Survey of chemical compounds in consumer products

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Survey, emission and evaluation of volatile organic chemicals in printed matter

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Contents

Preface

The Danish Environmental Protection Agency has initiated a survey of chemical compounds in consumer products. The purpose is to evaluate the exposure and risks to the people exposed to these chemical substances. The effort focuses the risk at direct exposure or contact with the products and indirect human exposure via the environment.

This report on "Survey, emissions and evaluation of volatile chemical compounds in printed matter" is a part of the Danish Environmental Protection Agency's programme "Survey of chemical compounds in consumer products ".

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The Graphic Association of Denmark has participated in selection and contact to printing houses and printing works in Denmark. The printing houses and -works have contributed with information and supplied the selected printed matter.

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Summary and conclusions

Monitoring of volatile organic compounds emitted from printed matter has been performed as part of a programme initiated by the Danish Environmental Protection Agency: "Survey of chemical substances in consumer products".

The purpose of the study was to monitor which chemicals and at which concentrations the consumer was exposed when reading or leafing through and keeping printed matter.

The annual consumption of printed matter like weekly and monthly magazines, journals, periodicals and unaddressed mail is approx. 61 kg per household. The amount equals 1.2 kg per week. Rotogravure was estimated to be 18% of the total volume. Thus the average weekly consumption was approx. 0.2 kg printed matter printed as rotogravure and approx. 1 kg as offset.

During the screening phase, 21 different printed matter were monitored and analysed for their qualitative emissions of volatile organic chemicals (VOCs). The printed matter comprised rotogravure, offset (rotation heatset and sheet offset) and flexographics using UV-curing inks. 143 substances were identified together with 20 groups of compounds that could not be separated in the analytical method (GC-MS-SIM). The measurements were performed as total emission measurements and the sources of the specific components (printing inks, paper, etc) are therefore unknown. However, a difference in emissions primarily attributable to the printing processes and the adapted printing inks, etc. was apparent.

Rotogravure printings such as catalogues, advertising matter, etc. emitted large quantities of VOCs of which toluene was the main fraction, 82 to 99%, and to a lesser extent terpenes and aldehydes. In offset the emissions contained especially long-chained aliphatic hydrocarbons, C9-19, followed by aldehydes. Monocyclic aromatics such as toluene and xylenes were also present in offset but at lesser concentrations. In flexographics, the primary chemical groups were alcohols and terpenes but much smaller concentrations were emitted compared to printed matter made by the previous two printing processes. The reason is probably the use of UV-curing inks where monomere acrylates polymerise to a solid ink layer. No monomere acrylates were observed in the analysis of the emissions

Based on the screening, 6 pieces of printed matter were selected for quantitative analysis of emitted compounds. The study simulated the situation where the consumer has the highest exposure, i.e. during reading and handling / leafing through the printed matter. The printed matter was cut up into 1 cm shreds, placed in glass container and the volatile emissions from the printed matter collected on absorbents. The sampling was performed just after the printed matter left the printing house or –works. Later the same procedure would be repeated after 1 to 5 days after printing to represent the sorting or handing out of the printed matter. And finally after 2 to 15 days after printing to represent the time where the printed matter reaches the consumer

It was observed that some of the volatiles reduced their emissions as time passed, e.g. toluene and alcohols, others evaporated at a later stage and peaked after a few days, e.g. aliphatic hydrocarbons. A third group of chemical substances increased their emissions during the study period. The latter was observed for the aldehydes and indicated that aldehydes in offset may be strongly adsorbed to the paper during the printing process and slowly released at a later stage, that is at the consumer.

The measured concentrations from the emitted chemicals are below the threshold limit values (TLV) intended for the working environment. As the threshold limit values are intended for the working environment and not for residential homes, the study relates to a values TLV times 0.01, i.e. using a safety factor of 100. The safety factor of 100 in relation to the value valid for the working environment is selected to include potential exposure to vulnerable groups (such as children, pregnant women, and persons weakened by illness) and because the total exposure consisting of a complex mixture of chemical compounds takes place during 24 hours per day. The threshold limit value for the working environment is set based on irritation of eyes and the inhalation system and other health affecting properties but also technical and economical relationships are included. In addition, LCI values are included in the evaluation. LCI (the Lowest Concentration of Interest) was developed in an EU-project on furniture VOC emissions and is intended for the indoor climate quality evaluation. LCI is based on inhalation and irritation or other effects including C-values or the lowest concentration having adverse effects. Only a few chemicals exceeded these thresholds values (TLV/100 and LCI). At larger exceeding of the used values, the evaluations are refined by a case-by-case assessment.

Toluene was the substance that raised most attention. In the study, maximum emissions up to 272 mg/kg printed matter were measured during one hour. However, as the maximal estimated exposure concentration of 23 mg/m^3 did not exceed NOAEC 150 mg/m^3 it was concluded that toluene was not expected to be a health problem to the average consumer.

Aldehydes are also noted but they exceed the TLV/100 and LCI values to a lesser extent: approx. a factor of 2. It might be disputable whether this may relate to any essential health effects.

The terpenerne, except alfa-pinene, only exceeded the threshold values when they were added up. However, alfa-pinene is allergenic and may cause allergic contact dermatitis. The significance of the concentration of total terpenes is unknown.

Nuisance such as odour was evaluated for selected chemicals. In the study only a few chemicals exceed the odour threshold in the reading, browsing / leaf through situation. Therefore, a consumer may only be able to identify a few chemicals by the odour. However, the adding of several chemical compounds exceeded the odour thresholds of groupings, i.e. the consumer may sense the odour of toluene, oils, terpenes, or just a general smell of chemicals. Of the chemicals included in the study this would be the case for aldehydes (propanal, pentanal, heptanal), toluene and the sum of terpenes and terpenoid compounds.

An entrance hall and living room scenario has been included in the study. The concentrations arising from leafing through the printed matter are estimated based on the average consumption of printed matter. The entrance hall and living room scenarios are based on air volumes of 10 m^3 and 50 m^3, respectively, and an air exchange rate of 0.5 per hour. The used LCI value is based on the C-value, and 1/100 of threshold limit value (TLV/100), were only exceeded by toluene for the entrace hall scenario. However, the level was below the experimental NOECS and thus toluene was not concidered a health problem for the average consumer.

The estimated emissions from single copies of printed matter when remaining untouched in the standard rooms were also included. The release and thus concentration of chemical compounds was considerably lower when the printed matter was left untouched. The contribution from each printed matter was based on the total volatile organic compounds (TVOC). Although the single contribution was small in this scenario, a consumer may have considerable amounts of printed matter lying around in the home. The effect of this relies on the amount, the ventilation, temperature and the nature of the printed matter. Thus, the printed matter may contribute to the residential total VOC load.

