Development of a material with reproducible emission of selected volatile organic compounds

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Für Kristin.

Manchmal sind Umwege der schönere Weg zum Ziel.

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Abstract

Building products and furniture are sources for indoor air pollutants. They emit volatile organic compounds (VOCs) which can affect human health. To investigate, the emission potential test specimens of building products are loaded into chambers which provide climate conditions close to that of indoor air. Here the samples emit VOCs which can be analysed by sampling air from the chamber onto adsorbent tubes and transferring them onto a measurement device.

To gain reliable results for this complex testing method reference materials are necessary. To address the lack of such references in emission testing, the present study focussed on the development of an artificial material with reproducible VOC emissions. Therefore a lacquer was mixed with the substances of interest. Afterwards, the mixture was cured under constant conditions and loaded into emission test chambers.

The emissions in the different chambers showed variations in the range of 10 % for common indoor air pollutants like hexanal, styrene, decane, naphthalene, limonene and hexadecane.

Zusammenfassung

Bauprodukte und Möbel sind Quellen für Schadstoffe im Innenraum. Sie emittieren leichtflüchtige organische Verbindungen (volatile organic compounds VOCs), welche einen negativen Einfluss auf die menschliche Gesundheit haben können. Um dieses Gefahrenpotential einschätzen zu können, werden Materialproben von Bauprodukten und Möbeln in Testkammern beladen, die konstante klimatische Bedingung bieten, die auch im Innenraum vorherrschen. In diesen Kammern emittieren die Proben VOCs, welche auf Adsorbentien gefangen und in Messgeräten analysiert werden können.

Um bei dieser komplexen Testmethode verlässliche Werte zu generieren, werden Referenzmaterialen benötigt. Da es aktuell in diesem Feld nur sehr wenig Referenzmaterialen gibt, befasst sich die vorliegende Arbeit mit der Entwicklung eines künstlichen Materials, welches VOCs reproduzierbar emittiert. Dafür wird ein flüssiger Lack mit ausgewählten Luftschadstoffen verrührt. Danach wird die Mischung unter konstanten Bedingungen ausgehärtet und in Emissionsmesskammern beladen.

Für typische Schadstoffe wie Hexanal, Styren, Decan, Naphthalin, Limonen und Hexadecan zeigt die Emission des Materials in verschiedenen Kammern Abweichungen im Bereich von 10 %.

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1 Introduction

Several investigations indicate that building products and furniture can emit harmful substances called volatile organic compounds (VOC). As between 15 and 16 hours per day [1] is spent indoors it is thought that this could cause a significant impact on human health.

To assess whether or not this risk is significant, identification of harmful substances from building products is essential. Therefore, specialised environmental laboratories analyse organic air pollutants either by investigating the room in question directly or by analysing emissions from several building products and furnishings. As the composition of every room is unique the latter method is more practical. The results of such measurements are important to identify sources of harmful emissions and to categorise products according to their emission behaviour.

The performance of environmental laboratories is usually controlled by round robin tests. Reference materials with identical properties are sent to the participants who analyse the samples under prescribed conditions. The results from the different laboratories are collected and statistical evaluated. In the case of emission testing from building materials and furnishing there is a lack of applicable references.

To solve this issue, an artificial reference material based on a lacquer will be investigated in this study. To ensure the homogeneity of the material, the liquid lacquer will be mixed with the investigated substances. After a certain amount of time, the lacquer-analyte-system changes its physical condition from liquid to solid and after loading it into emission test chambers it should show a reproducible emission profile.

2 Motivation and theoretical background

This chapter introduces the need for reference materials in emission testing. In order to facilitate comprehension of the following experiments and discussion some theoretical background is given.

In chapter 2.1.1 and 2.1.2 the process of emission is introduced in general. Part 2.2 turns the focus on the complex process of emission testing. The effect of possible sources deteriorating the method reproducibility is also described.

In chapter 2.3.1 reference materials as an essential tool to improve the quality of emission testing are described. Part 2.3.2 presents the innovative approach for a new material as central focus of this study.

Finally chapter 3.1.2 to 3.1.3 provide a theoretical overview of the analytical equipment and lacquers used.

2.1 Material emission

2.1.1 General aspects

An emission is the release of substances or radiation of a material. In the context of the present study this means the exhalation of mostly organic substances. These pollutants can be natural compounds of the material itself, like terpenes from wood. In addition they can have their origin in the manufacturing process like plasticisers or solvents in synthetic materials.

Beside these primary pollutant emissions secondary emissions may occur over time. For example, the emission of alcohols, aldehydes and carboxylic acids are oxidation products from the material itself in the presence of oxygen or ozone (see Wolkoff [2]).

The World Health Organisation (WHO) classifies those volatile substances concerning their boiling points into four groups:

Table 2.1: VOC-classification in accordance with WHO [3]

Abbreviation	Full name	Boiling range
VVOC	very volatile organic compounds	< 0 °C to (50 °C to 100 °C)
VOC	volatile organic compounds	(50 °C to 100 °C) to (240 °C to 260 °C)
SVOC	semi-volatile organic compounds	(240 °C to 260 °C) to (380 °C to 400 °C)
POM	particulate organic matter	> 380 °C

Volatile compounds show an emission profile that rapidly increases to a maximal concentration within a few hours followed by decay to lower levels. It ends with a period of slowly release of the remaining amount in the sample. Compounds with lower volatility (SVOC) emit at a slow rate to a constant value that lasts for a long period of time [4]. Figure 2.1 show these two contrary profiles.
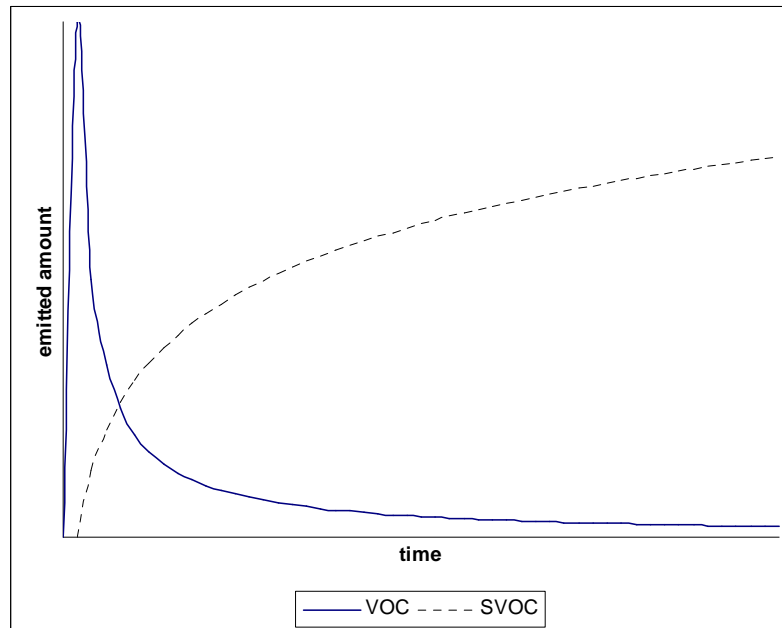
Figure 2.1: Different emission profiles for VOC and SVOC (model)

Many VOCs that can be found in indoor air such as alkanes, phthalates, aromatic hydrocarbons and terpenes are classified as irritants, narcotics, neurotoxins or carcinogens. Regarding their toxicological limit values, indoor concentration levels in µg/m³-ranges are too low to cause such drastic effects. The term "sick building syndrome" [5] summed non-specific syndromes that are related to long term VOC exposition, e.g. irritation of skin, eyes and nose combined with headache, fatigue and insomnia.

2.1.2 Emission modelling

Emissions are complex mass transfer processes which are not yet clarified. According to Sparks et al. [6] the driving force of emissions are the difference of the pollutant concentration, the combination of source, the source-air-interface and the surrounding (indoor) air. Liu et al. [7] collect different models to calculate these mass transfers for different types of sources. Key model parameters and models for solid and liquid materials as source are also provided. Although it is obvious that most

building materials are solid, liquid forms also exist, such as wood stains, varnishes and paints.

As key model parameters for the emission process Liu et al. [7] state the diffusion of the pollutant inside the source and the partition coefficient of the pollutant concentration between material-phase and gas-phase. Figure 2.2 summarises the emission mass transfer models in accordance to Haghighat and Huang [8] and Little et al. [9].
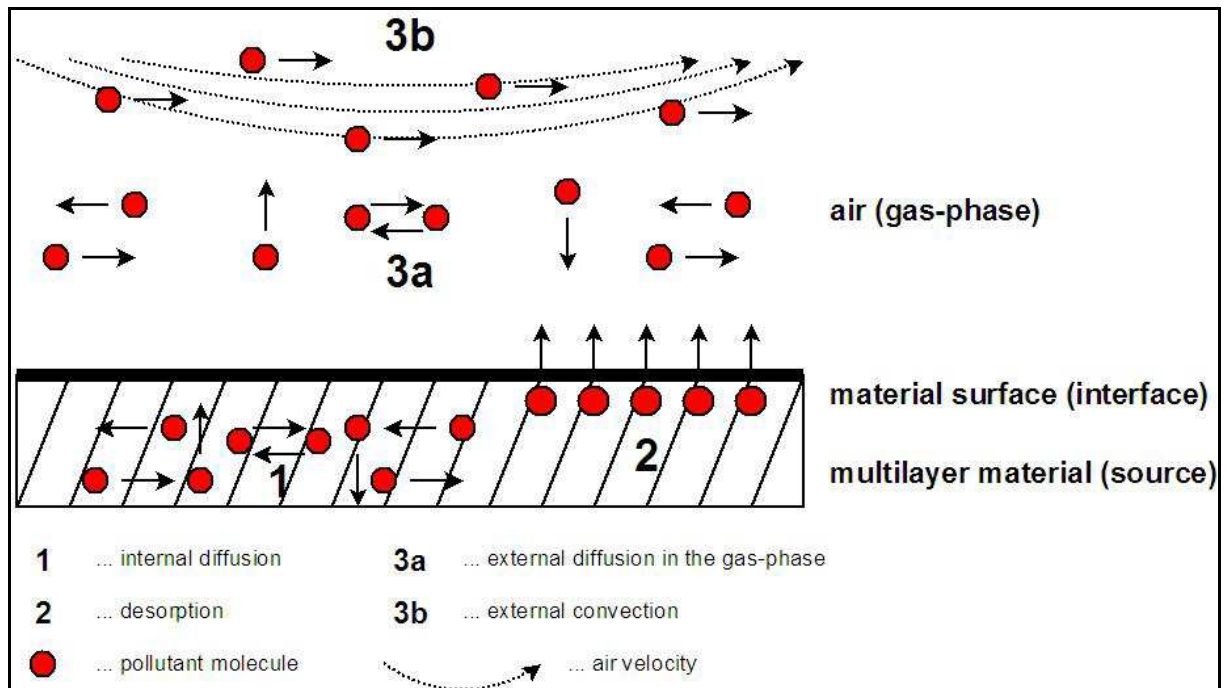
Figure 2.2: Overview of the emission process (two dimensional)

With regards to the lacquer system as reference material, the emission starts with the initial pollutant amount inside the lacquer phase. The unbounded molecules (red) diffuse undirected inside the material (1). Once the molecules reach the near surface material layer they change phase between the solid substances and the gaseous phase from the surrounding air (2). On the gaseous phase the pollutant molecules can diffuse unregulated (3a). If the air is agitated they are evacuated from the stream (3b).

In summary, it can be said that emissions are influenced by many mass transfer processes. Firstly there is diffusion inside the emission source and secondly there is convective mass transfer between the boundary layers of the source. Finally there is the (desorption) between the surface and the adjacent air.

Howard-Reed et al. [10] classify two types of sources of chemical emissions. On the one hand there is a *diffusion-controlled ("dry") source* whereby the emission is mainly limited by the diffusivity of the pollutant molecules combined with the temperature and the structure inside the material (see also Meininghaus and Uhde [11]). On the other hand there are *evaporation-controlled ("wet") sources*. In this case the emissions are mainly limited by the transfer of pollutant molecules from the material surface to the adjacent air. Here the volatility combined with the air velocity and turbulence is an important factor.

2.2 Emission testing

VOC-exhalations from building materials can be investigated with test chambers under predefined conditions. The ISO 16000-9 [12] provides standards to determine emissions from building products and furnishings.

According to Oppl [13] and Howard-Reed et al. [10] emission testing of building products consists of six main steps. Figure 2.3 shows these steps on the right hand side. On the left, the important influences are listed. Between the main steps important requests are shown.
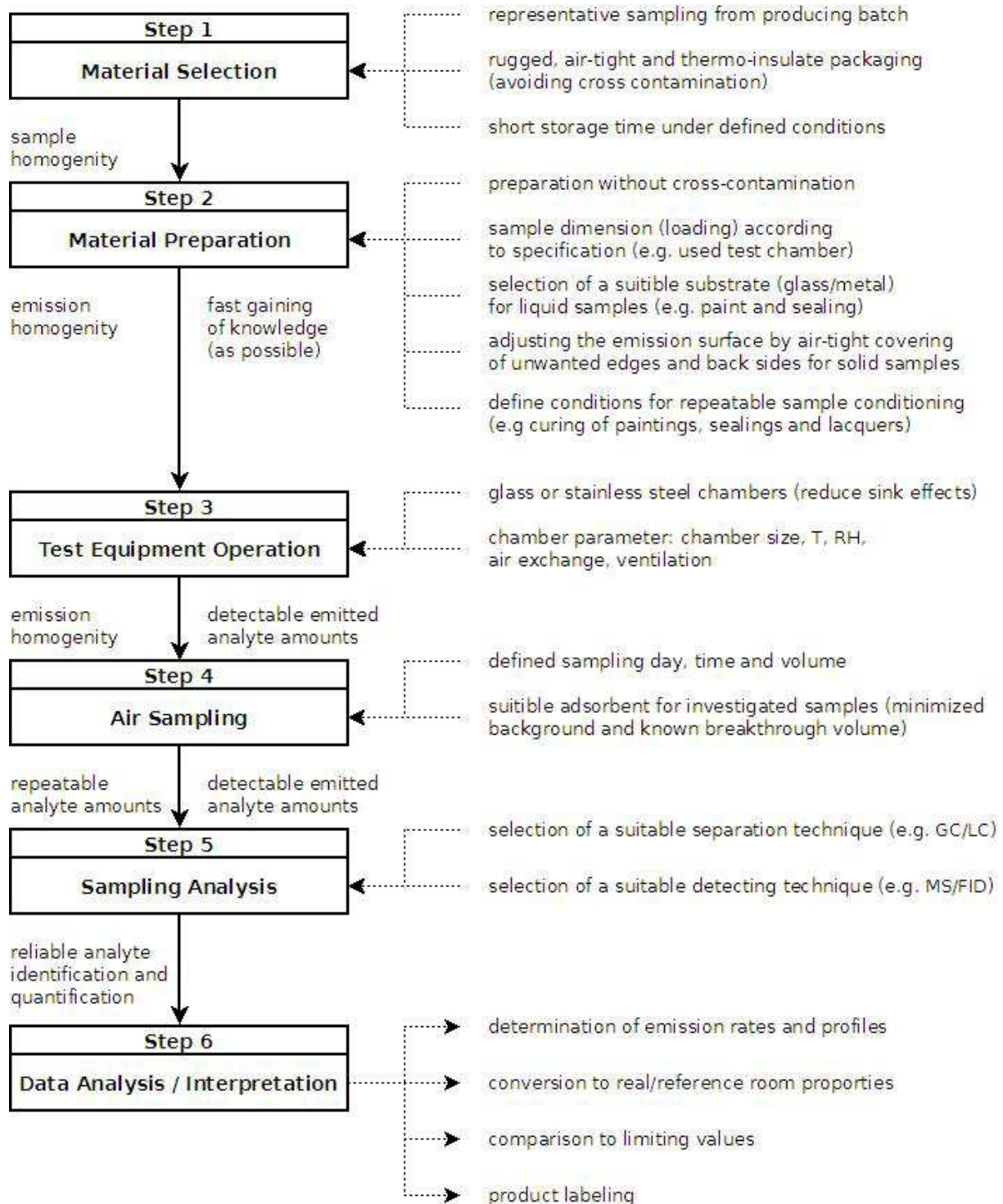
Step 1 **Material Selection**	representative sampling from producing batch
	rugged, air-tight and thermo-insulate packaging (avoiding cross contamination)
	short storage time under defined conditions

sample homogenity

Step 2 **Material Preparation**	preparation without cross-contamination
	sample dimension (loading) according to specification (e.g. used test chamber)
	selection of a suitible substrate (glass/metal) for liquid samples (e.g. paint and sealing)
	adjusting the emission surface by air-tight covering of unwanted edges and back sides for solid samples
	define conditions for repeatable sample conditioning (e.g curing of paintings, sealings and lacquers)

emission homogenity   fast gaining of knowledge (as possible)

| Step 3
Test Equipment Operation | glass or stainless steel chambers (reduce sink effects) |
| | chamber parameter: chamber size, T, RH, air exchange, ventilation |

emission homogenity   detectable emitted analyte amounts

| Step 4
Air Sampling | defined sampling day, time and volume |
| | suitible adsorbent for investigated samples (minimized background and known breakthrough volume) |

repeatable analyte amounts   detectable emitted analyte amounts

| Step 5
Sampling Analysis | selection of a suitable separation technique (e.g. GC/LC) |
| | selection of a suitable detecting technique (e.g. MS/FID) |

reliable analyte identification and quantification

Step 6 **Data Analysis / Interpretation**	determination of emission rates and profiles
	conversion to real/reference room proporties
	comparison to limiting values
	product labeling

*Figure 2.3: Overview of an emission testing procedure (T ... temperature, RH ... relative humidity)*

Figure 2.3 shows the complexity of the process. In step 1 a manufacturer specifies a material for testing. Often samples from different batches can cause different emissions. Thereafter the samples must be packed and shipped air-tight. In rare cases when, samples must be shipped under refrigeration conditions, they are

thermo-insulated. This preserves the characteristics of the material, avoids premature outgoing and cross contamination from the environment. Once the samples have reached the laboratory they have to be stored under defined conditions (e.g. refrigerating or at 23 °C and 50 % RH). These requirements ensure that a representative sample is taken from the manufactured batch.

In step 2 the material has to be prepared for the analysis. This step is closely associated to step 3 because the dimension of the investigated sample is strictly related to the size of the desired test chambers in relation to its real room amount. According to step 1 a clean working environment is necessary to avoid cross contaminations.

Afterwards the emission surface has to be adjusted. Emission surface is an essential parameter for emission testing. The loading factor as quotient of the surface (facing the room) and the room volume shall represent indoor properties. Solid materials like floorings or wooden particleboards are cut to size. Resulting emitting edges are sealed (e.g. with aluminium tape). Oppl [13] reported that emission of edges can differ significantly compared to the top surface. The treatment of liquid materials like lacquers, paints and sealants are more difficult. Defined amounts of the selected samples must be applied on a neutral substrate. Zhang and Niu [14] reported that the substrate can delay and change emissions. They first act as sink and adsorb analytes from the sample. The bounded substances can then be reemitted from the substrate (secondary emission). Hence, less-adsorptive substrates like glass or stainless steel are used. After applying the liquid sample onto a selected substrate the material must be cured under defined conditions. This process can be realised in emission test chambers because they provide constant climatic parameters.

This process leads to step three. Prepared samples for chamber testing are depictured in Figure 2.4 and Figure 2.5.
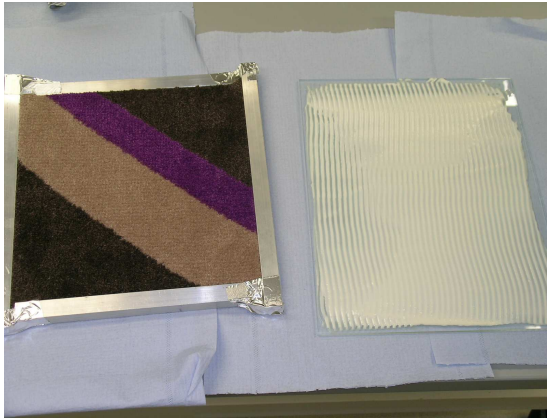
Figure 2.4: Test specimen of a carpet with sealed cutting edges (left) and suitable glue applied on glass (right)

Figure 2.5: Oriented strand boards with sealed cutting edges

Emission test chambers will be discussed further in chapter 3.1.2. They provide a defined environment for testing. To reduce sink effects they are made of glass or stainless steel [15]. For the test chamber parameters like humidity, temperature, ventilation and air change rate can be adjusted to predefined values close to indoor conditions.

After loading the test specimen into the chamber various substances are emitted. Under static conditions (without any air exchange) a partition-equilibrium between the sample and air are established over time for each substance. The concentration increases steadily until equilibrium is reached. Usually such tests are used to estimate the maximal air pollutant concentration in a real room without air change [16]. In reality air change must be taken into consideration. All rooms exchange air through windows, doors and air conditioning. Dynamic tests with defined chamber-flows are widely used. In this case the partition equilibrium is interrupted permanently and the substances emit consecutively from the sample.

Step 4 deals with the air sampling. ISO 16000-9 requires at least two sampling points. After three days samples are taken for early exposure tests. Long-term exposure can be investigated from sampling after 28 days. Gas analysis is usually carried out using gas chromatography (GC, later introduced in chapter 3.1.1). Sampling tubes with specific adsorbents are used for analyte collection. They concentrate the organic contaminants by separating them from the inorganic air compounds. It is a requirement for the adsorbent material to maximise the

accumulation of pollutants on the tube without breakthrough of the compounds in several litres of air. The tubes are desorbed thermally and the pollutants are separated from each other in the GC-column.

In step 6 the measurement data are assembled and interpreted. From the air concentrations at different times emission profiles and rates can be calculated. The manufacturer needs the outcome of the emission testing process to license their products if the results undercut limit values outlined in the legislation. The emission rates and concentrations are also the basis for the evaluation of products like the "Blue Angel". Such labels advertise their products against other competitors.

2.3 Challenges in emission testing

Comparative measurements on emission testing have previously resulted in significant variations. Howard-Reed et al. [17] and Horn et al. [18] report coefficient of variations up to 284 % with an average of greater than 40 % from seven studies that uses different indoor materials.

There are two main factors inducing these high variations. Firstly there is the complexity of the emission testing, as described in chapter 2.2. By modifying several parameters in the process, comparability to other tests are influenced significantly. For example, this includes different manufacturers and dimensions of the test chambers or different analysis methods. To address this, standardisation is an essential tool. It is impractical to develop regulations that match to all existing materials, chambers and analytes. Hence common standardisation focuses on single products with defined testing devices and specific compounds. One example is the "Standard Practice for Determination of Volatile Organic Compounds (Excluding Formaldehyde) Emissions from Wood-Based Panels Using Small Environmental Chambers Under Defined Test Conditions" (ASTM D6330 [19]).

The second main influential factor deteriorating the reproducibility of emission testing is the lack of reference materials. Round robin tests are comparative measurements between different laboratories evaluating their performance. Reference materials are necessary to provide all participants with a homogeneous sample with constant properties. This ensures comparability. As described in chapter 2.2 heterogeneity at the steps of material selection and preparation affect the testing results significantly. Therefore, identical samples for every laboratory participating in round robin tests are

desirable. While there are various reference materials in other sectors of environmental analysis (see [20]), they are missing for emission testing with the exception of the two approaches introduced below.

Another problem that should be addressed by a reference material is that the measured values should be traceable to SI units. In the case of emission testing this issue is displayed in Figure 2.6. Usually the chemical composition of the building materials is unknown. This means that the true amount of the analytes inside the sample is unknown and only the evaporated part is measurable. The amount, trapped on a sampling tube, is traceable with reference gas standard mixtures. They are based on evaporated weighed analyte amounts. The equilibrium between the air and sample concentration can only be assessed when a material with known composition is used. Hence it is possible to calculate losses of analyte amounts through wall adsorption and leakage of the test chambers.
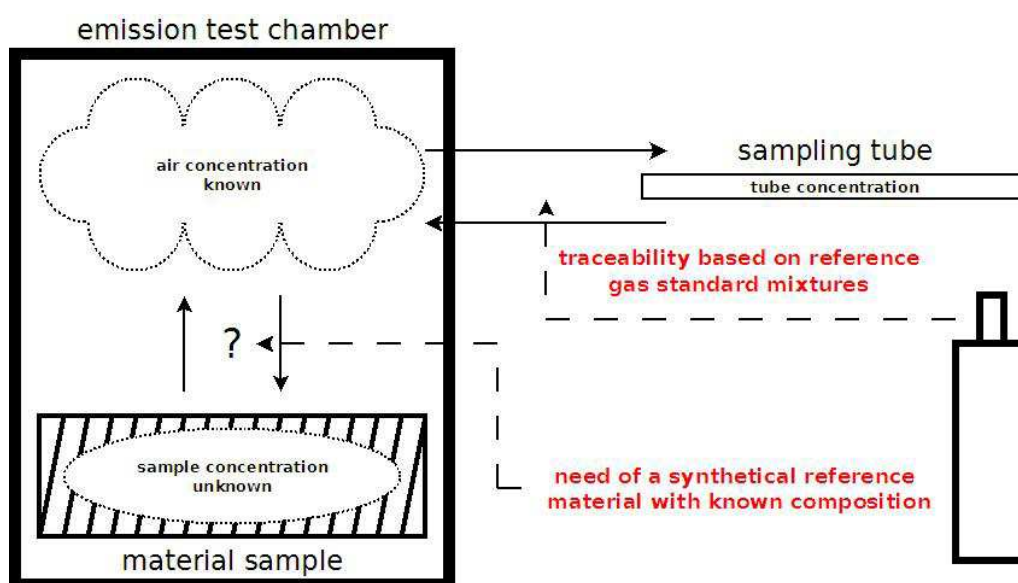
Figure 2.6: Overview of the traceability of emission testing

2.3.1 Reference materials in emission testing - state of the art

There are two basic approaches for reference materials for VOC-emission-testing, published by Wei at al. [21] and Howard-Reed et al. [17]. Both of them use only toluene as the investigated VOC. In 2014 Wei at al. [22] reported that they enable their reference material for the emission of formaldehyde. For both materials model calculations for predicting the emitted amounts are publicised.
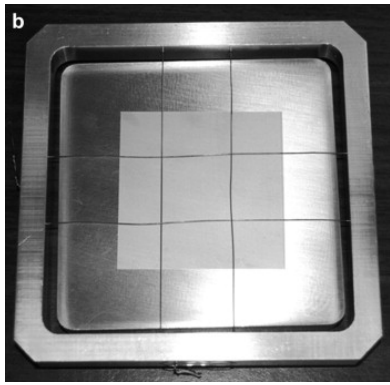
Figure 2.7: PMP-polymer-film loaded into a stainless steel sample holder (taken from [17])
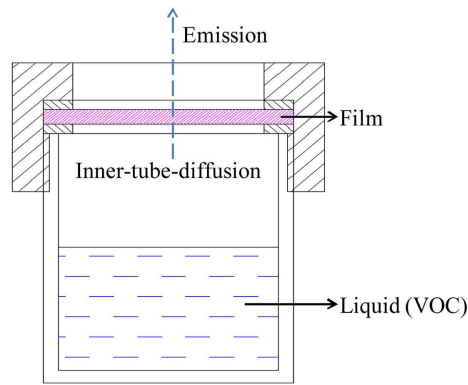
Figure 2.8: LIFE reference - schematic (left) and ion reality (right) (taken from [21])

The polymer PMP (polymethylpentene, a copolymer of 4-methylpentene and alpha-olefine, see Figure 2.7) is the material used by Howard-Reed et al. Small sheets of the polymer (length and width each 3.65 cm, thickness between 0.025 and 0.25 mm) are loaded with a known amount of toluene vapour. After placing the film on a sample holder and loading into a test chamber, toluene is emitted from the material surface.

The second reference is called "LIFE reference" (see Figure 2.8) which stands for liquid inner-tube diffusion-film-emission. This material consists of a cylindrical vessel made of PTFE (polytetrafluoroethylene, each 40 mm in length and diameter) in which the liquid purified VOC is loaded. The vessel is covered with a fastening piece that holds a thin film (aluminium oxide melamine-impregnated paper). It limits the vaporisation of the VOC and controls the emission rate after loading into an emission test chamber.

The emission curves of toluene for both materials differ because they address different problems. Figure 2.9 shows that the LIFE reference aims to set up a constant emission after a conditioning period for up to 1000 h inside the test chamber. This process can be considered rather as permeation than emission. In contrast the PMP-film simulates the behaviour of a real sample with a diffusion-controlled emission (see chapter 2.1.2). This typical graph (Figure 2.10) shows a steep increase to a maximal concentration followed by decay as mentioned before in chapter 2.1.1.
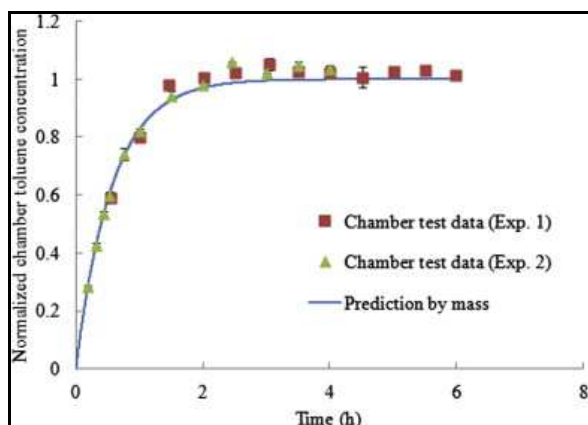
Figure 2.9: Emission profile of the LIFE-reference (taken from [21])
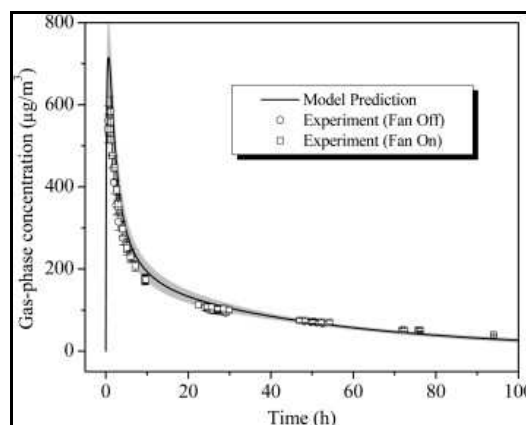
Figure 2.10: Emission profile of the PMP-film (taken from [17])

2.3.2 Problem-solving approach

The two references introduced above are limited to the VOC toluene and the VVOC formaldehyde. Various contaminants less volatile than those two substances can be found indoors. For example, there are plasticisers from synthetic or pesticides from treated wooden materials. However, the fact that the two references might work for such substances has not been published.

This problem is addressed in the present study by developing a new material that is able to release a broad spectrum of different volatile and less volatile organic contaminants. The basic matrix for the reference is a lacquer that can be mixed with either the solid or liquid pure VOCs in the liquid phase. Then the mixture is stirred to ensure a homogeneous distribution of the analytes. After a period of stirring, the lacquer cured under defined conditions. The solid lacquer acts as source similar to the PMP-film for further inter-laboratory comparisons.

The theoretical advantages to the aforementioned method are as follows:

- the agitation of the analytes inside the liquid lacquers ensures homogeneous distribution

- the composition of the cured lacquer system is known, hence the emitted analyte amounts are traceable to the weighed amount inside the cured lacquer

- the lacquer preparation is easy to handle

3 Materials, chemicals and methods

3.1 Materials and chemicals

3.1.1 TD-GC/MS

TD-GC/MS is the most commonly used technique to measure air pollutants. This technique connects thermal desorption (TD) with gas chromatography (GC) and mass spectrometry (MS). This chapter describes GC and MS only as overview because this is a well established technique in analytical chemistry.

The *GC technique* is used to separates gases. It consists of an injector, a separation column and a detector. The Injector evaporates dissolved compounds with high temperatures up to about 300 °C. Separation columns are made of fused silica which is coated with polyimide to reduce the brittleness of the silica. They are coated inside with a thin film mostly made of PDMS (polydimethylsiloxane). This is the stationary phase. This polymeric phase can be substituted with different amounts of phenyl- or cyanopropyl groups to improve the separation for more polar compounds. Polyethylene glycol phases are also used to separate polar compounds. The analytes are transported through these columns with inert carrier gases like helium, nitrogen or hydrogen. These gases act as mobile phase.

Mass spectrometry is a technique that separates ions with magnetic fields. Therefore the molecules from the GC-columns are ionised inside the MS-ion-source. A vacuum is also established to stabilise the emerging ions. One way to ionise the analyte molecules is the electron ionisation (EI). Here the molecules collide with accelerated electrons emitting from a glowing filament. The electrons are accelerated to 70 eV which is the mean energy to gain ions with one positive charge for a wide range of molecules. For labile molecules, chemical ionisation (CI) is preferred. At CI ionised reagent gases transferred only low energy which leads to less fragmentation in opposite to EI. Afterwards the separation system enables the ions to reach the detector separately to the molecule mass. Inside the detector the impinging molecule ions are transferred in detectable and countable electrons. As separation system in this study quadrupoles are used. More detailed information about GC/MS can be found in the reference works of Oehme [23] and Hübschmann [24].

At classic GC the standards are diluted in organic solvents. This solvent is separated from the analytes at the injector and the column. For VOCs the *thermal desorption*

(TD) enables the GC to analyse the substances directly in the gaseous phase. Therefore defined amounts of contaminated air must be trapped on special adsorbent tubes with sampling pumps at ambient conditions. The volatility of the contaminants defines the adsorbent material used inside the tubes. For VVOC mostly modified activated carbon is used while SVOC are usually sampled on glass wool materials. TENAX® TA is usually used to sample wide ranges of analytes with different volatilities. This polymer is based on 2,6-diphenyl-p-phenylene oxide.

The bounded analytes can be desorbed from the adsorbent material at higher temperatures inside a TD-oven. The maximum temperature of desorption is adjusted to the stability of the material and the analyte itself. Mostly temperatures between 280 and 340 °C are used. While with desorption the tubes are flushed with the carrier gas of the GC. The gas flow transports the analytes from the heated sampling tube to the GC. There the substances are desorbed from the material according to their volatility. First high volatile compounds evaporates from the material at lower than the less volatile at higher temperatures. Directly coupled to a GC the subsequent desorption and transport of the analytes from the TD-oven to the GC-column would lead to spreading peaks on the chromatogram. GC needs retention of the analytes at the column start for a good separation. Therefore the analytes are trapped at low temperature on a material at the GC-liner of the injector. This injector is equipped with a special adsorbent material (activated carbon, Tenax, glass wool). From this cold trap the analytes are desorbed simultaneously when the material is heated up quickly.

In the present study two different thermal desorption systems (TDS) were used. The system "Asterix" (GERTSEL/AGILENT) was used in part 4.1, while part 4.2 and 4.3 were analysed with "Idefix" (MARKES/AGILENT). Both systems are introduced in Table 3.3

3.1.2 Emission test chambers

Usually climate chambers are used to analyse samples under defined conditions. They keep the temperature, humidity, air flow and air change at constant values which is close to indoor air properties.

