Olfactometric determination of the odour detection threshold and the identification threshold of Naphthalene

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SUMMARY

In Germany naphthalene indoor air emissions occur especially in some older buildings (prior 1980’s) due to commonly used tar containing construction products. High accumulations of PAH in indoor air are associated with health- and odour related peculiarities through naphthalene. For toxicological evaluation, German indoor guide values can be used. For hygienic evaluation regarding the odour, an accepted odour detection threshold is missing.

To determine the odour detection threshold of naphthalene a two-day experiment was performed by using an olfactometer with 6 odour interfaces with 202 untrained participants. Naphthalene was supplied in ascending order between ~0.7 µg/m³ and ~70 µg/m³. The participants specify the first odour interface at which an odour was detected (odour threshold) and at which the specific smell of naphthalene was identified (identification threshold).

Analytical determination of the naphthalene concentrations was performed by air sampling with thermo-desorption tubes and analysis with TD-GC/MS. To determine the threshold levels, a log-normal probability plot was used to define the median of the distribution.

The odour detection threshold for Naphthalene was determined at a concentration of 2.3 ± 0.8 µg/m³, the identification threshold to 8.8 ± 3.2 µg/m³.

The results can be a reliable basis to derive odour guide values. Experts can use it to appraise indoor hygienic situations.

INTRODUCTION

Various building products used until the late 1980’s were based on tar containing PAH. These products were very popular due to their endurance. They also were easy to install (Zwiener and Mötzl, 2006). Since the 1990's it's known that these products lead to high accumulations of PAH in indoor air. Those accumulations can contain a broad mixture of several aromatic hydrocarbons e.g. acenaphthene, fluoranthene, methylnaphthalene or naphthalene (Heudorf and Angerer, 2001; Lederer and Angerer, 1998). Beside the toxicological effects, PAH, mostly naphthalene and naphthalene-similar compounds, are associated with odour nuisance (Umweltbundesamt, 2013).

German toxicological based guide values for Naphthalene exist since 2004 (Sagunski and Heger, 2004) and were revised lastly by the German Ad-hoc Working Group for Indoor Air Guide Values in 2013 (Umweltbundesamt, 2013). The new precautionary guide value is 10 µg/m³ and the hazard guide value is 30 µg/m³. In contrast to the previous guide values until 2013 these new guide values do not cover only naphthalene, but also naphthalene-similar compounds such as methylnaphthalene and incorporate them in a sum parameter. Those new guide values do not consider odour by naphthalene or methylnaphthalene. Although a few studies which named odour detection thresholds (ODT) for naphthalene exist, e.g. Devos et al. (1990) with 7.5 µg/m³ and Amoore and Hautala (1983) with 450 µg/m³, the German Ad-hoc Working Group considered them to be non-reliable. The main reason for that were missing framework and testing conditions.

Additionally, odour guide values were introduced in 2014 by the German Ad-hoc Working Group, which consider the hygienic situation in indoor air, to prevent odour nuisance (Umweltbundesamt, 2014). To derive odour guide values, it is needed, and requested by the German Federal Environmental Agency, to provide authoritative odour detection thresholds for naphthalene and naphthalene-similar compounds.

A determination of the odour detection threshold of naphthalene can be a reliable basis to derive odour guide values for naphthalene. These can be used in the evaluation of the indoor situations by experts.

METHODOLOGIES

Equipment

In order to carry out this experiment an olfactometer with seven odour interfaces (OI) was used (Co. anbus analytik GmbH, Fürth, Germany). It was built to comply with the requirements of the standard DIN ISO 16000-28. The scheme of the olfactometer is shown in figure 1.