The main release to the environment from printed matter after it has left the printing house, during use and disposal, is to the air compartment. However, it is assessed that that the contribution from printed matter in these parts of its "life cycle" is minimal when considering the contributions from other sources of similar compounds, e.g. combustion from fossil fuels and gasoline. The emission volumes can not be estimated due to a lack of data.

The overall conclusion is that no health risk exists to the consumer of printed matter. However, it can not be excluded that allergic reactions may be observed by sensitive consumers.

Abbreviations

ADI	Acceptable Daily Intake
BCF	Bioaccumulation factor, i.e. the ratio between the concentration in living organism and the surrounding environment
bw	Body weight
C-value	Contribution value Defined (in Miljøstyrelsen 2002) as an industrial air pollution control guideline, i.e. the maximum allowed contribution to the air pollution outside the boundaries of the enterprise.
DL	Detection limit
EC	Effect concentration
EC_{50}	Median effect concentration, i.e. the concentration where effects are observed in 50% of the test animals
GA	The Graphic Association in Denmark
h	Hour(s)
LC_{50}	Median lethal concentration, i.e. the concentration where 50% of the test animals are dead
LCI	Lowest Concentration of Interest LCI is defined as the lowest concentration of a certain substance, which according to our present knowledge at continued exposure in the indoor air will not cause damaging impact on humans. Most values are based on inhalation and irritation or other values including C-values and the lowest concentration with adverse effects *It should be noted that LCI-values are weighing factors indicating the relative hazard of substances and not a criteria for indoor air quality or a fixed threshold limit value.*
LC_{lo}	Lowest concentration where effects are observed
LD_{50}	Median lethal dose, i.e. the dosis where 50% of the test animals are dead
LOAEL	Lowest Observed Adverse Effect Level

MAK	Maksimaler Arbeitsplatz Konzentration: threshold limit value defined by German authorities
NOAEL	No Adverse Effect Level
RD_{50}	The air concentration of a chemical substance necessary to evoke a 50% decrease in respiratory rate (Alarie 1980).
TC_{lo}	Lowest toxic concentration with observed effects
TDI	Tolerable daily intake
TD_{lo}	Lowest toxic dosage with pbserved effects
TGD	Technical Guidance Document: EU guidance in risk assessment of chemicals
TLV	Threshold Limit Value that should not be exceeded in the working environment. Typically a time weighted average value over 8 hours (a working day) is used. The threshold limit value for the working environment is set based on irritation of eyes and the inhalation system and other health affecting properties but also technical and economical relationships are included.
TLV/100	The threshold limit value from the working environment divided with a safety factor of 100 is used as acceptable level for consumers in the report
TWA	Time Weighted Average
VOC	Volatile organic compounds

1 Introduction

The project "Survey, emission and evaluation of volatile organic chemicals in printed matter" was initiated by the Danish Environmental Protection Agency as a result of consumer enquiries on printed matter. The questions typically refer to smudging (rubbing off) or odour from printed matter.

The study on which chemicals that are emitted from printed matter are to establish a background documentation on whether the exposure to these chemicals are hazardous to the consumer or the environment.

The exposure to humans take place in two ways, the primary exposure by inhalation of chemicals evaporated from the printed matter and to a lesser extent by skin contact. The smudging (rubbing off) experienced mainly originated from printing inks from newspapers and offset advertising matter. The rubbing off may be annoying but is usually washable and, therefore, found to be less essential than the potential effects from evaporated chemical compounds. Therefore, the study has focused on discovering which chemicals were emitted from printed matter, the amount and for how long after printing.

The concept of printed matter is rather comprehensive but in this context limited to advertising matter, weekly and monthly magazines, membership and association journals and labels. Different forms of printing techniques are used in the production of these printed matter. The categories typically comprise offset, rotogravure and flexography with ultraviolet (UV)-curing inks. In these printed matter, different printing inks and additives are used.

The Danish Technological Institute has previously experienced emission of chemical compounds from printed matter where the evaporation was high enough to be a health hazard in the working environment. It concerned especially the emission of toluene from rotogravure during the distribution phase (Jelnes 1994). Later, the threshold limit for the emission of toluene from printed matter was set at 300 mg/kg printed matter in the working environment (The National Labour Inspection, Arbejdstilsynet 1995).

In connection with the case on toluene, a current sampling and measuring method was modified and improved by the Danish Technological Institute (Eggert 1995). The modified method has been used in this study.

The study is focused on volatile organic compounds (VOC). VOC's are defined as volatile organic compounds whose vapour pressure at 20°C (293.15°F) is at least 0.01 kPa, i.e. 10 Pa (0.075 mmHg) or has a comparative evaporation under the specific conditions of use (VOC bekendtgørelsen, Miljøministeriet 2002b, implementing the VOC directive (directive 1999/13/EC) in Denmark.

2 Printed matter

2.1 Consumption

Printed matter in this study comprises categories such as weekly magazines, periodicals, journals, advertising matter and labels.

Newspapers are not included because the consumer exposure of volatile chemical compounds is considered less essential in this context. The primary consumer exposure from newspapers is printing ink (e.g. carbon black) resulting in smudged hands and clothes but it is considered washable.

The consumption of printed matter is not transparent. Dansk Oplagskontrol (Danish Audit Bureau of Circulations) perform quarterly monitoring on a large part of published daily newspapers, journals, periodicals, and other magazines which is enlisted. It means however, that some journals and periodicals are not included in the statistics.

Statistics Denmark follows the import and export of paper in different categories and includes journals, periodicals. Statistics Denmark may provide information that may be related to printed matter if you know the used types of paper.

The Graphic Association of Denmark (GA) publishes "De Grafiske Fag" which contains statistics on the activities of the association. The statistics include consumption of paper and printing inks.

In the consumption of paper is only included qualities of paper that are free of wood fibres or contain a maximum of 10% mechanical pulp. In the table below the source (GA) inform that a part of the consumption is outside the graphic industry.

Table 2.1 Consumption of wood fibre free printing paper in Denmark (selected sorts of paper) in 1000 tonnes (GA 2001, 2002)

	1993	1994	1995	1996	1997	1998	1999	2000	2001
Production	99	102	97	97	114	116	102	119	116
Import	151	193	183	193	229	241	245	267	242
Export	67	82	87	78	90	94	101	104	96
Consumption*	183	213	193	212	253	263	246	282	262

*: Consumption = production + import - export

The consumption of printing paper was increasing at least until 1997 after which it fluctuates. The same applies to the consumption of printing inks (cf. table below).