Principal test chamber systems consist of the following parts: clean air generation, humidification, test chamber with a temperature control and ventilation (air mixing), control- and monitoring system.
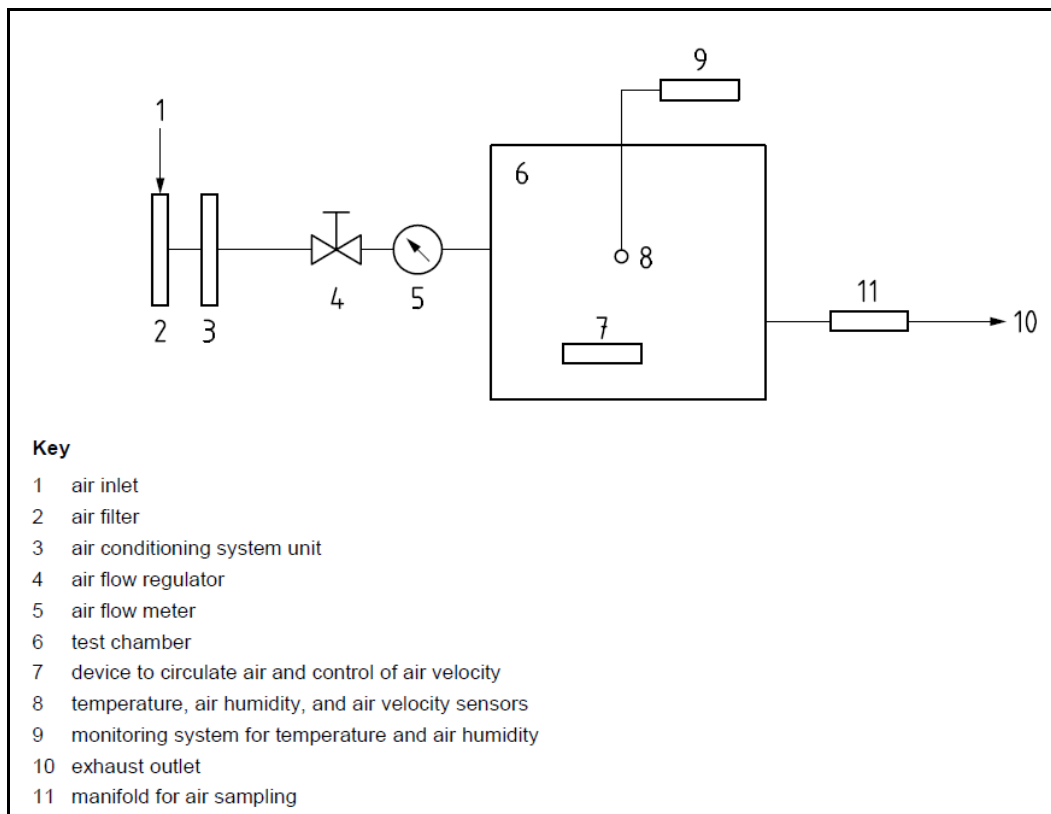
Key

1   air inlet
2   air filter
3   air conditioning system unit
4   air flow regulator
5   air flow meter
6   test chamber
7   device to circulate air and control of air velocity
8   temperature, air humidity, and air velocity sensors
9   monitoring system for temperature and air humidity
10 exhaust outlet
11 manifold for air sampling

Figure 3.1: General description of an emission test chamber (taken from [12])

Figure 3.1 shows a test chamber system according to ISO 16000-9 [12]. First the air supply (1) is cleaned with filters (2). Inside the air conditioning system (3) the pure air is mixed with steam. Flow controllers (4/5) adjust the mixing ratio and ensure a constant air flow. Afterwards the purified and humidified air flows through the inlet into the tempered test chamber (6). There air is then mixed by a fan (7) to avoid dead volumes which can act as a sink. The air leaves the chamber through the outlet (10).

Sensors inside the chambers (9) measure temperature and humidity continuously. They send the data for temperature and humidification back to controlling systems (3). As mentioned in chapter 2.2 where possible all parts of the chamber system are made of glass and stainless steel to avoid sink effects or secondary emissions.

Additionally, the chamber is equipped with sampling ports (11). These sealable ports enable air sampling with test tubes packed with adsorbent materials. With sealed ports the inlet air can leave the chamber through the outlet only. This ensures a defined air change. The sampling port is located at the at the chamber outlet (Figure 3.1).

Beside conventional test chambers with volumes in cubic meter ranges, there are various smaller chambers which are often custom made. This reduces the sample amount that has to be loaded. It can be said that those chambers are more economic because they need less space, conditioned air and amount of material samples. On the other hand their results must be correlated to bigger chambers because they are often prescribed in different standards.

One example of a custom made small chamber is the *24-l-desiccator* [25]. Figure 3.2 shows that those desiccators are equipped with a mixing fan that is operated through the lid. Three-neck adapters at the desiccator side provide an air in- and outlet. Additionally they can be used as sampling port. The supply air is conditioned and humidified with an external device which can be used for more desiccators. Together they are placed inside a 16-m³-chamber (Figure 3.3) which ensures a homogeneous temperature outside and inside the desiccator.

The desiccators consist of a base part and a cap with plain flange (300 mm diameter, both from TH. GEYER). Both parts are equipped with a glass joint socket (NS29/32). The socket of the lid is used to connect the blade stirrer (R 1385, VWR). The stirrer is driven by a DC micro motor (Mot110182 D26, INELTA) and both parts are coupled with a magnetic clutch (MRK 1/20, TH. GEYER). The socket of the desiccator base is used to equip a threefold glass connector for sampling, inlet und outlet air. The flow through the desiccator was measured with a soap film flow meter Gilibrator 2 from GILIAN. Further information is given also in chapter 3.1.2.

The desiccators and the 1-m³-chamber used in chapter 4.2.1 and following are located in climate chambers (WEISS UMWELTTECHNIK). This chamber is used to adjust the temperature of the desiccators. The air supply is conditioned by a purification packet (Oilfreepac OFP, DONALDSON). The humidification is adjusted by a self developed device similar to chapter 4.2.5.

The *Micro-Chamber/Thermal Extractor™ (µ-CTE™)* from MARKES (Figure 3.4) is a commercial device for the fast screening of materials emission. Six single chambers, each 44 ml are placed inside one heating block. A central flow of dry technical air is divided into one stream for each chamber. It enables air exchange and mixing [26]. Usually the µ-CTE is used to screen the emission of small material samples with a maximum diameter of 45 mm with high flows up to 200 ml/min (see [27] and [28]).

The emission process can also be accelerated for low volatile substances by increasing the temperature up to a maximum of 120 °C. As it exhibits high air exchange, the sampling tube on the lid of each of the six chambers can be loaded passively without pumps (Figure 3.5).

Beginning with experiment part 4.2 they were equipped with Mass flow controllers (MFCs, 4800 Series, BROOKS) to reduce the variation of the flow. For the investigations they operated at 25 °C. The flow was controlled with a flow meter (35806ML, ANALYT-MTC).
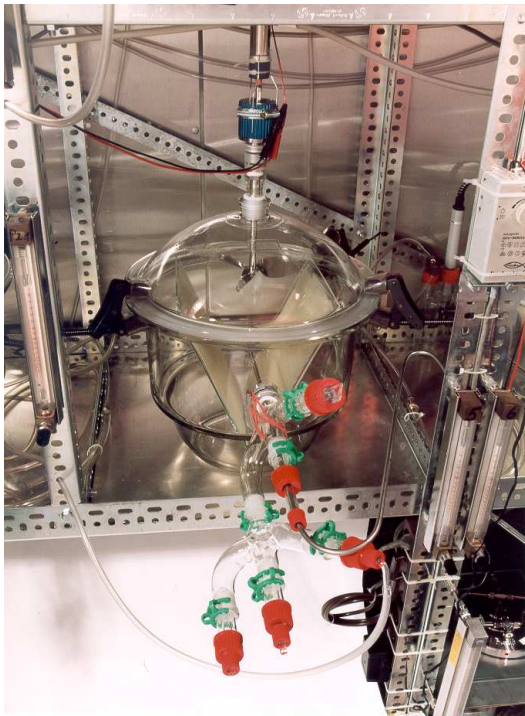
Figure 3.2: 24-l-chamber (desiccator) loaded with wooden sample
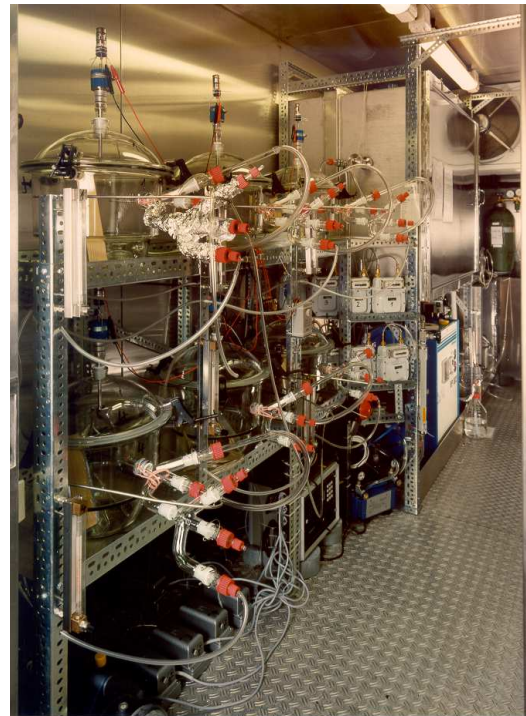
Figure 3.3: Several 24-l-chambers inside a 16-m³-chamber

Figure 3.4: Micro-Chamber/Thermal Extractor™ (μ-CTE™) from MARKES Int. (opened)
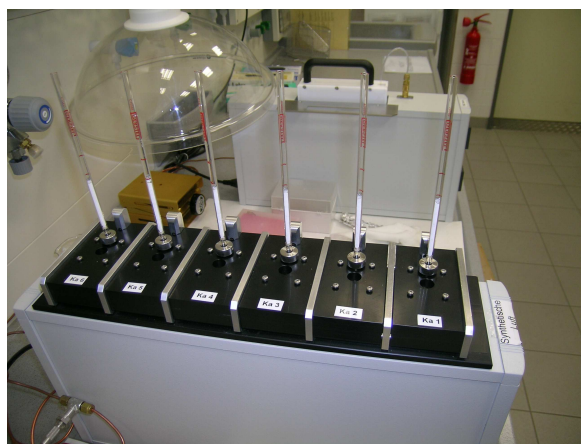
Figure 3.5: μ-CTE (closed) with sampling tubes

3.1.3 Lacquers

This chapter gives a short introduction into the complex field of lacquers and paintings. It informs of the requirements, classes and compositions of different lacquers. The following remarks are based on the "Glasurit-Handbuch Lacke und Farbe" [29] which describes lacquers from different point of views in a very extensive way.

In general, lacquers are substances that improve the surface properties of materials. Hence, the main tasks of coating is for protection against the destroying exposure of the environment (e.g. anticorrosive coating), embellishing the material through colour and brightness and finally improving physical and chemical functionality like hydrophobicity and roughness. Primarily lacquers consist of four basic materials: solvent, additives, pigments/filler and film forming substances (lacquer resin).

The lacquer resins consist of mostly organic substances of medium and higher molar mass. Silicones are almost the only substrate for inorganic resin. These compounds are either dissolved or dispersed.

There are two possible ways for the curing process. First there is *physical drying*. The covering film develops when the solvent evaporates from the solution or dispersion while the resin remains on the surface. On the other hand there is the *chemical cross-linking*. The main ingredients are highly reactive monomers that are dissolved by a solvent. When induced by light, heat or catalysts these monomers

polymerise to form a resin which covers the surface. The solvent then evaporates because the developing polymer loses solubility. Primary the process of curing does not depend on the chemical structure of the resin itself but on the presence of reactive chemical functional groups that provides polymerisation.

Pigments are necessary to cover the underground and colour the surface. The colour is based on either different inorganic salts or oxides like Ti_2O or organic substances with many conjugated double bonds. Additionally, inorganic pigments can increase the resistance against corrosion by deactivating the surface, for example on steel.

Mineral fillers are used to fill the dispersion and sustain the cured lacquer. Additionally they can improve the adhesion on the substrate and linkage following layers of lacquer as well as decreasing the surface brightness.

The group of *additives* is dominated by plasticisers. They act as non-evaporative solvents for the resins and control the hardness and brittleness of the cured lacquer. Other additives have the following functions: adjusting the viscosity of the mixture, prevent foaming, biocidal properties, anti-fouling properties and improving dispersion, wettability, curing and UV-absorption.

The main task for *solvents* or mixtures is to dissolve the other three main compounds. They turn the lacquer into one matrix and adjust the viscosity, flow properties and wetting. Besides water there are a lot of organic solvents in use, like aliphatic hydrocarbons (e.g. benzine), aromatic hydrocarbons (e.g. styrene, toluene, xylene), glycol-ethers and -esters, alcohols (glycerine), ketones (e.g. Methyl isobutyl ketone, MIBK) and other special solvents like N-methylpyrrolidone.

The lacquers used in chapter 4.1.2 were produced by the manufacturer MEFFERT. Six of them were acrylic based (incorporating water as solvent) and six were based on alkyd polymers (incorporating organic solvents). The acrylic lacquers contained water, a dispersion of acrylat and polyurethane, glycols, additives, preservatives (methyl-, benzyl- and chlor-isothiazolinone) and pigments (if it is a coloured lacquer). These lacquers are labelled with the Blue Angel eco-label for low emissions. The alkyd lacquers contained the alkyd resin, additives, white spirit and pigments (if coloured).

3.1.4 Chemicals

For the investigation the five VOCs styrene (100-42-5, ALFA AESAR, 99.5 %), N-methyl-α-pyrrolidone (872-50-4, NMP, FLUKA, > 99.9 %), 2-ethyl-1-hexanol (104-76-7, E.H., ALDRICH, 99.6 %), 1,2-dimethyl-phthalate (131-11-3, DMP, ALFA AESAR, 99 %), n-hexadecane (544-76-3, C16, ALDRICH, 99 %) and the two SVOC lindane (58-89-9, ALDRICH, 99.8 %) and 1,2-di-n-butyl-phthalate (131-11-3, DBP, ALDRICH > 98 %) were selected.

All of these substances can be found in indoor air as they are emitted from different building materials like flooring. C16 is the link between VOC and SVOC according to the standard ISO 16000-6 [30]. NMP and DBP (a plasticiser like DMP) are "substances of very high concern" according to the ECHA (European Chemical Agency) - candidate list because of their toxicity for reproduction [31]. E.H. and styrene are reactants for many synthetic materials. For example E.H. is an important reactant for the synthesis of the widely used plasticiser bis(2-ethylhexyl) phthalate (DEHP) [32].

The spectrum of the polarity expressed as partition coefficient log $P_{oct/wat}$ can be seen in Figure 3.6. Figure 3.7 shows the range of volatility of the investigated substances expressed as boiling point T_B. Table 3.1 shows additional selected physical parameters. The chromatographic separation of the investigated substances is shown in Figure 3.8.

Table 3.1: Overview of selected physical parameters of the investigated substances [33] [34]

analyte	CAS	molar mass M [g/mol]	melting point T_m [°C]	boiling point T_B [°C]	log $P_{oct/wat}$
styrene	100-42-5	104.15	-31	145	3.05
E.H.	104-76-7	130.23	-76	182	2.86
NMP	872-50-4	99.13	-24	203	-0.54
DMP	131-11-3	194.19	6	282	1.56
C16	544-76-3	226.45	18	287	6.2
lindane	58-89-9	290.83	113	323	3.55
DBP	131-11-3	278.35	-35	340	4.72
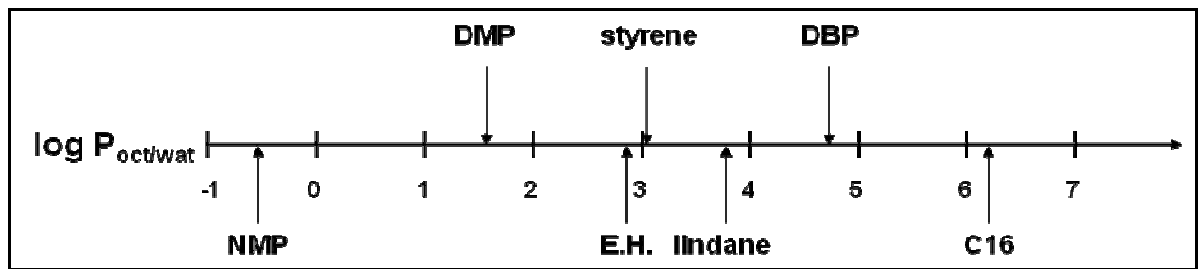
Figure 3.6: Overview of the polarity range of the investigated substances expressed as $P_{oct/wat}$

Figure 3.7: Overview of the boiling point range of the investigated substances
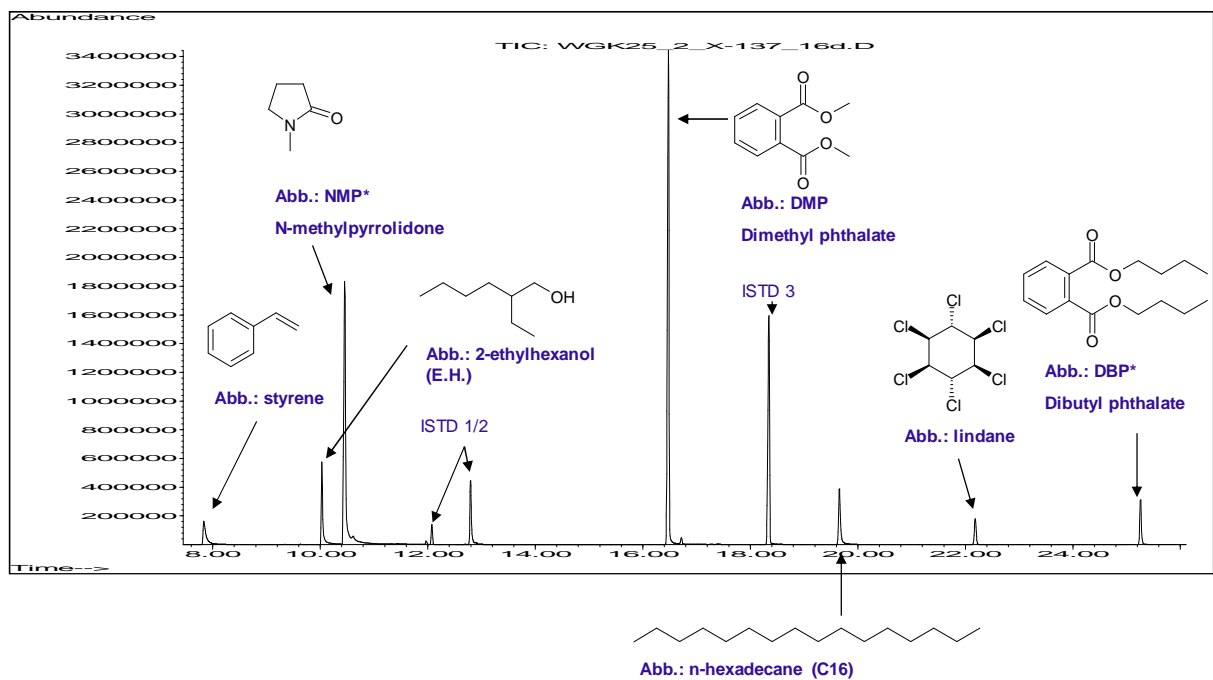
Figure 3.8: Chromatographic separation of the investigated substances (*...SVHC – substances of very high concern [31]; see Table 3.3 for measurement parameters; ISTD .. internal standard)

In chapter 4.3 odorous compounds were added. Hexanal (66-25-1, Aldrich, 98 %) is a secondary emitter, e.g. from wooden samples. It is formed by oxidative elimination. R-(+)-limonene (138-86-3, limonene, ALDRICH, 97%) and is also emitted from wooden samples. Naphthalene (91-20-3, J. T. BAKER, 99.9 %) is emitted from synthetic materials that were produced with oil. 2-Ethylhexyl acrylate (103-11-7, E.H.-acryl, ALDRICH, 98 %) is a reactant for acrylic sealants.

Decane (124-18-5, C10, MERCK, > 99 %), which is emitted from wooden and synthetic materials, was added to include a volatile substance in the range of styrene and hexanal.

Table 3.2: Overview of selected physical parameters of the additional substances [33] [34]

analyte	CAS	molar mass M [g/mol]	melting point T_m [°C]	boiling point T_B [°C]	log $P_{oct/wat}$
hexanal	66-25-1	100.16	-56	129	1.78
C10	124-18-5	142.28	-30	174	5.01
limonene	138-86-3	136.24	-89	175	4.50
E.H.-acryl	103-11-7	184.28	-90	214	4.29
naphthalene	91-20-3	128.17	80	218	3.35

3.2 Methods

3.2.1 TD-GC/MS

The TDSA from GERSTEL (Figure 3.9) operates glass TD-tubes. 20 of these tubes can be loaded into the auto-sampler. From this sampler, the tubes are loaded automatically into the TD-oven. There they are desorbed and flushed with He. With a small transfer line (Figure 3.10) the analytes stream to the cold injection system (CIS) which is cooled simultaneously to about -100 °C. The analytes are then cold-trapped until the defined heating cycle of the tube inside the oven finishes. After this period of time the CIS is heated up quickly and the trapped analytes are flushed to the GC-column. The system uses liquid Nitrogen for cooling. A pneumatic unit adjusts the different transport flows of He through the TDS, it also allows splitting steps.

The second TDS used is the Unity-1-system from MARKES coupled with a ULTRA-50:50-auto-sampler (Figure 3.11). The tubes can be collected on the ULTRA-auto-

sampler. The tubes are heated up and flushed with carrier gas and they stream over a heated transfer line into the ultra. The analytes then become trapped on a cold trap tube which is equipped with an adsorbent material. As the trapping temperature is usually no lower than -5 °C, only gaseous Nitrogen and Peltier elements are needed for cooling. After quickly heating the trap, the analytes are flushed together into the GC-column. The complex pressure control of the UNITY allows splitting the analyte-flow at every part of the TDS. For example, it is possible to divide the flow from the TD-oven or the trap and transport a portion of it back to the sampling tube. This can be used to analyse a sample from one tube for a second time. On the contrary the TDS from GERSTEL desorbs the analytes from one tube completely, therefore the sample cannot be analysed again from the same tube. To enable the recollection of samples, the UNITY needs a complex pneumatic system with high pressures, thus the TD-tubes are made mostly on stainless steel and they must be tightened with caps before loading them into the ULTRA-50:50 (Figure 3.12).

Figure 3.9: TDSA with glass sampling tubes inside the autosampler (GERSTEL)

Figure 3.10: Transfer line of the TDSA (GERSTEL)
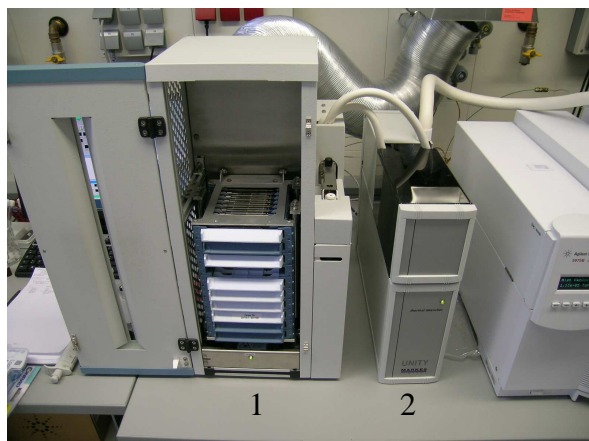
Figure 3.11: ULTRA 50:50 (1) and UNITY1 (2) (MARKES Int.)
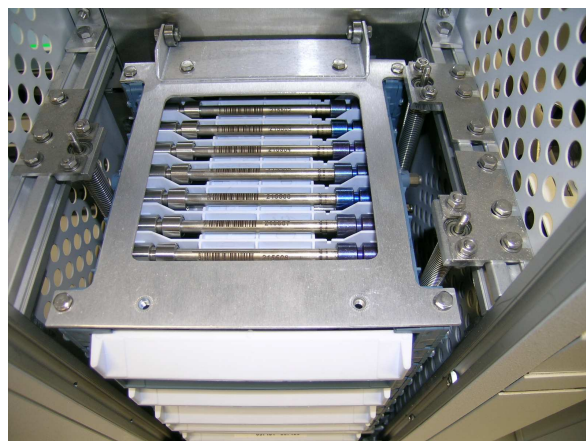
Figure 3.12: Capped steel sampling tubes inside the Ultra 50:50 autosampler

The GERSTEL-tubes were conditioned for two hours at 280 °C inside a GERSTEL TC 2 (tube conditioner). The MARKES-tubes were conditioned for half an hour at 280 °C inside a MARKES TC20 (tube conditioner). Both conditioners operated with a N_2-flow of 100 ml/min. For both applications Tenax TA was used as adsorbent.

Table 3.3: Measurement parameters of the TD-GC/MS system "Asterix" and "Idefix" (see chapter 3.1.1)

		Asterix	Idefix
GC	model	AGILENT 6890	AGILENT 6890
	column	RESTEK Rxi 5-ms (60 m, 25 mm, 0.25 µm)	
	column flow	1.4 ml/min (constant flow)	1.5 ml/min (constant flow)
	carrier gas	helium (ALPHAGAZ AIR LIQUIDE)	
	oven temperature program	40 °C for 4 min; with 10 °C/min to 150 °C for 1 min; with 8 °C/min to 300 °C for 5 min	60 °C for 2 min; with 10 °C/min to 300 °C for 5 min
MS	model	AGILENT 5973N	AGILENT 5975B
	transfer line	300 °C	300 °C
	ion source	EI, 230 °C	
	quadrupole	150 °C	
	mode	full scan: 40 – 440 amu	
TDS	model	GERSTEL TDS A + GERSTEL CIS 4	MARKES UNITY 1
	tube desorption program	30 °C for 1 min; with 30 °C/min to 260 °C for 5 min; flow: 50 ml/min (splitless)	290 °C for 10 min; flow: 50 ml/min (splitless)
	CIS/cold trap program	-120 °C for 0.05 min; with 12 °C/s to 300 °C for 3 min; flow: 1.4 ml/min (splitless)	5 °C; with 12 °C/s to 300 °C for 5 min; flow: 1.5 ml/min + 6 ml/min split flow (ratio: 1:5)
	liner	glass wool	Tenax TA
	transfer line	300 °C	180 °C

3.2.2 Calibration

The substances were externally calibrated. From each substance weighed amounts were diluted in methanol (MeOH, for organic residue analysis, J.T. Baker) in volumetric flasks of 10 ml. Depending on the purity of the substances the final concentrations were all approximately 10 µg/µl. From these stock solutions defined amounts were transferred to a volumetric flask of 10 ml and filled up with MeOH. The adjusted concentration of the mix was approximately 200 ng/µl. This methanolic solution was diluted according to the following steps: 180, 160, 140, 120, 100, 80, 60, 50, 40, 20, 10, 4, 2 and 1 ng/µl.

From each of these 15 levels 1 µl was spiked with glass syringes of 5 µl (HAMILTON) onto adsorbent tubes. 1 µl of an internal standard (ISTD) was also added. This ISTD consisted of 20 ng/µl of cyclodecane (293-96-9, ALDRICH, 95 %) and naphthalene-d_8 (1146-65-2, ALDRICH, 99 %) as well as 51.5 ng/µl of 2,4,6-tribromophenol (118-79-6, ALDRICH, 99 %). Afterwards MeOH was flushed with a 1 l of N_2 (ALPHAGAZ AIR LIQUIDE) on a GERSTEL TSPS (standard tube preparation system).

The tubes that were spiked with the 15 levels were subsequently analysed with the TD-GC/MS. The measured area counts calculated from the chromatograms were linked with the mass of analyte on the tube with linear regression. The calibration data can be found in Table 8.1 to Table 8.6.

3.2.3 Quantification

The internal standard was used to calculate differences in the adsorption performance of the sampling tubes. Therefore the measured ISTD-area-counts from each tube of one measurement sequence were averaged. For each tube the ratio of the ISTD amount on the associated tube and the ISTD-average was calculated. This factor was multiplied with the measured analyte amounts.

Furthermore, the concentrations were calculated based on ISO 16000-9 [12]. The analyte amount trapped onto the sampling tube (m_S) in relation to the sampled volume (V_S) results in the mass concentration (ρ_X). This parameter is often expressed as µg/m³.

As there is a wide spectrum of commercially available and self build emission test chambers with different volumes and operating flows the parameter L and q are often used to correlate results from different chambers. For comparison SER_A is more

practical than ρ_X because it considers important chamber parameters like air change, emission surface and flow.

Table 3.4 summarises regularly used parameters in emission testing with their associated calculations.

Table 3.4: Typical parameters and their calculations in emission testing (partially in accordance to ISO 16000-9 [12])

abbr.	unit	name	calculation
m_S	ng	analyte amount trapped onto the sampling tube	-
V_S	m³	sampling volume	-
V	m³	chamber volume	-
$\dot{V}$	m³/h	chamber air flow	-
t	h or d	time after start of the test	-
A	m²	emission surface	-
ρ_X	mg/m³	mass concentration of a VOC$_X$ inside the emission test chamber	$\rho_X = \dfrac{m_S}{V_S}$
L	m²/m³	product loading factor	$L = \dfrac{A}{V}$
n	1/h	air change rate	$n = \dfrac{\dot{V}}{V}$
q	m³/(m²·h)	area specific air flow rate	$q = \dfrac{\dot{V}}{A} = \dfrac{n}{L}$
SER_A	µg/(m²·h)	area specific emission rate	$SER_A = \rho_X \cdot q$

3.2.4 Lacquer preparation

The basic lacquer preparation can be seen in Figure 3.13.

In the first step the lacquer can was opened. After stirring the mixture with a glass rod weighed amounts were poured into screw cap bottles of 100 ml (wide neck, VWR). For larger batches Erlenmeyer flasks were also used. A magnetic stir bar (cylindrical, VWR) was added afterwards and the vessel was placed on a magnetic stirrer

(HEIDOLPH MR 3001 K). Under simultaneous stirring the defined amounts of the pure analytes were added with glass syringes (HAMILTON). Solid substances had to be diluted in MeOH beforehand. The mixture was then stirred for one hour with closed bottles or flasks.

Finally, Petri dishes (35 mm or 94 mm diameter; GREINER BIO ONE) were filled gravimetrically with the lacquer mixture. Into the µ-CTE 2 g were loaded while for the desiccator 20 g were weighed. These Petri dishes were loaded into the emission test chambers.
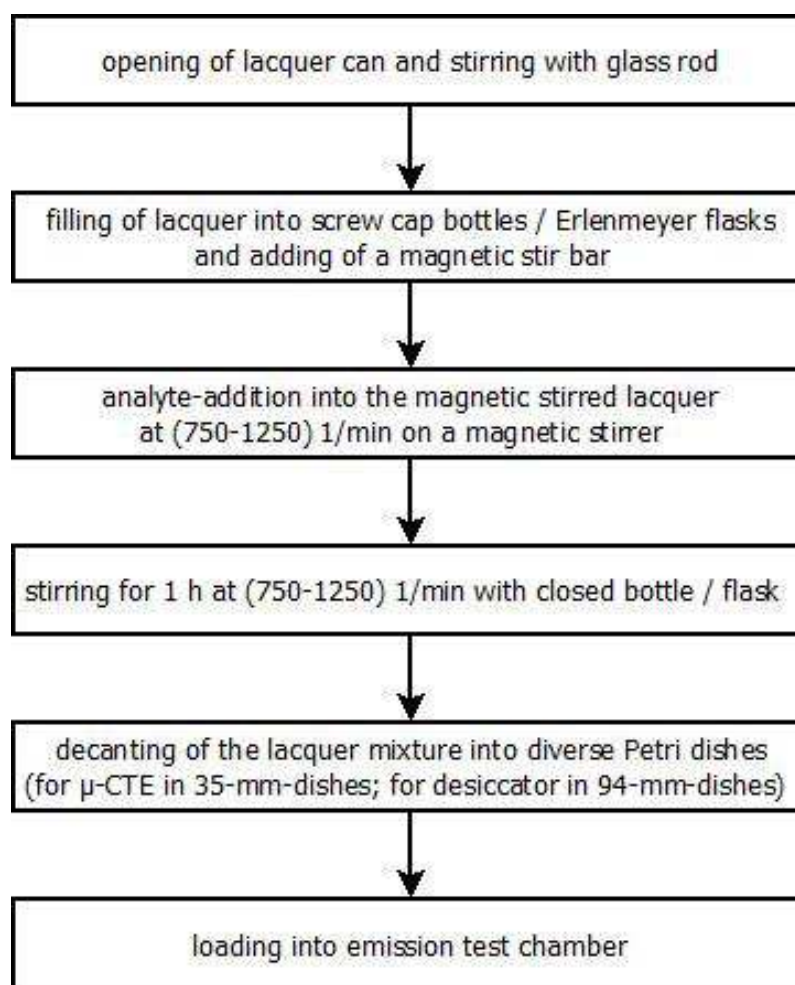
Figure 3.13: Lacquer preparation scheme

Figure 3.14: Lacquer mixture inside a 100 ml amber screw cap bottle on a magnetic stirrer

Figure 3.15: Addition of the pure analyte into the agitated lacquer with a glass syringe

For the lacquer preparation it was important to state how much analyte in relation to the lacquer was used. This lacquer spiking can be calculated by two ways. Commonly the mass fraction ω is used. This means the quotient between the mass of each analyte m_A introduced and the mass of the whole lacquer batch m_B (mass of lacquer + all analytes + solvent):

$$\omega = \frac{m_A}{m_B} = \frac{\rho_A \cdot V_A}{m_B}$$

For subsequent lacquer spiking this mass fraction is not helpful. The mass m_B depends on how long it takes to prepare the mixture. Solvent evaporates while the lacquer is stirred during the preparation. For a reproducible lacquer spiking it is better to know the lacquer specific mass fraction ω_L which means the ratio of the mass of analyte and the mass of lacquer m_L.

$$\omega_L = \frac{m_A}{m_L} = \frac{\rho_A \cdot V_A}{m_L}$$

For liquid analytes in both mass fractions m_A can be expressed as a product between the spiked analyte volume V_A multiplied by the associated density ρ_A.

3.2.5 Sampling

In the emission test chambers active sampling was performed with FL-1001 FLEC-pumps from SCP. They are designed to provide a constant flow over time. To sample 1 l a flow of 100 ml/min was chosen for a time of 10 min. The pump flow was calibrated by the manufacturer and checked every six months in the laboratory.

Figure 3.16: FLEC-pump from SCP

At the µ-CTE sampling tubes were loaded passively by the high chamber flow (see chapter 3.1.2). 250 ml was sampled. While sampling the through flow each tube was measured with a flow meter. The ratio of the desired sampling volume of 250 ml and the flow through the tubes resulted in the sampling time. After this time the tubes were removed from the µ-CTE.

3.2.6 Uncertainty

According to the "Guide to the expression of uncertainty in measurement" (GUM; [35]) the combined standard uncertainty u of a value y can be estimated with the law of propagation of uncertainty. This means that the uncertainties of the parameters x_i influencing y are squared and summed. The square root of this sum is the combined uncertainty u(y):

$$u(y) = \sqrt{\left(\frac{\partial y}{\partial x} \cdot u(x_1)\right)^2 + ... + \left(\frac{\partial y}{\partial x} \cdot u(x_n)\right)^2}$$

For the lacquer system, y stands for the measured air concentration ρ_x inside the test chamber. According to Table 3.4 ρ_x stands for the quotient of the analyte amount trapped onto the sampling tube m_S and the sampled air volume V_S. Therefore the combined relative uncertainty can be summarised as:

$$u_{rel}(\rho_X) = \sqrt{u_{rel}^2(m_S) + u_{rel}^2(V_S)}$$

The uncertainty of V_S is mainly determined by the deviation of the sampling pump performance. This uncertainty was calculated from the relative standard deviation of repetitive sampling of 1 l with 100 ml/min. The sampled volume was measured with a gas meter (BRAND Germany).