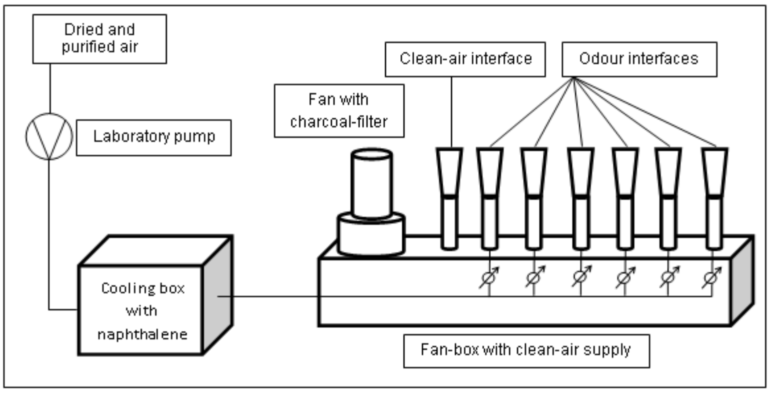

Figure 1. Scheme of the used olfactometer

Pure naphthalene was used (4 g, ≥99.7 %, 84679 FLUKA). Dried (silica gel) and purified (charcoal) indoor air is saturated with the pure naphthalene through a laboratory gas washing bottle. To keep the concentration of the saturated air constant over time, the air was cooled down to approximately 11°C by using a cooling box. Furthermore a constant pressure difference between in- and output of the cooling box was sustained using throttle valves. The naphthalene-saturated air was continuously monitored using a PID (ppbRAE 3000 pro, RAE Systems) to assure a constant concentration. This naphthalene saturated air was then dosed into each of the six odour interfaces through float-type flow meter (Co. Analyt-MTC GmbH, Germany). In a pre-trial the reasonable adjustments for the flow meter were determined (approx. 0.7 – 70 µg/m³ naphthalene) and kept over the time of the experiment.

Air sampling & analytics

The whole experiment was divided into three time periods, approx. three hours each. The determination of the actual naphthalene concentrations from the odour interfaces was performed by active air sampling with thermo-desorption tubes (Tenax TA/Carbopack X). Three identical 2-channel pumps with built-in mass flow meters were used (Holbach BiVOC 2). The air-sampling was conducted at the end of each period (Volume flow 0.1 – 0.2 L/min, sampling volume 0.5 – 3.0 L, sampling time up to 15 min). The first and third sampling point was conducted as double determination. Single determination was used at the second point.

The samples were analysed by TD-GC/MS (TD: Shimadzu TD-20, desorption temperature: 250°C for 8 minutes, GC: Shimadzu GC-2010, carrier gas: helium 5.0, column: DB-MS5, 60 m x 0,25 mm x 0,25 µm, MS: Shimadzu QP-2010 Ultra+). All proceedings were performed according to DIN ISO 16000-6 (2012), except the use of an adsorbents-combination.

Framework Conditions

The experiment was carried out on two consecutive days in Detmold, Germany, at the University of Applied Sciences (UAS) HS-OWL. In the context of the annual open day in May 2014, 202 participants took part.

The olfactometer was set up in building no. 2 of the UAS. To prevent an accumulation of naphthalene in indoor air, the olfactometer was placed under opened roof windows to ensure exhaust ventilation. Furthermore the location was sufficiently far away from the main entrance door (7 m) and from the canteen door (10m) to prevent interfering air flows and canteen odours. The climatic parameters were measured tree times during the experiment (day one: 22.4 °C, 45 % rH, 994 hPa., day two: 16.8 °C, 53 % rH, 994 hPa, day two: 18.7 °C, 59 % rH, 990 hPa)

Experiment

In order to achieve the objectives it was necessary to use as many participants as possible in a experiment to get a representative sample of the general population.

At first the participants were asked to fill in a questionnaire and state their anonymised personal information (gender, age and smoker/non-smoker), as well as the current date and time. In the next step the participants had to perform a smell tests using “sniffin sticks” with different concentrations of methylnaphthalene (University of Technology Dresden, Germany).This test had the purpose of assuring the ability to smell naphthalene and get focused for the main task.

In the next step, the participants had to determine the odour detection threshold. The task was to pick the OI, which differs from the clean-air interface in olfactory matter. Thereby it was important, that the participants didn’t need to identify the smell of naphthalene in this step. Therefore it was necessary to smell the OI in ascending order.

To determine the identification threshold, the participants had to name the OI, where the odour could be identified as naphthalene. In order to identify it, the participants were allowed to smell the sixth OI (highest naphthalene concentration) to get an idea of the smell-character. After this, to prevent odour adaption, they had to wait approx. 30 s. Then again the participants hat to smell the interfaces in ascending order to name the OI for the identification threshold.

Calculation method

In general, odour thresholds are described as the minimal concentration of an olfactory active substance, which leads to an olfactory reaction by 50% of the test subject group. Therefore the odour detection threshold is also referred as the ODT_{50}-value (Umweltbundesamt, 2014).

The standard DIN EN 13725 (2006) describes the normative determination of odour detection thresholds. It tries to avoid huge subject groups by using a small group (4 to 8 persons) of qualified test persons with a standardised sense of smell and uses mathematic operations, as well as classification of the test subjects, to compensate the low number of test subjects. Since 202 test subjects participated in this experiment, there is no need to apply the DIN EN 13725 standards for odour detection threshold determination. A huge amount of participants results in better statistics.