Table 2.2 Consumption of printing inks in Denmark in tonnes (GA 2001, 2002)

	1993	1994	1995	1996	1997	1998	1999	2000	2001
Production	9.981	11.216	11.222	11.361	12.318	13.814	13.371	13.100	13.917
Import	4.439	5.061	6.400	7.176	7.629	7.801	8.520	10.366	9.058
Export	3.142	3.582	3.677	3.786	5.329	6.265	7.757	6.756	8.586
Consumption*	11.278	12.695	13.945	14.751	14.618	15.350	14.134	16.710	14.389

*: Consumption = production + import - export

2.2 Number of enterprises

The graphic industry makes up the number of VAT-registered enterprises to 2323 enterprises at the end of 1999. Considering small enterprises which have an annual turnover below 0.5 million D.kr. (approx. 0.06 mio. Euro) as hobby operations the remaining number of graphic enterprises excluding newspapers and other publishing and printing enterprises is estimated to approx. 1400 (GA 2002).

2.3 Printing

The production of printed matter is only briefly mentioned as to understand from where and how the observed compounds may be included in the manufacturing processes and to explain used concepts.. The definitions are extracted from the Danish VOC regulation, which also includes printing houses (Miljøministeriet 2002b).

2.3.1 Printing techniques

Printing of text and/or images is in short a process where printing ink by some kind of printing form by the use of an image carrier is transferred directly or via an intermediate carrier to a the substrate to be printed. Included is adapted printing techniques such as lacquering, coating and lamination.

2.3.1.1 Rotogravure

In publication gravure, the process is employed in the web printing of magazines, brochures, catalogues etc. Publication gravure utilises hard resins dissolved in toluene or aliphatic solvents. Drying is achieved by solvent evaporation. The printing ink is transferred from the printing area consisting of tiny cells on an etched cylinder to the paper web. The short path from ink reservoir to the material to be printed on only permits the use of rapidly evaporating solvents. Publication gravure covers the printing of magazines, advertisement matter, brochures, labels etc.

Another form of rotogravure exists, called packaging gravure. In packaging gravure, printing is also performed using fluently printing inks drying by evaporation. The printing substrate is paper, plastic films, aluminium foils, etc. In contrast to publication gravure, toluene and aliphatic solvents are not employed. Instead, ethyl acetate and alcohols (e.g. ethanol, 1- and 2-propanols, ethoxypropanols) are used as solvents.

Transfer of printing ink directly to the printing subject via a printing unit for each colour means that the paper web has to pass a drying device between each printing unit. It also means that certain demands are required of the solvents of the printing inks and their evaporation ability. The drying ability has to be large enough to ensure sufficient drying at the used drying device (hot air current, air ventilation, heating, etc.) Toluene is a typical solvent fulfilling these requirements (cf. section on printing inks)

2.3.1.2 Offset

Offset printing comprises printed matter produced by plane printing method where the printing form contains hydrophilic and hydrophobic areas. In the printing process, the printing form passes a moisturer (wetting unit) with a roller. The wetting agent applied ensures a separation between the fatty oleophilic inks and the repel of inks in the non-printing areas. The printing inks dry (cur) by a chemical reaction (oxidation). The ink is transferred from hydrophobic areas to a rubber blanket that transfers the colour to the paper ("to set off")

In sheet-fed offset printing, the colour is set off on paper sheets. In sheet-fed printing the printing form is fastened to the printing machines plate cylinder.

Other offset printing techniques comprises rotation press (newspaper offset and heatset web offset). Newspaper offset is not included in the study but the printing inks dry by penetration into the paper ("coldset").

2.3.1.3 Heatset

Heatset web is printing on paper web in contrast to sheet fed offset printing The image carrier of the printing form consists of printing regions (lipophilic areas) in the same plane as the non-printing areas (hydrophilic areas). Drying takes place by leading the web through a heater where a hot air current passes the web. Heatset web is used in the printing of weekly magazines, advertising matter, catalogues etc.

When the web leaves the last printing unit the colour is still wet. Drying takes place by leading the web through a heater where the paper is heated to 120 to 140°C. Thereby the printing inks contents of volatile mineral oils evaporate. After cooling by passing cooling rollers the print is added a mixture of silicone and water to make the paper more smooth and to protect the print during cutting. The printed matter are then bundled and stacked.

2.3.1.4 Flexografic printing

Flexografic printing means printing with liquid printing inks that dries by evaporation or UV-curing. The printing inks are transferred from a printing plate of rubber or elastic polymere (plastic) where the image carrier is raised inked elements contrary to non-printing non-raised areas (letterpress printing).

2.4 Paper

The paper used is usually coated or calendered paper with a weight of 50 to 150 g/m^2.

Coated paper is paper that during its manufacture is covered with a surface layer. The surface layer consists of a pigment (usually chalk) and a binding agent, e.g. latex (Hansen and Petersen 1993). The use of coated paper results in a glossy and sharp print.

Calendered paper is paper that during the production process is calendered, i.e. the web has been lead through two rollers compressing the paper and thereby giving it a smooth surface.

2.5 Printing inks

All printing inks consist mainly of pigments/colouring agents, binders, solvents and additives.

The colouring agents consist of pigments or solvent colours of which the pigments present the major part. Pigments and additives in colorants used in rotogravure are almost identical. The content of pigments and fillers in rotogravure is approx. 10% and in heatset 15 to 20% (Bauer 1993).

Additives may have different purposes such as controlling the viscosity of printing inks and reduce smudging. The additives may be e.g. different kinds of wax often based on polyethylene.

The printing colours may also contain resin and mineral oils (unspecified basic oils: distillates, hydrogenated heavy naphthenes).

2.5.1 Solvents

The main difference between printing inks to offset, heatset and rotogravure is the solvents. The solvents keep the printing ink liquid during the printing process.

