



## LEVELS OF SELECTED ORGANIC COMPOUNDS IN MATERIALS FOR CANDLE PRODUCTION AND HUMAN EXPOSURE TO CANDLE EMISSIONS

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### Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDD), dibenzofurans (PCDF) selected chlorinated pesticides, polycyclic aromatic hydrocarbons (PAH) and some volatile organic compounds (VOC) were analysed in the exhaust fumes of candles made from different waxes and finishing materials. To guarantee defined burning conditions a chamber was developed for the sampling of the exhaust fumes. Using a simple exposure model, the inhalative uptake of PCDD/PCDF by an adult person was calculated for different scenarios. It was shown that additional uptake of PCDD/PCDF caused by candle emissions does not contribute significantly to the total daily intake of these compounds. Emissions of PCDD/PCDF, benzo(a)pyrene and the VOC were then compared to limit value for working places. Even when many candles would be burnt at the same time in a small room, concentrations of the compounds investigated stay below 1 % of the tolerable limit values. © 1997 Elsevier Science Ltd. All rights reserved

*Keywords:* PCDD/PCDF, PAH, VOC, candle emissions, exposure assessment, inhalation.

### 1 INTRODUCTION

In Germany, about 90,000 tonnes of candles are being produced annually (Statistisches Bundesamt 1993). The three materials used for candle production are paraffin, stearin, and beeswax. Paraffin contributes to more than 90 % of the total production volume, whereas stearin is used to some percentage, and beeswax with approx. 1,000 t/a contributes about 1 % (Schütz 1994). Some reports assume that fumes from candles made of paraffin, an „oil-refinery“ product, may be more toxic than candles made of the „natural“ materials stearin and beeswax. Consequently, there was a need to investigate the concentration of potential pollutants in the various raw materials as well as in the exhaust fumes of candles.

Most candles being sold in Germany have a surface with different colours or lacquers. This finish is normally made by dipping the raw candles into a special liquid wax mixture (paraffin and polyethylene wax) containing the dye pigments. Thus, colouring affects only a thin surface layer of the candles. A further surface finishing can be done in a second step by dipping candles into liquid lacquer. This technique also minimizes the consumption of finishing materials for typical candles as used in this study.

## 2 EXPERIMENTAL

### 2.1 Raw Materials

Uncoloured and coloured commercially available candles made of paraffin, stearin and beeswax, wicks, candle colours, and lacquers were provided by German manufacturers. The candles with a length of 240 mm, a width of 23 mm and an approximate weight of 80 g were finished with about 80 mg dye or 80-240 mg lacquer. All materials were representative examples of products used by candle manufacturers in Germany.

For each type of wax a different brand of wick is being used to guarantee optimised combustion conditions; so we checked three types of wicks used in candles made of paraffin, stearin and beeswax. The wicks as well as the crude waxes were analysed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDF), chlorophenols, and chlorobenzenes. Additionally, wicks were analysed for chlorinated pesticides ( $\alpha$ - and  $\gamma$ -hexachlorocyclohexane, *p,p'* and *o,p'*-DDT)

A composite sample combining six of the most commonly used colours (red, yellow, dark-red, blue, green, and violet) and a composite sample of three lacquers (matt, glossy, and gold) were analysed for potential contamination with polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Both composites contained equal amounts of each colour and lacquer, respectively.

Thus, a total of eight raw material samples were analysed for the selected set of organic compounds.

### 2.2 Chamber Experiments and Sampling

Chamber experiments were performed to determine the emissions of selected organic compounds in candle exhaust fumes. A crucial point in the determination of emission concentrations is the simulation of realistic conditions for burning candles. Therefore, a special sampling device was developed which allowed the sampling of the exhaust fumes under defined burning conditions with a constant oxygen concentration and without turbulences (Schwind *et al.* 1994). In the chamber (volume = 1.2 m<sup>3</sup>) nine candles were burnt at the same time. For all experiments pre-cleaned air (passed through a polyurethane-foam filter) was used. The air exchange and flow rate in the chamber was adjusted to guarantee realistic burning conditions.