For µ-CTE-sampling the tubes were loaded passively by the chamber flow over a specific amount of time. The deviation of the stopwatch combined with the time that was needed to pull the tubes from the sampling port could not be calculated. However, compared to the deviation of the chamber flow it was negligible. The deviation of the flow through the µ-CTE was calculated as relative standard deviation of the flow, measured while sampling and randomly over the whole loading cycle. With equipped mass flow controller the deviation of the flow could be lowered from 5 to 1 %.

The uncertainty of m_S is influenced by the stability of the measurement system (TD-GC/MS), the adsorption performance of the sampling tubes and the variance in the lacquer emission. Figure 3.17 shows that this last variance is determined by the process parameter of the chamber while curing and emission testing as well as by the variation of the lacquer preparation. In this study the lacquer system as a reference material was under development. Hence not enough data was available to develop models calculation the influence of the process parameters and the variations in the sample preparation on the emission performance. Therefore these parameters are shown but cannot be included in the uncertainty of m_S.

The performance of the measurement system and the adsorption performance can be estimated with repetitive analysis of sampling tubes spiked with equal analyte amounts. Therefore each of the six sampling tubes were spiked with a solution that

contained 40 and 100 ng/µl of each compound. The uncertainty of m_S was calculated as averaged relative standard deviation of the results from each tube.
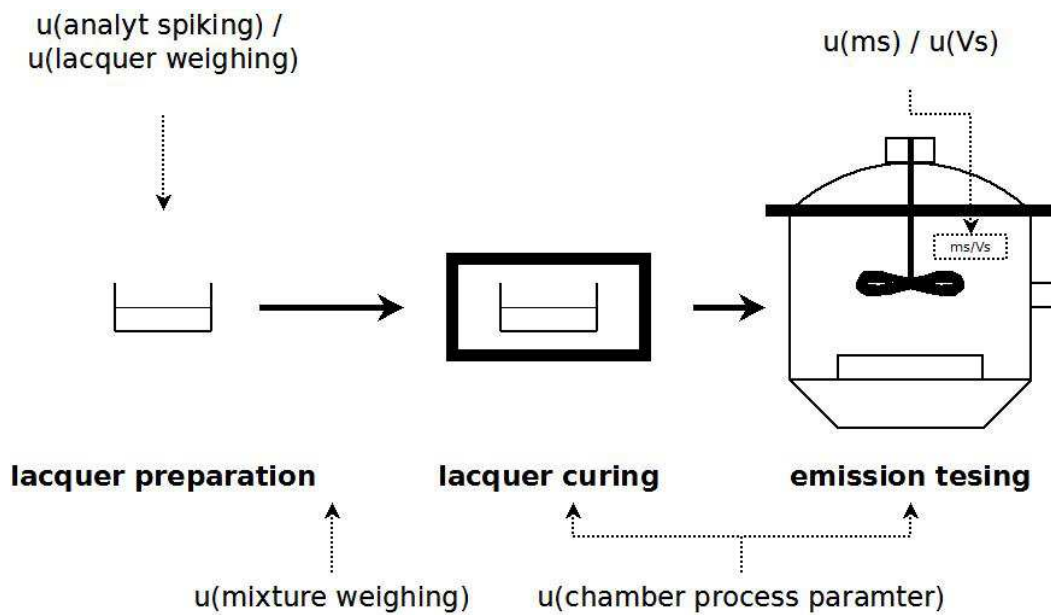
Figure 3.17: Uncertainties influencing the preparation, curing and emission testing of the lacquer system (u ... uncertainty, m_S ... analyte amount trapped onto the sampling tube, V_S ... sampled air volume)

Table 3.5: Uncertainties (u_{rel}) for the measured air concentration ρ_x on two different TD-GC/MS-systems ("Asterix"/"Idefix") calculated from the uncertainties of the analyte mass trapped onto the adsorbent tube (m_s) and the sampled volume (V_s; "pump" ... active sampling with pump; "w/o. / w. MFC" ... passive sampling on µ-CTE equipped without/with MFC) - part 1

	hexanal	styrene	C10	E.H.	limonene	NMP
$u_{rel}(V_{S,pump})$ [%]	2.0	2.0	2.0	2.0	2.0	2.0
$u_{rel}(V_{S,w/o.\ MFC})$ [%]	5.0	5.0	5.0	5.0	5.0	5.0
$u_{rel}(V_{S,w.\ MFC})$ [%]	1.0	1.0	1.0	1.0	1.0	1.0
"Asterix"						
$u_{rel}(m_S)$ [%]	5.5	6.8	4.3	6.4	4.9	8.9
$u_{rel}(\rho_{x,pump})$ [%]	5.8	7.0	4.8	6.7	5.3	9.1
$u_{rel}(\rho_{x,w/o.\ MFC})$ [%]	7.4	8.4	6.6	8.1	7.0	10.2
$u_{rel}(\rho_{x,w.\ MFC})$ [%]	5.6	6.8	4.4	6.5	5.0	8.9
"Idefix"						
$u_{rel}(m_S)$ [%]	7.6	5.6	4.8	5.8	5.3	6.7
$u_{rel}(\rho_{x,pump})$ [%]	7.9	5.9	5.2	6.1	5.7	7.0
$u_{rel}(\rho_{x,w/o.\ MFC})$ [%]	9.1	7.5	6.9	7.7	7.3	8.4
$u_{rel}(\rho_{x,w.\ MFC})$ [%]	7.7	5.7	4.9	5.9	5.4	6.8

Table 3.6: Uncertainties (u_{rel}) for the measured air concentration ρ_x on two different TD-GC/MS-systems ("Asterix"/"Idefix") calculated from the uncertainties of the analyte mass trapped onto the adsorbent tube (m_s) and the sampled volume (V_s; "pump" ... active sampling with pump; "w/o. / w. MFC" ... passive sampling on µ-CTE equipped without/with MFC) - part 2

	naphthalene	E.H.-acryl	DMP	C16	lindane	DBP
$u_{rel}(V_{S,pump})$ [%]	2.0	2.0	2.0	2.0	2.0	2.0
$u_{rel}(V_{S,w/o.\ MFC})$ [%]	5.0	5.0	5.0	5.0	5.0	5.0
$u_{rel}(V_{S,w.\ MFC})$ [%]	1.0	1.0	1.0	1.0	1.0	1.0
"Asterix"						
$u_{rel}(m_S)$ [%]	6.1	3.7	5.7	4.3	5.6	4.9
$u_{rel}(\rho_{x,pump})$ [%]	6.4	4.2	6.1	4.8	5.9	5.3
$u_{rel}(\rho_{x,w/o.\ MFC})$ [%]	7.9	6.2	7.6	6.6	7.5	7.0
$u_{rel}(\rho_{x,w.\ MFC})$ [%]	6.2	3.8	5.8	4.5	5.6	5.0
"Idefix"						
$u_{rel}(m_S)$ [%]	3.6	4.5	3.4	5.1	4.4	4.2
$u_{rel}(\rho_{x,pump})$ [%]	4.1	4.9	3.9	5.5	4.8	4.7
$u_{rel}(\rho_{x,w/o.\ MFC})$ [%]	6.2	6.7	6.0	7.1	6.7	6.5
$u_{rel}(\rho_{x,w.\ MFC})$ [%]	3.7	4.6	3.5	5.2	4.5	4.3

Table 3.7: Uncertainties influencing the reproducibility of the emission of the lacquer system that cannot be included into the calculation of the combined uncertainty

u	uncertainty	calculation
analyte spiking	3 % (100-µl-syringe) 0.5 % (500-µl-sysringe)	checkout with pure water
lacquer weighing	0.01 %	balance calibration protocol
mixture weighing	0.02 % (20-g-samples) 0.002 % (2-g-samples)	balance calibration protocol
camber process parameter	4 % (temperature) 5 % (relative humidity) 5 % (air change)	long-term monitoring

4   Experimental

In this chapter the experimental design is described. Preparation schemes summarise the lacquer preparations with the respective analyte composition. The different symbols are depicted in Figure 4.1.
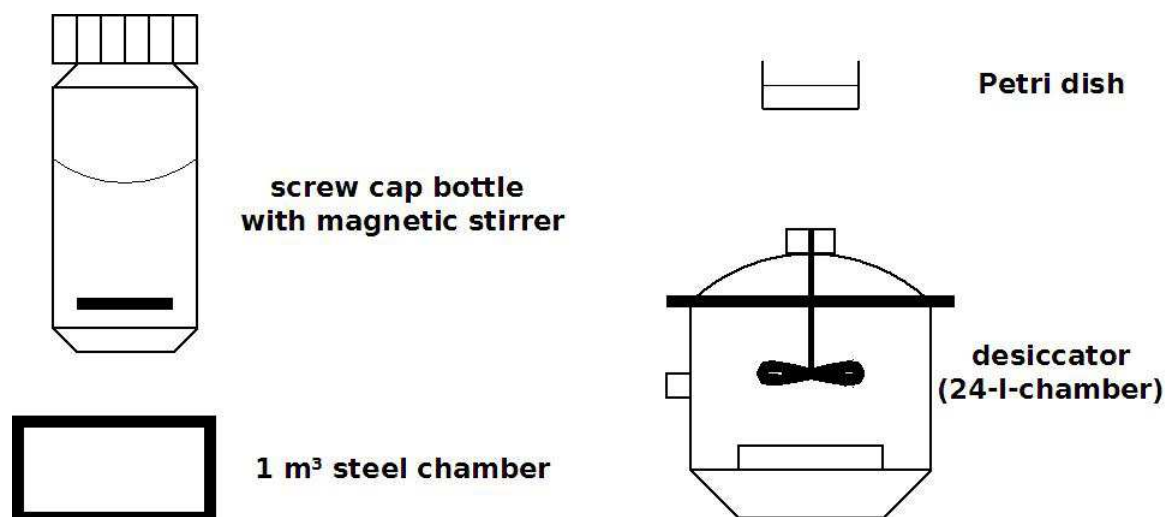
Figure 4.1: Symbol descriptions used for the preparation schemes

4.1   Preliminary testing

4.1.1   Chamber selection

Developing the optimal lacquer mixture requires various experiments concerning lacquer selection, preparation, optimisation and stability testing. Conducting these tests in 1-m³-chambers would be too time-consuming. When cleaning the chambers must be wiped out with special solvents or they can be desorbed thermally. Additionally each experiment would need huge amounts of sample. 24-l-chambers can provide equal parameters but they are smaller and they can measure approximately four to six samples with the same required space. However, cleaning once again is very complex and afterwards they need approximately one day to equilibrate.

Figure 4.2 shows the size-difference of a conventional chamber of 1 m³ in opposite a micro-chamber. The µ-CTE combines six single chambers which enables parallel testing in one instrument, but it must be kept under consideration that no humidification is provided.

Figure 4.2: Size-comparison of a micro-chamber (front) in opposite of a 1-m³-chamber (back)

To show that the micro-chamber is a suitable substitution for conventional ones the emission curves of styrene, limonene (a fragrance compound from the chemical class of terpenes) and Octamethylcyclotetrasiloxane ("siloxane-D4", from silicone materials) were determined from a sealant. From this sealant four times each 3.3 g were loaded into the micro-chamber and each 16.2 g were loaded into four 24-l-chambers ("desiccator"). Sampling was carried out at intervals of 1 (24 h), 3 (72 h), 6 (144 h), 8 (192 h), 10 (240 h), 13 (312 h) and 15 (360 h) days after loading.

Quantification was performed with toluene-equivalents. This is often used in emission testing to gain results for a wide range of analytes without calibrating them. Therefore their concentration is calculated by comparing their area counts with the area counts of a toluol-calibration.

Table 4.1 below shows additional experimental parameters.

Table 4.1: Operating parameters of the μ-CTE and 24-l-chamber ("desiccator")

Value	μ-CTE	μ-CTE	desiccator	desiccator	desiccator
Experiment section	4.1; 4.2.4	4.2	4.1; 4.2.2	4.2.3	4.3
V (chamber volume) [m³]	0.000044	0.000044	0.024	0.024	0.024
d (dish diameter) [m]	0.035	0.035	0.094	0.094	0.094
A (emission surface) [m²]	0.001	0.001	0.007	0.007	0.007
V^* (Chamber-flow) [l/h]	1.8	0.9	127	108	100
L (product loading factor) [m²/m³]	21.87	21.87	0.3	0.3	0.3
n (air change rate) [1/h]	40.91	20.45	5.3	4.5	4.2
q (area specific air flow rate) [m³/(m²h)]	1.87	0.94	18.3	15.6	14.4
T (temperature) [°C]	25	25	23	23	23
RH (relative humidity) [%]	-	-	50	50	50

4.1.2 Lacquer selection

12 lacquers from one manufacturer (this improves comparability) were purchased from a local building supplies store. Six of them are based on acrylic (water as solvent) and six on alkyd (organic solvents) polymers. From the two main groups lacquers with equal colours and surface designs were selected. Figure 4.3 shows the nomenclature that consists of three letters for each pre-chosen lacquer:
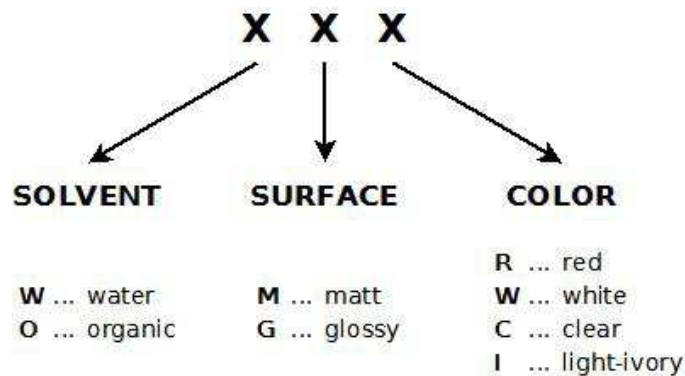
Figure 4.3: Nomenclature of the tested lacquers (w…acrylic, o…alkyd)

The following lacquers were purchased (WGI is similar to WGW, but WGW is not available): WGC, WGI, WGR, WMC, WMW, WMR, OGC, OGW, OGR, OMC, OMW and OMR.

To test their emission performance, 55 g of each lacquer was spiked with 50 µl of each of the tested substance, except lindane. 2.5 ml of a methanolic lindane-solution of 20 µg/ml was spiked into the lacquer. After stirring for one hour, 2 g of each lacquer mixture was placed into two Petri dishes and loaded into two different chambers of one µ-CTE for determination in duplicate. Figure 4.4 summarises the preparation. The sampling was done at intervals of 1 (24 h), 3 (72 h), 7 (168 h), 9 (216 h), 11 (264 h), 14 (336 h), 16 (384 h), 18 (432 h) and 21 (504 h) days after loading. The nomenclature for the tests was extended by adding the weighed amount (e.g. 55 g) and the loaded amount (e.g. 2 g), for example WGC55_2.
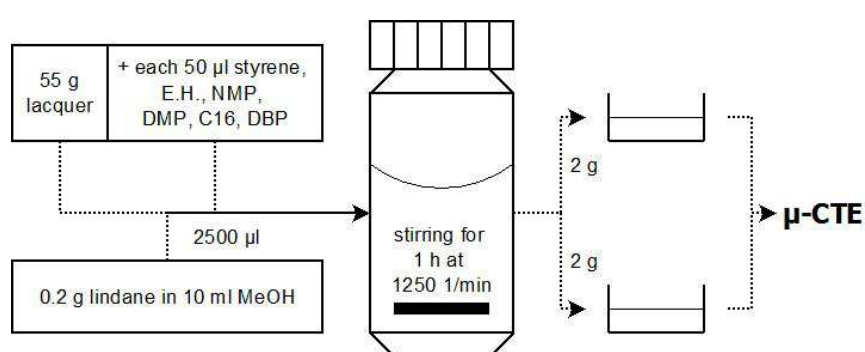
Figure 4.4: Preparation scheme for experiment 4.1.2

Table 4.2 shows the calculated ω_L-values for the selected analytes in accordance to chapter 3.2.4. For lindane, which is dissolved in MeOH, the concentration c_l must be used instead of ρ_A.

Table 4.2: Calculation of the added analyte amounts (c_l used instead ρ_A)*

analyte	ρ_A [mg/µl]	V_A [µl]	m_A [mg]	m_L [g]	ω_L [mg/g]
styrene	0.91	50	45.5	55	0.83
E.H.	0.83	50	41.5	55	0.75
NMP	1.03	50	51.5	55	0.94
DMP	1.19	50	59.5	55	1.08
C16	0.77	50	38.5	55	0.70
lindane	0.02*	2500	50	55	0.91
DBP	1.04	50	52.0	55	0.95

To test the emissions, 16 g of each pure lacquer was filled in a Petri dish and loaded into a 24-l-chamber and sampling was done at intervals of 3 (72 h), 7 (168 h) and 21 (504 h) days after loading.

4.1.3 Increasing the SVOC emission

Chapter 4.1.2 showed that the WGC lacquer was the most suitable substrate. It also turned out that although all of the substances were added in the same amounts, the emissions of lindane and DBP were low. To increase the emissions two approaches were investigated. In the first one (left side of Figure 4.5), two batches containing 2 g (WGC55_2) and 4.5 g (WGC55_4.5) of a WGC-mixture with the same amounts of DBP and lindane were placed into Petri dishes to check a potential influence of the filling amounts on the emission behaviour. In the second approach (right side of Figure 4.5) the concentration of each of the two analytes in the mixtures were increased to 4.08 mg/g lindane and 6.72 mg/g for DBP in a WGC-mixture of 25 g (WGC25_2). From each mixture two samples were loaded into the μ-CTE and sampling was performed at intervals of 1 (24 h), 3 (72 h), 7 (167 h), 9 (216 h), 11 (264 h), 16 (384 h), 18 (432 h), 21 (504 h), 23 (552 h) and 25 (600 h) days after loading.
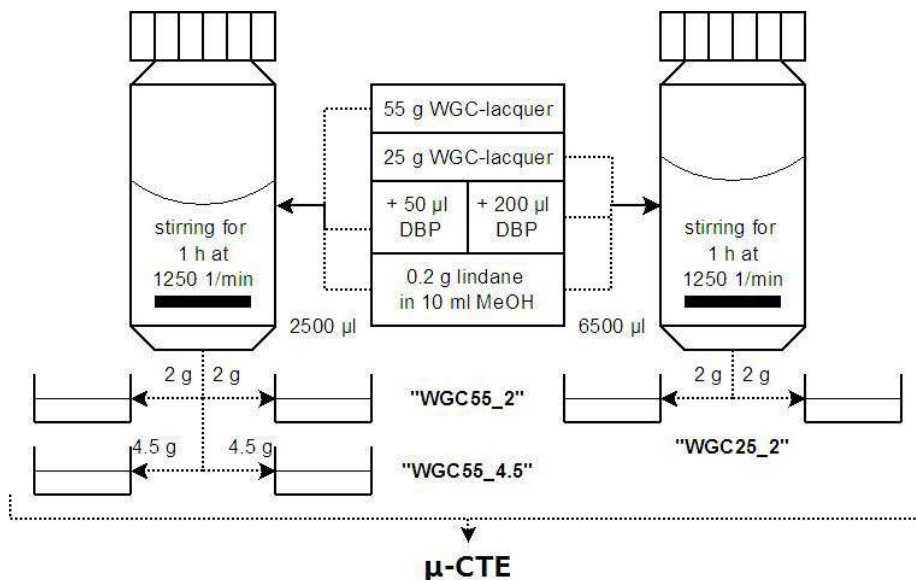
Figure 4.5: Preparation scheme for experiment 4.1.3

4.1.4 Optimisation of the lindane-spiking

In the previous experiments lindane was dissolved in methanol to improve the solubility of the solid substance inside the lacquer. In this chapter the effect that

lindane can have when added to the mixture was tested. Figure 4.6 shows the preparation. Two batches were prepared, on the left side lindane was dissolved and on the right it was added pure. For maximum comparability the lacquer and associated analyte amounts were set so that both batches had similar ω-values. After one hour of stirring an aliquot of each batch was sampled while the rest of the mixture was stirred further. After another hour the next sample from the batch with the solid lindane was taken. This procedure was repeated three times. Finally, after four hours of stirring, the last sample was taken from the two batches. The sampling was performed at intervals of 2 (48 h), 4 (96 h), 7 (167 h), 9 (216 h) and 11 (264 h) days after loading into the µ-CTE.
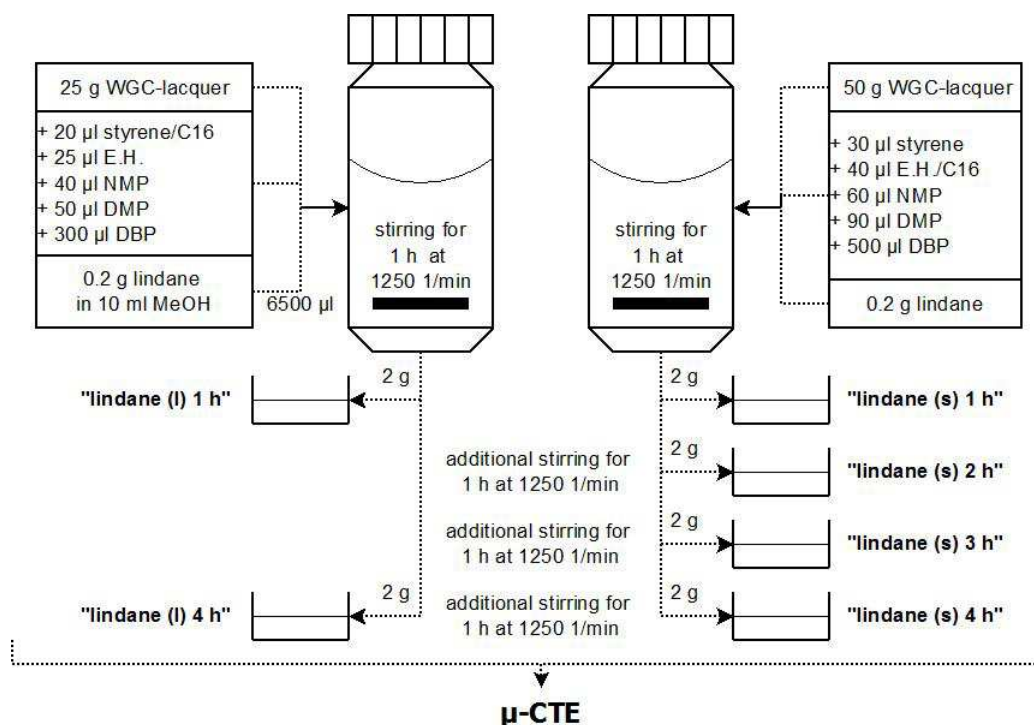
Figure 4.6: Preparation scheme for experiment 4.1.4

4.1.5 Influence of methanol

Combined with chapter 4.1.4 the influence that methanol has on the emissions of the lacquer mixture were investigated.

Figure 4.7 shows the preparation. A lacquer mixture of 55 g was prepared, stirred for one hour and afterwards separated into two equal aliquots. 6.5 ml of methanol was added to one of these two batches (right side of Figure 4.7). These two mixtures were stirred again and each of the three samples were loaded into one micro-

chamber. After 14 days storage in the refrigerator the two batches were stirred again and the sampling of each three aliquots for loading into the micro-chamber was repeated. In both cases the sampling was performed at intervals of 2 (48 h), 7 (167 h), 9 (216 h) and 11 (264 h) days after loading.
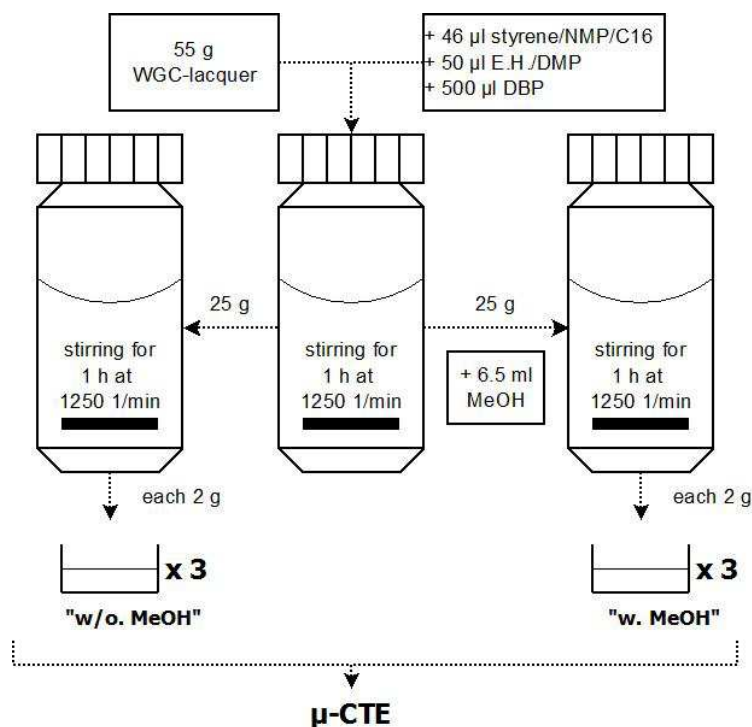
Figure 4.7: Preparation scheme for experiment 4.1.5 (w ... with, w/o ... without)

4.1.6 Stability testing I

The repeatability and reproducibility are indicators to assess the homogeneity of the material emission.

To determine the reproducibility as a relative standard deviation (RSD(repro)) of the emissions of different equally threaded lacquer mixtures (batch 1 - 3), 50 g of a WGC-mixture containing all seven substances was prepared three times and loaded into a µ-CTE. The six chambers of the µ-CTE were each loaded with 2 g of the same lacquer-system so that a deviation between the emissions inside the six chambers could be determined. This relative standard deviation averaged between the three single batches at the different sampling days results in the repeatability RSD (repeat). The sampling was performed at intervals of 2 (48 h), 4 (96 h), 7 (167 h), 9 (216 h) and 11 (264 h) days after loading.

For this experiment the µ-CTEs were equipped with mass flow controllers (MFCs) which kept the chamber flow constant. According to chapter 3.2.6 without MFC the chamber flow over the whole sampling cycles showed deviations up to 5 % while the controlled flow deviated less than 1 %.
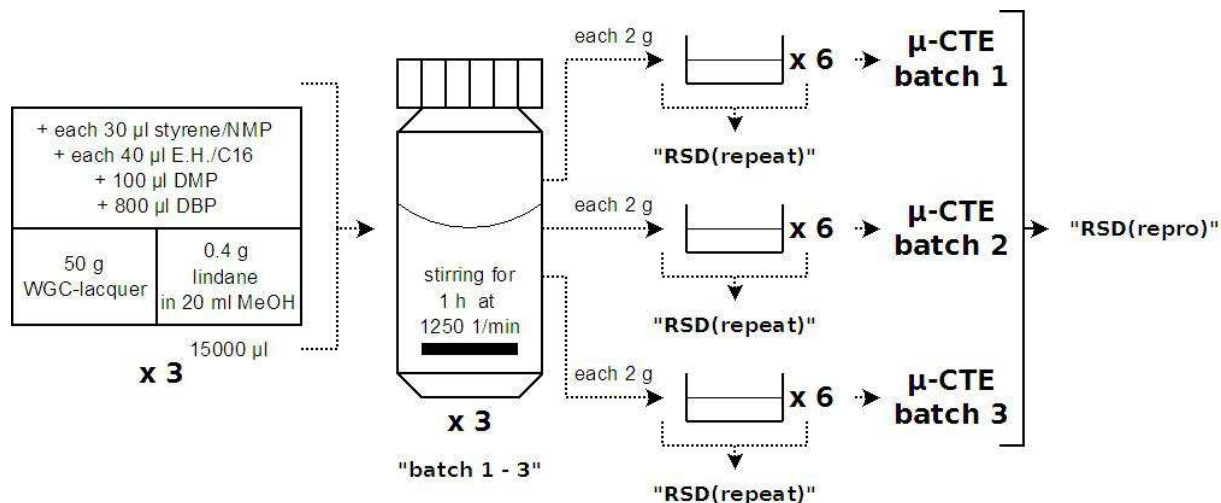
Figure 4.8: Preparation scheme for experiment 4.1.6

4.2 Optimisation of the curing process

The curing of lacquers under defined conditions is a crucial parameter. In the previous chapter the lacquer mixtures were cured inside the µ-CTE with its harsh conditions concerning the high chamber flow and the low humidity. In this chapter the investigation on the best suited way for lacquer curing are explained. For this the desiccator and the 1-m³-chamber were used because they operate with humidified air supply, therefore the loading factor chosen could smaller because of their higher chamber volume combined with lower flows. The 1-m³-chamber for curing operated at 750 l/h flow, 23 °C and 50 % RH.

4.2.1 Curing process in the µ-CTE

This experiment, displayed in Figure 4.10, aims to determine the differences in the emission in case the µ-CTE itself or the 1-m³-chamber is used to cure the liquid lacquers. Therefore two equal batches of lacquer were prepared. From each batch six aliquots of 2 g were filled inside 35-mm-Petri-dishes. The six samples from batch 1 are loaded directly into one µ-CTE. Firstly, the dishes from batch 2 were loaded into the 1-m³-chamber for 44 h and subsequently into the second µ-CTE. The air sampling was performed at intervals of 2 (48 h), 4 (96 h), 7 (168 h), 11 (264 h) and 14 (336 h) days after loading into the µ-CTE, and the 1-m³-chamber respectively.

Figure 4.9: Lacquer samples loaded into a 1-m³-chamber for curing

Starting with this chapter the µ-CTEs were equipped with mass flow controllers (MFCs). This enabled the micro-chamber to operate at lower flows. Without MFC the variation in the flow through the µ-CTE increased dramatically (> 5 % over 7 days) when it was set below 30 ml/min. The MFC enables a flow of 15 ml/min with deviations of less than 1 % over a period of two weeks. Lowering the flow to 15 ml/min in both the current and the previous chapters resulted in an air change rate n of 21 h^{-1} with an area-specific air flow rate close to 1 m³/m²h. With lower flows it would be possible to adjust the air change of the µ-CTE to conventional test chambers but this would extend the sampling time for typical sampling volumes such as 250 ml. As well the ram pressure of the sampling tubes (approximately 10 mbar for 30 ml/min) would extend the influence of the flow inside the chamber.
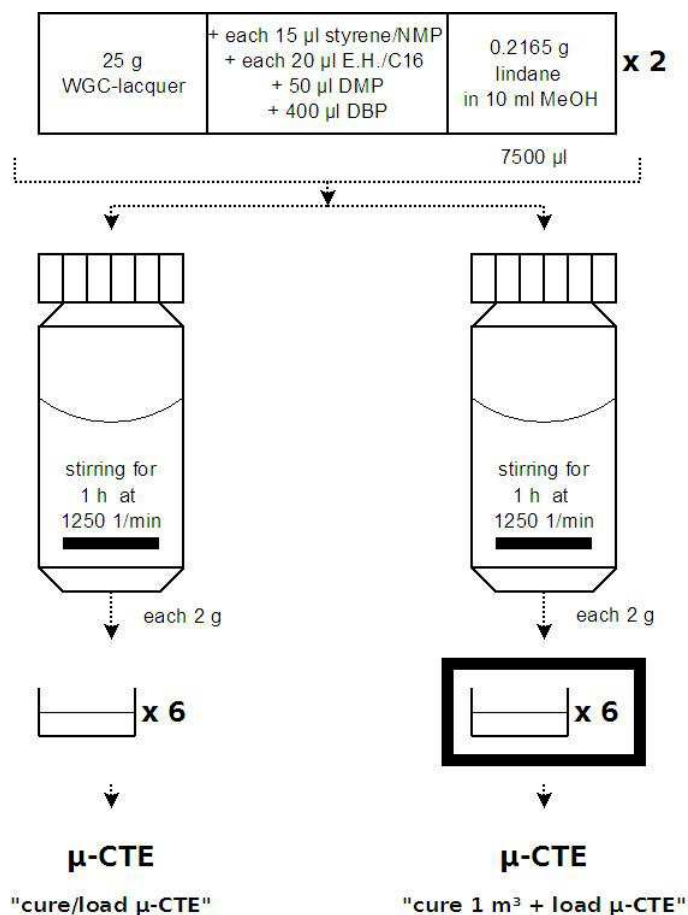
Figure 4.10: Preparation scheme for experiment 4.2.1

4.2.2 Curing process for the desiccator

Here the curing process inside the desiccator is investigated. Therefore three equally prepared lacquer-batches (see Figure 4.11) were produced. Four aliquots of 30 g from one batch were filled into 94-mm-Petri-dishes and directly loaded into four desiccators. From the other two batches four aliquots of 30 g were also filled into Petri dishes but they were loaded previously for 46 h into a 1-m³-chamber for curing and afterwards into the desiccators. The desiccators that were loaded with the samples from batch 2 have active fans, while for batch 3 the fans were disconnected. The operation parameters for the desiccators can be found in Table 4.1. Air samples were taken after 3 (72 h), 5 (120 h), 7 (168 h), 10 (240 h), 12 (288 h), 14 (336 h) and 17 (408 h) days

| 90 g WGC-lacquer | + 80 µl styrene/NMP/C16
+ 100 µl E.H.
+ 150 µl DMP
+ 1500 µl DBP | 1 g lindane in 50 ml MeOH | x 3 |