In printing inks to heatset is used mineral oils (kerosene distillates with a boiling point of approx. 210-250°C) which is more volatile than the mineral oils used in other kinds of offset printing. The content of mineral oils in heatset is 25-40% (Bauer 1993). In Ullmann (1993), the information on typical formulations deviates a little from the Bauer (1993) information:

Table 2.3 Typical formulation for heatset web offset inks (Ullmann 1993):

Organic pigments	15 - 25 wt%
Binders:	
Hard resins	25 - 35 wt%
Soft resins + drying oils	5 - 15 wt%
Mineral oils (boiling point 200-300ºC)	25 - 40 wt%
Additives	5 - 10 wt%

wt%: weight percentage

In addition Ullmann (1993) also presents a typical formulation for sheet-fed offset printing inks:

Table 2.4 Typical formulation for sheet-fed offset inks (Ullmann 1993):

Organic pigments	12 - 20 wt%
Binders:	
Hard resins	20 - 25 wt%
Soft resins + drying oils	20 - 30 wt%
Mineral oils (boiling point 250-300ºC)	20 - 30 wt%
Additives	5 - 10 wt%

wt%: weight percentage

In printing inks to rotogravure a large amount of solvent, especially toluene, is used. Toluene is very volatile with a vapour pressure of 3000 Pa at 20°C and 3800 Pa at 25°C. The advantage is quick drying and a high printing speed. The content of toluene in ready-to-use printing inks is 60-75% (Bauer 1993).

Table 2.5 Typical formulation of publication rotogravure inks (Ullmann) 1993:

Pigments	ca. 8 - 15 wt%
Resins	ca. 15 - 20 wt%
Toluene (solvent)	ca. 60 - 70 wt%
Additives	ca. 0.5 - 5 wt%

It is not possible to use as volatile solvents in heatset as in publication gravure. The printing ink has to be set off at a rubber blanket before transferred to the paper. If the drying is too quick, problems will be created in the colour transfer.

2.5.2 Binders

Binders are used to make the pigments adhere to the paper. In both heatset and rotogravure different resins are used as binders. In heatset printing inks alkyde and in rotogravure resinates may be used. Hard resins are rosin modified with phenols and aldehydes. Soft resins and drying oils are used as solvents for hard resins. They are usually fatty alkyds. Drying oils include plant oils.

2.5.3 Wetting agent

Wetting agents used in heatset contain different alcohols, e.g. isopropanol which may make up as much as 10-15% (Petersen and Skjærbæk 1998).

Table 2.6 Typical formulation of wetting agent concentrates (applied at a concentration of 2-5%) (Ullmann):

Buffer system	4 - 8 wt%
Alkohols	5 - 20 wt%
Surfactants (tensides)	0 - 1 wt%
Hydrophilic polymers	1 - 7 wt%
Complexing agents	0 - 2 wt%
Preservatives	0 - 4 wt%
Water, added to make up to 100%	58 - 90 wt%

2.5.4 UV-curing inks

UV-curing printing inks and lacquers are used in printing self-adhesive labels by flexography, screen printing (serigraphy) of posters, lacquering of printed matter, normally printed by offset, etc. (Silfverberg and Sørensen 1998). The use of UV-curing printing inks and lacquers in Denmark is usually in flexographic printing where labels are the dominating area (Lund and Wallström 1999).

UV-curing printing inks and lacquers contain reactive, high viscosity binders, so called pre-polymer acrylates, which by the curing process (a polymerisation taking place after exposure to ultraviolet light) are transformed into a solid layer of ink or lacquer. Ink or lacquer contains photoinitiators, i.e. light sensitive compounds, which by radiation become active and initiate the curing process.

Low viscosity reactive monomer acrylates or methacrylates are used as thinners. Furthermore the inks contain pigments and small amounts of additives (Silfverberg and Sørensen 1998).

Drying does not release volatile compounds since UV-curing printing inks do not contain solvents in the usual sense. However, a curing of the total ink layer is a prerequisite. If the ink layer is too thick some of the ink may not cure (polymerise) sufficiently and may lead to potential exposure from acrylate monomers. Residue acrylic monomers may later cause contact dermatitis if exposed to skin. Acrylic monomers are recognised as skin irritating and may cause contact dermatitis (Thomsen 1990, CEPE 2002).

Thus, theoretically no volatile compounds are released from UV-cured printing inks and lacquers. However, it is noted in Silfverberg and Sørensen (1998) that printed matter where UV-curing inks and lacquers are used, sometimes may have an unpleasant smell/odour. The statement indicates that some compounds may evaporate from the printed matter. The authors indicate that it may be impurities in the used raw materials or reaction products from the substrate printed on. Residues from ozonation at the UV-lamp may also be a potential source.

2.6 Emissions during printing

Printing facilities are as other enterprises subjected to regulations for the working environment and requirements to internal emissions are made. Most emissions from the printing process is collected and either recycled (e.g. up to 98% of toluene) or incinerated before release to the external environment.

Emissions during the distribution (e.g. at post offices) previously examined (Hansen and Petersen 1993, Jelnes 1994) is also regulated relating to the working environment (EU 1999, Miljøministeriet 2002). In rotogravure focus has been especially on toluene where emissions from printed matter in the working environment is regulated (Arbejdstilsynet 1995).

In heatset, the releases may be volatile petrodistillates and aliphatic aldehydes formed under heating of the mineral oils. The aldehydes may release unpleasant odours as the compounds may be malodorous like acetaldehyde, n-butylaldehyde, crotonaldehyde (2-butenal), propionic aldehyde, or valerianealdehyde (pentanal) (Lauritsen 1991).

2.7 Printed matter in the household

The amount of printed matter reaching the consumer has for instance been assessed in a study calculating the potential consumption of paper and cardboard from private households in the year 2000 (Højen and Petersen 2002). The potential paper and cardboard consumption has been distributed on categories presented in the table below.

Table 2.7 Potential paper and cardboard consumption, 2000 (Højen and Petersen 2002)

Category	Potential [tonnes]	kg per household		
		Average	Min.	Max.
Daily newspapers	113 160	46.3	25.2	66.5
Local papers	39 148	16.0	2.2	51,6
Weekly and monthly magasines	30 889	12.6	9.0	22.3
Trade-/membership journals 1)	20 410	8.3	7.9	10.1
Distribution af telefone books 2)	9 211	3.8	0.6	7.7
Unaddressed mail 3)	98 202	40.2	27.9	52.1
Addressed mail	41 683	17.1	17.1	17.1
Other, paper	18 578	7.6	7.6	7.6
Cardboard	61 100	25.0	25.0	25.0
Total	432 381	176.9	137.1	220.4

1) Amount of the country divided by numer of households in the municipalities

2) Only covering telephose books not distributed by Post Denmark as the amount from Post Denmark is included under unaddressed mail

3) Excluding housholds registered as not wanting advertising matter

The total potential annual consumption of paper and cardboard in private households is estimated to 432,000 tonnes eller 177 kg. per household. The estimated country average covers large differences in both categories and in the total amount. The variation in each category is presented as an interval in kg/household per municipality. In one municipality, a potential annual consumption of 137 kg/household was observed. However, another municipality may estimate approx. 83 kg more paper per household or a total of 220 kg/household. The relationship is tied to the volume and character of the distributed printed matter (Højen and Petersen 2002).