During three sampling cycles (two hours each) a volume of about 30 m<sup>3</sup> of air was collected and adsorbed on a combined polyurethane-foam/XAD-filter for the analysis of PCDD/PCDF and PAH. The total emission stream of the candles was collected for further analysis.

The determination of formaldehyde, acetaldehyde, and acroleine (= 2-propenal) as representatives of the volatile organic compounds (VOC) could be done with a volume of 0.04 to 0.06 m<sup>3</sup> (40-60 L) by collecting only a part of the emission stream over a period of one hour in a separate sampling intervall.

We analysed the emissions of three candles without any finish (beeswax, stearin, and paraffin, respectively), and 13 paraffin candles with different colours and surface finish (for details see Table 4).

## 2.3 Analysis

Analysis of PCDD/PCDF was performed with high resolution gas chromatography coupled with high resolution mass spectrometry (Varian HRGC 3400/Finnigan MAT 90 HRMS) using two columns of different polarity for the analysis of homologue groups and 2,3,7,8-substituted congeners. Quantification was done using isotope dilution method with an additional recovery standard for 2,3,7,8-Cl<sub>4</sub>DD. Chlorinated phenols were analysed for mono- through pentachlorinated and chlorobenzenes for mono- through hexachlorinated compounds. Pesticides (HCH and DDT) were detected with a gas chromatograph coupled with a mass sensitive detector (GC/MSD, Hewlett-Packard GC 5890/MSD 5970) using a HP Ultra 2 column. Quantification was made with an external standard solution containing all compounds of interest. The 16 polycyclic aromatic hydrocarbons (PAH) according to the EPA list No. 610 (EPA 1984) were also detected on the Hewlett Packard HRGC/MSD system using internal standards.

Aldehydes (formaldehyde, acetaldehyde, and acroleine) were collected on a glass fibre filter spiked with 2,4-dinitrophenylhydrazine for the *in situ* derivatisation of the compounds of interest. After extraction the hydrazone-derivatives of formaldehyde, acetaldehyde, and acroleine were analysed with a high performance liquid chromatography system coupled with a UV-detector at a wavelength of 260 nm.

For reasons of quality control, several blank values were determined for all compounds prior to the analysis of raw material and emission samples.

## 3 RESULTS

### 3.1 Levels in Raw Material

Concentrations of chlorinated organics and PAH in wax are summarised in Table 1. Chlorophenols and chlorobenzenes - known precursors for the formation PCDD/PCDF - could be detected in the raw material as well as dioxins and furans. Levels of chlorobenzenes in stearin wax were more than a factor of two higher than in paraffin and beeswax.

Within the group of PAH, naphthalene was most abundant in paraffin candles and contributes to more than 70 % to the  $\Sigma$  PAH. Keeping in mind that paraffin is made in the oil refinery process this is not surprising. However, it is remarkable that beeswax contained the highest levels of compounds present in ambient air: The amount of chlorophenols is 8 to 17fold higher and levels of PCDD/PCDF are 7 to 18 fold increased in comparison to the other materials. Polycyclic aromatic hydrocarbons such as pyrene, fluoranthene, phenanthrene, and naphthalene can frequently be found in the gas phase of ambient air. As a consequence, these compounds are significantly higher in beeswax than in paraffin or stearin and contribute to more than 65 % to the sum of 16 PAH in this wax.

Table 1: Concentration of PAH, chlorophenols, chlorobenzenes and PCDD/PCDF in wax materials

Compound	Dimension	Paraffin Wax	Stearin Wax	Beeswax
$\Sigma$ PAH	$\mu\text{g}/\text{kg}$	462	205	1.35
$\Sigma$ Chlorophenols	$\mu\text{g}/\text{kg}$	14.8	32.3	256
$\Sigma$ Chlorobenzenes	$\mu\text{g}/\text{kg}$	130	330	120
PCDD/PCDF	ng I-TEQ/kg	0.59	1.62	10.99

As shown in Table 2 levels of PCDD/PCDF, chlorophenols, and chlorobenzenes in all types of wicks were significantly lower than in wax. No HCH-isomers could be detected and DDT-isomers were only present in wicks used for paraffin candles.