40000 µl

stirring for 1 h at 1250 1/min

stirring for 1 h at 1250 1/min

stirring for 1 h at 1250 1/min

each 30 g   each 30 g   each 30 g

x 4   x 4   x 4

x 4   x 4   x 4

"cure/load desiccator"   "cure 1 m³ + load desiccator"   "cure 1 m³ + load desiccator + no fan"
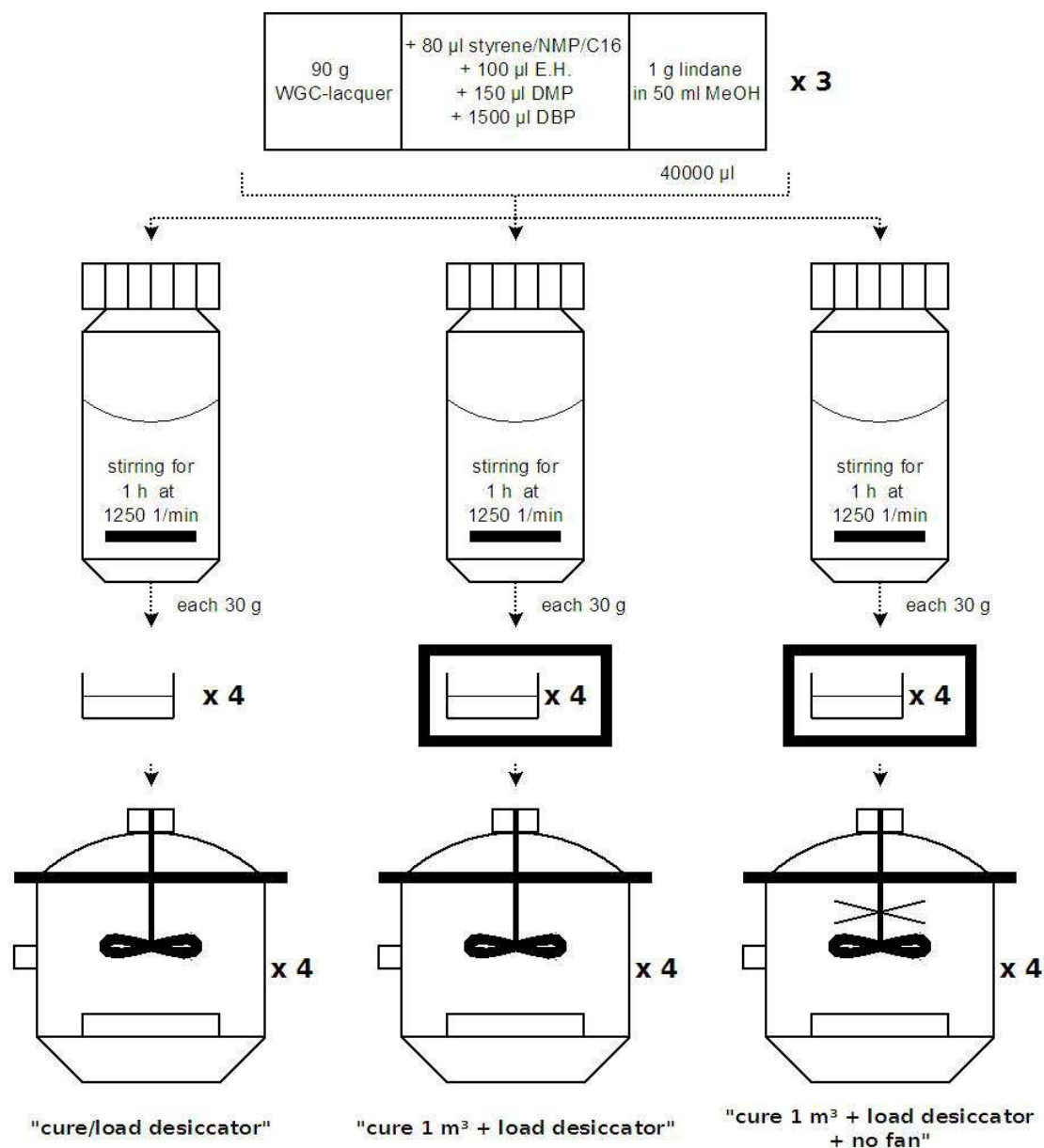
Figure 4.11: Preparation scheme for experiment 4.2.2

4.2.3 Stability testing II

This experiment combines the previous two chapters. Figure 4.12 shows that from three equally prepared lacquer batches aliquots were taken for loading in three ways: directly into the µ-CTE, directly into the desiccators and by intermediately stopping for curing inside the 1-m³-chamber for 96 h. This was repeated in the same way for two additional equally prepared batches. Hence, similar to experiment 4.1.6 the reproducibility can be calculated as RSD of the emission between the three equally prepared batches. Air samples were taken at both test chamber types after 5 (120 h), 7 (168 h), 11 (264 h) and 14 (336 h) days after the first loading.
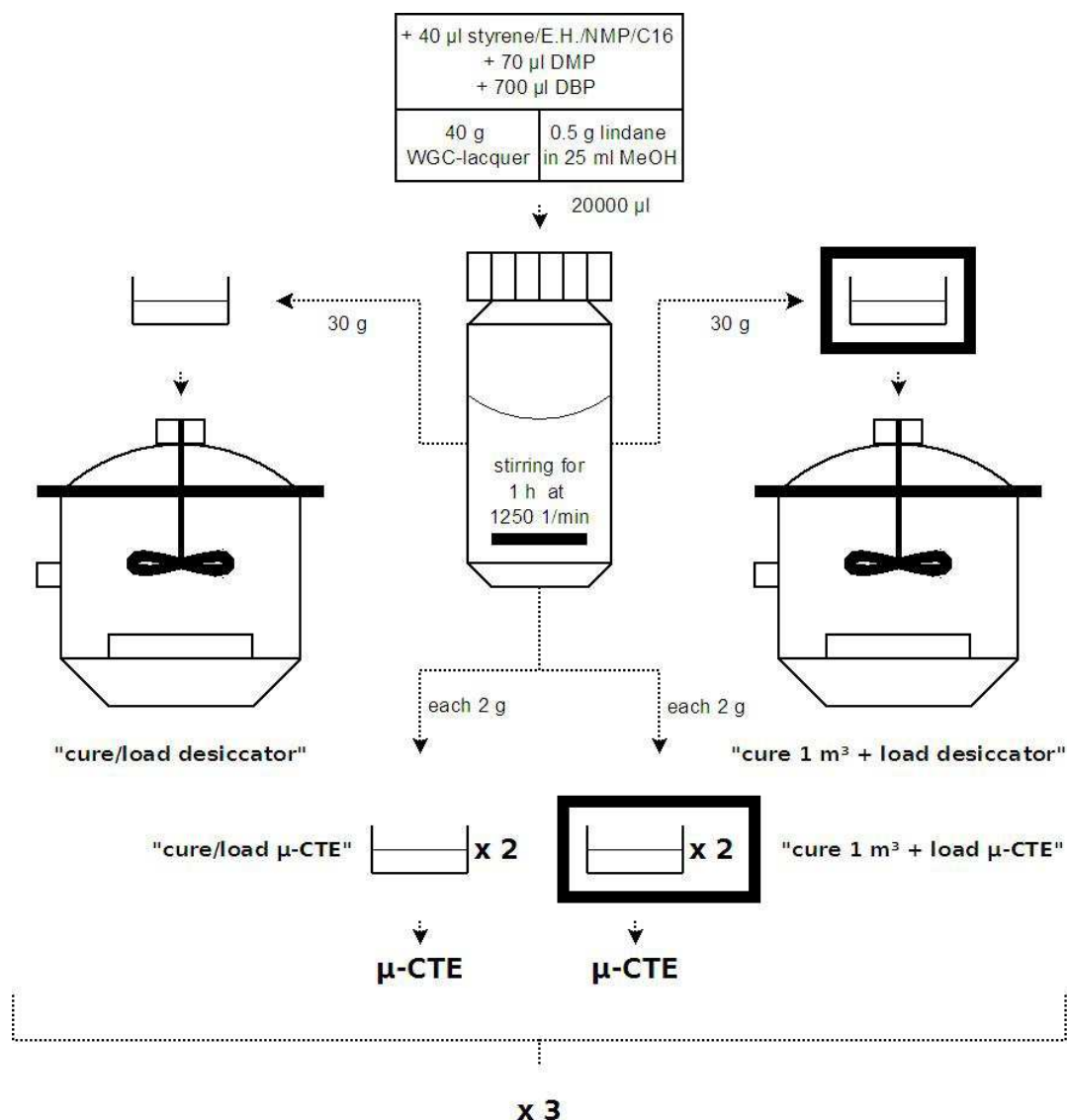
Figure 4.12: Preparation scheme for experiment 4.2.3

4.2.4 Influence on emissions at different chamber flows

In this experiment the emissions of the lacquer system were analysed using different flows through the µ-CTE. As it can be seen in Figure 4.13 two aliquots of 2 g from a mixture were loaded either into a µ-CTE that was operated at 30 ml/min or two aliquots were loaded into a µ-CTE that was operated at 15 ml/min. To observe the emission from both the liquid and the cured lacquer, samples were taken after 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 24 h, 26 h, 28 h, 30 h, 48 h, 50 h, 52 h, 54 h, 72 h, 76 h, 78 h, 98 h, 100 h, 168 h, 192 h after loading.
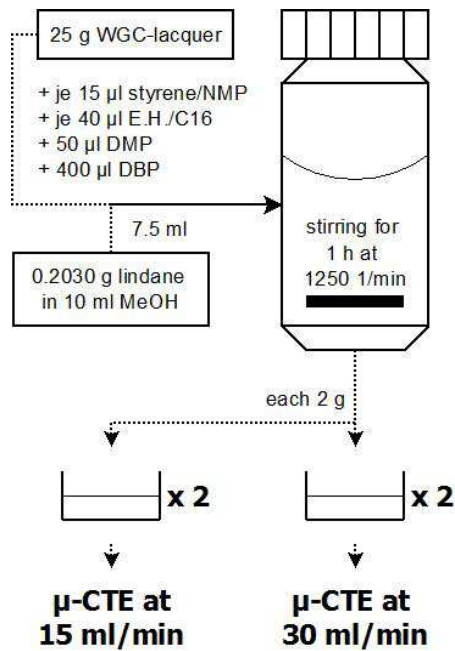
Figure 4.13: Preparation scheme for experiment 4.2.4
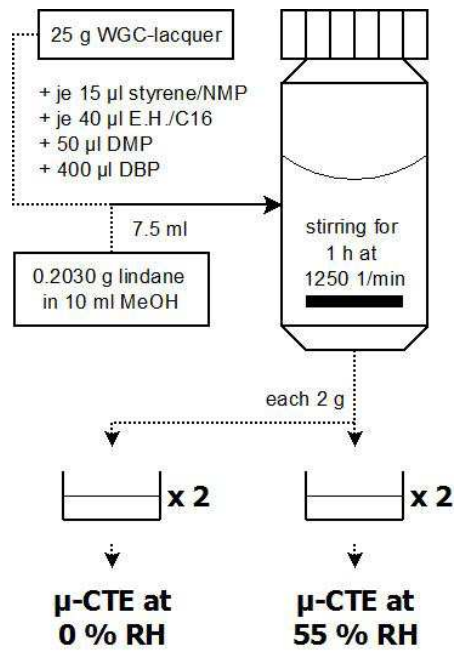
Figure 4.14: Preparation scheme for experiment 4.2.5

4.2.5 Influence on emission at different humidities

In the following experiment 4.2.4, the emissions of the same mixture were measured under different humidities. Figure 4.14 shows that two aliquots of 2 g were loaded into a µ-CTE that was operated at 0 % RH and also two aliquots into a µ-CTE that was operated at 55 % RH. In accordance with experiment 4.2.4, the curing process and the emissions afterwards should be observed. Therefore samples were taken after 1 h, 2 h, 3 h, 4 h, 5 h, 24 h, 26 h, 28 h, 50 h, 52 h, 72 h, 76 h, 168 h, 192 h, 240 h, 264 h after loading. The flow was set to 15 ml/min for both µ-CTEs.

As previously mentioned in chapter 4.1.1 the µ-CTE does not provide humidification. To humidify the air supply of the µ-CTE a simple humidification device was developed (see Figure 4.15). Figure 4.16 shows the construction set-up. Dry air from the MFC was split into two streams by a T-piece (1). With a needle valve (2) the split ratio of dry and saturated air was adjusted. One part of the air was led through a water reservoir (3) where the air is saturated with water. At a second T-piece (4) the humidified air was mixed with dry air from the first T-piece and flows to the µ-CTE. A sensor (ALMEMO 2890-9 data logger with a FHA646-R climate sensor both from AHLBORN) measures and records the relative humidity of the µ-CTE supplying air.
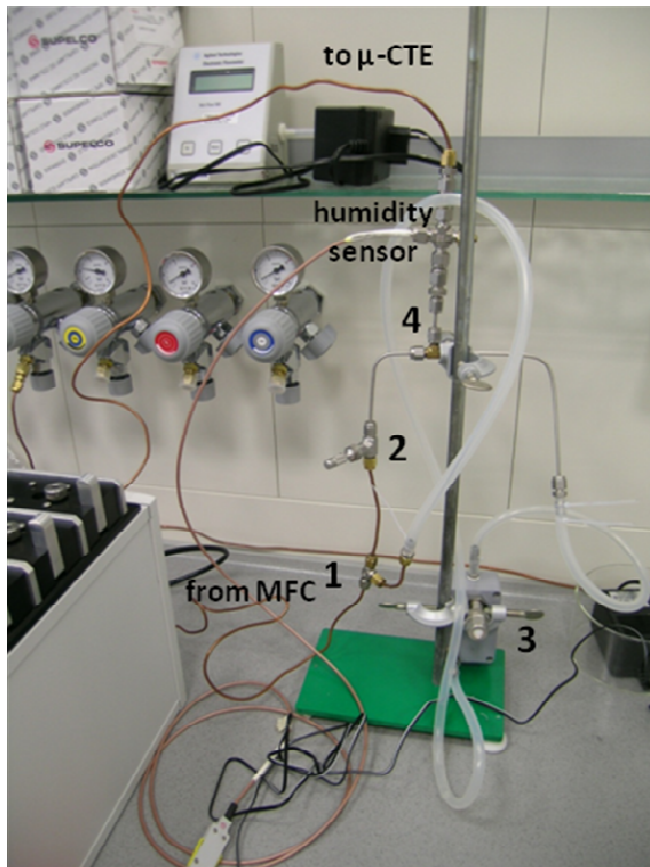
*Figure 4.15: Improvised humidification device
(1 ... T-piece; 2 ... needle valve; 3 ... water
reservoir; 4 ... T-piece)*
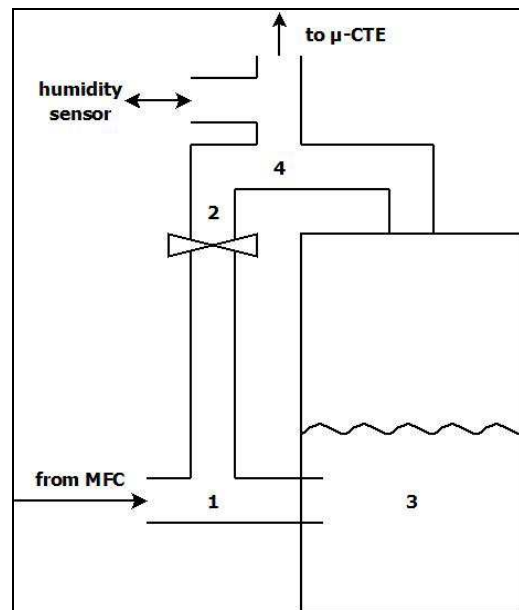
*Figure 4.16: Systematic scheme of the
improvised humidification device
(1 ... T-piece; 2 ... needle valve; 3 ...
water reservoir; 4 ... T-piece)*

4.3 Round robin test optimisation

The developed lacquer should be used as reference material for a round robin test on emission testing with climate chambers according to ISO 16000-9 [12]. These tests are organised by Federal Institute for Material Research and Testing (Bundesanstalt für Materialforschung und -prüfung BAM, Germany) every two years with about 50 participants all over the world.

Before the lacquer system could be used as reference some additional tests had to be performed. Firstly odorous compounds were added. Afterwards a mixture was developed where all substances emit quantifiable amounts at sampling day 3 and 7 after loading. It should be tested in which packaging the lacquer should be sent to the participants. Finally the homogeneity of one of the lacquer batch inside desiccators and a 1-m^3-chamber was investigated.

4.3.1   Additional analytes and optimal spiking amounts

Additional analytes hexanal, n-decane (C10), 2-ethylhexyl acrylate (E.H.-acryl) and naphthalene were added to the mixture. The substances were spiked in amounts that are comparable to styrene, E.H. and C16 because they show similarity in both boiling points and polarity (see Table 3.1 and Table 3.2).

Common used TD-GC/MS (thermal desorption) systems have their linear calibration range between 1 ng to 150 ng depending on the substance. With a sampling volume of 1 l this results in air concentrations of 1 - 150 µg/m³. Different lacquer mixtures were prepared. After curing inside the 1-m³-chamber and loading into desiccators the emissions after three and seven days were analysed. These are typical sampling points in emission testing. The measured air concentration should range between 10 to 120 µg/m³.

4.3.2   Shipping and storage

At round robin tests it is important to ensure that the samples reach the participants without any changes in their properties. With this step it should be ensured that all laboratories receive comparable samples.

The lacquer mixture cannot be shipped in liquid. Chapter 4.2 shows that the curing process is the crucial parameter that defines the emissions of the lacquer system. Slight differences in the parameters while the mixture cures can lead to poor emission reproducibility. Moreover, several regulations restrict the shipping liquids to other countries. This leads to extending transfer times and possibly changing the sample. Therefore it is more feasible to ship the solid lacquers which were cured previously in bigger chambers.

In this experiment a lacquer mixture was prepared (see 4.3.1) and poured into six Petri dishes and loaded into a µ-CTE (15 ml/min; 0 % RH). There were cured for four days. After this time all Petri dishes were sealed with a lid and three were covered in aluminium foil. The other three were packed in a LDPE-bag (low density polyethylene, 0.1 mm thickness), vacuumed and sealed. The vacuum prevents additional emission by eliminating the air. The six samples were stored for three days in the laboratory at 21 °C. They were then unpacked and loaded into a µ-CTE which operated at 15 ml/min chamber flow of dry air. Samples were taken one, two and four days after the loading.

Figure 4.17: Lacquer samples vacuumed in a LDPE bag (on top) and packed in aluminium foil (below)
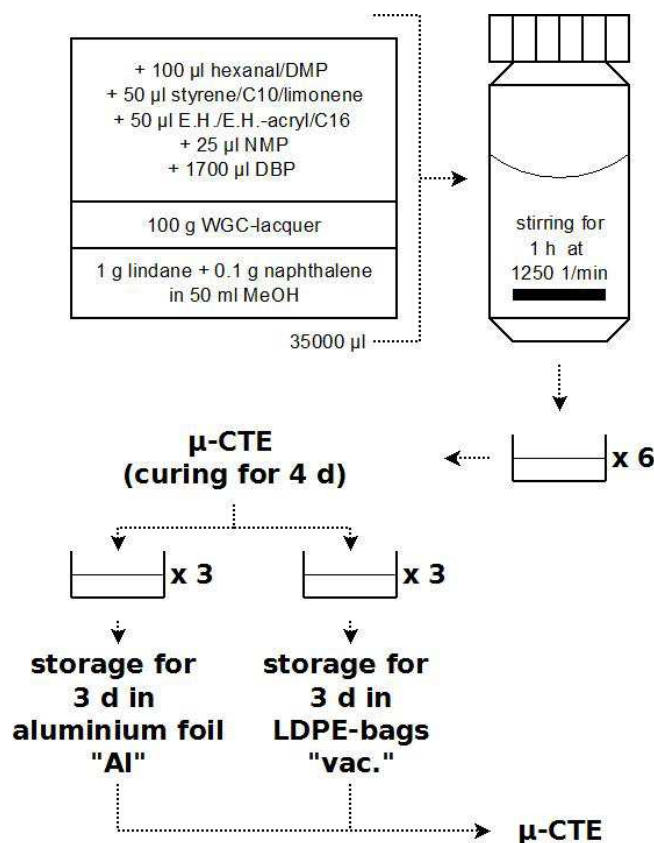
Figure 4.18: Preparation scheme for experiment 4.2.4

4.3.3 Stability testing III

In this experiment a lacquer mixture was prepared (see Figure 4.19) and filled in 17 Petri dishes. These Petri dishes were loaded into a 1-m³-chamber for a curing period of four days. Afterwards eight samples were loaded into eight desiccators. Five samples were also loaded into a 1-m³-chamber (VÖTSCH) for emission testing. Sampling was done for all chambers three and seven days after loading.

The remaining four Petri dishes (retained samples) were packed and sealed in the aluminium composite foil CLIMPAC 2810 (METPRO Verpackungsservice GmbH) and stored for eight days in the laboratory at 21 °C. After this period they were unpacked and directly loaded into four desiccators. The sampling was undertaken for all chambers after three and seven days. It was also performed seven days after loading.

The CLIMPAC-foil consist of the following parts: outer layer (12 µm thickness, PET (polyethylene terephthalate)), barrier layer (8 µm, aluminium foil) and the inner layer

(100 µm, LDPE). The foil is steam-tight and protects the sealed sample from outside light and humidity influences.

The desiccators operated at a flow rate of 100 l/h and were loaded with one Petri dish with a diameter of 0.094 m and a lacquer amount of 20 g. To gain comparable emissions, the 1-m³-chamber that operated at 500 l/h five filled Petri dishes had been loaded.

The chamber air was analysed with the GERSTEL-TDS "Asterix" (see Table 3.3).
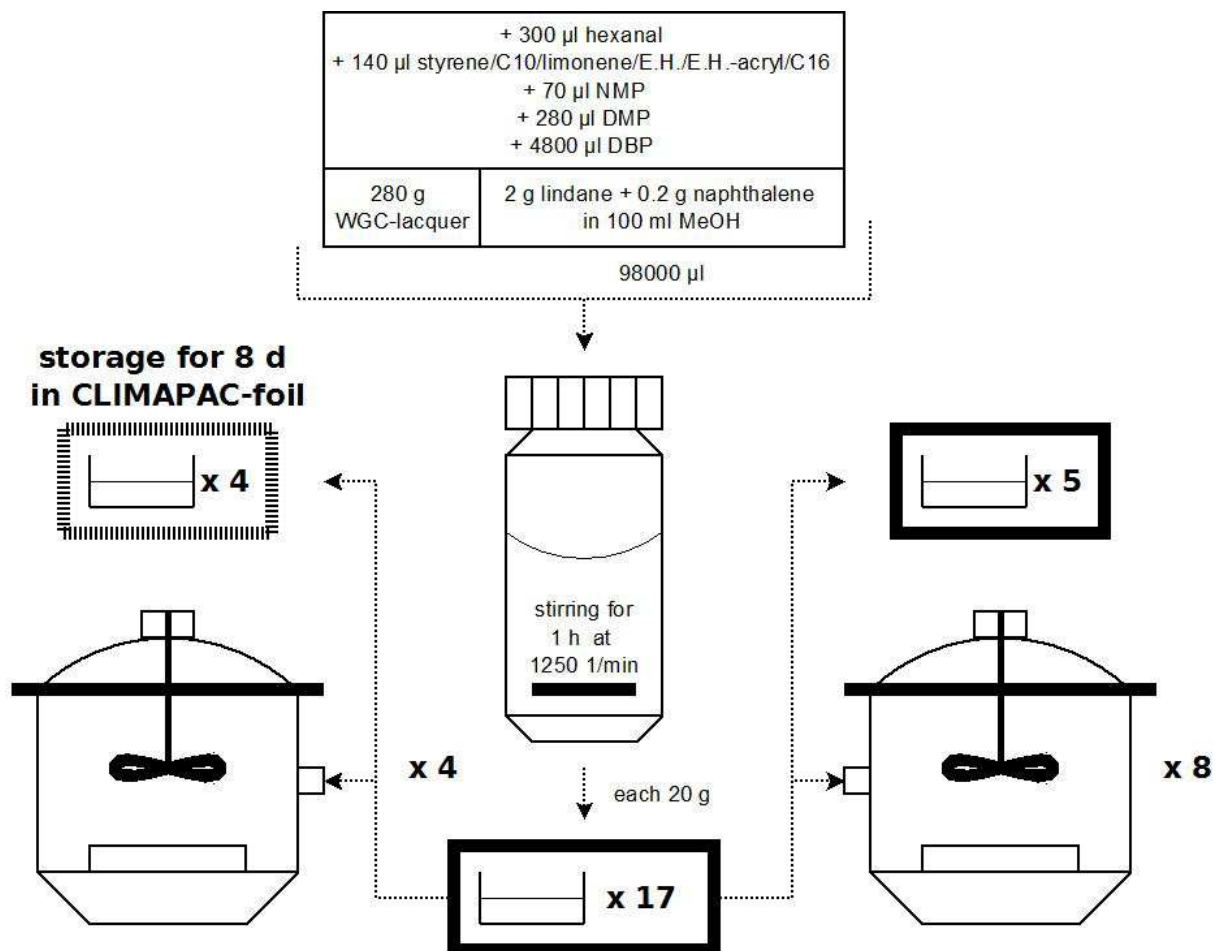
Figure 4.19: Preparation scheme for experiment 4.3.3
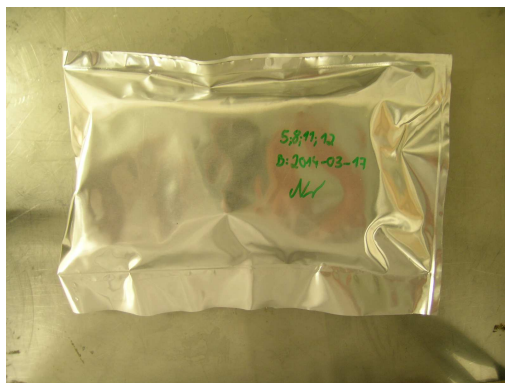
Figure 4.20: Four lacquer samples packed in sealed CLIMAPAC-foil

5   Results and Discussion

5.1   Preliminary testing

5.1.1   Chamber selection

In order to compare samples and include the different process parameters of the investigated chambers, the results are converted to area specific emission rates (SER$_A$). It is obvious that the emission curves for the three substances are comparable when referring to the time course (see Figure 5.1 to Figure 5.3). The differences between the emission rates can be explained with various curing processes based on different environmental parameters of the two investigated chambers. Finally it can be summarised that it is possible to substitute the conventional chambers with the µ-CTE.
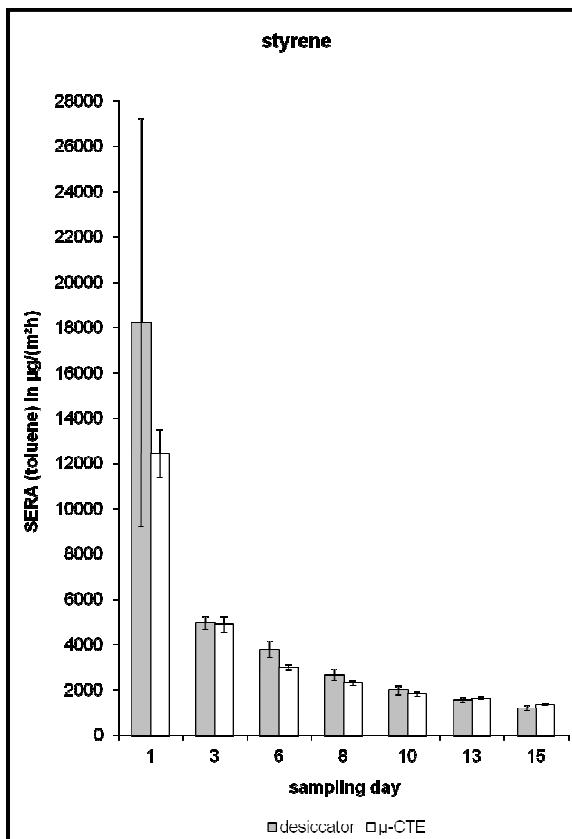
Figure 5.1: Emission curves of styrene from a sealant sample loaded into a desiccator (light grey) and a µ-CTE (white)
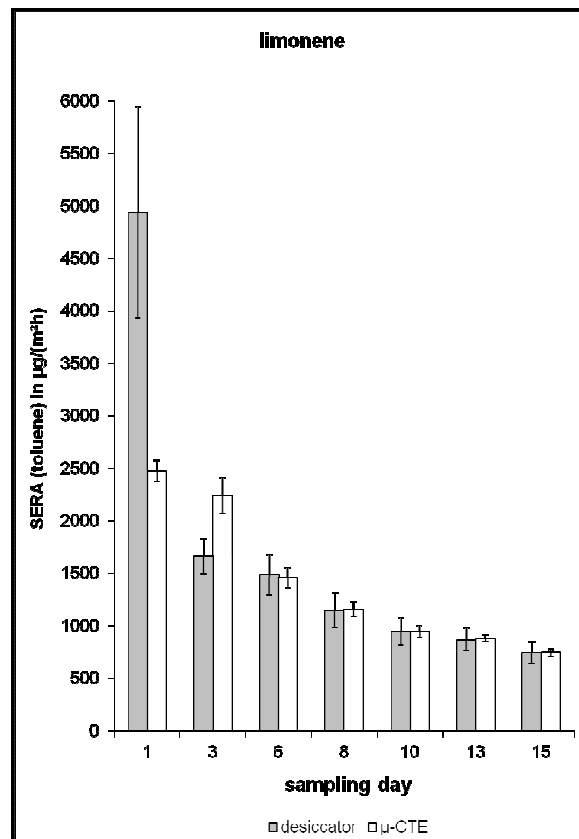
Figure 5.2: Emission curves of limonene from a sealant sample loaded into a desiccator (light grey) and a µ-CTE (white)
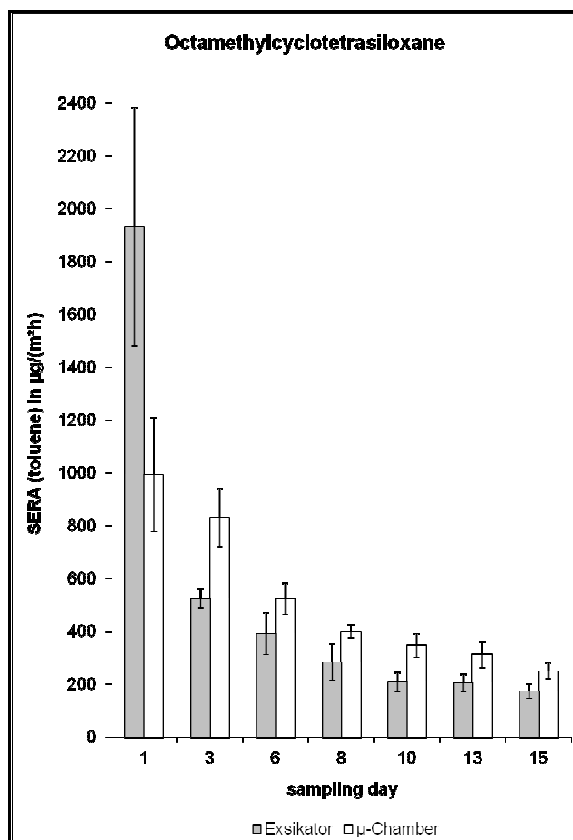
Figure 5.3: Emission curves of octamethylcyclotetrasiloxane from a sealant sample loaded into a desiccator (light grey) and a µ-CTE (white)

5.1.2 Lacquer selection

It is of upmost importance that the lacquer-system emits the added substances in detectable amounts. Firstly the alkyd-lacquers mixtures were prepared in accordance to chapter 4.1.2 and loaded into the µ-CTE.