From Table 2.7, the categories "weekly and monthly magazines", "trade and membership journals" and "unaddressed mail" is used in the estimation of consumption of printed matter per household. They add up to 61.1 kg/household and a maximum of 84.5 kg printed matter. The uncertainties regarding a minor contribution from telephone books distributed by Post Denmark is assumed equalling an unknown amount of printed matter in "unaddressed mail", i.e. advertising matter send directly on request etc.

The association of Danish distribution enterprises (Brancheforeningen af Danske Distributionsvirksomheder, BDD) has information on the average number of distributed printed matter covering private and Post Denmark distributions. BDD informs that a number of 1934 million printed matter are distributed to Danish households in 2001 corresponding to 15/week or 38 kg per household. Of these approx. 18% is produced in rotogravure (BDD 2002).

Based on this information the consumption of printed matter is 61.1 kg per household annually, corresponding to 1.2 kg per week. Rotogravure processed printed matter is assumed to be 18% corresponding to 0.2 kg and the remaining part offset corresponding to approx. 1 kg.

2.8 Disposal

At disposal, printed matter is recycled, incinerated or landfilled. Volatile organic compounds are estimated to be released during the processes. During recycling the VOCs may be emitted or remain in the paper pulp (cf. below). By landfilling, the VOCs remaining in then printed matter will slowly be released during the degradation of the paper. By incineration the VOCs are estimated to be destroyed during the incineration process.

The study focused on the release of VOC in the initial and consumer phase. The residual emissions and the residuals remaining in the paper and printing inks at disposal were not measured. As illustrated by rotogravure below the residuals remaining in the paper at disposal may be significant.

Rotogravure
In Hansen and Petersen (1993), it is estimated that 16% of the rotogravure printed matter is disposed of by landfilling, 23% is reused (recycled) and 61% incinerated. The main fraction of residual volatile organic compounds in printed matter that is incinerated is assumed destroyed during the process of incineration or transformed into other compounds. The study from 1993 (Hansen and Petersen 1993) indicates that approx. 9 tonnes of toluene each year is released from landfilled and recycled rotogravure printed matter. The result is based on a total volume of 40,000 tonnes of rotogravure with a residue content of 690 mg/kg extractable toluene in the printed matter. Unfortunately the value is based on one single measured concentration and thus may not be representative.

According to current regulations, at least 60% paper and cardboard should be collected and recycled by 2004 at the latest (Tønning 2000). If assumed that most municipalities fulfil the requirement of 55% in 2002, the release to the atmosphere may be estimated to approx. 13 tonnes of toluene.

Toluene is still used to a great extent even though a technical progress such as heating, paper types and formulations of printing ink has happened during the later years and may have reduced the emission.

2.9 Recycling

At recycling printed matter, all paper has to go through a de-inking process where printing inks, lacquer, glue and other impurities are removed before new paper can be made from the fibres.

Two main principles are used: washing and flotation. Both methods start with the printed matter being suspended in large amounts of water under mechanical and chemical influence.

In the "washing" process, inks and additives of the original paper are washed out while the cellulose fibres are concentrated. The method is mostly used in America.

In the "flotation" process, which is the most used method in Europe, chemicals are added that make the cellulose fibres swell and reject the printing inks. By letting air bubble though the solution, impurities are brought to the surface where they can be removed by defoaming.

In the recycling process a fraction of the residue toluene may be released while a fraction may remain in the solution. It is assumed that the main fraction will be released to the air compartment (99% according to a Mackay I distribution model). The technique of letting air bubble through the solution may increase the release rate.

3 Exposure

To form the basis for the planning of the chemical analyses, a screening study was initiated. A screening of the emissions from 21 selected printed matter within the categories rotogravure, offset (heatset and sheet-fed offset) and flexography, was performed. The primary selection was based on the printed matter category and the final selection was based on the availability of the selected printed matter. For instance, printed matter is distributed rather quickly after printing meaning that the final choice could depend on which printed matter that was available at the sampling time (September 6 to 12, 2002).

After the first screening of the 21 printed matter and on the basis of results of the chemical screening, the Danish Environmental Agency selected 6 items of printed matter for further analysis of VOC content and quantity of chemical substances.

3.1 Emission measuring methods

3.1.1 Sampling and analyses

The printed matter for the first screening was sampled directly at the printing works right after their printing. At the printing works a number of printed matter located within the piles was sampled. This was done to ensure a realistic impression of the emission potential (cf. methods in Eggert 1995).

3.1.2 Screening of volatiles

The qualitative screening was performed as a headspace analysis. A known amount of printed matter was shredded into 1 cm strips and quickly placed in "red cap" glass containers at 45 g/l container volume. The container was heated to 100°C for 1 hour after which gas samples was collected. The heating ensures that all potential volatile compounds were released. The gas samples was analysed using capillary column gaschromatography combined with mass spectrophotometric detection (GC-MS). The results showed which organic compounds evaporated from the printed matter and their relative distribution.

In the headspace analyses most potential volatile organic compounds except the low molecular weight aldehydes are identified. By the headspace analyses of the 21 printed matter, 143 single chemicals were identified. Besides 20 groups of compounds were found that were so closely located on the chromatograms that they could not be separated and inconclusively identified, e.g. aliphatic hydrocarbons with close numbers of carbon chain lengths, linear or branched, etc.

The results are presented in Appendix 2 (summary) and detailed in Appendix 4 (Analysis report).

Already based on the screening analysis, general trends could be identified for the volatile organic compounds (VOCs). For instance rotogravure printed matter had a common feature in large amounts of organic solvents of which toluene was the main compound. Offset (heatset and sheet offset) had a common feature in hydrocarbons where long chained alkanes (C8-C19) constituted the main fraction.

Both observations could be seen as an expression of the basic printing techniques. In rotogravure printing are used organic solvents that not always have time to evaporate even if technical progress has been implemented. In offset, oils containing hydrocarbons are used. Residues of these hydrocarbons still evaporate long after the printing process is over.

3.1.3 Quantitative measurements

The quantitative measurements were performed after a meeting at the Danish Environmental Protection Agency where it was discussed which compounds that could be the most interesting to focus on.

The selected printed matters are listed in the table below. The specific names of the printed matter are made anonymous, as it was not the purpose to focus on a specific printed matter but to get a general insight on the exposures of VOCs from the printed matter based on measured emissions.

Before the actual measuring, the background concentration in the inlet air was measured and subtracted from the measured result.