Table 2: Chlorinated pesticides, chlorophenols, chlorobenzenes, and PCDD/PCDF in different types of wicks

Compound	Dimension	Type of Wick Used for...		
		Paraffin Candles	Stearin Candles	Beeswax Candles
$\alpha$ -HCH	$\mu\text{g}/\text{kg}$	<0.5	<0.5	<0.5
$\gamma$ -HCH	$\mu\text{g}/\text{kg}$	<0.5	<0.5	<0.5
<i>p,p'</i> -DDT	$\mu\text{g}/\text{kg}$	6.0	<1.0	<1.0
<i>o,p'</i> -DDT	$\mu\text{g}/\text{kg}$	13.0	<1.0	<1.0
$\Sigma$ Chlorophenols	$\mu\text{g}/\text{kg}$	1.23	0.94	0.74
$\Sigma$ Chlorobenzenes	$\mu\text{g}/\text{kg}$	0.67	0.34	0.35
PCDD/PCDF	ng I-TEQ/kg	0.18	0.12	0.08

The concentrations of PCDD/PCDF in colours and lacquers are shown in Table 3. Only composite samples were analysed and therefore no information on the composition of specific colours or lacquers is available. Levels of PCDD and PCDF in both samples are low and do not indicate dioxin contamination. Pesticides, chlorophenols, chlorobenzenes and PAH were not analysed in these samples.

Table 3: PCDD/PCDF concentrations in candle colours and lacquers

Compound	Dimension	Composite Sample of 6 Colours	Composite Sample of 3 Lacquers
$\Sigma$ PCDD	ng/kg	9.4	524
$\Sigma$ PCDF	ng/kg	8.9	1,874
PCDD/PCDF	ng I-TEQ/kg	0.5	6.5

As a general statement it can be concluded that levels of organic pollutants found in raw materials for candle manufacturing are low. With the exception of some organochlorines and PAH in beeswax and the naphthalene levels in paraffin candles, no specific pattern of contamination can be assigned to a product's origin.

### 3.2 Emissions from Burning Candles

Measured emission were calculated as emission factors adjusted to the amount of substance released when 1 g of wax is being burnt. These values allow a direct comparison between different types or brands of candles. As shown in Table 4, emission factors vary with the type of colour and lacquer of the candles. High emissions of *e.g.* dioxins are not necessarily connected with high levels of PAH, and even within the VOC no clear relation exists. Low levels of acrolein were only detected in emissions of two candles without finish and was below the detection limit in all other samples. On the other hand, the amount of acetaldehyde is significantly higher from candles with surface finish.

Although pure beeswax contained the highest levels of PCDD/PCDF and chlorophenols (see Table 1), the emission of beeswax candle gave the lowest dioxin concentrations (Table 4). Possibly the higher combus-

tion temperature in the flame of beeswax candles effectively impedes the thermal formation of PCDD/PCDF in the flame but supports the destruction of dioxins being present in the wax.

Table 4. Emission factors of PCDD/PCDF, PAH, benzo(a)pyrene (= BaP) and selected VOC of candles with and without finish (n.d. = not detected)

Type of Candle and Surface Finish	PCDD/PCDF pg I-TEQ/g	PAH ng/g	BaP ng/g	Acetaldehyde ng/g	Formaldehyde ng/g	Acroleine ng/g
Beeswax candle, no finish, no colour	0.004	5.29	n.d.	n.d.	4.7	n.d.
Stearin candle no finish, no colour	0.037	4.75	n.d.	n.d.	3.7	5.4
Paraffin candle, no finish, no colour	0.020	156	0.01	n.d.	14.1	0.1
Paraffin candle with colourless dipping layer	0.030	11.47	0.09	28.4	6.6	n.d.
Paraffin candle, yellow	0.021	8.20	0.06	61.8	5.2	n.d.
Paraffin candle, red	0.023	8.91	0.10	26.0	6.3	n.d.
Paraffin candle, dark-red	0.021	7.97	0.08	46.6	4.5	n.d.
Paraffin candle, blue	0.027	9.32	0.08	39.3	12.5	n.d.
Paraffin candle, green	0.028	7.03	0.05	43.1	7.0	n.d.
Paraffin candle, violet	0.032	6.55	0.04	51.9	6.1	n.d.
Paraffin candle with colour mixture	0.031	9.23	0.05	32.1	5.1	n.d.
Paraffin candle with matt lacquer	0.019	8.77	0.13	58.3	n.d.	n.d.
Paraffin candle with glossy lacquer	0.026	7.36	0.04	57.3	6.5	n.d.
Paraffin candle with gold lacquer	0.024	8.92	0.07	36.4	6.6	n.d.
Paraffin candle with lacquer mixture	0.047	7.25	0.06	54.3	6.5	n.d.
Paraffin candle, red and matt lacquer	0.042	7.53	0.05	39.3	4.5	n.d.
Minimum value	0.004	4.75	n.d.	n.d.	3.7	n.d.
Maximum value	0.047	156	0.13	61.8	14.1	5.4

