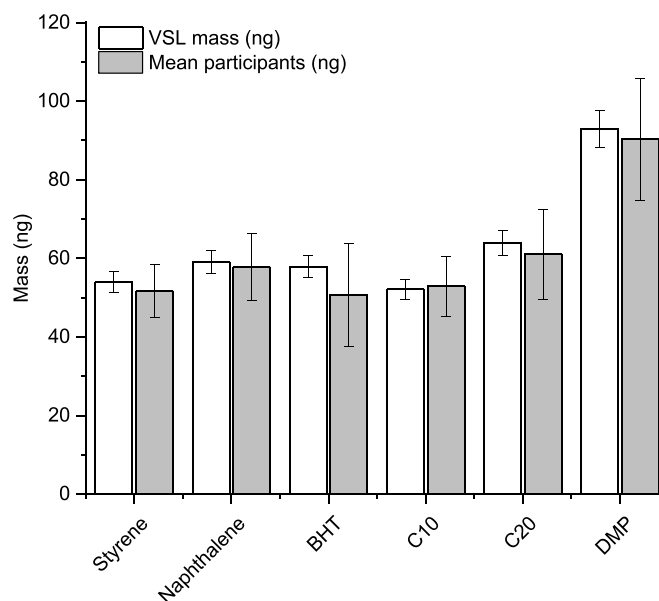
Each participant reported the results of the three sampled sorbent tubes for each VOC obtained by substance specific analysis [29]. By comparing the participants' results and the VSL sampled VOC mass (table 8), the consistency of preparation of these reference materials was determined (figure 6). The relative difference (D_i) has been determined based on equation (7):

$$D_i = \frac{\overline{m}_{i(\text{part})} - m_i}{m_i} \quad (7)$$

where

$\overline{m}_{i(\text{part})}$: mean mass VOC i participants (ng).

The standard deviations of all measurement results reported by the participants for styrene, naphthalene, C10, C20 and DMP fall within the expanded uncertainty associated with the VSL mass (5% ($k = 2$)). The relative difference (D_i) between the overall mean and VSL mass is less or equal to 5%, with exception of BHT. For BHT, a significant difference of 14% is observed. It should be noted that most participants provided glass or uncoated SS tubes and that the dispersion of the measurement results is very large (25%). Based on the results of the storage and stability study, BHT is known to be degrading inside uncoated SS tubes with TTA sorbent material and this could explain the appreciated deviation with the VSL mass. Furthermore, there was no information on the history of the participants sorbent tubes and storage after preparation by the participants. These factors may have an impact on the degradation process.

**Figure 6.** Comparison between the mean value of the RRT participants reported results with the VSL mass for all VOCs. Error bars give the expanded uncertainty for the VSL masses (5% ($k = 2$)) and the standard deviation of the participants' measurement results.**Table 9.** Reference values and relative expanded uncertainties for the VOCs in SilcoNert[®] coated SS tubes with TTA as sorbent material.

VOC	Reference value (ng)	U (%) ($k = 2$))
Styrene	Theoretical value	5
BA	Theoretical value—4%	10
Naphthalene	Theoretical value	8
D6	Theoretical value	6
BHT	Theoretical value—4%	5
C10	Theoretical value	5
C16	Theoretical value—3%	9
C18	Theoretical value—7%	11
C20	Theoretical value—12%	11
DMP	Theoretical value	6
DEP	Theoretical value—8%	12
DBP	Theoretical value—12%	12

3.4. Reference values and uncertainty

The results of the validation of the dynamic system, the storage and stability study and the RRT results lead to the conclusion that, to assign a reference value, a correction factor must be applied to the theoretical values for some VOCs (table 9). For BA, BHT, C18 and DEP a correction is applied based on the deviation found during the validation (table 5). The correction applied for C16, C20, and DBP is based on the results for the storage and stability study (table 7). From the studies, it appeared also necessary to revise the uncertainty budget of the reference values taking into account type of sorbent tube, homogeneity, reproducibility and stability issues (table 9). Therefore, the overall uncertainties of BA, D6,

naphthalene, C16, C18, C20, DMP, DEP and BDP have now included as safety margin based on the $s(R)$ results from the validation study (table 5) and the $s(r)$ results from the storage and stability study (table 7). Based on the stability study the assigned uncertainties cover a stability period of 6 months for the standard reference materials of VOCs in sorbent tubes.

4. Conclusion

EN 16516 defines the test procedure for the determination of emissions of VOCs from building materials into indoor air [11]. Metrological traceable reference materials are key for the validation, calibration and quality control of such test procedures. With the developed dynamic system it is possible to obtain SI-traceable gas-phase standards of VOCs in air. Reference materials of the VOCs can be obtained by sampling of the gas-phase standard into TTA sorbent material in preferably SilcoNert[®] coated SS tubes. Accurately known masses between 10 ng and 1000 ng can be sampled with relative expanded uncertainty between 5% and 12% ($k = 2$). The stability of the reference materials is 6 months when stored in the freezer at $-20\text{ }^{\circ}\text{C}$.

The feasibility of preparing SI-traceable reference materials has been demonstrated in the RRT. The average of the participants results for the VOCs, with exception of BHT, is within the given expanded uncertainty of the mass sampled. In return, the result of the RRT shows that the participants are performing well in analysing VOCs by TD-GC/MS.

The use of SVOC reference materials on sorbent tubes employed as SI-traceable reference materials is fit-for-purpose and sets directions for a regular RRT for these challenging measurements.

In extension to this work, in the EMPIR project ‘Metrology for the determination of emissions of dangerous substances from building materials into indoor air’ (20NRM04 MetrIAQ) novel emission reference materials and primary reference gas standards in accordance with EN 16516 are under development.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: [10.5281/zenodo.7347503](https://doi.org/10.5281/zenodo.7347503).

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