Three measurements on each printed matter has been performed (table 3.1):

1st measurement is performed just after printing. On the rotogravure printed matter printed outside Denmark, the first measurement was performed on the day it reaches Denmark; approx. 7 to 10 days after printing.

2nd measurement is performed 1 to 5 days after printing. This measurement represents sorting, shop, distributor etc..

3rd measurement is performed at 2 to 15 days after printing, i.e. when the printed matter reaches the consumer at his home.

Table 3.1 Printed matter sampling date, measuring day and way of storage

Printed matter	ID no	Printing date	Measured on	Days after printing	Storing
Rotogravure	2	01.10.2002	01.10.2002 02.10.2002 03.10.2002	0 1 2	Bundle (100 pcs) Bundle (100 pcs) 10 pieces
Rotogravure	3	26.09.2002	03.10.2002 07.10.2002 11.10.2002	7 11 15	Bundle (100 pcs) Bundle (100 pcs) 10 pieces
Flexography with UV-curing inks (label)	4	04.10.2002	04.10.2002 09.10.2002 11.10.2002	0 5 7	Ca. 5 m wined up Ca. 5 m wined up Ca. 5 m wined up
Offset	8	06.10.2002	07.10.2002 10.10.2002 11.10.2002	1 4 5	10 pieces 10 pieces 10 pieces
Offset	17	16.10.2002	16.10.2002 18.10.2002 23.10.2002	0 2 7	10 sheets 10 sheets 10 sheets
Offset	19	09.10.2002	09.10.2002 14.10.2002 16.10.2002	0 5 7	10 pieces 10 pieces 10 pieces

Measurements are performed by sheering the printed matter in approx. 1 cm strips that are weighed and placed in a 5.6 l glass container. A known volume of air is sucked through the container and then through suitable adsorption material. The adsorption material used to sample the exit gas was Tenax-tubes, charcoal- and DNPH-tubes. Tenax- and charcoal tubes are suitable for adsorption of volatile organic compounds (VOC's). Silicagel impregnated with dinitro-phenyl-hydrazine (DNPH-tube) is suitable for the collection of aldehydes, acetone and 2-butanon.

An air sample was extracted over 60 minutes with an air flow of 0.65 l/min. The total air volume sucked through the container was 117 litre corresponding to 39 litre of air sucked through each of the three filters (tubes) per hour. The air temperature was 23°C at 50% relative humidity.

After extraction of the compounds from the adsorbent charcoal and tenax tubes by carbondisulphide and diethylether, respectively, the chemical analyses and quantitative measurements of the volatile organic compounds took place using deuterium-isotope labelled internal standards. The eluates were analysed using GC-MS-SIM detection. The DNPH-tubes was extracted by acetonitrile and analysed using liquid chromatography with a diode detector: HPLC-UV. Double detection was performed on each eluate and the average calculated.

For all analyses quantification were performed in relation to calibration standards of the detected compound or closely related compounds (NIST database).

3.1.4 Results

To estimate the exposure the results for each printed matter is presented as:

- Concentration evaporated to the air from the shredded paper (µg/m^3).
- Amount of emitted compound per printed matter (µg/printed matter)
- Amount of emitted compound per kg printed matter (µg/kg printed matter)

Details of the chemical analyses of the adsorbants can be found in the chemical analysis report (Appendix 4).

The result of the qualitative measurements is presented below (table 3.2). The summary table illustrate that rotogravure differs significantly by the release of large amounts of toluene and terpene oils/terpenes, flexographic by alcohols and offset by the release of aliphatic hydrocarbons. Common to all is toluene, aldehydes and single ketones.

Differences in composition and amounts are mentioned separately for each printed matter (cf. below).

Table 3.2 Summary of measured volatile compounds in selected printed matter

Observed VOCs	CAS	EINECS	Printed matter, ID no.:					
			2 (roto)	3 (roto)	4 (flex)	8 offset	17 offset	19 offset
Charcoal/Tenax tube:								
Toluene	108-88-3	203-625-9	x	x	x	x	x	x
Octane	111-65-9	203-892-1	x					
Naphthalene	91-20-3	202-049-5	x		x			
C_9H_{12}, arom hydrocarbon			x	x	x		x	
$C_{10}H_{14}$, arom hydrocarbon				x				
alfa-Pinene	7785-26-4	232-077-3	x	x				
Camphene	79-92-5	201-234-8	x	x				
beta-Pinene	127-91-3	204-872-5	x	x				
d-Limonene	5989-27-5	227-813-5	x	x				
2-Propynylbenzene	300-57-2	206-095-7	x					
2,3-Dimethylphenol	526-75-0	208-395-3	x					
1-Methylindane	767-58-8	212-184-1	x					
Xylenes, ethylbenzene	1330-20-7 100-41-4	205-535-7 202-849-4		x			x	x
Cyclohexanone	108-94-1	203-631-1			x			
1-Butanol	71-36-3	200-751-6			x			
2-Hexanol	626-93-7	210-971-4			x			
Butylacetate	123-86-4	204-658-1			x			
n-Butylether	142-96-1	205-575-3			x			
Propanoic acid butylester	590-01-2	209-669-5			x			
3-Methyl-4-heptanone	15726-15-5	239-820-0			x			
2-Ethyl-1-hexanol	104-76-7	203-234-3			x			
C9 H10					x			
C10 H16					x			
C8 H16					x			
Acetic acid, ethylhexylester	103-09-3	203-079-1			x			
Other terpenes			x	x	x		x	
C9-12 aliphatic hydrocarbons						x	x	x
C13-19 aliphatic hydrocarbons						x	x	x
Styren		202-851-5					x	
C10 H12 O2							x	
DNPH tube:								
Formaldehyde	50-00-0	200-001-8	x	x	x	x	x	x
Acetaldehyde	75-07-0	200-836-8	x	x	x	x	x	x
Acrolein	107-02-8	203-453-4						
Propanal	123-68-6	204-623-0	x	x	x	x	x	x
Acetone	67-64-1	200-662-2	x	x	x	x	x	x
Butanal	123-72-8	204-646-6	x	x	x	x	x	x
Pentanal	110-62-3	203-784-4	x	x	x	x	x	x
Hexanal	66-25-1	200-624-5	x	x	x	x	x	x
Benzaldehyde	100-52-7	202-860-4	x	x	x	x	x	x
2-Butanon	78-93-3	201-159-0	x	x	x	x	x	x

Below is presented a summary of the measured results for each printed matter. Because the type of printing is the most important factor, even though the paper also may affect the results, the printed matter is not specified further. For the measurements is used what the printing works had of "fresh" printed matter if the intended printed matter was unavailable. The printed matter therefore may not necessarily have to be the same as the ones used in the screening. However, it has been ensured that the printing inks and paper are identical.