In the first step the questionnaire was digitalised into a dynamic calculation mask. This allowed filtering data and counting statements regarding the detection and identification threshold. This results in a density distribution which plots the number of statements for each naphthalene-concentration (at each OI) for the detection threshold and the identification threshold (fig. 2).

The Plot indicates that the distribution is more likely a log-normal distribution than a normal distribution (or Gaussian distribution). The main statement of the Weber-Fechner law also implies, that sensory inputs and the perceived intensity underlie a logarithmic coherence. (Dehaene, 2003)

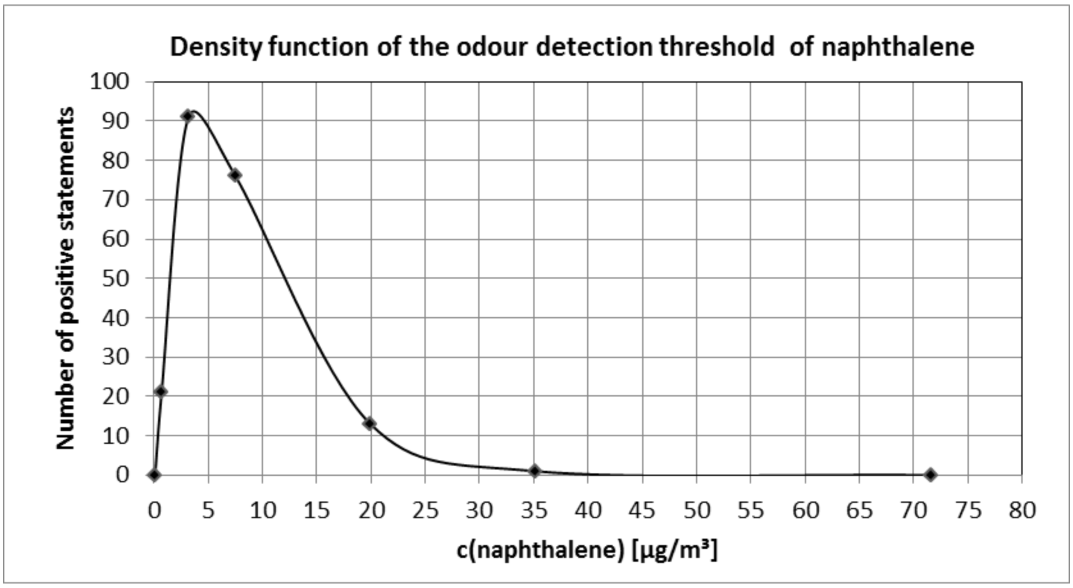

Figure 2. Density function of the odour detection threshold

To calculate the ODT_{50} from this distribution it is necessary to determine the median of this distribution. Therefore an evaluation-version of “XSel12.1” was used (Ronniger, 2014). This software is able to plot the distribution data into a logarithmic probability plot. Furthermore it is possible to determine the median and the coefficient of determination. The same procedure applies to the identification threshold.

RESULTS AND DISCUSSION

Air samples

The analysis results of the air samples are shown in table 1. The values were calculated as the arithmetic mean of all sampling periods.

Table 1. Naphthalene concentrations at each odour interface

Arithmetic mean values of measured naphthalene-concentrations at the odour interfaces [µg/m³]							
Clean-air interface	**OI 1**	**OI 2**	**OI 3**	**OI 4**	**OI 5**	**OI 6**	**Ambient air**
0.1	0.7	3.2	7.5	20.0	35.2	71.6	0.3

The accuracy of these results underlies, like every measurement, systematic uncertainty. One reason for this can be found in alternating volume flow of the olfactometer. Schmidt (2011) determined a deviation of 5 % during long-term measurements.

A further aspect is the attachment of the thermodesorption-tubes above the odour interfaces during air sampling. They were attached to a rail and the tube-opening was 4 cm above the odour interface. This is the actual distance the participants kept with their nose from the odour interfaces.

Additionally the chemical analysis also underlies an uncertainty. As a result of the last two round robin tests (AGÖF 2011 and 2012) the mean measurement inaccuracy of the used TD-GC/MS system is 37 %. This value contains deviations caused by the air-sampling method, the measurement and the analysis.

The deviations between each sampling period are also considered. Different ways of calculating the concentrations, such as fragmentation of the participants into three groups for each measurement period showed that the final result is not affected by these variations.

Odour detection threshold

For the determination of the odour detection threshold, all 202 participants were included into the calculation. Table 2 shows the calculation basis for the median determination of the log-normal distribution. As observed, all participants were able to detect an odour at least at OI 5. Therefore only the first five OI were used for further calculation.