The chromatograms for day 1 and 3 (Figure 5.4) showed huge peaks that overlay the signals for styrene, E.H. and NMP. The negative influences of those signals were increased by the fact that the chromatogram was measured in SIM mode (single ion monitoring) whereby only selected ions are displayed. These peaks can be ascribed to the self emission of the alkyd-lacquers. Additionally, this emission plugged the measurement system. This can be seen in Figure 5.5. An empty glass tube was measured directly after a sampled tube. Usually the blank tubes show a flat baseline. Subsequent measurement of additional blank tubes indicated that those signals between 10 and 15 min decay slowly. Cleaning the TDS-system was the only way to eliminate this contamination completely. It appears that the lacquer amount combined with its self emission was too high for the measurement system. Only

lower sampling volumes could reduce this contamination but this would lead to low detectable analyte amounts and because this plugging self emission could be observed for all alkyd lacquers this class must have been excluded from further investigations. In addition, they were barely soluble in common solvents which complicated the cleaning of the laboratory equipment needed for the preparation.
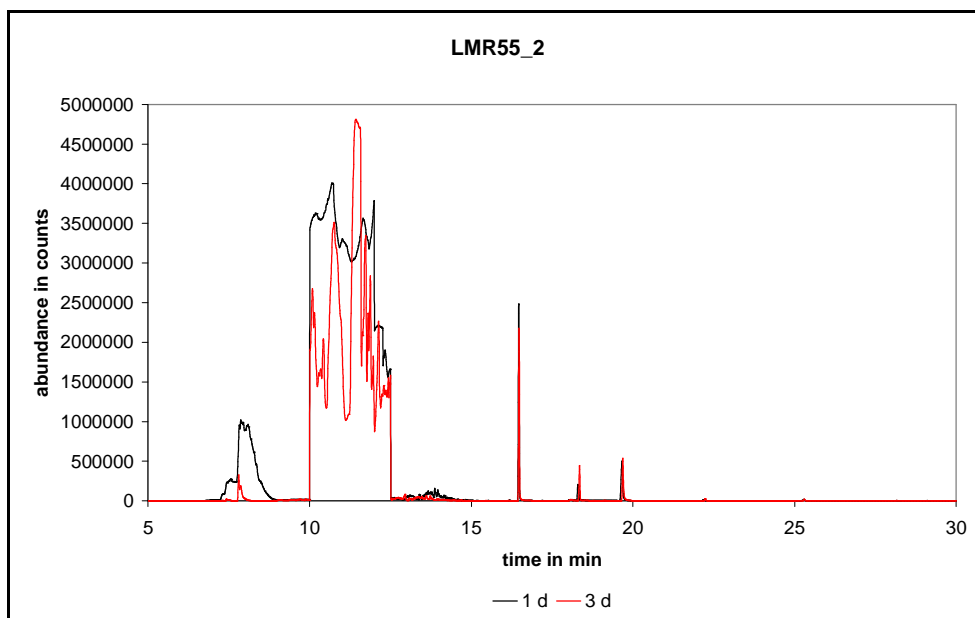
Figure 5.4: SIM-chromatogram of the self-emission of the lacquer OMR on sampling day 1 (black line) and 3 (red line) – (SIM…single ion monitoring)
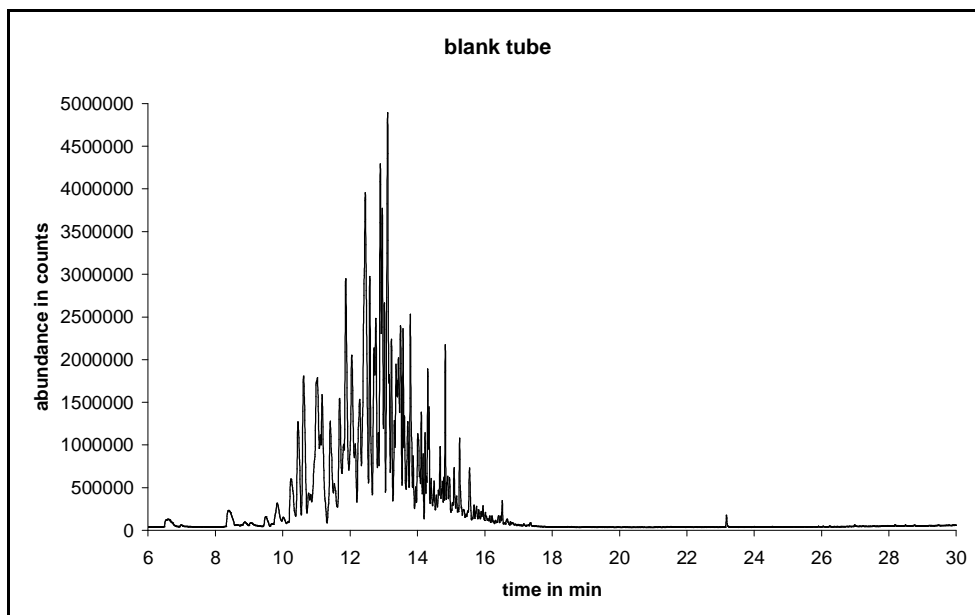
Figure 5.5: TIC-chromatogram of a subsequently measured blank tube (clean and unfilled glass tubes) - (TIC…total ion count)

In contrast the acrylic lacquers showed almost no self emission, hence it was possible to detect the emission of the added analytes over time without any lacquer interference. Exemplary for the group of VOCs Figure 5.6 shows the emission profile of styrene. The curve was comparable to the behaviour of E.H. and NMP. Those three substances showed a typical decreasing curve which can be observed for other VOCs (see chapter 2.2). The curve for DMP in Figure 5.7, which is comparable to the emissions of C16, decays only slowly. This behaviour is typical for less volatile substances.
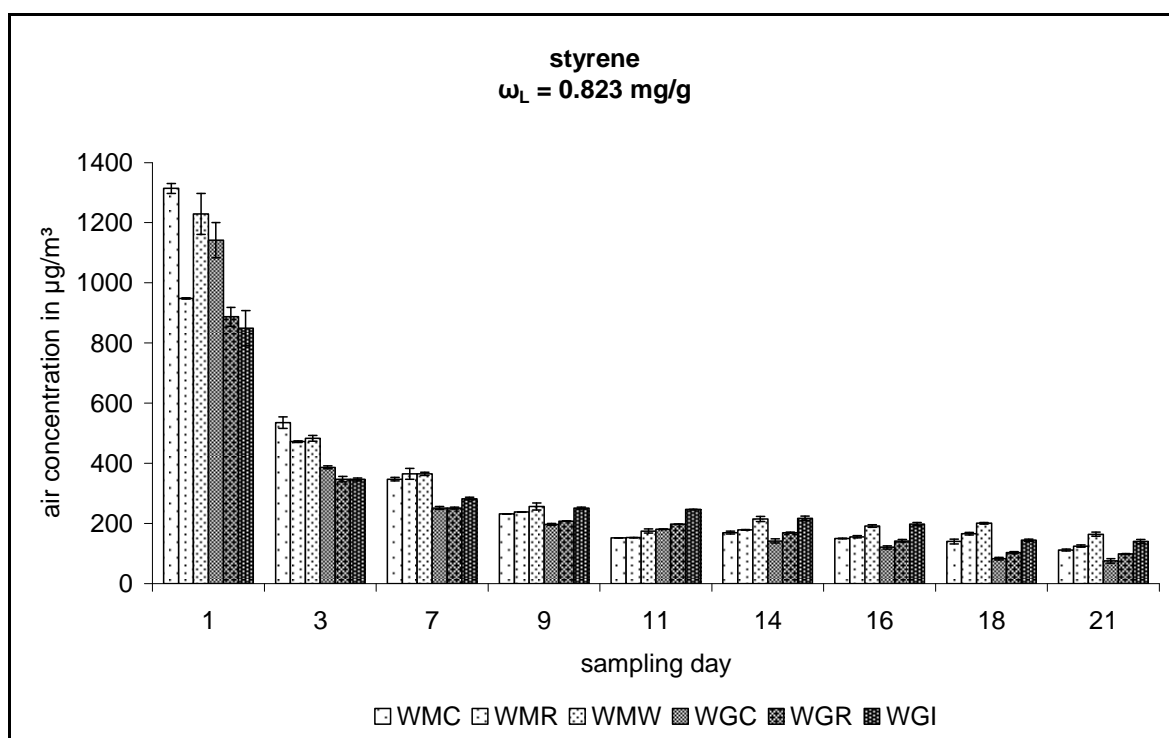
Figure 5.6: Emissions of styrene from different lacquer types in µ-CTE on different sampling days - two samples per lacquer (equal to E.H. and NMP)

The last two substances lindane and DBP (shown in Figure 5.8) showed only low emissions mostly below the limit of quantification (LOQ), although they were added to the lacquer in the same amount compared with the other analytes.
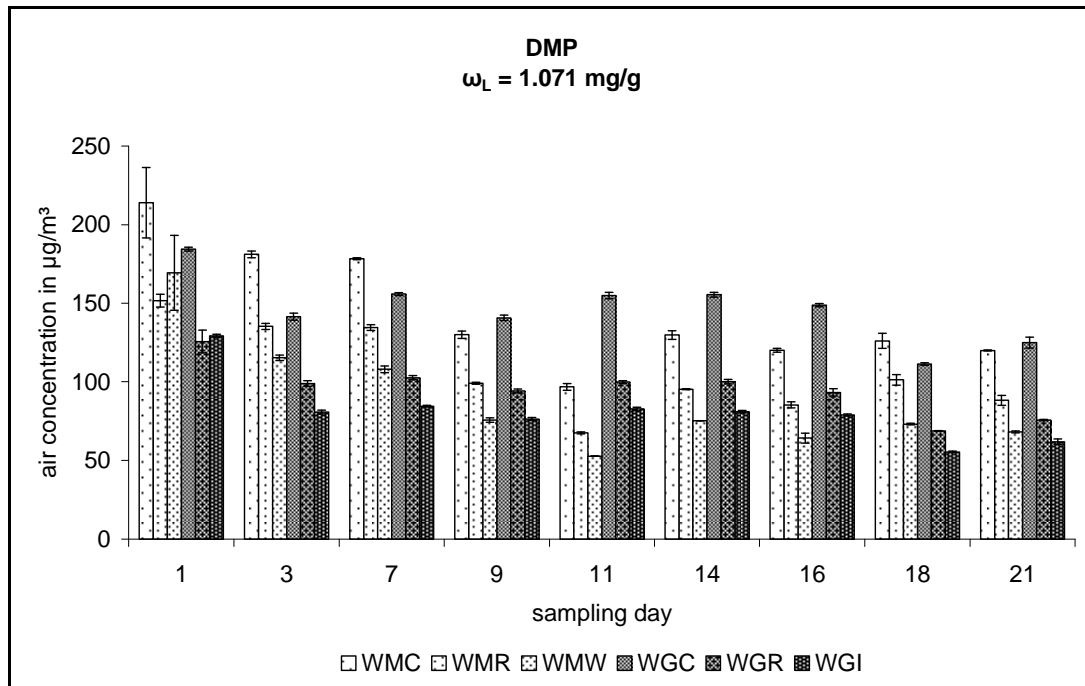
Figure 5.7: Emissions of DMP from different lacquer types in µ-CTE on different sampling days - two samples per lacquer (equal to C16)
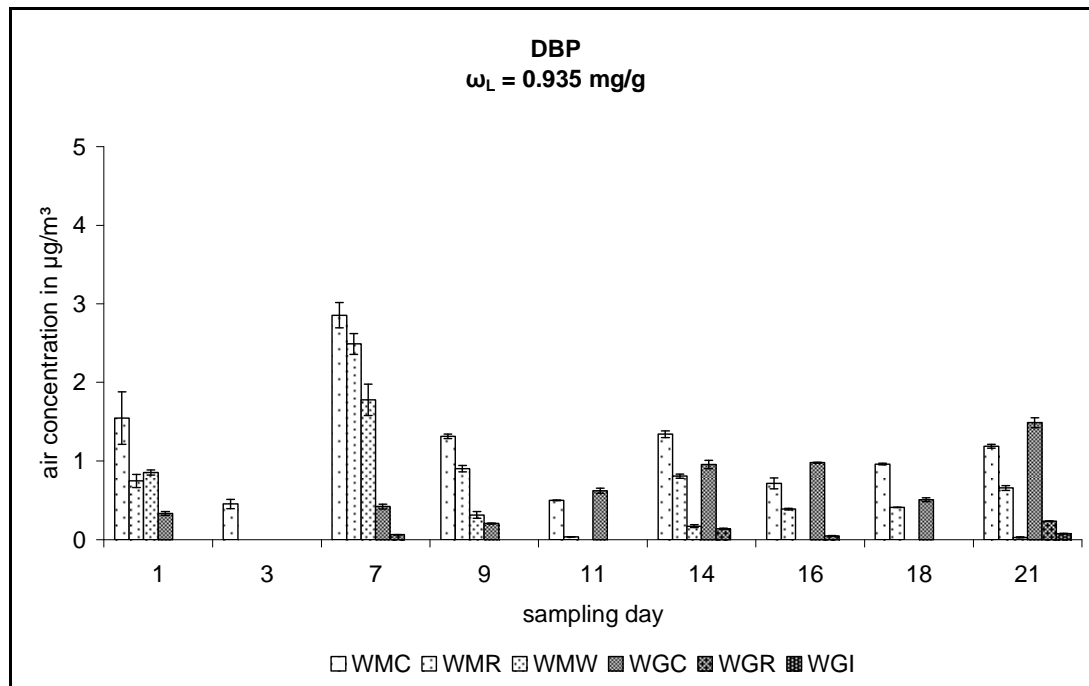
Figure 5.8: Emissions of DBP from different lacquer types in µ-CTE on different sampling days - two samples per lacquer (equal to lindane)

Table 5.1: Averaged (n = 2) minimum and maximum emitted analyte amounts of the water-based lacquers over a sampling cycle of 21 days

		styrene	E.H.	NMP	DMP	C16	lindane	DBP
	ω_L [mg/g]	0.823	0.752	0.935	1.071	0.693	0.888	0.935
WMC	Min [µg/m³]	111	67	159	97	109	10	< LOQ
	Max [µg/m³]	1314	2138	1162	214	455	50	2.86
WMR	Min [µg/m³]	125	79	176	68	175	5	< LOQ
	Max [µg/m³]	948	1552	802	152	376	9	< LOQ
WMW	Min [µg/m³]	164	70	150	53	158	4	< LOQ
	Max [µg/m³]	1229	1699	542	169	361	9	2.49
WGC	Min [µg/m³]	75	53	179	111	159	6	< LOQ
	Max [µg/m³]	1142	1630	1155	184	400	11	< LOQ
WGR	Min [µg/m³]	98	61	168	69	153	4	< LOQ
	Max [µg/m³]	887	1144	646	126	258	6	< LOQ
WGI	Min [µg/m³]	140	55	137	55	142	4	< LOQ
	Max [µg/m³]	849	947	818	129	325	6	< LOQ

Table 5.1 summarises the seven emission curves for the single substances. It shows the minimum and the maximum emitted amounts over the whole sampling cycle of 21 days.

As previously mentioned the air concentrations of the less volatile lindane and DBP are very low. This problem is subsequently addressed in chapter 5.1.3.

For choosing the preferred lacquer among those six the first is chosen based on the emitted amounts. The reference material must emit the selected substances at a detectable range. Table 5.1 shows that WMC, WMW and WGC are emitted the most. Therefore the choice had to be made between them. WMW was excluded because after curing fissures were created on the surface (Figure 5.9 on the left side). This heterogeneous surface complicates the calculation of the emission surface and leads to poor emission reproducibility. These fissures could be observed for all of the coloured lacquers. They also had a higher viscosity than the clear ones which made

decantation and filling much more difficult. Finally, only the clear-lacquer mixtures remain in liquid form after spending a number of years in closed bottles. This is very important for the long term stability and storage.

Figure 5.9: Surfaces of various water-based lacquers inside Petri dishes with a diameter of 9.6 cm (WGR, WGI, WGC each 15 g)

The two remaining lacquers WGC and WMC showed similar emission profiles. The WGC-lacquer was preferred because it was easier to handle and the surface appeared more homogeneous.

5.1.3 Increasing the SVOC emission

From Table 5.1 it becomes obvious that the emissions of the less volatile lindane and DBP were very low although they were added with equal amounts compared to the other substances.

Experiment 4.1.3 describes two ways to increase the SVOC-emission of the lacquer system: the increase of spiking (WGC25_2) or the loaded lacquer-mixture-amount (WGC55_2 → WGC55_4.5). Table 5.2 summarises the emission of the two lacquer batches displayed in Figure 4.5 over the whole sampling cycle of 25 days.

Table 5.2: Minimum and maximum emitted analyte amounts of lindane and DBP from two lacquer batches (WGC25/WGC55) with different loaded lacquer amounts (2 g, 4.5 g) over a sampling cycle of 25 days

		lindane	DBP
ω_L [mg/g]		5.00	8.23
WGC25_2	Min [µg/m³]	37	13
	Max [µg/m³]	63	22
ω_L [mg/g]		0.87	0.94
WGC55_2	Min [µg/m³]	6	< LOQ
	Max [µg/m³]	13	1.40
WGC55_4.5	Min [µg/m³]	6	< LOQ
	Max [µg/m³]	13	1.28

The results of WGC55_2 and WGC55_4.5 showed that the emitted amounts were independent from the lacquer amount if the concentration of the analyte is similar. Additionally, the emission of both substances can be enhanced by increasing the analyte concentration inside the lacquer (WGC25_2).

To explain these observations the emission can be considered as distribution equilibrium, because the compounds diffuse from the lacquer surface into the gaseous air-phase (see Liu et al. [7] and chapter 2.1.2). The partition coefficient K_d of a compound A results in the concentration of A in the surrounding air (c_{air}) divided by the concentration of A inside the lacquer surface ($c_{lacquer}$):

$$K_d(A) = \frac{c_{air}(A)}{c_{lacquer}(A)}$$

The constant K_d is independent of concentration. Hence an increased $c_{lacquer}$ results in an increased c_{Air}. If $c_{lacquer}$ is kept constant, c_{Air} is influenced in the same way.

Chapter 4.3.1 shows that this assumption could be transferred to the other substances. It turns out that the high emission of the volatile analytes can be reduced by adding lower amounts to the lacquer.

Therefore it can be assumed that the emissions can be controlled by the lacquer spiking. The results of chapter 5.1.6 showed that this assumption is limited. Above a

certain concentration inside the lacquer the emissions of lindane and DBP could not be enhanced by adding more substance into the mixture. The volatility of those two substances limited an increased emission, hence the spiking of those two substances was kept at about 10 - 20 mg/g.

5.1.4 The influence of methanol

Experiment 4.1.4 aims to determine the influence of lindane and the associated solvent methanol. It was the only solid substance among the analytes. Figure 5.10 shows the emission profile of lindane which was added as methanolic solution ("lindane (l)") or pure ("lindane (s)") to the lacquer. The results showed that the emissions from lindane are higher when it is dissolved in methanol. Hence MeOH seemed to improve the solubility of lindane inside the lacquer mixture.
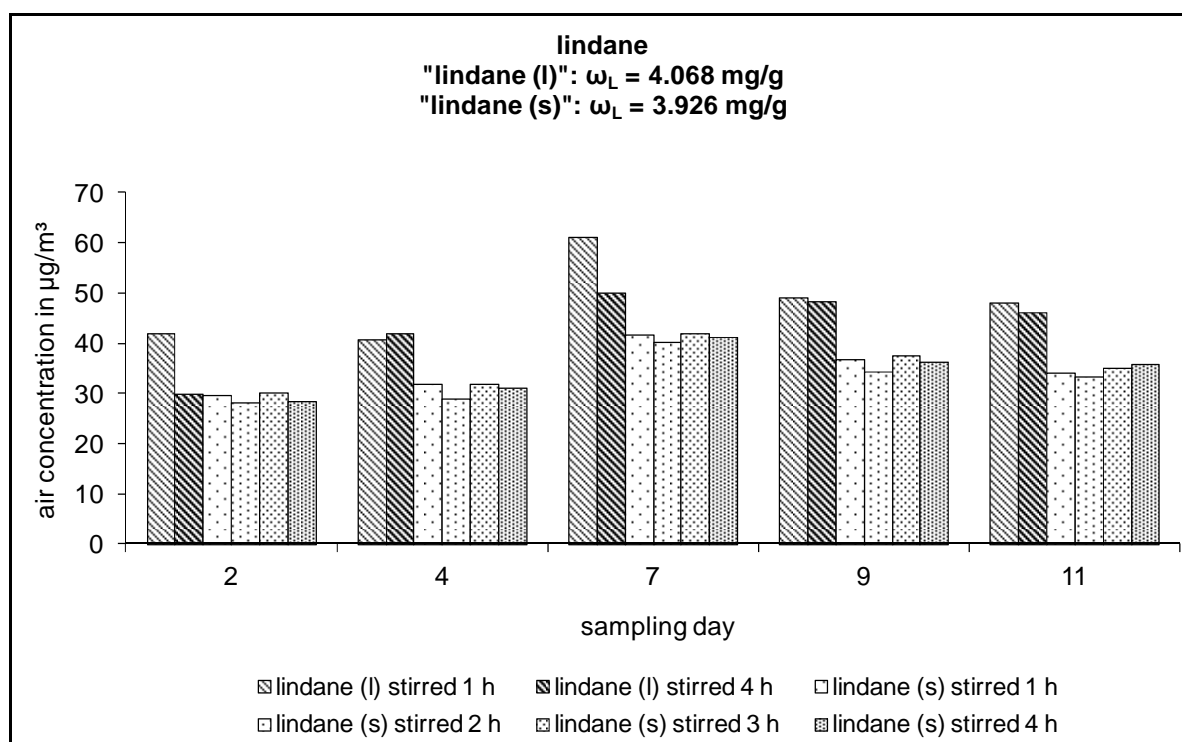
Figure 5.10: Emitted lindane amounts, either dissolved in MeOH ("lindane (l)") or added pure ("lindane (s)"), over a period of 11 days with different stirring times

The dotted columns show that the stirring time did not affect lindane emissions significantly. It can be assumed that the less volatile lindane remained inside the liquid mixture over the whole homogenisation process.

Figure 5.11 to Figure 5.22 compare the results for the compounds except lindane for both experiments 4.1.4 and 4.1.5. Experiment 4.1.4 was designed in a way that the

mass fractions ω and the results could be compared directly. In experiment 4.1.5 the dilution caused from methanol must be taken into account. Hence a factor between the two masses of these experiments was included into the results.
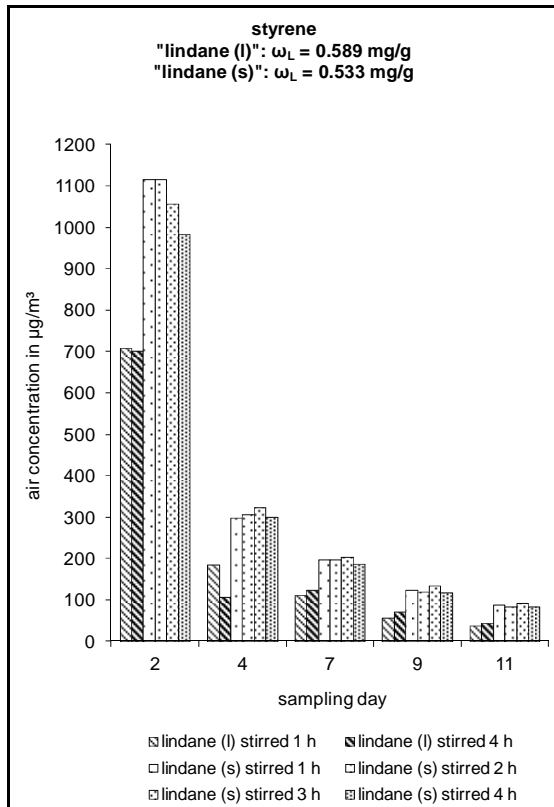
Figure 5.11: Emissions of styrene with/without MeOH at different stirring times (see 4.1.4)
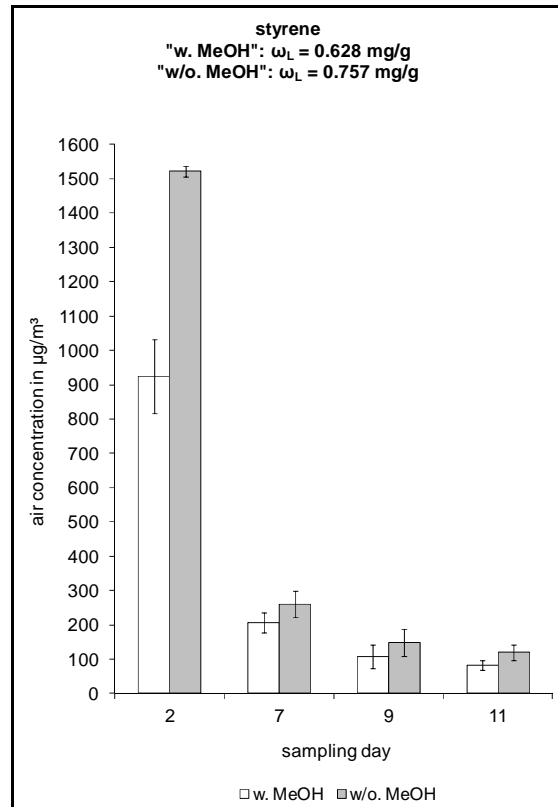
Figure 5.12: Emissions of styrene with and without MeOH (see 4.1.5)
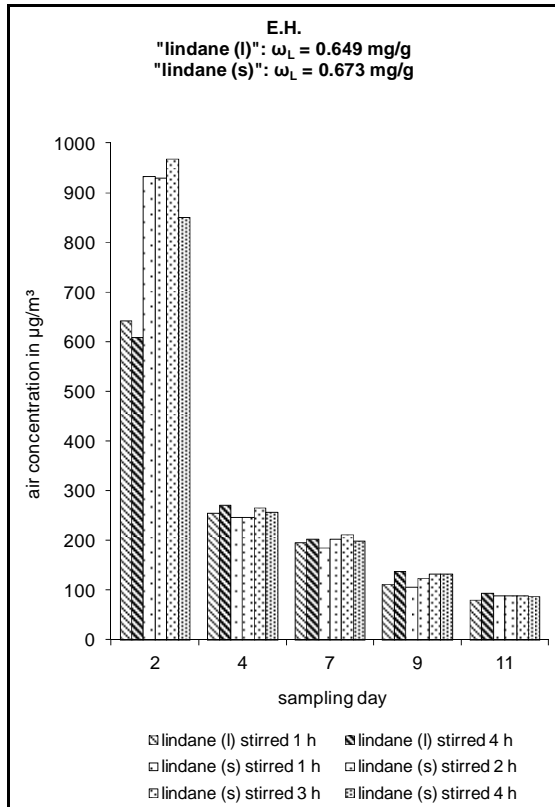
Figure 5.13: Emissions of E.H. with/without MeOH at different stirring times (see 4.1.4)
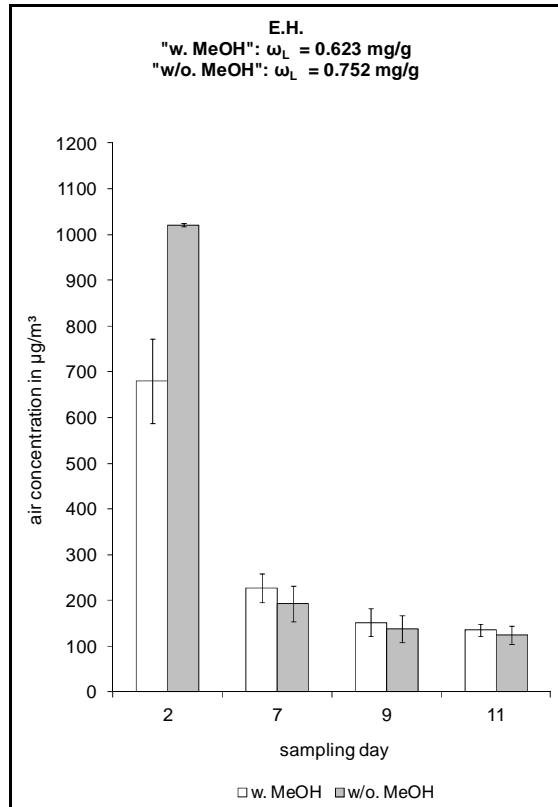
Figure 5.14: Emissions of E.H. with and without MeOH (see 4.1.5)
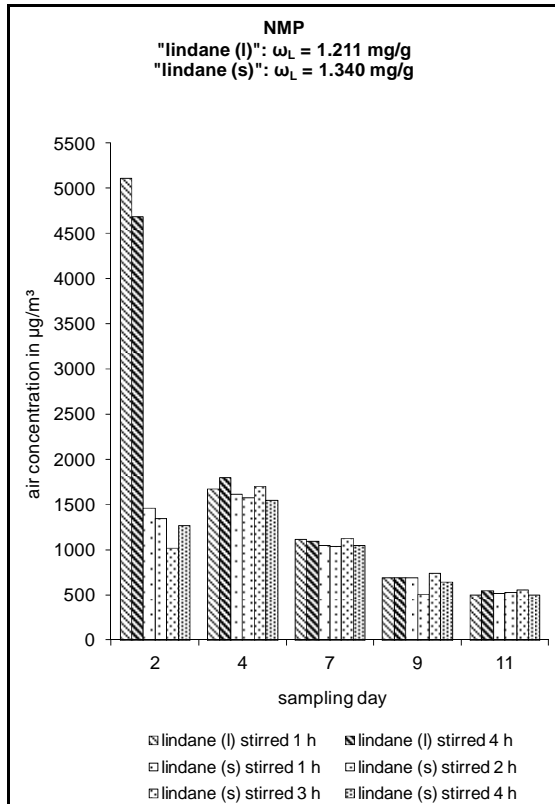
Figure 5.15: Emissions of NMP with/without MeOH at different stirring times (see 4.1.4)
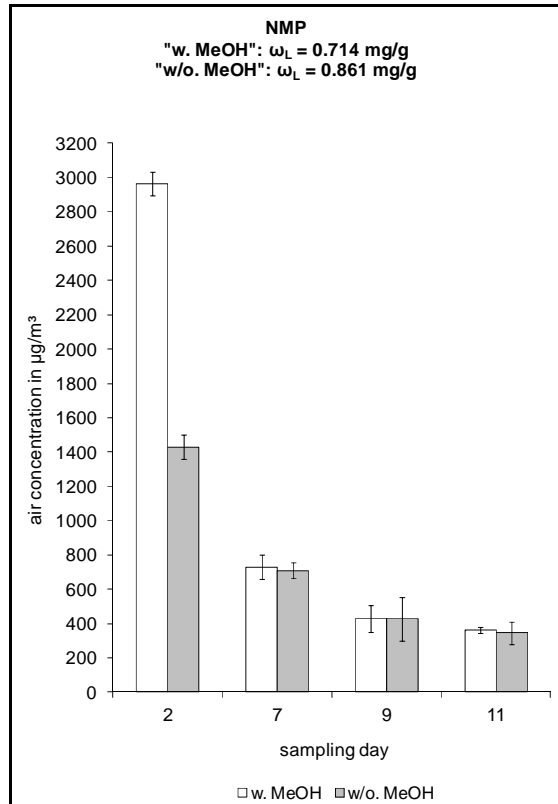
Figure 5.16: Emissions of NMP with and without MeOH (see 4.1.5)
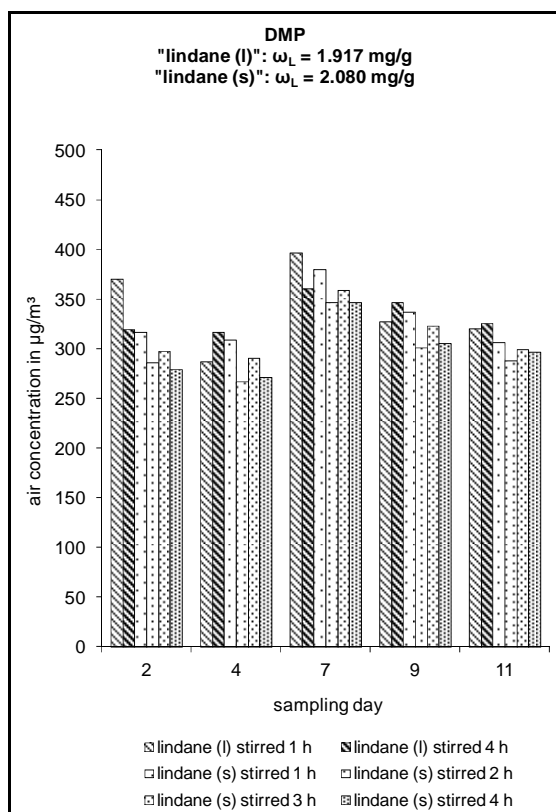
Figure 5.17: Emissions of DMP with/without MeOH at different stirring times (see 4.1.4)
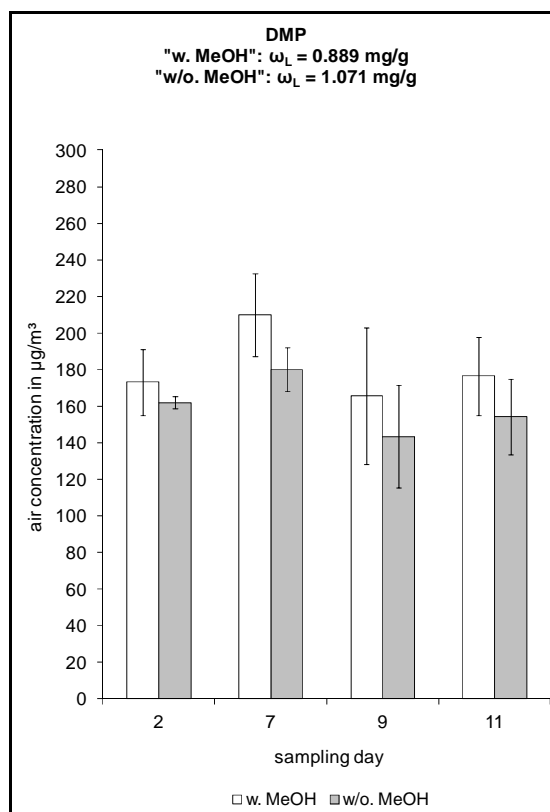
Figure 5.18: Emissions of DMP with and without MeOH (see 4.1.5)
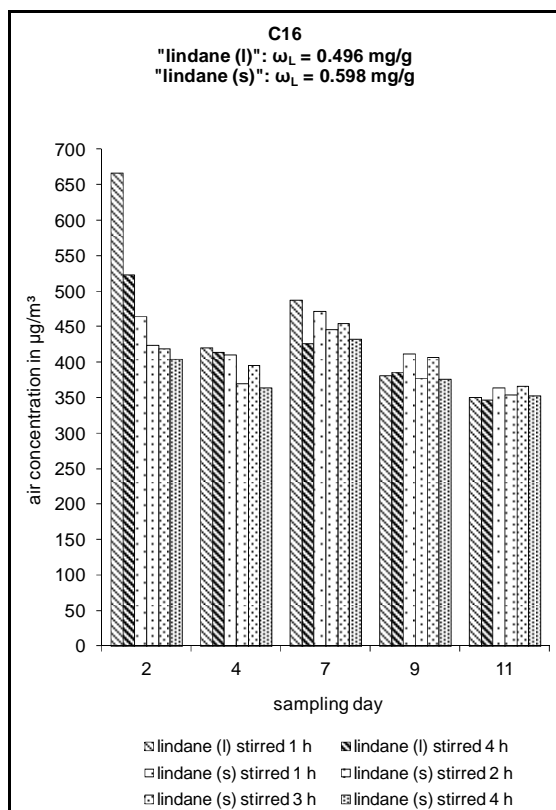
Figure 5.19: Emissions of C16 with/without MeOH at different stirring times (see 4.1.4)
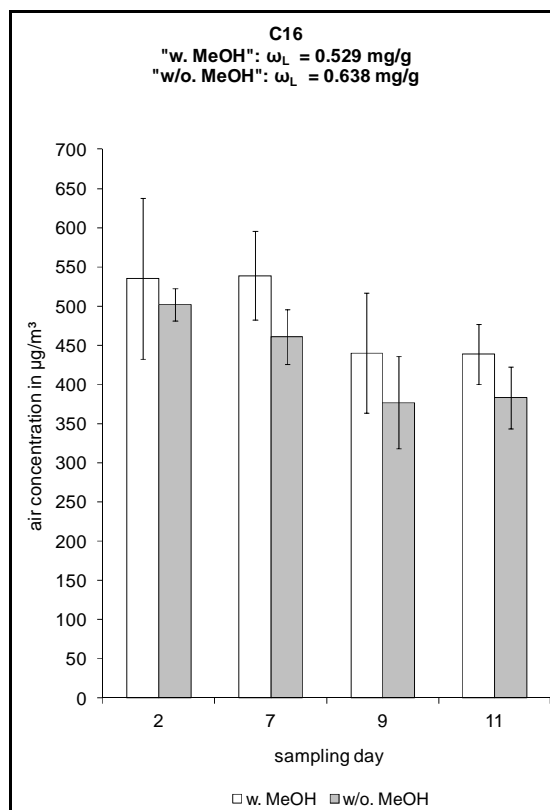
Figure 5.20: Emissions of C16 with and without MeOH (see 4.1.5)
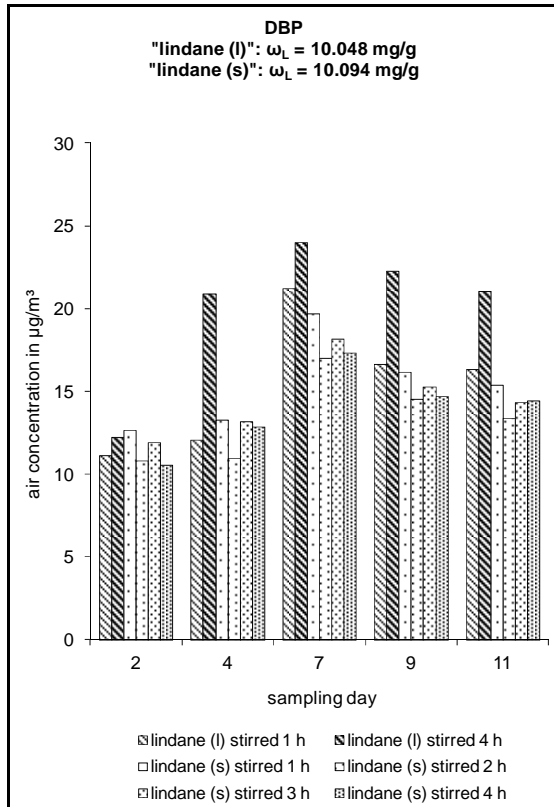
Figure 5.21: Emissions of DBP with/without MeOH at different stirring times (see 4.1.4)
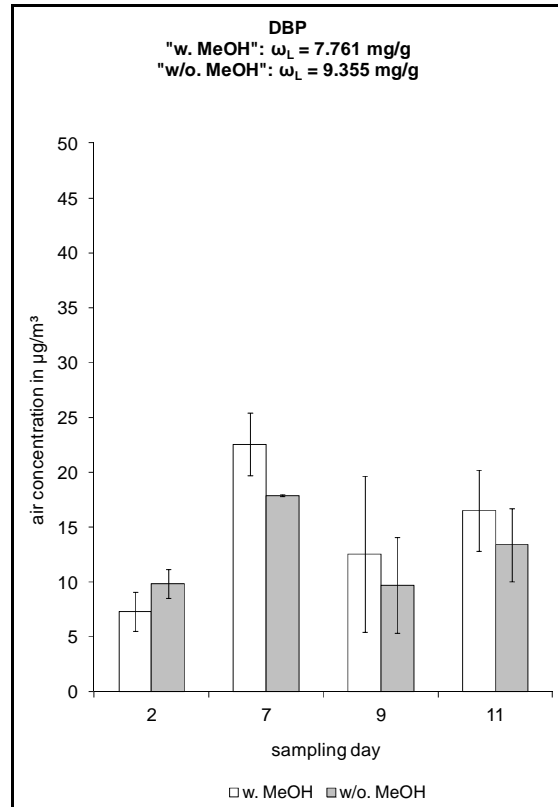
Figure 5.22: Emissions of DBP with and without MeOH (see 4.1.5)

The dotted and shaded columns show that for almost all substances the stirring time does not significantly influence their associated emission profiles. Only DBP in Figure 5.21 showed higher emissions after four hours of stirring.