The specific emission volume (= volume air per amount of wax being burnt) of all candles varied very little and an average value of 0.09 m<sup>3</sup>/per g wax was calculated independent of the surface finish. Dividing the specific emission factors from Table 4 by the emission volume of 0.09 m<sup>3</sup>/per g wax, the emission values in pg I-TEQ/m<sup>3</sup> or ng/m<sup>3</sup> of the candles can be calculated. For exposure assessment we only used emission factors.

#### 4 EXPOSURE ASSESSMENT TO EMISSIONS FROM CANDLES

An exposure assessment for the emissions of organic pollutants from burning candles is done using two different approaches:

- (1) A simple exposure model was applied to calculate human uptake of PCDD/PCDF *via* inhalation;
- (2) Indoor air concentration caused by burning candles were compared to German limit values and to emissions in cigarette smoke

#### 4.1 A Model for the Inhalative Uptake of PCDD/PCDF-Emissions

For a well defined volume, e.g. in a living room, a simple model can describe the human uptake of a compound *via* inhalation. The air exchange rate is not considered in this equation.

$$Dose = \frac{Ef \cdot M}{V} \cdot B \cdot T \cdot Rf \cdot \frac{1}{BW}$$

where: dose amount of substance inhaled (pg I-TEQ per kg body weight)  
 Ef Emission factor of a specific candle (pg I-TEQ/g wax)  
 M Mass of wax being burnt (g wax)  
 V Volume of the room (m<sup>3</sup>)  
 B Breathing volume (for adults 0.6 m<sup>3</sup>/h)  
 T Exposure time (h)  
 Rf Resorption factor of the compound in the lungs: Rf = 1 (100 % resorption)  
 BW Body weight (for adults: 70 kg)

With this equation the calculation of different exposures with respect to exposure time, air volume and type of emission source, expressed as specific emission factor can be done. Results of two examples are shown in Table 5. All values were calculated using the emission factor of a paraffin candle finished with a mixture of lacquers. This candle gave the highest emission factor for PCDD/PCDF in the experiment (see Table 4). The inhalative uptake after a exposure time of one hour in a small or a large room (V = 40 m<sup>3</sup> and V = 80 m<sup>3</sup>) was calculated. An exposure time of three hours to the emissions of 30 candles into equal room volumes certainly is an extreme situation and may represent the maximum inhalative uptake of PCDD/PCDF from candle emissions.

Results of the scenarios are reported in Table 5 and were compared with background exposure data of PCDD/PCDF (Umweltbehörde Hamburg 1995) in Germany. The average uptake of PCDD/PCDF *via* inhalation in Germany for an adult person with a body weight of 70 kg is about 1.5 pg I-TEQ/person (or 0.02 pg I-TEQ per kg body weight and day) and contributes to less than 2 % of the total daily intake (approx. 115 pg I-TEQ/person or 1.65 pg I-TEQ per kg body weight and day, respectively).