Table 2. Overview of the odour detection threshold statements

Odour interface	OI 1	OI 2	OI 3	OI 4	OI 5	OI 6
No. of positive odour detection threshold statements	21	91	76	13	1	0
Percentage of overall statements [%]	10.4	55.4	93.1	99.5	100	100

The determination of the odour detection threshold via calculating the median is illustrated in figure 3. The median is calculated as 2.34. Therefore, involving the measurement uncertainties of 37 %, the odour detection threshold for naphthalene is 2.3 ± 0.8 µg/m³.

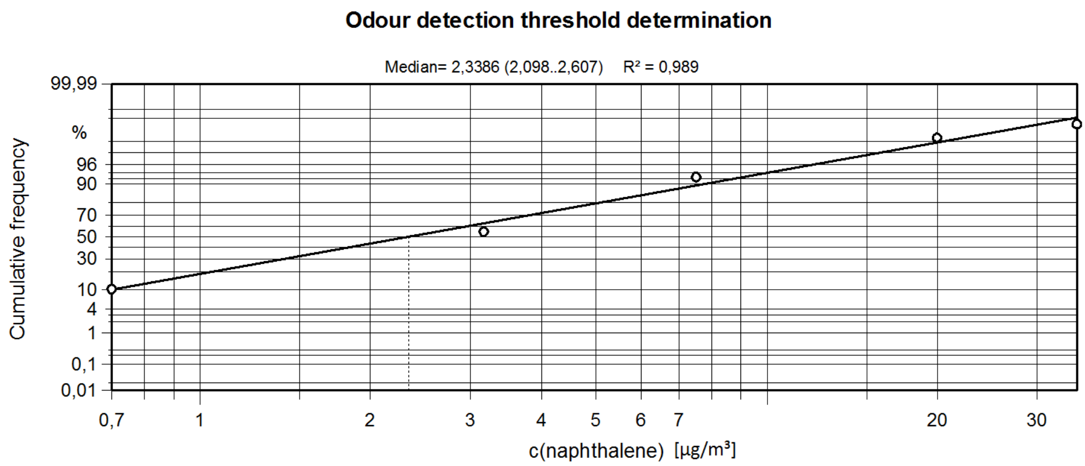

Figure 3. Determination of the odour detection threshold of naphthalene

To validate this result, the methodology was applied to different participant groups (Table 3). This allows a general comparison of the results regarding the ability to smell at different ages and between smokers and non-smokers. The results correspond with other studies regarding these subjects (Doty et al., 1984; Vennemann et al., 2008).

Table 3. Overview of different participant groups

Participant group	Number of participants	Percentage of all participants [%]	Odour detection threshold naphthalene [µg/m³]
Age 12-19	31	15.4	2.5
Age 20-29	80	39.6	2.0
Age 30-39	10	5.0	2.5
Age 40-49	24	11.9	3.2
Age 50-59	43	21.3	3.1
Age 60-74	14	6.9	4.1
Smoker	24	11.9	3.0
Non-smoker	178	88.1	2.3
Male	76	37.6	2.4
Female	126	62.4	2.4

Because of using a randomly mixed participants group the result for the detection threshold of naphthalene only represents the population distribution in a limited way for Germany concerning age, smokers and non-smokers (Statistische Ämter des Bundes und der Länder, 2011). Nevertheless the variations of the ODT_{50} depending on the several groups seem to be small (between 2.0 and 4.1 µg/m³, see table 3).

Odour identification threshold

The same procedure was conducted to determine the odour identification threshold. The data used for the calculation is given in table 4. As a result the log-normal probability plot determinates the identification threshold as 8.8 ± 3.2 µg/m³.

Table 4. Overview of the odour identification threshold statements

Odour interface (OI)	1	2	3	4	5	6
No. of positive odour identification threshold statements	2	10	67	85	20	18
Percentage of overall statements [%]	1.0	5.9	39.1	81.2	91.1	100

The identification threshold is approx. 3.6 times higher than the detection threshold. Other studies show, that detection and identification thresholds can differ by a factor of 10 (Schmidt et al., 2011). The disadvantage of the used method is, that the participants knew, that they will smell naphthalene in an ascending order. So it is possible, that the statements were distorted by this circumstance. Furthermore the participants might be confused by the difference between detection and identification threshold.

CONCLUSIONS

This study resulted in a reliable ODT_{50} due to well designed and described testing conditions. The determined ODT_{50} for naphthalene is significantly lower than former detection thresholds in previous studies.
Furthermore the ODT_{50} of naphthalene lies considerably beneath the German toxicological based guide values. This is relevant for a complete evaluation of the indoor hygienic situation by experts.

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