For styrene in Figure 5.11 and Figure 5.12 it can be stated that the emissions are enhanced when methanol is left out of the mixture. This can be explained by the fact that styrene is volatile and evaporates together with the solvent while curing, therefore a large amount of styrene gets lost from the mixture together with methanol. With the exception of day two, Figure 5.13 to Figure 5.16 show that the emissions of NMP and E.H. were not influenced by MeOH. In day two the curing process still took place and for both substances the emissions were lower when methanol was used. As with lindane, from DMP over C16 to DBP the figures from experiment 4.1.5 indicate that the emissions seemed to benefit from the addition of methanol.

Figure 5.23 shows that without MeOH the lacquer contracted while curing. This led to fissures at the edges of the lacquer film inside the Petri dishes. In accordance to

chapter 5.1.2 for the alkyd lacquers such fissured surfaces lead to heterogeneous emissions. On the contrary Figure 5.24 shows that MeOH provided a plane lacquer surface after curing.
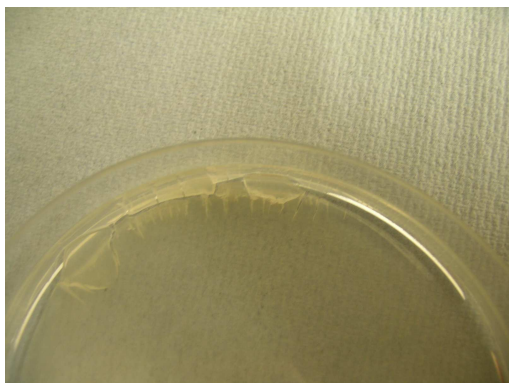
Figure 5.23: Fissures on the surface of a cured lacquer mixture without MeOH

Figure 5.24: Plane surface of a cured lacquer mixture without containing MeOH

In general MeOH could not be substituted with other bipolar solvents. Acetone is a common analyte for a lot of synthetic building products which complicates accurate measurement of acetone emissions. Ethyl acetate and ethanol also emit from building products. Their boiling points are also too high which extends the curing time, because they evaporate slower.

5.1.5 Interim conclusion I

The previous experiments show that the WGC-lacquer was able to emit the pre-chosen seven substances. MeOH should be used to dissolve the solid lindane and to enhance the emissions of the less volatile compounds, if their emissions are to be determined. The associated negative influence on styrene is acceptable and its emissions could be well-controlled with the spiked amount. The emission-controlling function of the spiking also applies for the more volatile analytes up to C16.

The stirring step with a closed cap ensured that the analytes were distributed homogenously inside the mixture. Volatile analytes like styrene also remained inside the lacquer while mixing. One hour stirring seemed to be enough. Only the emissions of DBP can be enhanced by longer stirring, however this would excessively extend the preparation time.

It could also be observed that sampling while curing may increase the measurement variations. After curing almost all compounds emission profiles stabilised.

Finally, it is difficult to optimise the emission profiles when considering of all analytes equally as their physical and chemical properties differ substantially. The preparation parameters described above are therefore a compromise between the different effects.

5.1.6 First stability testing

Table 5.3 summarises the results of experiment 4.1.6. The emissions of styrene, DMP, C16 and lindane varied mostly below 10 %. In terms of emission testing this indicated that both the emission of one mixture and equally prepared batches were both repeatable and reproducible. The emissions of NMP were relatively stable with deviations of less than 20 %. For E.H. up to day 7 there is a process that disturbs the emission profile. This cannot currently be explained. The deviations for DBP stabilise after one week below 20 %. The low air concentrations combined with the SVOC-typical tendency to show sink effects lowers the repeatability and reproducibility of the emission. Those sink effects cannot be described and controlled completely [36].

Table 5.3: Average (AV) and relative standard deviation (RSD(repro)) of three identical prepared spiked lacquer samples over different sampling days; RSD(repeat) stands for the mean RSDs of the six chambers of one µ-CTE over different sampling days

sampling day	spiking [mg/g]	styrene 0.430	E.H. 0.523	NMP 0.488	DMP 1.864	C16 0.482	lindane 4.801	DBP 13.022
2	AV [µg/(m²h)]	1500	1000	4800	850	980	100	20
	RSD(repro) [%]	5	26	15	4	7	5	27
	RSD(repeat) [%]	1	32	4	8	7	10	21
4	AV [µg/(m²h)]	410	160	1900	720	740	92	21
	RSD(repro) [%]	3	35	16	5	7	3	39
	RSD(repeat) [%]	3	15	3	8	6	12	23
7	AV [µg/(m²h)]	100	77	1000	760	710	100	35
	RSD(repro) [%]	1	34	17	5	9	4	13
	RSD(repeat) [%]	4	6	7	8	7	10	13
9	AV [µg/(m²h)]	32	75	670	700	630	93	27
	RSD(repro) [%]	2	20	18	3	9	3	18
	RSD(repeat) [%]	10	8	10	7	5	10	13
11	AV [µg/(m²h)]	< LOQ	44	460	670	570	91	25
	RSD(repro) [%]	< LOQ	9	18	7	12	11	14
	RSD(repeat) [%]	< LOQ	10	15	7	6	8	13

5.2 Curing

5.2.1 Curing process in the μ-CTE

The following figures show the results for experiment 4.2.1. The white columns present the emitted amounts from the samples which were loaded directly into the μ-CTE. Their results were normalised to 1. The grey columns show the emission rates of the samples that are firstly loaded into the 1-m³-chamber for curing. They were calculated in relation to the white ones. The line graphs stand for the associated RSDs from each μ-CTE as a measure for the repeatability.

For most substances the RSD-values after curing inside the 1-m³-chamber are below 10 %. However for DBP an outlier from this rule can be observed.
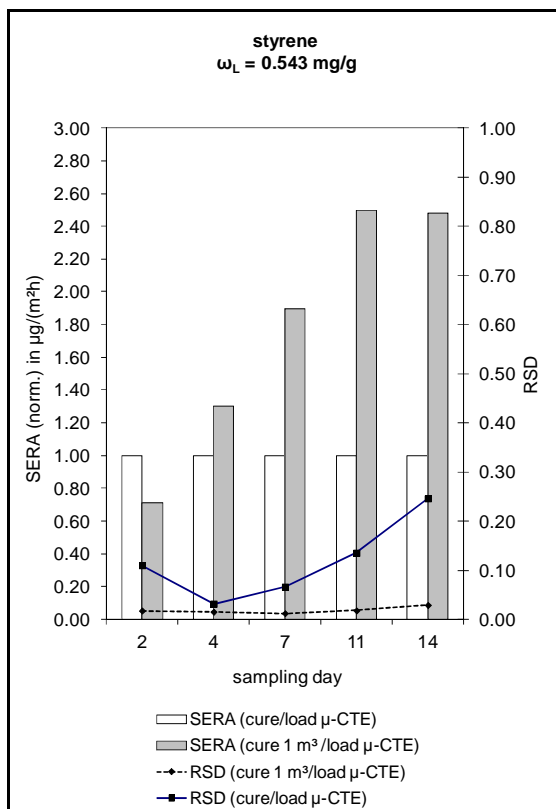
Figure 5.25: Emissions of styrene after different curing processes (µ-CTE)
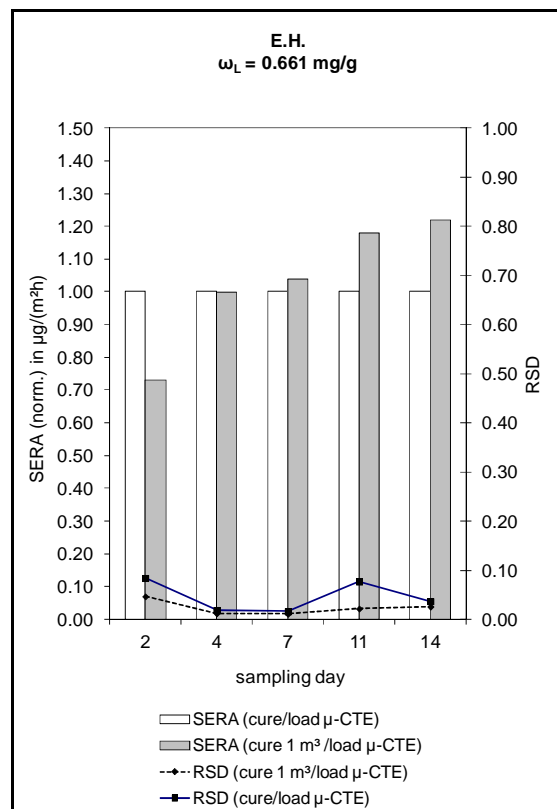
Figure 5.26: Emissions of E.H. after different curing processes (µ-CTE)
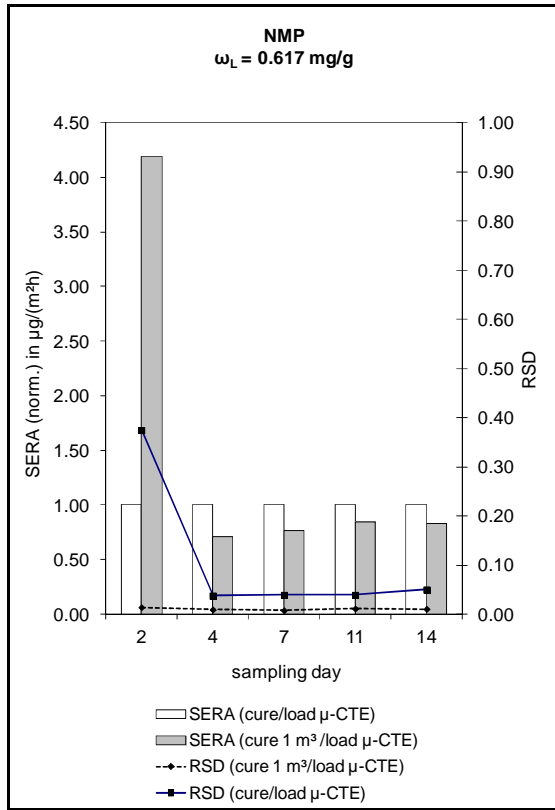
Figure 5.27: Emissions of NMP after different curing processes (µ-CTE)
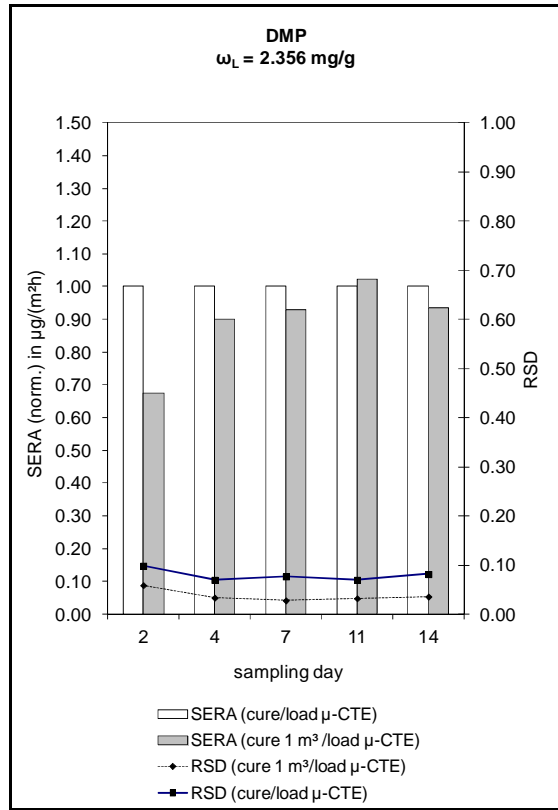
Figure 5.28: Emissions of DMP after different curing processes (µ-CTE)
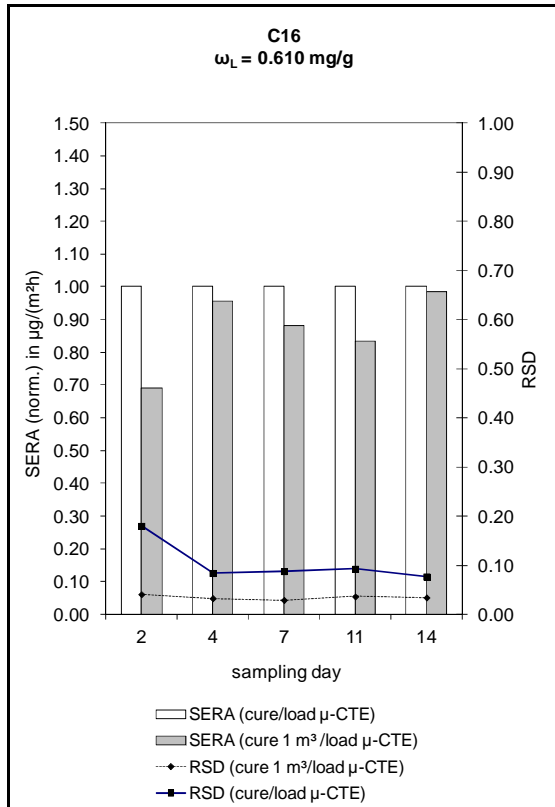
Figure 5.29: Emissions of C16 after different curing processes (µ-CTE)
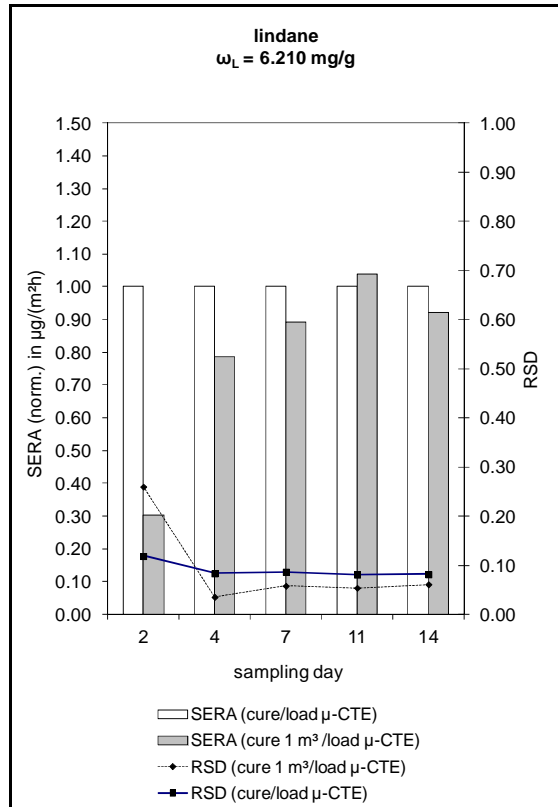
Figure 5.30: Emissions of lindane after different curing processes (µ-CTE)

70
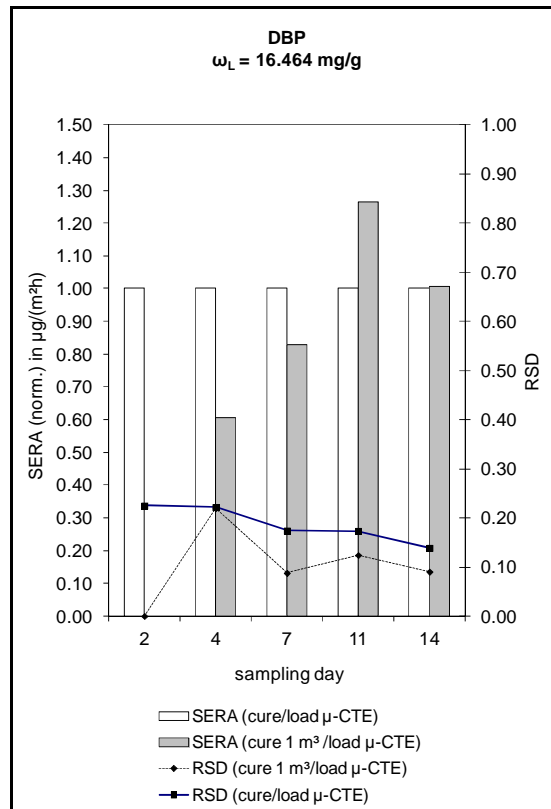
Figure 5.31: Emissions of DBP after different curing processes (µ-CTE)

For styrene in Figure 5.25 it is obvious that emissions were increased when curing takes place inside the 1-m³-chamber. This means that the lacquer mixture lost more analyte while curing inside the µ-CTE. This can be explained by the fact that the air change rate inside the µ-CTE was much higher. Hence, the mixture was leached from the volatile styrene when unsaturated air constantly streams over the lacquer surface. The same can be observed for E.H, however because of its lower volatility (see Figure 3.7) the effect was weaker.

Theoretically the same should be applied to NMP but Figure 5.27 shows that the emissions were enhanced when curing takes place inside the µ-CTE. This contrary behaviour can be explained by the high hydrophilicity of NMP (see Figure 3.6). The lacquer mixture, which was transferred from the external chamber to the µ-CTE contained water, because the steel chamber air was humid. When it came into contact with the dry air inside the µ-CTE the lacquer lost water quickly, but due to its good solubility in water NMP also evaporated quickly. This is shown by the high emissions on sampling day two.

For the other substances the emissions aligned between the two ways of curing over time. Figure 5.28 and Figure 5.29 show that the emissions for DMP and C16 aligned after two days. Lindane in Figure 5.37 and DBP in Figure 5.38 needed much more time to emit on the same level. It appears that the volatility of these four substances determined the time to align the emission. The less volatile substances also tended to show sink effects, therefore DBP could not be detected at sampling day two. The walls of the µ-CTE must be saturated with DBP before it could emit into the air. This fact also increased the alignment time.

5.2.2 Curing process for the desiccator

In the previous chapter 5.2.1 the parameters of the curing chambers differ when referring to humidity, air change rate and chamber size.

The 1-m³-chamber and the desiccator in this chapter had similar climate and flow rate parameters. Only the air velocity and the chamber size differ. This results in similar emissions which can be seen in Figure 5.32 to Figure 5.38 (white and light grey columns). This means that for all substances except DBP the emissions aligned after 3 days. The difference was within the RSD values between 10 to 20 % (line graphs). For DBP the emission aligns within one week. Again the low volatility combined with the tendency to interact with sinks delays the alignment.

The influence of the fan must be observed separately (dark grey columns). For the volatile styrene, E.H. and NMP the movement of the air caused by the fan showed had a negligible effect. The difference ranged mostly within the RSD between 10 to 20 %. This indicates that that lacquer mixture acts as a diffusion-controlled source. Chapter 2.1.2 described that the air velocity shows only minor influences on such sources. For the less volatile substances from DMP up to DBP the lacquer acts as an evaporation-controlled source. Here volatility and turbulences are determining parameters for the emission profile. This can be seen in Figure 5.35 to Figure 5.38. The dark grey columns show that the emissions were inhibited by the low air turbulence over the sample caused by the disabled fan. The low air velocity leads to low air concentrations because molecules that are bounded to sinks are desorbed much slower. Clausen et al. [37] and Mull [38] also describe the influence of external mass transfer (caused either by a fan or high air exchange) on the emission of SVOCs.
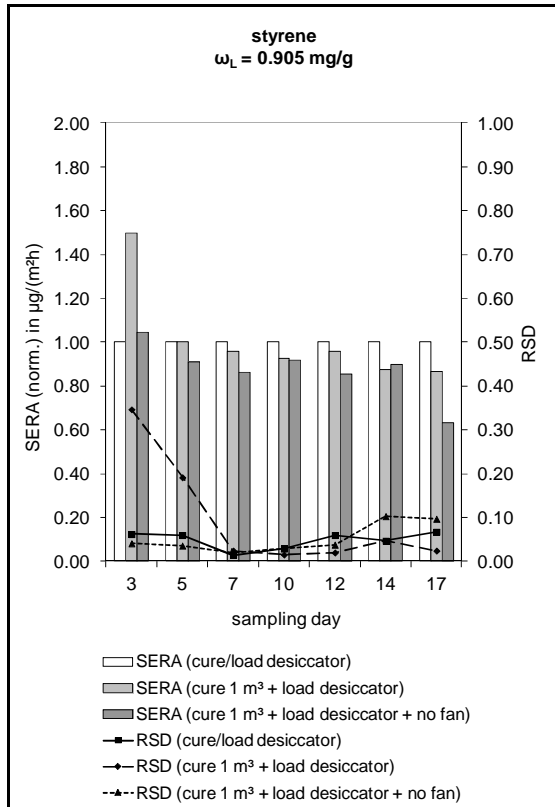
Figure 5.32: Emission profile of styrene after different curing processes (desiccator)
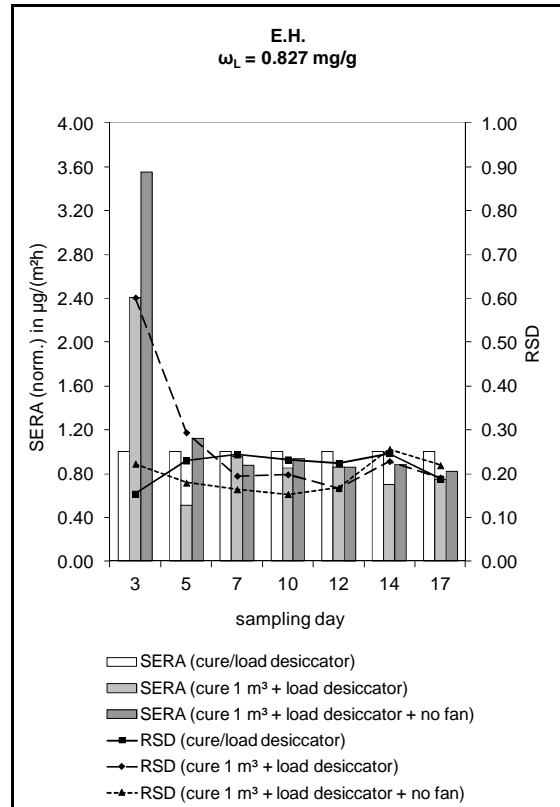
Figure 5.33: Emission profile of E.H. after different curing processes (desiccator)
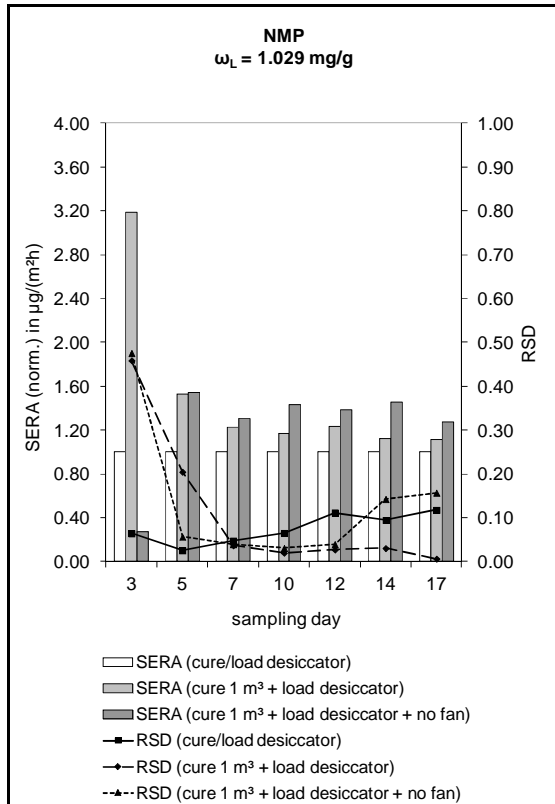
Figure 5.34: Emission profile of NMP after different curing processes (desiccator)
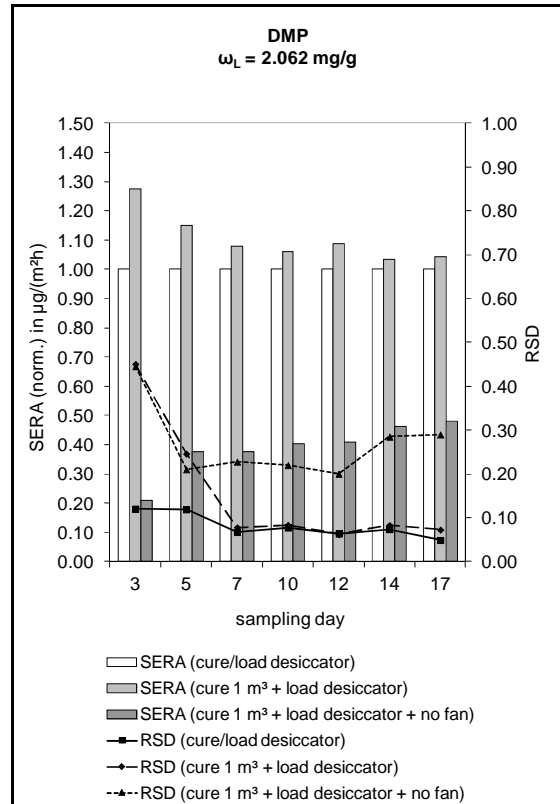
Figure 5.35: Emission profile of DMP after different curing processes (desiccator)

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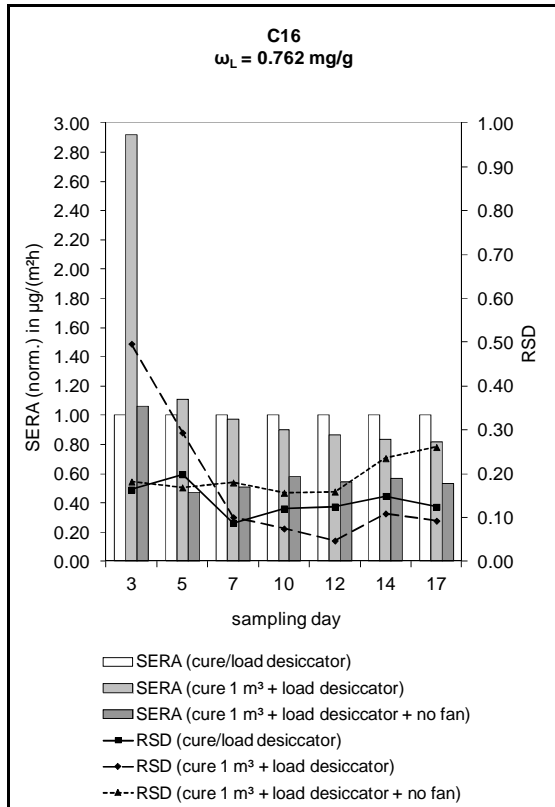
Figure 5.36: Emission profile of C16 after different curing processes (desiccator)
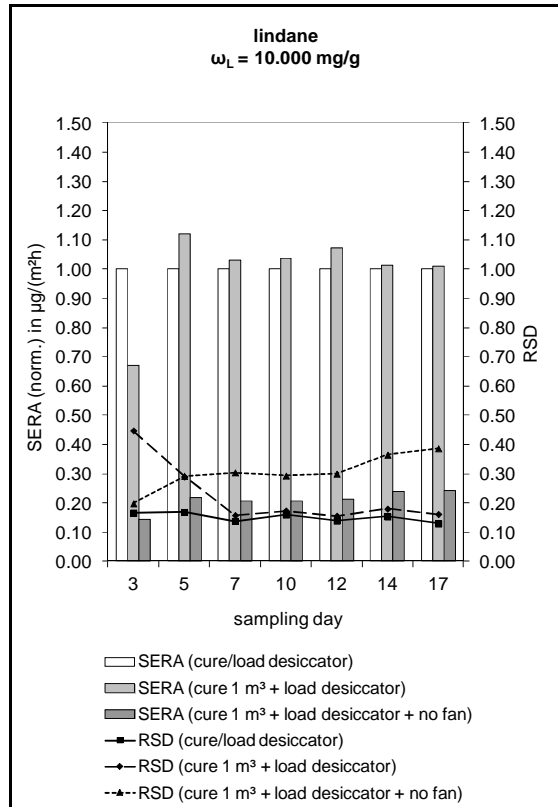
Figure 5.37: Emission profile of lindane after different curing processes (desiccator)
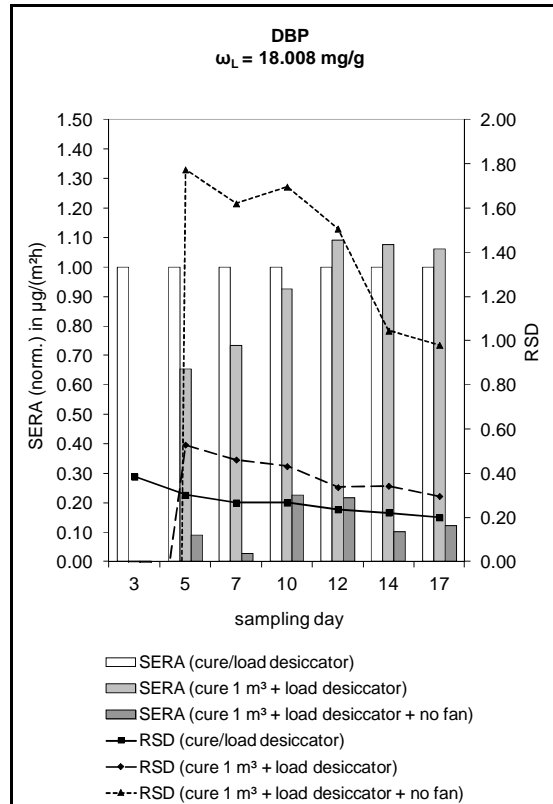
Figure 5.38: Emission profile of DBP after different curing processes (desiccator)

5.2.3 Stability testing II

Table 5.4 and Table 5.5 show the results for the mean emissions, repeatability and reproducibility.

Table 5.4: Mean SER$_A$ and reproducibility (RSD) of the emissions of styrene, E.H. and NMP for each of the three equal lacquer batches loaded into the µ-CTE and the desiccator combined different curing processes

day	styrene 0.643 mg/g AV [µg/(m²h)]	styrene RSD [%]	E.H. 0.579 mg/g AV [µg/(m²h)]	E.H. RSD [%]	NMP 0.720 mg/g AV [µg/(m²h)]	NMP RSD [%]
cure/load µ-CTE						
5	230	± 6	1300	± 13	4600	± 11
7	67	± 2	580	± 13	2100	± 7
11	13	± 5	150	± 11	130	± 3
14	10	± 2	110	± 10	120	± 9
cure 1 m³ + load µ-CTE						
5	240	± 11	1200	± 12	2600	± 3
7	48	± 17	520	± 14	1200	± 4
11	9	± 9	160	± 5	340	± 2
14	8	± 8	120	± 4	210	± 4
cure/load desiccator						
5	6500	± 30	5500	± 38	9800	± 17
7	2900	± 10	3000	± 12	300	± 15
11	700	± 6	1500	± 23	1500	± 9
14	450	± 6	940	± 22	940	± 11
cure 1 m³ + load desiccator						
5	6900	± 9	7000	± 7	22000	± 5
7	2800	± 9	2900	± 4	7600	± 18
11	710	± 15	1400	± 6	3100	± 17
14	390	± 10	940	± 11	1800	± 8

Table 5.5: Mean SER_A and reproducibility (RSD) of the emissions of DMP, C16, lindane and DBP for each of the three equal lacquer batches loaded into the µ-CTE and the desiccator combined different curing processes

day	DMP 1.443 mg/g AV [µg/(m²h)]	RSD [%]	C16 0.543 mg/g AV [µg/(m²h)]	RSD [%]	lindane 7.000 mg/g AV [µg/(m²h)]	RSD [%]	DBP 12.605 mg/g AV [µg/(m²h)]	RSD [%]
cure/load µ-CTE								
5	270	± 5	360	± 4	75	± 4	61	± 6
7	200	± 4	260	± 7	61	± 1	50	± 9
11	130	± 5	150	± 9	39	± 3	34	± 5
14	120	± 10	150	± 11	36	± 6	29	± 10
cure 1 m³ + load µ-CTE								
5	290	± 9	340	± 1	86	± 7	47	± 14
7	210	± 2	240	± 9	82	± 5	56	± 12
11	140	± 9	160	± 7	43	± 5	39	± 11
14	120	± 12	160	± 11	37	± 9	29	± 12
cure/load desiccator								
5	4400	± 32	4100	± 17	1500	± 40	550	± 109
7	3600	± 48	2800	± 33	1400	± 55	580	± 122
11	2100	± 3	1500	± 40	1100	± 19	480	± 79
14	2100	± 12	1000	± 42	1000	± 16	240	± 69
cure 1 m³ + load desiccator								
5	8300	± 18	8100	± 2	2200	± 42	310	± 31
7	5400	± 17	4000	± 7	1700	± 34	310	± 23
11	3400	± 19	2200	± 12	1500	± 23	470	± 52
14	2200	± 19	1300	± 7	1000	± 23	390	± 51

For the µ-CTE the reproducibility of the emissions for DMP, C16 and lindane did not differ significantly concerning the curing process. For DBP the results diverge less if curing and sampling took place in the same chamber. In this case only the sinks of

the µ-CTE disturbed the homogeneity of the emissions. Changing the chamber for the emission testing led to two possible sinks: sinks of the 1-m³-chamber (curing) and the µ-CTE (testing). For E.H. and styrene the variations were distributed more homogeneously if the chamber was not changed. On the contrary, the reproducibility of the emissions of NMP benefited significantly if the lacquer mixture cured inside the 1-m³-chamber. The humidification inside this chamber appeared to improve the reproducibility of the NMP-emissions. Lastly, it turned out that compared to chapter 5.1.6the variations for E.H., NMP and DBP could be improved significantly.

Concerning the desiccator, the reproducibility of almost all of the substances is improved if curing took place inside the 1-m³-chamber. Therefore it is possible to reproduce the emission profiles of the majority of the analytes with variations below 20 %. Only the results for lindane and DBP varied to a greater degree.

Compared to the results of the µ-CTE the reproducibility for all substances inside the desiccator was poorer. For the less volatile lindane and DBP this can be explained with the lower loading factor. Inside larger chambers there is more surface area that can act as sink. This lowered the reproducibility of the additional low SVOC-emissions. The emissions of the remaining more volatile substances were higher compared to the µ-CTE because of the lower air change rate. This indicates that small variations of the process parameters of the desiccators had a greater influence on the homogeneity of the emissions.