3.1.4.1 Printed matter no. 2 (rotogravure)

Measured concentrations and calculated values are presented in the table below.

Table 3.3 Results of emission measurements of printed matter no. 2 (rotogravure)

Compound	µg/m³ *			µg/printed matter			µg/kg printed matter		
Day	0	1	2	0	1	2	0	1	2
Toluene	161538	135897	82051	92049	72821	45960	544669	430894	271955
Octane	62	85	72	35	45	40	207	268	238
Naphthalene	59	44	41	34	23	23	199	138	136
C_9H_{12}, arom hydrocarbon	26	41	46	15	22	26	86	130	153
alpha-Pinene	82	90	92	47	48	52	277	285	306
Camphene	87	118	126	50	63	70	294	374	416
beta-Pinene	<0.2	<0.2	<0.2						
d-Limonene	28	44	51	16	23	29	95	138	170
2-Propynylbenzene	28	44	51	16	23	29	95	138	170
2,3-Dimethylphenol	38	23	18	22	12	10	130	73	59
1-Methyl-indane	41	51	49	23	27	27	138	163	161
Other terpenes	821	692	897	468	371	503	2767	2195	2975
Sum: charcoal/tenax	162810	137128	83495	92774	73481	46769	548957	434797	276739
Formaldehyde	28	23	19	22	18	17	129	106	100
Acetaldehyde	142	115	71	84	64	42	496	379	249
Acroleine	<0.03	<0.03	<0.03						
Propanal	28	45	24	15	24	12	90	140	74
Acetone	179	77	49	107	46	32	632	272	190
Butanal	5	3	3	3	2	2	19	11	11
Pentanal	4	2	1	3	2	1	16	9	5
Hexanal	53	12	8	32	8	6	190	46	36
Benzaldehyde	26	110	72	19	63	44	113	372	263
2-Butanone	2	4	3	1	2	2	5	11	11
Sum DNPH tube	467	391	249	286	228	159	1690	1347	939
Total VOC sum	163277	137519	83744	93059	73708	46928	550646	436144	277678

*: Emission measured from test sample of 34.7 g. The printed matter weighed 169 g.

The emission of volatile organic compounds measured during 1 hour for printed matter no. 2 is presented in the table below. It is observed that even if the release of some compounds decrease with time while others need time before release takes place (time-lag) the total emission is reduced with time. For printed matter no. 2, the emission half-life is 2 days if exponential decrease is assumed.

Table 3.4 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
0	93,059	550,646
1	73,708	436,144
2	46,928	277,678

The toluene emission was substantial. An important factor could be that it concerns a weekly magazine, which has a short delivery time from printing to consumer (approx. 2 days).

It is noted that toluene emission exceeds the 300 mg/kg printed matter agreed as threshold limit for the distribution environment (Arbejdstilsynet 1995) during the first two days.

Subjective evaluation of odour

The printed matter has a strong odour of toluene and to a lesser extent of terpenes. The odour intensity decreases with time.

3.1.4.2 Printed matter no. 3 (rotogravure)

Measured concentrations and calculated values are presented in the table below.

Table 3.5 Results of emission measurements of printed matter no. 3 (Rotogravure)

Compound	µg/m³ *			µg/printed matter			µg/kg printed matter		
Day	7	11	15	7	11	15	7	11	15
Toluene	66667	41026	25385	39476	22195	12143	237805	133705	73153
Xylenes, ethylbenzene	282	308	208	167	166	99	1006	1003	599
Naphthalene	<0.2	<0.2	<0.2						
C_9H_{12}, arom hydrocarbon	69	64	72	41	35	34	247	209	207
alpha-Pinene	667	615	513	395	333	245	2378	2006	1478
Camphene	203	197	164	120	107	79	723	643	473
beta-Pinene	100	103	97	59	55	47	357	334	281
d-Limonene	164	187	192	97	101	92	585	610	554
$C_{10}H_{14}$ arom hydrocarbon	174	197	205	103	107	98	622	643	591
Other terpenes	2949	3667	3821	1746	1984	1828	10518	11950	11010
Sum: charcoal/tenax	71274	46364	30656	42204	25083	14665	254241	151103	88345
Formaldehyde	< 0.1	<0.1	-	6	0.8	-	35	5	-
Acetaldehyde	87	78	67	54	45	34	325	270	206
Acroleine	<0.03								
Propanal	17	20	20	14	15	13	86	88	77
Acetone	115	142	179	73	81	90	442	490	540
Butanal	4	3	5	3	2	3	16	13	16
Pentanal	1	3	4	0.8	2	2	5	13	13
Hexanal	13	42	55	8	23	27	50	140	152
Benzaldehyde	20	45	33	12	25	16	73	149	96
2-Butanone	0,2	0.1	1.0	0.5	0.3	0.7	2.7	1.7	4
Sum DNPH tube	257	334	364	171	194	183	1031	1167	1104
Total VOC sum	71532	46698	31020	42375	25277	14849	255272	152270	89449

*: Emission measured from test sample of 32.8 g. The printed matter weighed 166 g.
-: below detection limit

The emission of volatile organic compounds measured during 1 hour for printed matter no. 3 is presented in the table below. It is observed that some of the compounds decrease with time while others need time before release takes place (time-lag) and finally for some the release increases. However, the total emission is reduced with time. For printed matter no. 3, the emission half-life is 5.5 days if exponential decrease is assumed.

Table 3.6 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
7	42,375	255,272
11	25,277	152,270
15	14,848	89,449

The toluene emission complies with the threshold value for distributors of 300 mg/kg printed matter (Arbejdstilsynet 1995) when the printed matter that is printed abroad reaches the country.

Subjective evaluation of the odour

The printed matter has an odour of toluene and strong odour of terpenes. The odour intensity decreases with time.

3.1.4.3 Printed matter no. 4 (flexography)

Measured concentrations and calculated values are presented in the table below.