Table 5: Uptake of PCDD/PCDF *via* inhalation from emissions of paraffin candles finished with a mixture of lacquers (b.w. = body weight)

Exposure Characteristics	Room Volume V = 40 m <sup>3</sup>	Room Volume V = 80 m <sup>3</sup>
Emissions of 1 candle (= 6 g wax) for 1 hour exposure time	0.00006 pg I-TEQ/kg b.w.	0.00003 pg I-TEQ/kg b.w.
Increase of inhalative uptake per event	+ 0.28 %	+ 0.14 %
Increase of total daily intake per event	+ 0.004 %	+ 0.002 %
Emissions of 30 candles (= 540 g wax) for 3 hours exposure time	0.016 pg I-TEQ/kg b.w.	0.008 pg I-TEQ/kg b.w.
Increase of daily inhalative uptake per event (100 % = 0.02 pg I-TEQ/kg · d)	+ 75 %	+ 37 %
Increase of total daily intake per event (100 % = 1.65 pg I-TEQ/(kg · d))	+ 0.96 %	+ 0.48 %

The additional exposure to emissions from candles contributes less than 1 % of the total daily intake *via* all paths (Table 5). Considering only the uptake by inhalation, 30 candles increase the daily exposure *via* this path by up to 78 %. Keeping in mind that an event as described above with the exceptional use of candles occurs only very seldom the impact on human exposure from the use of candles is negligible.

#### 4.2 Comparison to Existing Limit Values

To compare the exposure to aldehydes and benzo(a)pyrene from candle emissions with another realistic situation we used same room volume and amounts of wax being burnt as described above and compared values to the exposure of smoke of one cigarette in a room of 40 m<sup>3</sup>. As a worst-case scenario the highest emission factors from Table 4 were used and 3 h burning time was assumed. This corresponds to the consumption of 540 g of wax.

PCDD/PCDF and other organic compounds emitted with cigarette smoke are reported in the literature (Ball *et al.* 1990, DFG 1985). Candle and cigarette emissions are compared in Table 6.

Table 6: Calculated concentrations of chemicals in indoor air: Comparison between cigarette smoke and candle exhaust (Room volume: 40 m<sup>3</sup>)

Compound	Levels in Indoor Air after...		Type of Candle Causing Maximum Indoor Air Concentration
	Smoking 1 Cigarette	Burning 30 Candles	
Formaldehyde (µg/m <sup>3</sup> )	38	0.190	Paraffin, no finish
Acetaldehyde (µg/m <sup>3</sup> )	no data	0.834	Paraffin with yellow colour
Acroleine (µg/m <sup>3</sup> )	23	0.073	Stearin, no finish
Benzo(a)pyrene (µg/m <sup>3</sup> )	0.003	0.002	Paraffin with lacquer matt
PCDD/PCDF (pg I-TEQ/m <sup>3</sup> )	0.0016	0.635	Paraffin with mixture of lacquers

For risk assessment, Maximum Workplace Concentrations (MAK-values) or Technical Guideline Concentrations (TRK-values) can be used (see Table 7). As these limit values were established for a worker's environment and a daily exposure time of eight hours, they represent a threshold value below which health effects do not occur in adult persons. Both, MAK- and TRK-values cannot be used for long-term exposure to substances present in ambient air (DFG 1993). All calculated indoor air concentrations are well below any limit value. It is remarkable that even the extreme situation of burning 30 candles produces much lower levels of organic pollutants than the smoke of a single cigarette. Only in the case of the PCDD/PCDF, the emissions from 30 candles would be above those from a single cigarette but resulting indoor air concentration is less than 1.3 % of the tolerable TRK-value (see Table 7).

Table 7: MAK and TRK values for the compounds investigated (DFG 1993)

Compound	MAK-Value	TRK-Value
Formaldehyde	600 µg/m <sup>3</sup>	--
Acetaldehyde	90,000 µg/m <sup>3</sup>	--
Acroleine	250 µg/m <sup>3</sup>	--
Benzo(a)pyrene	--	5 µg/m <sup>3</sup>
PCDD/PCDF	--	50 pg I-TEQ/m <sup>3</sup>

### Acknowledgements

The skilful help of Dr. Alsorachi from the Landesgewerbeanstalt (LGA) Nuremberg, Germany, in developing the chamber experiments is gratefully acknowledged.

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