5.2.4 Curing at different chamber flows

Figure 5.39 to Figure 5.45 show the emission curves for the analytes at 15 and 30 ml/min chamber flow through the µ-CTE.
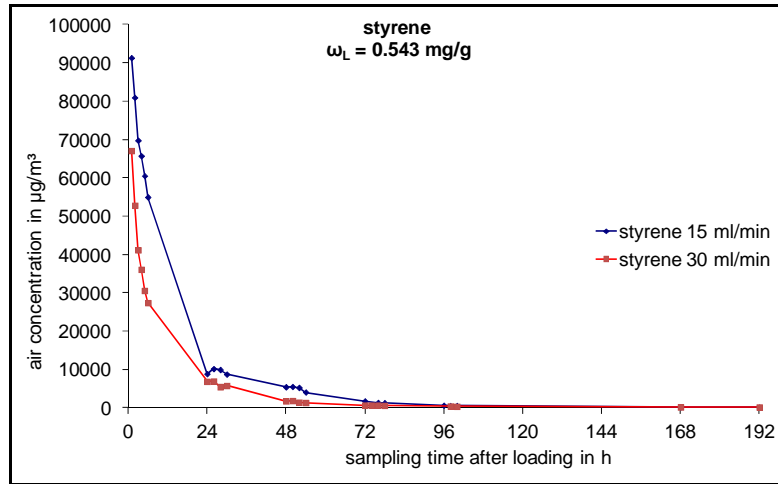
Figure 5.39: Styrene emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
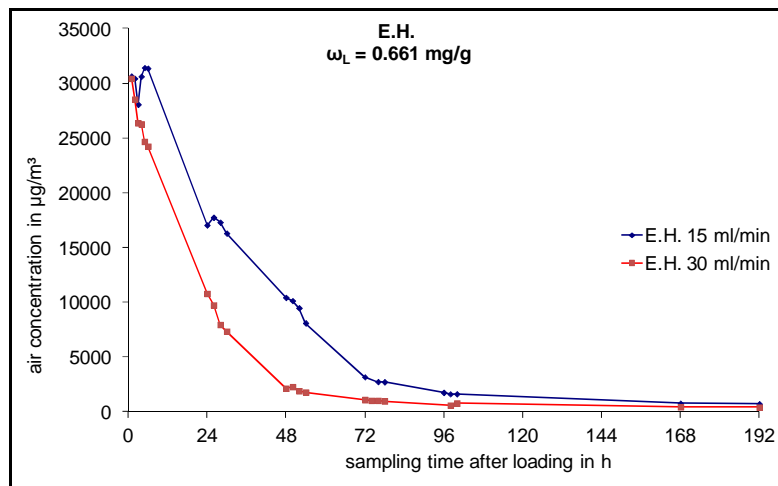
Figure 5.40: E.H. emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
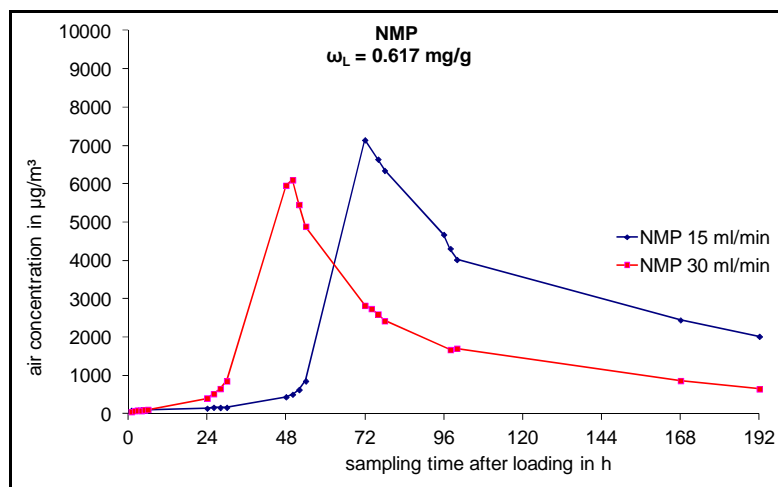
Figure 5.41: NMP emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
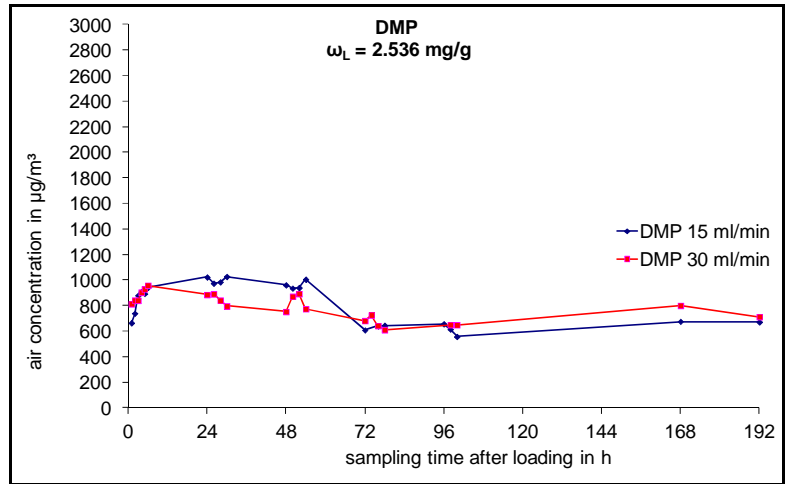
Figure 5.42: DMP emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
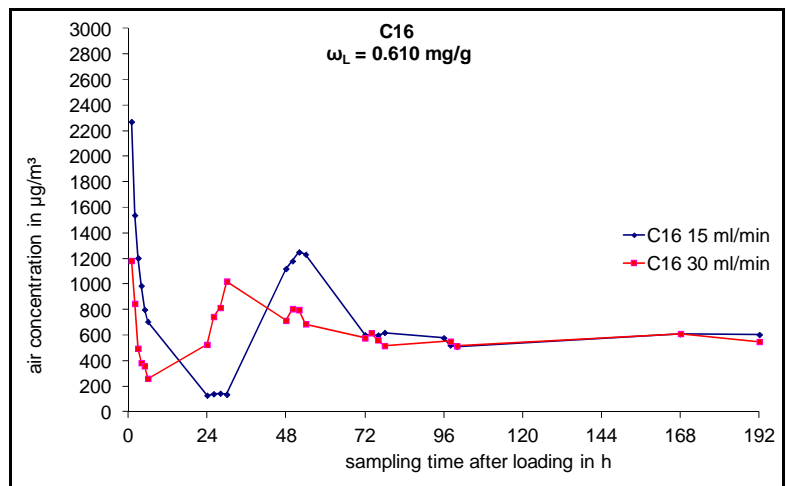
Figure 5.43: C16 emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
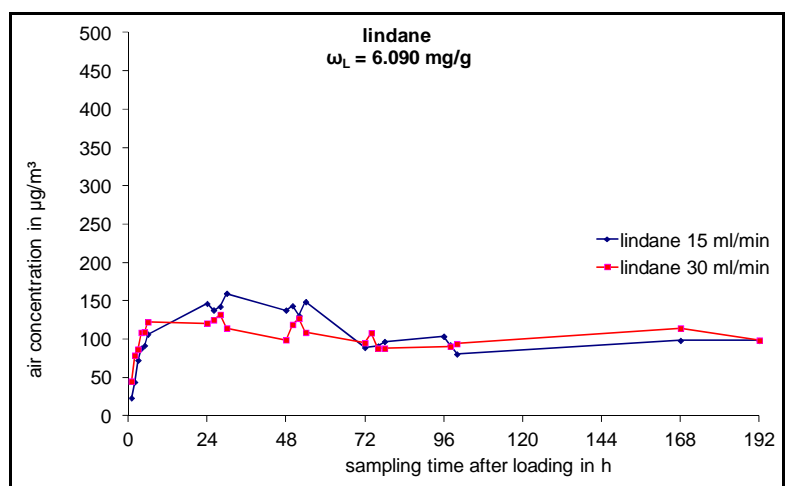
Figure 5.44: Lindane emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)
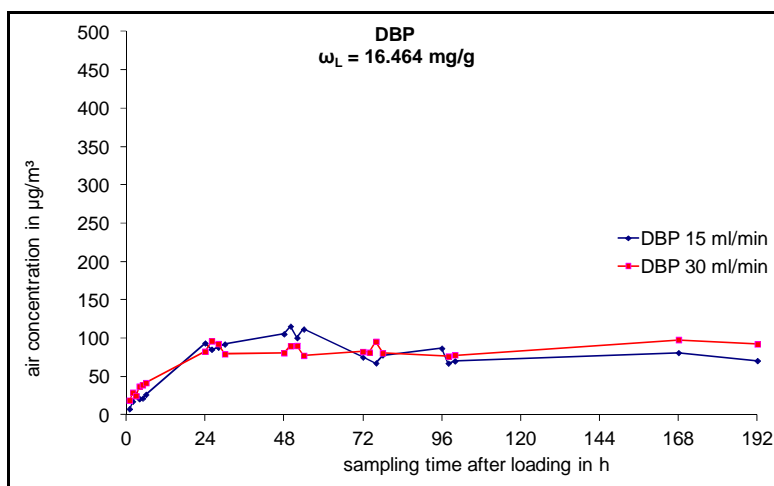
Figure 5.45: DBP emissions of one lacquer batch at 15 and 30 ml/min chamber flow (0 % RH)

It is obvious that the emission of DMP, lindane and DBP are not influenced by the chamber flow rate (Figure 5.42, Figure 5.44 and Figure 5.45).

High chamber flows diluted the emissions of the volatile E.H. and styrene (Figure 5.39 and Figure 5.40). Hence, the measured air concentrations at 30 ml/min were lower compared to the amounts at 15 ml/min.

Figure 5.41 and Figure 5.43 show that the maximum point on the emission curve of NMP and C16 shifted when the flow was increased. At lower flows less water evaporated from the lacquer mixture, hence more time was needed for the curing process. It appeared that as long as the mixture was liquid hardly any NMP emission was detectable. On the contrary C16 showed high emissions which subsided when the lacquer turned into a solid and increased again afterwards. Those two substances showed that the point of curing was delayed by one day.

After curing the emission of C16 aligned over time between the two flows in the same way as was observed for DMP, lindane and DBP. For all the other substances the air concentration remained at a higher level at lower chamber flows.

5.2.5 Curing at different humidities

Figure 5.46 to Figure 5.52 show the emission curves for the analytes at 15 and 30 ml/min chamber flow through the µ-CTE.
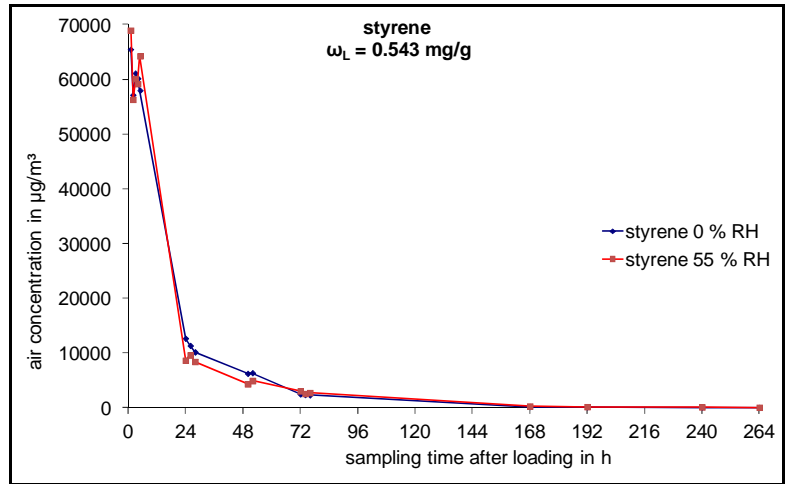
Figure 5.46: Styrene emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
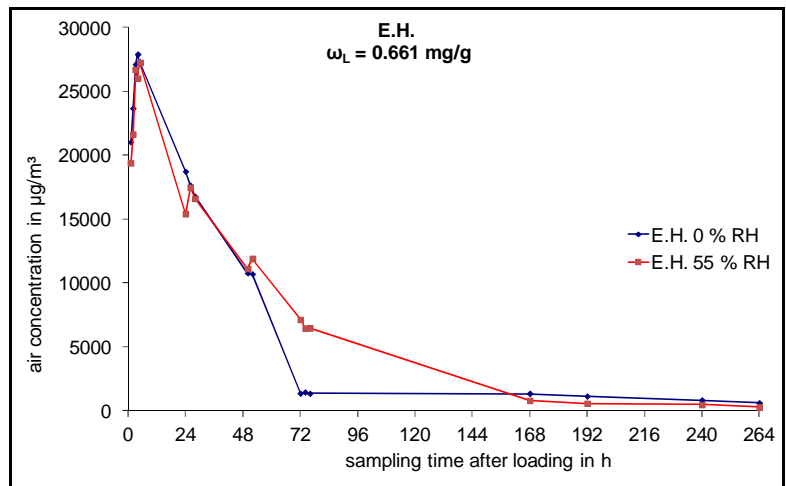
Figure 5.47: E.H. emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
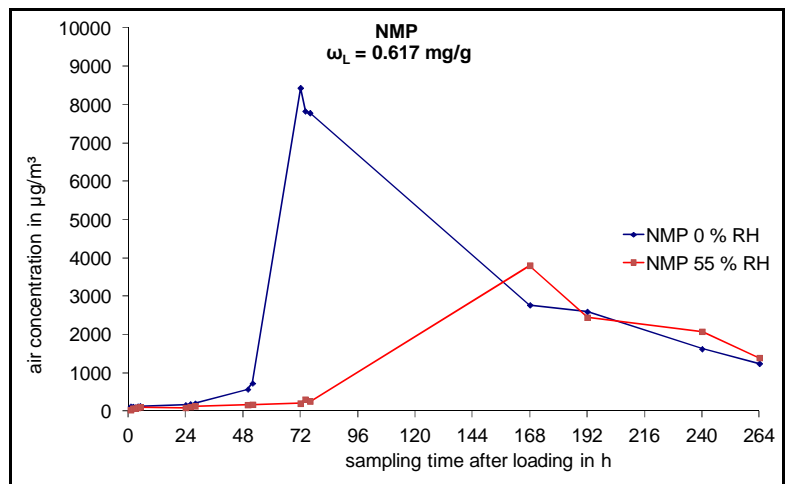
Figure 5.48: NMP emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
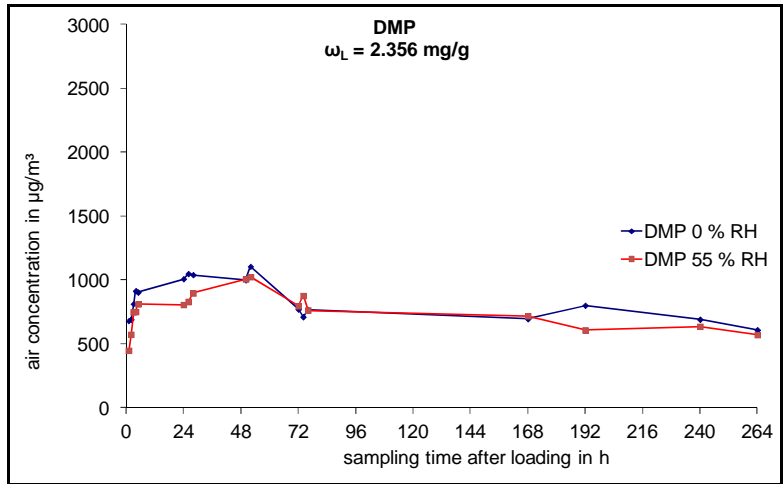
Figure 5.49: DMP emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
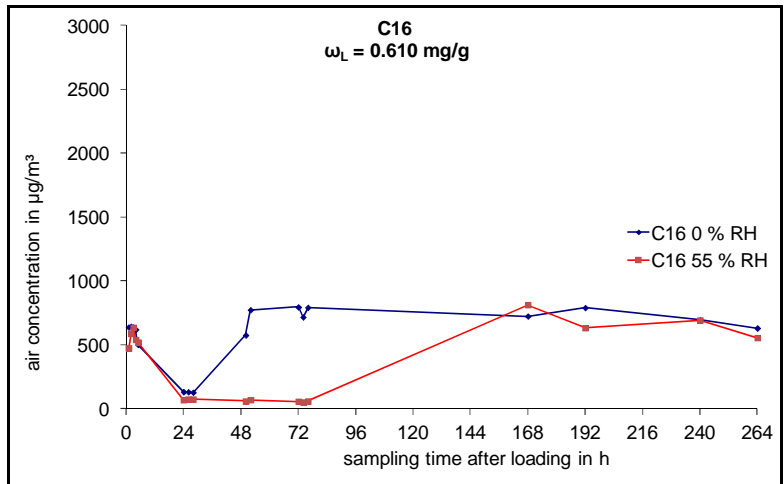
Figure 5.50: C16 emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
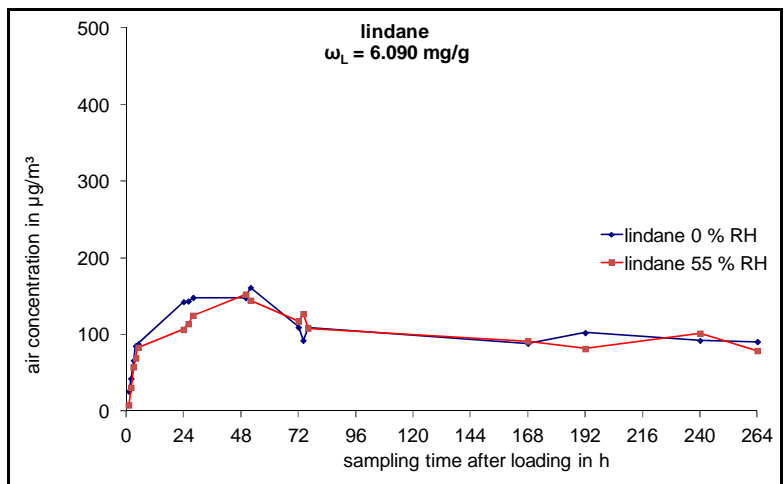
Figure 5.51: Lindane emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)
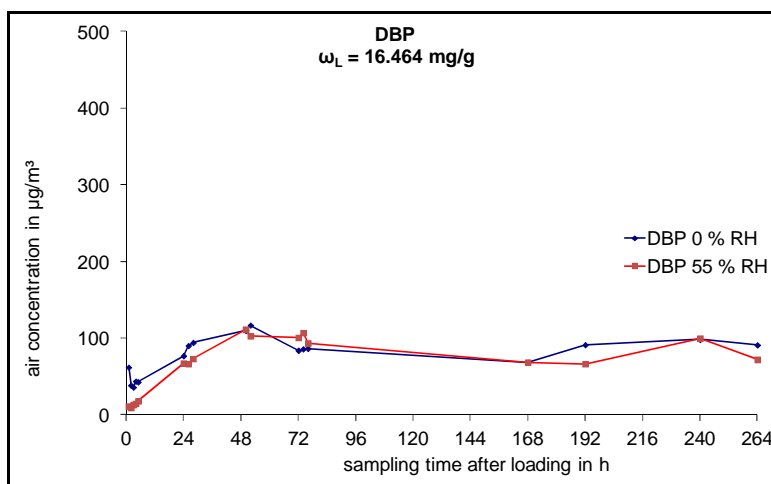
Figure 5.52: DBP emissions of one lacquer batch at 0 and 55 % RH (15 ml/min flow)

It appears, that humidification did not influence the emissions of styrene, DMP, lindane and DBP significantly (Figure 5.46, Figure 5.49 and Figure 5.51 to Figure 5.52). E.H. shows a minor impact. Figure 5.47 shows that over time, the emission is slightly higher if the chamber air is humidified. Similar results were published in literature, for example Liu et al. [35] observed that the toluene emission from a diffusion-controlled source was uninfluenced by the humidity.

In accordance to the previous chapter 5.2.4 the curves of NMP and C16 in Figure 5.48 and Figure 5.50 were shifted. Again delaying curing influenced the emissions. In contrast to chapter 5.2.4 the air concentrations aligned over time for both substances.

5.2.6 Interim conclusion II
In contrast to the previous experiments discussed in chapters 4.2.4 and 4.2.5 sampling was also performed before the lacquer mixture was cured. This procedure determines the emission behaviour entirely. It can be stated that low air change rates extend the curing time as well as humidified air.

As mentioned in chapter 5.2.2 the lacquer system acted as a diffusion-controlled source for volatile compounds and as evaporation-controlled source for less volatile substances. For example, the results of chapters 5.2.3, 5.2.4 and 5.2.5 showed that emissions from DMP, lindane and DBP were quite independent of the way curing occurs. The humidification, chamber flow, or air change rates, did not disturb the emission significantly. Only the air velocity on the surface caused by the desiccator

fan had a major impact on the emissions (chapter 5.2.2). As described in 5.1.3 increasing the analyte amount inside the lacquer results in higher air concentrations, if evaporation does not limit the emissions produced. Reliable results for such compounds can be achieved if the test chamber air is homogeneous and sinks should be at best avoided or saturated.

On the contrary chapter 5.2.1 and 5.2.4 indicate that styrene and E.H. were influenced significantly by the air change rate. As mentioned in chapter 5.2.2 the lacquer acted as diffusion-controlled source. As long as the chamber air was not saturated and the diffusion of the compound inside the lacquer was not limited those analytes evaporated at a continuous rate. High air change rates diluted the VOC concentration inside the chamber, hence the emitted amounts were lower at higher flows inside the µ-CTE in 5.2.4. Therefore reliable results for such compounds can be achieved if the air change is kept at best constant especially while curing, where the lacquer loses the majority of volatile analytes.

In general humidity had a minor influence on the emissions of the lacquer system. C16 and NMP were special cases. They are the most non-polar, respectively polar, compounds among the investigated substances. Their emission is additionally influenced significantly by the curing process which is influenced by the chamber flow, mixing and humidity. Only after curing the lacquer acted as diffusion-controlled source for NMP and as evaporation-controlled source for C16.

Finally Figure 5.53 to Figure 5.55 show that the homogeneity of the lacquer surface could be improved by the chamber flow and its corresponding size. At 30 ml/min (Figure 5.53) inside the µ-CTE the liquid mixture is pushed to one edge of the Petri dish. There it cures while fissures develop on the opposite sides. At lower flows (e.g. 15 ml/min, Figure 5.54) the mixture is less influenced by the flow and the lacquer distributes more evenly inside the Petri dish. This behaviour is enhanced inside the 1-m³-chamber with its low flow compared to the chamber size, which results in a plane and homogeneous surface (Figure 5.55).
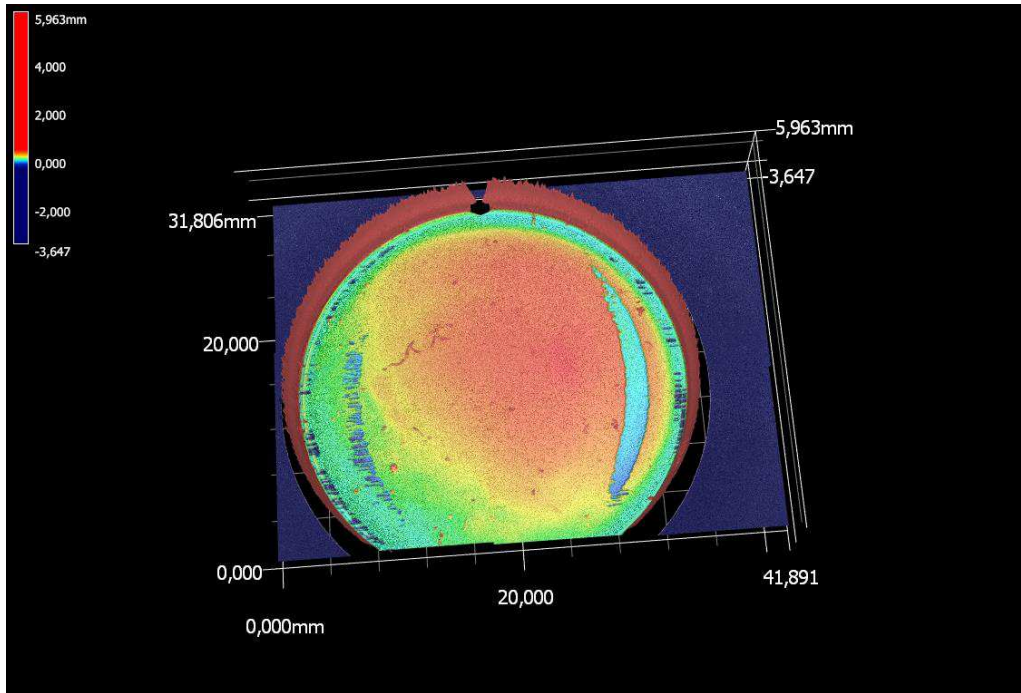
Figure 5.53: Surface of a lacquer sample cured inside the µ-CTE at 30 ml/min and 0 % RH (35-mm-Petri dish, measured with a VR 3000 from KEYENCE)
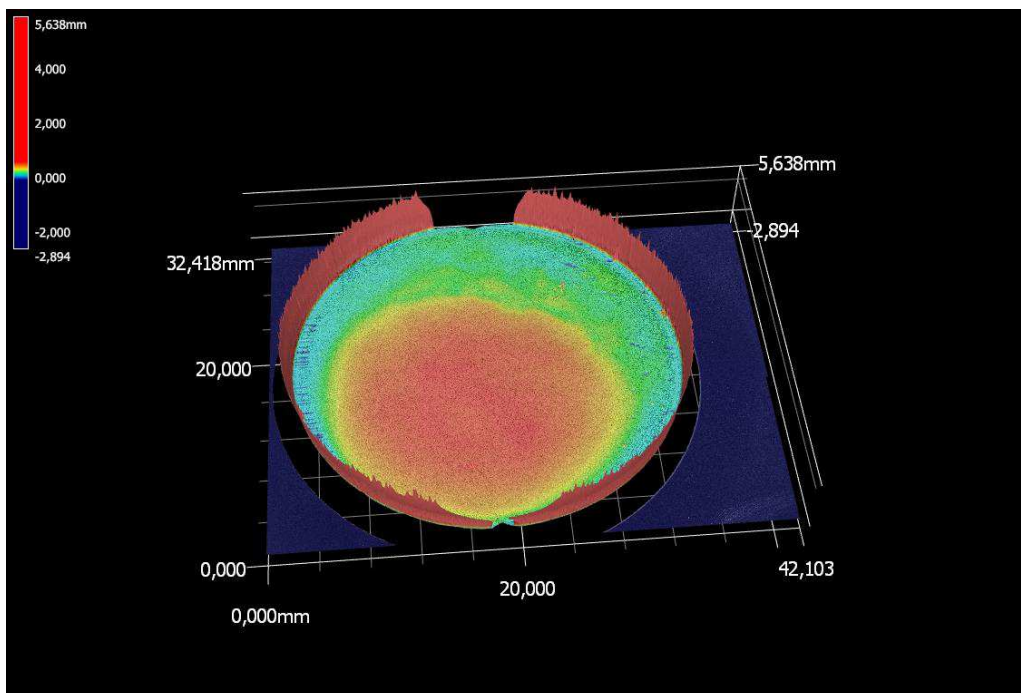
Figure 5.54: Surface of a lacquer sample cured inside the µ-CTE at 15 ml/min and 0 % RH (35-mm-Petri dish, measured with a VR 3000 from KEYENCE)
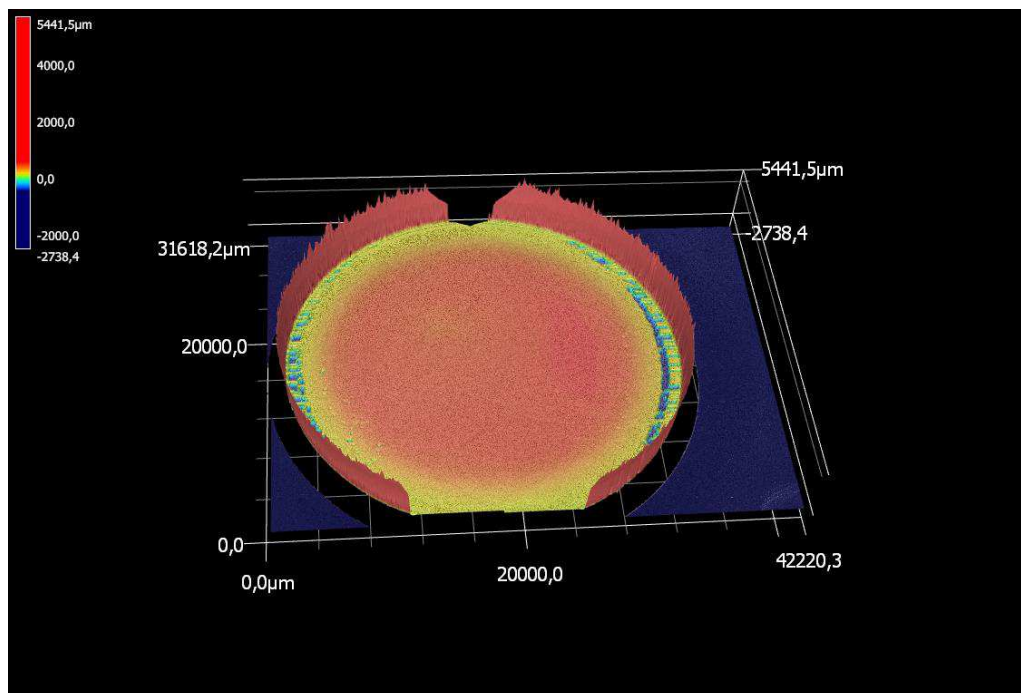
Figure 5.55: Surface of a lacquer sample cured inside an external 1-m³-chamber at 750 l/h and 50 % RH (35-mm-Petri dish, measured with a VR 3000 from KEYENCE)

5.3 Round robin test optimisation

5.3.1 Optimal Spiking

It turned out that hexanal and naphthalene showed an emission behaviour that was comparable to styrene (in comparison to Figure 5.39 at 15 ml/min). Their emission decays constantly during and after curing of the mixture. The emissions of C10, limonene and E.H.-acryl also decay, however similar to C16 while curing a maximum in the emission developed over time (in comparison to Figure 5.43 at 15 ml/min).

According to the spiking, the emissions of C10, limonene, E.H.-acryl was comparable to E.H. if they are added in the same amount to the mixture. Hexanal must be spiked in the same way as DMP because its high volatility means large amounts are lost while curing. Like lindane, naphthalene is a solid substance, therefore it was diluted in MeOH together with lindane and added as a solution. As it is more volatile than lindane only 10 % of the lindane amount was added to the MeOH-solution.

Table 5.6 and Table 5.7 depict a lacquer mixture whereby all substances are emitted in quantifiable amounts.

Table 5.6: Air concentrations of a lacquer mixture three and seven days after loading into a 24-l-chamber (cured three days in a 1-m³-chamber) - part 1

	hexanal	styrene	C10	E.H.	limonene	NMP
spiking ω_L [mg/g]	0.79	0.45	0.36	0.41	0.41	0.26
amount after 3 d [µg/m³]	19	90	133	61	120	74
amount after 7 d [µg/m³]	12	36	67	40	74	41

Table 5.7: Air concentrations of a lacquer mixture three and seven days after loading into a 24-l-chamber (cured three days in a 1-m³-chamber) - part 2

	naphthalene	E.H.-acryl	DMP	C16	lindane	DBP
spiking ω_L [mg/g]	0.80	0.44	1.18	0.38	12.95	17.49
amount after 3 d [µg/m³]	201	95	121	107	55	23
amount after 7 d [µg/m³]	115	60	106	75	64	37

5.3.2 Shipping and storage

Table 5.8 below shows that the emitted amounts were lower when the samples were stored in the evacuated bags. This difference between the two ways of storage was lessened for the less volatile substances starting with DMP (see Table 5.9 and Table 5.10). The low emissions of these compounds were not affected by the suction of the air from the bag, thereby making the emitted amounts comparable. While sucking the vacuum the lacquer lost huge amounts of the more volatile analytes which lead to the lower emissions afterwards.

Table 5.8: Mean SER$_A$ (AV) and RSD (n = 3) of six equal cured lacquer samples, three of which were stored in aluminium foil ("Al") and three in an evacuated LDPE bag (vac.) over four days - part 1

| d | stor. | hexanal 0.79 mg/g | | styrene 0.45 mg/g | | C10 0.36 mg/g | | E.H. 0.41 mg/g | |
		AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]
1	vac.	18	± 20	88	± 6	337	± 6	681	± 2
	Al	23	± 21	244	± 5	1118	± 6	771	± 8
2	vac.	9	± 15	49	± 12	224	± 12	494	± 6
	Al	14	± 36	129	± 15	595	± 14	587	± 5
4	vac.	6	± 23	21	± 7	106	± 8	339	± 4
	Al	8	± 24	43	± 18	226	± 20	382	± 2

Table 5.9: Mean SER$_A$ (AV) and RSD (n = 3) of six equal cured lacquer samples, three of which were stored in aluminium foil ("Al") and three in an evacuated LDPE bag (vac.) over four days - part 2

| d | stor. | limonene 0.41 mg/g | | NMP 0.26 mg/g | | naphthalene 0.80 mg/g | | E.H.-acryl 0.44 mg/g | |
		AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]
1	vac.	627	± 3	966	± 1	1630	± 2	878	± 5
	Al	1286	± 3	1161	± 7	2008	± 8	924	± 8
2	vac.	415	± 7	755	± 3	1288	± 2	674	± 4
	Al	769	± 5	902	± 5	1537	± 5	793	± 7
4	vac.	246	± 7	506	± 9	925	± 5	507	± 7
	Al	384	± 13	613	± 3	1055	± 3	546	± 6

Table 5.10: Mean SER_A (AV) and RSD (n = 3) of six equal cured lacquer samples, three of which were stored in aluminium foil ("Al") and three in an evacuated LDPE bag (vac.) over four days - part 3

d	stor.	DMP 1.18 mg/g AV [µg/(m²h)]	RSD [%]	C16 0.38 mg/g AV [µg/(m²h)]	RSD [%]	lindane 12.95 mg/g AV [µg/(m²h)]	RSD [%]	DBP 17.49 mg/g AV [µg/(m²h)]	RSD [%]
1	vac.	116	± 4	203	± 7	37	± 1	16	± 9
	Al	120	± 8	193	± 5	37	± 6	18	± 7
2	vac.	113	± 3	192	± 2	37	± 2	24	± 5
	Al	115	± 5	198	± 4	38	± 6	26	± 6
4	vac.	120	± 5	201	± 5	41	± 3	32	± 9
	Al	118	± 8	196	± 5	40	± 6	34	± 7

5.3.3 Stability testing III

Table 5.11 to Table 5.13 below show the mean emissions of eight equal lacquer samples loaded into eight desiccators with their associated deviations. The emissions of five aliquots from the same mixture loaded into a 1-m³-chamber can be seen. Finally, the averaged air concentration and the combined deviations are calculated.

For all substances the emissions of the 1-m³-chamber were comparable to the desiccators. The uncertainty of the emissions, expressed as RSD were uninfluenced by either including or excluding the results from the 1-m³-chamber. The deviation ranged for all analytes below 20 % at sampling day 7 except for DBP. In two of the eight desiccators hardly any DBP could be detected which increased the uncertainty. Sinks seemed to prevent stable emissions.

Table 5.11 to Table 5.13 also show the averaged emitted amounts of the retained samples loaded into four desiccators. The percentage loss of the analytes emissions are calculated from the quotient of the analyte concentration in the retained sample c_r and the total concentration c_t of the nine different chambers:

$$loss = 100\% \cdot \left(1 - \frac{c_r}{c_t}\right)$$

For almost all substances the loss ranged between 20 to 40 %. The exceptions were styrene and C10, where about 60 % was unaccounted for. Based on their high volatility higher amounts evaporate from the lacquer inside the foil. The same should be applied to hexanal but the emissions from the retained samples ranged at LOQ, therefore the calculated loss was not significant. For DBP the emissions of the packed and sealed retained samples were very low which led to a higher loss. Potentially the surface of the foil may act as an additional sink.

Table 5.11: Mean air concentration (AV) of eight desiccators (RSD, n = 8), one 1-m³-chamber and combined (total, RSD n = 9); retained samples from the same batch were stored sealed in foil for eight days and loaded afterwards into four desiccators (n = 4) - part 1

d	chamber	hexanal 0.85 mg/g		styrene 0.45 mg/g		C10 0.36 mg/g		E.H. 0.41 mg/g	
		AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]
3	24 l	16	± 10	76	± 7	140	± 7	63	± 7
	1 m³	14	-	70	-	131	-	57	-
	total	15	± 10	76	± 7	139	± 7	63	± 7
7	24 l	7	± 11	25	± 6	59	± 6	30	± 5
	1 m³	6	-	23	-	55	-	28	-
	total	7	± 11	25	± 6	59	± 6	30	± 6
7	retained	5	± 7	12	± 7	25	± 5	20	± 6
	loss [%]	31		52		58		33	

Table 5.12: Mean air concentration (AV) of eight desiccators (RSD, n = 8), one 1-m³-chamber and combined (total, RSD n = 9); retained samples from the same batch were stored sealed in foil for eight days and loaded afterwards into four desiccators (n = 4) - part 2

d	chamber	limonene 0.41 mg/g		NMP 0.26 mg/g		naphthalene 0.80 mg/g		E.H.-acryl 0.44 mg/g	
		AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]
3	24 l	130	± 6	85	± 19	204	± 7	111	± 6
	1 m³	120	-	87	-	188	-	103	-
	total	129	± 7	85	± 18	202	± 7	110	± 6
7	24 l	65	± 5	40	± 14	105	± 5	55	± 5
	1 m³	60	-	40	-	97	-	53	-
	total	64	± 5	40	± 13	101	± 5	55	± 5
7	retained	37	± 3	29	± 10	76	± 3	41	± 5
	loss [%]	42		28		25		26	

Table 5.13: Mean air concentration (AV) of eight desiccators (RSD, n = 8), one 1-m³-chamber and combined (total, RSD n = 9); retained samples from the same batch were stored sealed in foil for eight days and loaded afterwards into four desiccators (n = 4) - part 3

d	chamber	DMP 1.18 mg/g		C16 0.38 mg/g		lindane 12.95 mg/g		DBP 17.49 mg/g	
		AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]	AV [µg/m³]	RSD [%]
3	24 l	126	23	128	9	59	31	22	88
	1 m³	122	-	121	-	62	-	31	-
	total	126	22	127	9	60	29	23	80
7	24 l	88	19	66	16	56	17	27	48
	1 m³	85	-	67	-	53	-	30	-
	total	88	18	66	15	55	16	27	45
7	retained	65	± 14	54	± 9	39	± 15	7	± 70
	loss [%]	26		18		29		74	

6   Conclusion and Outlook

The present study indicates the applicability of the lacquer system as a candidate reference material. The lacquer is able to emit the investigated substances with a wide range of volatility and polarity in detectable amounts.

The sample preparation was easy to handle. In less than three hours the mixture could be prepared, depending on the mass of the lacquer batch and analytes needed. Adding methanol helped to dissolve solid compounds, reduced the lacquer viscosity which facilitated the homogenisation of the mixture and increased the SVOC emissions. It also prevented the lacquer from contracting while curing which improved the homogeneity of the lacquer surface.

The curing process was the most important step when defining the VOC emission. Therefore climate parameters like temperature, humidity, air change and air flow should be at best kept constant. For less volatile substances the air mixing and flow above the lacquer surface mainly determined the emission profile.

In an intra-laboratory comparative test the emissions could be repeated with variations of less than 20 % in nine single chambers. For the large part of the analytes the deviations ranged below 10 %. In this test two typical chamber types with volumes of 24 l and 1 m³ were used. The difference in the chamber volume could be included with a factor for the lacquer amount including the chamber flow.

For inter-laboratory comparisons losses of analytes while shipping must be taken into account. It showed that for almost all substances there was a loss of about 20 to 40 % in the emissions when cured lacquer samples were stored for eight days and sealed in steam-tight CLIMPAC-foil. Such losses must be compensated with higher analyte spiking to the liquid mixture while sample preparation.

Although the study indicated that the lacquer was applicable for a wide range of different analytes there were some limitations, e.g. SVOCs showed only low emissions. Their low vapour pressures prevent higher emissions when more analyte was added to the mixture. The tendency to adsorb onto sinks also increased the uncertainty of the SVOC measurement. For VOCs, the emissions can be adjusted by altering the analyte amount that is added to the mixture. It must be taken into account however, that a large part of the volatile compounds get lost while curing. It can be summarised that, when additional analytes are added to the mixture, preliminary

testing is needed to determine the analyte concentration resulting in detectable emissions.

For further testing optimising the SVOC-emission is important. Their low vapour pressure combined with the tendency to interact with sink complicated reliable testing. The developed preparation method is a compromise between a wide range of different substances. For low boiling compounds investigations according less adsorptive surfaces and long-term testing is necessary to improve the emission stability.

When working towards creating a certified reference material additional testing must be undertaken. Homogeneity and traceability are the most important properties for a reference material. For homogeneity inter-laboratory round robin tests are necessary. The study showed that packing the cured lacquer into steam-tight CLIMPAC-foils was the best way to ship the samples to the testing laboratories. Once the homogeneity is determined, models predicting the emission profiles can be developed. From these models parameters can be calculated that influence the emission process. This will improve the quality of emission testing with its fundamental role to protect human health from gaseous contaminants caused by indoor materials.

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8 Appendix

8.1 Abbreviations

µ-CTE	Micro-Chamber/Thermal Extractor™
ASTM	American Society for Testing and Materials
AV	average
BAM	Federal Institute for Material Research and Testing (Bundesanstalt für Materialforschung und -prüfung)
C10	n-decane
C16	n-hexadecane
CI	chemical ionisation
CIS	cold injection system
d	sampling day
DBP	dibutyl phthalate
DEHP	di-2-ethylhexyl phthalate
DMP	dimethyl phthalate
E.H.	ethyl hexanol
E.H.-arcyl	2-ethylhexyl acrylate
ECHA	European Chemical Agency
EI	electron ionisation
FID	flame ionization detector
GC	gas chromatography
ISTD	internal standard
ISO	International Organization for Standardization
L	product loading factor
LDPE	low density polyethylene
LIFE	liquid inner-tube diffusion-film-emission
LC	liquid chromatography
LOQ	limit of quantification
m	slope

MeOH	methanol
MFC	mass flow controller
MIBK	methyl isobutyl ketone
MS	mass spectrometry
n	air change rate / number of samples or measurements
n_y	y-intercept
NMP	N-methyl-2-pyrrolidone
OGC	organic-solvent-based glossy clear lacquer
OGW	organic-solvent-based glossy white lacquer
OGR	organic-solvent-based glossy red lacquer
OMC	organic-solvent-based matt clear lacquer
OMR	organic-solvent-based matt red lacquer
OMW	organic-solvent-based matt white lacquer
$P_{oct/wat}$	partition coefficient
PET	polyethylene terephthalate
PMP	polymethylpentene
POM	particular organic matter
PTFE	polytetrafluoroethylene
q	area specific air flow rate
R^2	coefficient of correlation
RH	relative humidity
(R)SD	(relative) standard deviation
SER_A	area specific emission rate
SI	International System of Units
SIM	single ion monitoring
stor.	storage
SVOC	semi-volatile organic compounds
TD(S)	thermal desorption (system)
TIC	total ion chromatogram

u	uncertainty
VOC	volatile organic compound
VVOC	very volatile organic compound
w.	with
w/o.	without
WGC	water-based glossy clear lacquer
WGI	water-based glossy light-ivory lacquer
WGR	water-based glossy red lacquer
WMC	water-based matt clear lacquer
WMR	water-based matt red lacquer
WMW	water-based matt white lacquer
WHO	World Health Organization

8.2 List of figures

8.3   List of tables

8.4 Additional measurement data

8.4.1 Calibration data

The values of slope (m), y-intercept (n), coefficient of correlation (R²) and the limit of quantification (LOQ) were calculated based on DIN 32645 [39] with the EXCEL-macro B.E.N. (ARVECON).

Table 8.1: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (n_y), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 1

Level	hexanal			styrene		
	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	199.98	2385527	11809282	208.69	4989141	82915487
2	179.98	1912645	11181402	187.82	3853445	79444251
3	159.98	1979775	9981754	166.95	4042211	71938892
4	139.99	1701394	8717577	146.08	3431423	62742256
5	119.99	1509281	7993767	125.22	3004854	58412601
6	99.99	1219897	6524903	104.35	2447134	47475151
7	79.99	1069232	5145278	83.48	2079570	38027734
8	59.99	823564	4043914	62.61	1569069	30400306
9	49.99	685805	3385214	52.17	1267395	25842513
10	40.00	515408	2677846	41.74	993238	20076152
11	20.00	303054	1450465	20.87	550276	10925888
12	10.00	191411	728464	10.43	293175	5485923
13	4.00	78254	264403	4.17	118029	2153305
14	2.00	40529	175163	2.09	49644	1171957
15	1.00	47178	69134	1.04	23974	631412
m [area/ng]		11432.48	60822.70		22830.34	412755.87
n_y [area]		74844.67	211733.21		60777.56	2334909.80
R²		0.991	0.997		0.991	0.993
LOQ [ng]		7.64	5.12		7.99	15.62

Table 8.2: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (n_y), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 2

Level	C10			limonene		
	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	202.08	5412488	13186555	205.33	3373392	21282917
2	181.87	4396203	12669207	184.80	2828018	20357313
3	161.66	4389961	11628098	164.26	2725147	18614442
4	141.46	3727854	10225728	143.73	2319380	16439720
5	121.25	3270447	9675586	123.20	1996334	15473679
6	101.04	2716397	7974378	102.66	1708969	12840139
7	80.83	2306263	6512296	82.13	1405290	10571427
8	60.62	1725660	5380175	61.60	1044427	8725609
9	50.52	1437305	4626993	51.33	871978	7514844
10	40.42	1131889	3664903	41.07	686509	5995060
11	20.21	627513	2084694	20.53	370365	3392565
12	10.10	336342	1068392	10.27	193973	1773835
13	4.04	133254	428821	4.11	79208	679090
14	2.02	65909	245297	2.05	40558	362792
15	1.01	30621	142456	1.03	23603	187907
m [area/ng]		25816.17	67365.92		15991.21	106477.11
n_y [area]		84499.79	672028.03		33873.85	1109420.38
R²		0.995	0.990		0.997	0.990
LOQ [ng]		8.79	15.72		6.88	29.58

Table 8.3: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (n_y), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 3

Level	E.H. amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	NMP amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	201.73	4289476	39683558	201.96	1322345	30512306
2	181.56	3451861	37473778	181.76	1356155	27881534
3	161.38	3380287	32988983	161.57	1054842	24686633
4	141.21	2896688	30234926	141.37	1007825	21661722
5	121.04	2484054	27218410	121.17	855048	19203759
6	100.86	2097688	22760832	100.98	705105	16023814
7	80.69	1709990	18394232	80.78	569968	12130677
8	60.52	1269293	14881391	60.59	380363	9657077
9	50.43	1095236	12447214	50.49	282241	7637206
10	40.35	794862	10146421	40.39	214248	6059592
11	20.17	475513	5611924	20.20	114789	3163024
12	10.09	233354	2658135	10.10	31050	1444199
13	4.03	90955	1048383	4.04	0	496364
14	2.02	61104	559864	2.02	0	250866
15	1.01	72098	292906	1.01	0	133041
m [area/ng]		20284.89	200676.67		7087.40	153260.33
n_y [area]		35016.25	1345715.13		-30532.08	22410.92
R²		0.996	0.993		0.991	0.999
LOQ [ng]		8.81	21.13		28.1	8.69

Table 8.4: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (nᵧ), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 4

Level	naphthalene			E.H.-acryl		
	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	200.04	7874375	33206462	210.00	11466860	162058057
2	180.03	6442665	31577956	189.00	9998357	152428560
3	160.03	6319439	27890715	168.00	8842066	135202675
4	140.03	5431621	25400674	147.00	7461151	123425589
5	120.02	4631175	22455347	126.00	6340101	106973221
6	100.02	3837875	19370463	105.00	5464783	92484931
7	80.02	3220917	15754777	84.00	4314930	75207430
8	60.01	2436504	12770316	63.00	3205046	60115306
9	50.01	1983253	10719259	52.50	2667006	50625470
10	40.01	1510707	8704313	42.00	2181135	40620436
11	20.00	782225	4827372	21.00	1087101	22283257
12	10.00	385999	2323382	10.50	552845	10958504
13	4.00	140223	899048	4.20	229693	4283507
14	2.00	72087	446789	2.10	107954	2236668
15	1.00	29427	223102	1.05	77610	1143870
m [area/ng]		38284.05	169525.77		53057.08	785418.04
nᵧ [area]		27507.45	1246414.27		-67790.01	5175699.18
R²		0.996	0.992		0.998	0.994
LOQ [ng]		6.43	22.25		8.92	19.87

Table 8.5: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (n$_y$), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 5

Level	DMP			C16		
	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	209.88	10333198	125684138	211.35	7391180	38405267
2	188.89	8856344	116440434	190.21	6563133	36479443
3	167.90	7735336	102721980	169.08	5815844	32733401
4	146.92	6473684	93988603	147.94	4964789	29874776
5	125.93	5547873	84778567	126.81	4300948	27193360
6	104.94	4817325	69830076	105.67	3677182	23205492
7	83.95	3630894	53622410	84.54	2919938	18910626
8	62.96	2662903	43216854	63.40	2160486	15387117
9	52.47	2208245	35402240	52.84	1793027	12978754
10	41.98	1844069	27799778	42.27	1441491	10457575
11	20.99	874746	14974284	21.13	723206	5965112
12	10.49	431056	6884923	10.57	384380	2941621
13	4.20	183534	2523197	4.23	139440	1173306
14	2.10	71283	1294748	2.11	51114	637246
15	1.05	66391	674564	1.06	51757	331470
m [area/ng]		47267.86	612645.64		34524.17	186019.15
n$_y$ [area]		148393.87	1970695.58		-13151.11	1818392.49
R²		0.995	0.996		0.999	0.991
LOQ [ng]		21.45	19.99		6.96	29.00

Table 8.6: Analyte amount and averaged area response (AV, n = 3) of a 15-point-calibration with slope (m), y-intercept (n_y), coefficient of correlation (R²) and the limit of quantification (LOQ) calculated from a linear regression curve on the two measurement devices "Asterix" and "Idefix" - part 6

Level	lindane			DBP		
	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"	amount [ng]	AV [area] "Idefix"	AV [area] "Asterix"
1	203.60	2763590	19185442	201.10	17680201	171536891
2	183.24	2472114	17852482	180.99	16046823	161769274
3	162.88	2072774	15611689	160.88	13133984	143375195
4	142.52	1691393	14588015	140.77	10709025	134339791
5	122.16	1489843	12880801	120.66	9466237	122089867
6	101.80	1294403	10578672	100.55	8125456	101928424
7	81.44	969984	8310107	80.44	5929314	83731165
8	61.08	703680	6416654	60.33	4254067	64690317
9	50.90	596007	5176729	50.27	3550805	54330251
10	40.72	506231	3897988	40.22	3040031	42137529
11	20.36	235207	1959912	20.11	1322155	22731292
12	10.18	124762	851776	10.05	604657	11106507
13	4.07	52924	285144	4.02	273253	3981962
14	2.04	0	181421	2.01	126500	2127172
15	1.02	0	79415	1.01	99387	1072280
m [area/ng]		13213.77	97576.70		86040.91	881960.39
n_y [area]		-48342.06	12128969.82		439872.41	5737324.32
R²		0.994	0.996		0.992	0.992
LOQ [ng]		20.46	14.41		18.05	25.09

8.4.2 Chapter 4.1.1

Table 8.7: Averaged area specific emission rates (n = 4) and RSD-values of styrene, octamethylcyclotetrasiloxane and limonene from a sealant sample loaded into four desiccators, respectively four chambers of a µ-CTE over a sampling cycle of 15 days

d	chamber	styrene AV [µg/(m²h)]	styrene RSD [%]	octamethylcyclotetrasiloxane AV [µg/(m²h)]	octamethylcyclotetrasiloxane RSD [%]	limonene AV [µg/(m²h)]	limonene RSD [%]
1	µ-CTE	12429	± 9	993	± 22	2474	± 4
	desiccator	18216	± 50	1931	± 23	4940	± 20
3	µ-CTE	4888	± 7	828	± 13	2242	± 8
	desiccator	4949	± 6	525	± 7	1658	± 10
6	µ-CTE	2987	± 4	523	± 11	1454	± 7
	desiccator	3784	± 10	392	± 20	1481	± 13
8	µ-CTE	2295	± 5	399	± 6	1160	± 6
	desiccator	2654	± 10	284	± 25	1146	± 14
10	µ-CTE	1815	± 5	346	± 13	945	± 6
	desiccator	1971	± 10	208	± 17	944	± 14
13	µ-CTE	1622	± 3	312	± 16	876	± 4
	desiccator	1540	± 8	205	± 16	867	± 13
15	µ-CTE	1349	± 2	250	± 12	742	± 5
	desiccator	1193	± 10	173	± 16	739	± 14

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Table 8.8: Averaged emissions (n = 2) of a water-based matt clear lacquer (WMC) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WMC d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	1314	2138	159	214	109	12	< LOQ
3	535	256	1162	181	455	11	< LOQ
7	347	168	659	178	425	14	3
9	232	117	422	130	323	50	< LOQ
11	152	75	275	97	237	22	< LOQ
14	169	91	303	130	307	15	< LOQ
16	150	82	271	120	293	10	< LOQ
18	140	80	249	126	288	11	< LOQ
21	111	67	213	120	254	12	< LOQ

Table 8.9: Averaged emissions (n = 2) of a water-based matt red lacquer (WMR) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WMR d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	948	1552	249	152	224	8	< LOQ
3	472	264	802	135	376	8	< LOQ
7	365	192	556	135	373	9	< LOQ
9	238	137	277	99	256	7	< LOQ
11	152	82	176	68	175	5	< LOQ
14	179	104	264	95	231	6	< LOQ
16	155	91	230	85	212	6	< LOQ
18	165	100	248	101	234	7	< LOQ
21	125	79	200	88	193	6	< LOQ

Table 8.10: Averaged emissions (n = 2) of a water-based matt white lacquer (WMW) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WMW d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	1229	1699	421	169	307	9	< LOQ
3	483	211	542	115	361	8	< LOQ
7	365	155	358	108	311	9	3
9	256	106	203	76	224	6	< LOQ
11	174	70	150	53	158	4	< LOQ
14	214	89	192	75	214	6	< LOQ
16	191	81	171	64	193	6	< LOQ
18	201	84	175	73	207	6	< LOQ
21	164	71	153	68	178	6	< LOQ

Table 8.11: : Averaged emissions (n = 2) of a water-based glossy clear lacquer (WGC) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WGC d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	1142	1630	179	184	159	10	< LOQ
3	386	218	1155	141	400	6	< LOQ
7	251	146	615	156	393	9	< LOQ
9	196	116	457	141	355	8	< LOQ
11	180	112	412	155	369	10	< LOQ
14	142	95	339	155	354	10	< LOQ
16	120	81	283	149	321	11	< LOQ
18	83	57	198	111	245	8	< LOQ
21	75	53	188	125	240	10	< LOQ

Table 8.12: Averaged emissions (n = 2) of a water-based glossy red lacquer (WGR) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WGR d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	887	1144	355	126	227	6	< LOQ
3	347	197	646	99	258	4	< LOQ
7	251	147	426	103	252	6	< LOQ
9	208	123	341	94	233	5	< LOQ
11	197	122	322	100	241	6	< LOQ
14	169	110	291	100	232	6	< LOQ
16	142	91	240	93	208	6	< LOQ
18	102	66	171	69	159	4	< LOQ
21	98	61	168	76	153	5	< LOQ

Table 8.13: Averaged emissions (n = 2) of a water-based glossy light-ivory lacquer (WGI) prepared with seven substances over a sampling cycle of 21 days loaded into a µ-CTE

WGI d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	849	947	818	129	325	5	< LOQ
3	346	142	414	81	225	4	< LOQ
7	282	110	294	85	225	5	< LOQ
9	251	97	239	76	212	5	< LOQ
11	246	98	240	83	221	6	< LOQ
14	217	89	219	81	209	6	< LOQ
16	198	80	199	79	195	6	< LOQ
18	144	58	137	55	145	4	< LOQ
21	140	55	142	62	142	6	< LOQ

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Table 8.14: Emitted analyte amounts of lindane and DBP from two lacquer batches (WGC25/WGC55) with different loaded lacquer amounts (2 g, 4.5 g) over a sampling cycle of 25 days loaded into a µ-CTE

	WGC25_2		WGC55_2		WGC55_4.5	
d	lindane [µg/m³]	DBP [µg/m³]	lindane [µg/m³]	DBP [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
1	63	20	13	< LOQ	13	< LOQ
3	44	14	8	< LOQ	10	< LOQ
7	63	22	12	1	11	< LOQ
9	48	17	8	< LOQ	8	< LOQ
11	42	16	7	< LOQ	7	< LOQ
16	51	22	8	1	8	1
18	37	13	6	< LOQ	6	< LOQ
21	49	18	8	< LOQ	8	< LOQ
23	43	16	6	< LOQ	7	< LOQ
25	47	17	7	< LOQ	7	< LOQ

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Table 8.15: Emission of a lacquer batch where lindane was added dissolved in MeOH stirred for one and four hours loaded into a µ-CTE

	d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
lindane (l) stirred 1 h	2	708	641	5109	370	667	42	11
	4	185	255	1674	287	419	41	12
	7	111	195	1108	396	487	61	21
	9	55	112	688	327	381	49	17
	11	37	80	497	320	349	48	16
lindane (l) stirred 4 h	2	701	608	4682	319	522	30	12
	4	105	271	1796	317	414	42	21
	7	122	203	1097	360	426	50	24
	9	70	137	686	347	385	48	22
	11	44	93	543	325	347	46	21

Table 8.16: Emission of a lacquer batch where lindane without MeOH stirred for one, two, three and four hours loaded into a μ-CTE

	d	styrene [μg/m³]	E.H. [μg/m³]	NMP [μg/m³]	DMP [μg/m³]	C16 [μg/m³]	lindane [μg/m³]	DBP [μg/m³]
lindane (s) stirred 1 h	2	1115	932	1464	316	464	30	13
	4	297	245	1613	309	410	32	13
	7	196	184	1046	379	472	42	20
	9	122	106	689	337	412	37	16
	11	88	89	519	306	363	34	15
lindane (s) stirred 2 h	2	1115	929	1346	286	424	28	11
	4	306	245	1573	267	370	29	11
	7	195	203	1040	346	446	40	17
	9	119	123	509	300	377	34	15
	11	83	89	529	288	353	33	13
lindane (l) stirred 3 h	2	1055	967	1012	297	418	30	12
	4	322	266	1699	290	396	32	13
	7	204	211	1121	358	454	42	18
	9	133	132	740	323	406	37	15
	11	92	88	557	299	365	35	14
lindane (l) stirred 4 h	2	981	850	1268	279	404	28	11
	4	299	257	1549	271	363	31	13
	7	185	199	1045	346	433	41	17
	9	116	133	645	305	376	36	15
	11	84	87	495	296	353	36	14

Table 8.17: Averaged (n = 3) emissions and SD-values of styrene, E.H. and NMP of lacquer batches with and without MeOH over a sampling cycle of 11 days loaded into a µ-CTE

	d	styrene		E.H.		NMP	
		AV [µg/m³]	SD [µg/m³]	AV [µg/m³]	SD [µg/m³]	AV [µg/m³]	SD [µg/m³]
w. MeOH	2	924	± 107	680	± 92	2964	± 67
	7	206	± 29	228	± 31	730	± 70
	9	108	± 34	152	± 31	431	± 78
	11	82	± 14	135	± 14	363	± 16
w/o. MeOH	2	1522	± 15	1021	± 4	1429	± 71
	7	261	± 38	193	± 39	709	± 45
	9	148	± 39	138	± 30	427	± 126
	11	119	± 22	125	± 20	346	± 67

Table 8.18: Averaged (n = 3) emissions and SD-values of DMP, C16 and DBP of lacquer batches with and without MeOH over a sampling cycle of 11 days loaded into a µ-CTE

	d	DMP		C16		DBP	
		AV [µg/m³]	SD [µg/m³]	AV [µg/m³]	SD [µg/m³]	AV [µg/m³]	SD [µg/m³]
w. MeOH	2	173	± 18	535	± 103	2	± 7
	7	210	± 23	539	± 56	3	± 23
	9	166	± 37	440	± 77	7	± 13
	11	177	± 21	439	± 39	4	± 16
w/o. MeOH	2	162	± 3	502	± 21	10	± 1
	7	180	± 12	461	± 35	18	± 0
	9	144	± 28	377	± 59	10	± 4
	11	154	± 21	383	± 40	13	± 3

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Table 8.19: Averaged emissions (n = 6) and RSD-values of a lacquer batch loaded into μ-CTEs over a sampling cycle of 14 days that cured either directly inside the μ-CTE or for 44 h inside a 1-m³-chamber - part 1

cure/ load	d	styrene AV [µg/(m²h)]	styrene RSD [%]	E.H. AV [µg/(m²h)]	E.H. RSD [%]	NMP AV [µg/(m²h)]	NMP RSD [%]	DMP AV [µg/(m²h)]	DMP RSD [%]
μ-CTE	2	1529	± 11	2184	± 8	616	± 37	634	± 10
/	4	509	± 3	1291	± 2	2625	± 4	520	± 7
μ-CTE	7	134	± 7	813	± 2	1584	± 4	504	± 8
	11	27	± 14	501	± 8	1003	± 4	522	± 7
	14	7	± 25	297	± 4	657	± 5	480	± 8
1 m³	2	1090	± 5	1594	± 7	2578	± 6	427	± 9
/	4	662	± 5	1287	± 2	1854	± 4	468	± 5
μ-CTE	7	253	± 4	845	± 2	1205	± 3	469	± 4
	11	68	± 5	591	± 3	845	± 5	534	± 5
	14	18	± 9	362	± 4	546	± 5	449	± 5

Table 8.20: Averaged emissions (n = 6) and RSD-values of a lacquer batch loaded into µ-CTEs over a sampling cycle of 14 days that cured either directly inside the µ-CTE or for 44 h inside a 1-m³-chamber - part 2

		C16		lindane		DBP	
	d	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]
cure/load µ-CTE	2	1327	± 33	128	± 12	79	± 22
	7	771	± 6	99	± 8	59	± 22
	9	702	± 7	89	± 9	57	± 17
	11	653	± 6	88	± 8	68	± 17
	14	470	± 34	77	± 8	58	± 14
	2	593	± 29	39	± 39	< LOQ	-
cure 1 m³/ load µ-CTE	7	628	± 5	77	± 5	36	± 33
	9	483	± 35	79	± 9	47	± 13
	11	614	± 4	92	± 8	87	± 19
	14	243	± 3	71	± 9	58	± 14

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Table 8.21: Averaged emissions (n = 4) and RSD-values of lacquer batches loaded into desiccators over a sampling cycle of 17 days that cured either directly inside the desiccator or for 46 h inside a 1-m³-chamber with switched on/off fan inside the testing chamber - part 1

cure/ load	d	styrene AV [µg/(m²h)]	RSD [%]	E.H. AV [µg/(m²h)]	RSD [%]	NMP AV [µg/(m²h)]	RSD [%]	DMP AV [µg/(m²h)]	RSD [%]
24 l / 24 l	3	4133	± 6	1157	± 15	5997	± 6	2913	± 12
	5	3230	± 6	1985	± 23	3572	± 3	2598	± 12
	7	2473	± 1	1608	± 24	2697	± 5	2331	± 7
	10	1658	± 3	1223	± 23	1912	± 7	2041	± 8
	12	1282	± 6	1085	± 22	1594	± 11	1892	± 6
	14	999	± 5	1041	± 25	1379	± 9	1770	± 7
	17	704	± 7	866	± 19	1133	± 12	1634	± 5
1 m³ / 24 l	3	6198	± 35	2789	± 60	19129	± 46	3714	± 45
	5	3235	± 19	1024	± 29	5468	± 20	2992	± 25
	7	2367	± 2	1536	± 20	3315	± 4	2516	± 8
	10	1538	± 2	1039	± 20	2239	± 2	2164	± 8
	12	1228	± 2	934	± 17	1968	± 3	2059	± 6
	14	874	± 5	729	± 23	1547	± 3	1829	± 8
	17	610	± 2	650	± 19	1264	± 1	1705	± 7
1 m³ / 24 l no fan	3	4321	± 4	4113	± 22	1647	± 48	610	± 45
	5	2942	± 4	2229	± 18	5511	± 6	978	± 21
	7	2133	± 2	1406	± 16	3517	± 4	877	± 23
	10	1526	± 3	1147	± 15	2740	± 3	822	± 22
	12	1098	± 4	939	± 17	2210	± 4	776	± 20
	14	899	± 10	918	± 26	2013	± 14	819	± 28
	17	445	± 10	709	± 22	1443	± 16	786	± 29

Table 8.22: Averaged emissions (n = 4) and RSD-values of lacquer batches loaded into desiccators over a sampling cycle of 17 days that cured either directly inside the desiccator or for 46 h inside a 1-m³-chamber with switched on/off fan inside the testing chamber - part 2

cure/ load	d	C16		lindane		DBP	
		AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]	AV [µg/(m²h)]	RSD [%]
24 l / 24 l	3	2661	± 16	955	± 17	323	± 38
	5	2125	± 20	926	± 17	353	± 30
	7	1509	± 9	921	± 14	387	± 27
	10	1212	± 12	866	± 16	380	± 27
	12	1135	± 13	823	± 14	372	± 24
	14	1063	± 15	802	± 15	363	± 22
	17	955	± 12	787	± 13	373	± 20
1 m³ / 24 l	3	7768	± 50	642	± 45	< LOQ	-
	5	2362	± 29	1039	± 29	231	± 53
	7	1465	± 10	950	± 16	284	± 46
	10	1097	± 7	899	± 17	352	± 43
	12	984	± 5	883	± 16	407	± 34
	14	890	± 11	813	± 18	391	± 34
	17	783	± 9	795	± 16	396	± 30
1 m³ / 24 l no fan	3	2822	± 18	138	± 20	< LOQ	-
	5	1001	± 17	201	± 29	32	± 177
	7	770	± 18	190	± 30	10	± 162
	10	700	± 16	178	± 29	86	± 170
	12	619	± 16	176	± 30	81	± 151
	14	603	± 24	192	± 36	38	± 105
	17	506	± 26	191	± 39	46	± 98

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Table 8.23: Emission rates of a lacquer batch loaded into a µ-CTE over a sampling cycle of 8 days that operated at 15 ml/min

d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
				15 ml/min			
1	91309	30642	85	664	2270	23	8
2	80950	30436	84	738	1539	44	17
3	69763	28064	89	879	1203	72	26
4	65708	30618	98	907	986	88	21
5	60508	31419	99	893	799	92	21
6	54971	31360	95	942	705	106	26
24	8861	17042	140	1023	128	146	93
26	10172	17743	165	974	140	138	85
28	9933	17295	160	984	143	142	88
30	8748	16300	162	1026	135	160	92
48	5423	10427	438	961	1119	138	105
50	5508	10137	503	935	1180	143	115
52	5264	9478	628	939	1250	131	100
54	4073	8097	853	1005	1231	149	112
72	1756	3169	7140	608	601	89	75
76	1363	2743	6638	639	599	91	67
78	1294	2714	6344	644	619	97	78
96	625	1756	4672	656	578	104	87
98	543	1618	4308	615	521	92	67
100	545	1625	4020	557	510	80	70
168	183	772	2442	675	608	98	81
192	136	717	2015	672	603	98	71

Table 8.24: Emissions of a lacquer batch loaded into a μ-CTE over a sampling cycle of 8 days that operated at 30 ml/min

d	styrene [μg/m³]	E.H. [μg/m³]	NMP [μg/m³]	DMP [μg/m³]	C16 [μg/m³]	lindane [μg/m³]	DBP [μg/m³]
				30 ml/min			
1	67092	30430	53	812	1183	45	19
2	52818	28538	74	842	847	79	29
3	41164	26363	91	840	496	87	25
4	36052	26270	80	903	383	109	37
5	30535	24671	96	929	358	109	39
6	27387	24237	105	958	260	122	42
24	6835	10792	405	886	526	121	83
26	6906	9739	521	891	743	125	96
28	5476	7954	652	842	815	132	93
30	5793	7343	851	796	1021	114	79
48	1748	2125	5958	753	714	99	81
50	1802	2277	6098	871	806	119	90
52	1387	1892	5458	892	798	127	90
54	1303	1774	4889	773	687	109	77
72	686	1098	2823	681	577	95	82
76	640	1035	2736	725	618	108	81
78	633	1026	2598	643	561	88	95
96	604	981	2422	610	517	88	81
98	430	588	1667	649	550	91	76
100	372	775	1700	648	515	94	78
168	172	447	862	800	611	114	98
192	140	409	646	713	549	99	92

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Table 8.25: Emissions of a lacquer batch loaded into a µ-CTE over a sampling cycle of 11 days that operated at 0 % RH

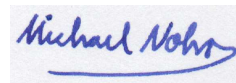| d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
			0 % RH				
1	65467	21038	126	680	639	26	62
2	57145	23686	118	691	645	42	38
3	61119	27122	105	813	639	66	36
4	60158	27914	124	915	620	85	44
5	57967	27299	134	904	502	88	43
24	12674	18736	158	1009	133	143	77
26	11357	17638	186	1049	132	144	90
28	10164	16764	201	1041	128	148	94
50	6252	10781	571	1000	576	148	110
52	6367	10714	730	1106	775	161	117
72	2507	1370	8434	772	796	110	84
74	2385	1462	7831	711	718	92	86
76	2339	1360	7783	769	793	109	86
168	209	1352	2770	697	725	88	68
192	140	1140	2597	801	791	102	91
240	71	845	1625	692	695	92	98
264	43	622	1245	609	632	91	91

Table 8.26: Emissions of a lacquer batch loaded into a µ-CTE over a sampling cycle of 11 days that operated at 55 % RH

d	styrene [µg/m³]	E.H. [µg/m³]	NMP [µg/m³]	DMP [µg/m³]	C16 [µg/m³]	lindane [µg/m³]	DBP [µg/m³]
				55 % RH			
1	68941	19394	37	448	475	8	11
2	56299	21637	73	575	589	31	9
3	60125	26713	79	749	636	58	13
4	59142	26038	97	751	542	69	15
5	64238	27255	107	812	521	83	18
24	8643	15423	94	808	70	107	67
26	9619	17482	115	831	75	114	67
28	8407	16613	133	898	75	125	73
50	4345	11132	164	1007	60	152	111
52	4942	11915	172	1025	70	144	103
72	3028	7152	205	797	58	117	101
74	2573	6466	306	878	52	127	107
76	2755	6476	262	764	60	108	93
168	285	811	3804	719	814	92	68
192	179	577	2444	608	634	81	66
240	126	484	2079	637	693	101	100
264	70	290	1392	571	555	79	72

9   Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Quellen und Hilfsmittel angefertigt habe.

Die den Quellen wörtlich oder inhaltlich entnommenen Stellen sind als solche kenntlich gemacht.

Berlin, den 21.1.2015   Michael Nohr

10 Lebenslauf

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Beruflicher Werdegang:
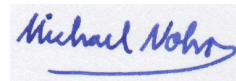
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