Table 3.7 Results of the emission measurements of printed matter no. 4 (flexography)

Compound	µg/m³ *			µg/printed matter			µg/kg printed matter		
Day	0	5	7	0	5	7	0	5	7
1-Butanol	15	-	-	0.057	-	-	67	-	-
2-Hexanol	23	-	-	0.085	-	-	100	-	-
Toluene	67	19	10	0.246	0.083	0.059	289	98	70
Butylacetate	56	-	-	0.208	-	-	244	-	-
Cyclohexanone	85	5	-	0.312	0.023	-	367	27	-
n-Butylester	156	-	-	0.576	-	-	678	-	-
Propanoic acid butylester	108	-	-	0.397	-	-	467	-	-
3-Methyl-4-heptanone	21	18	-	0.076	0.078	-	89	93	-
C_9H_{12} arom. hydrocarbon	218	108	-	0.803	0.474	-	944	558	-
2-Ethyl-1-hexanol	244	95	15	0.897	0.417	0.089	1056	491	105
C9H10	38	28	-	0.142	0.124	-	167	146	-
C10H16	28	-	-	0.104	-	-	122	-	-
Acetic acid, 2-ethyl-hexylester	256	64	21	0.944	0.282	0.119	1111	332	140
Naphthalene	90	28	18	0.331	0.124	0.104	389	146	122
C8H16	92	38	10	0.340	0.169	0.059	4000	199	70
Terpenes	769	462	179	2.833	2.031	1.038	3333	2389	1221
Sum: charcoal/tenax	2267	865	254	8.349	3.807	1.468	9822	4479	1727
Formaldehyde	33	7	41	0.162	0.078	0.298	191	91	350
Acetaldehyde	72	9	7	0.281	0.061	0.067	330	72	79
Acroleine	-	-	-	-	-	-	-	-	-
Propanal	1	-	-	-	-	-	<0.1	-	-
Acetone	30	6	17	0.142	0.063	0.146	167	75	171
Butanal	2	1	0.3	0.010	0.005	0.003	11	5	4
Pentanal	158	10	3	0.621	0.049	0.024	730	57	28
Hexanal	7			0.038	0.008	0.015	44	9	17
Benzaldehyde	122	1		0.477	0.039	0.030	561	45	35
2-Butanone	1	1	0.5	0.005	0.005	0.003	6	5	3
Sum DNPH tube	436	35	68	1.7	0.3	0.6	2040	351	672
Total VOC sum	2703	900	322	10	4	2	11863	4830	2399

*: Emission measured from test sample of 27 g. The single printed matter (labels) weighed 0.85 g.

-: below the detection limit or less than the background concentration in the laboratory

The release of the volatile organic compounds measured over 1 hour for printed matter no. 4 is presented in the table below. It is observed that the total VOC emission decreases with time. For printed matter no. 4, the half-life of emission is 2 days if exponential decrease is assumed.

Table 3.8 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
0	10	11,864
5	4	4,830
7	2	2,399

UV-curing inks and lacquers contain high viscose reactive binders which by the hardening process polymerise to solid layer of ink or lacquer. For flexographic printed matters the emission after production is low compared to the other printed matter. At flexographic printing the emission of VOC is strongly reduced when the printed matter reaches the consumer.

The printed matter is a self-adhesive label, i.e. an adhesive is located on the back of the label. Potential release from the adhesive is included in the results of the analysis.

Subjective evaluation of odour

The printed matter has a distinct odour of non-identifiable solvents. The odour intensity decreased with time.

3.1.4.4 *Printed matter no. 8 (offset, heatset)*

Measured concentrations and calculated values are presented in the table below.

Table 3.9 Results of the emission measurements of printed matter no. 8

Compound	µg/m^3 *			µg/printed matter			µg/kg printed matter		
Day	1	4	5	1	4	5	1	4	5
Toluene	19	18	28	13	11	18	59	50	80
Xylenes	<0.2								
C_9-C_{13} aliph. Hydrocarbons	<5	1103	564	<52	663	352	<12	3014	1598
C_{13}-C_{19} aliph. hydrocarbons	5128	8974	6154	3501	5397	3835	15915	24533	17433
Sum: charcoal/tenax	5147	10095	6476	3514	6071	4205	15974	27597	19111
Formaldehyde	0.33	<0.1	<0.1	8	5	5	35	21	25
Acetaldehyde	9	18	10	9	13	9	42	61	40
Acroleine	<0.03	-	-						
Propanal	3	13	1	1.2	7	0	6	31	-
Acetone	18	26	8	18	21	11	81	94	48
Butanal	1.3	4	2	1.1	3	1.5	5	13	7
Pentanal	1.8	7	2	1.8	5	1.6	8	23	7
Hexanal	59	107	12	43	66	10	193	302	43
Benzaldehyde	0	0	-	2.0	1.6	0.3	9	7	1.5
2-Butanone	0.8	1.8	-	0.5	1.1	-	2	5	-
Sum DNPH tube	93	177	35	84	122	37	381	556	174
Total VOC sum	5240	10273	6781	3598	6194	4242	16355	28153	19282

*: Emission measured from test sample of 37.7 g. The printed matter weighed 220 g.

-: below the detection limit or less than the background concentration in the laboratory

The emission of volatile organic compounds measured during 1 hour for printed matter no. 8 is presented in the table below. It is observed that the release from some of the compounds decreases with time, while others need a period before the release takes place (time-lag). The total emission of VOC decreases with time. For printed matter no.8 the emission peaked around day 4 and then decreases. The exact peak time can not be estimated from the measuring points. For printed matter no. 8 the emission half-life is 2 days if exponential decrease of emission after the peak is assumed. However, as the estimate is based on two measuring points the estimate should be used with reservation.

Table 3.10 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
1	3,589	16,355
4	6,194	28,153
5	4,242	19,282

Subjective evaluation of odour

The printed matter has an odour of oil (hydrocarbon). The odour intensity decreases with time.

3.1.4.5 Printed matter no. 17 (offset)

Measured concentrations and calculated values are presented in the table below.

Table 3.11 Results of emission measurements of printed matter no. 17

Compound	µg/m³ *			µg/printed matter			µg/kg printed matter		
Day	0	2	7	0	2	7	0	2	7
Toluene	44	16	19	20	8	10	135	56	70
Xylenes	28	22	19	13	11	10	88	73	68
Styrene	5	-	-	2			16		
C_9H_{12}, arom hydrocarbon	54	64	49	25	32	26	167	218	175
C_9H_{12}, arom hydrocarbon	28	28	26	13	14	14	88	96	92
C_8-C_{12}, aliph. Hydrocarbon	513	897	538	236	452	287	1592	3052	1938
C_{13}-C_{19}, aliph. Hydrocarbon	1359	1282	846	624	645	451	4218	4360	3046
Terpenes	177	164	128	81	83	68	549	558	462
C10 H12 O2	82	90	79	38	45	42	255	305	286
Sum: charcoal/tenax	2290	2564	1705	1052	1290	908	7106	8719	6138
Formaldehyde	8	4	5	9	7	9	58	50	59
Acetaldehyde	44	35	35	22	20	21	151	133	142
Acroleine	<0.03								
Propanal	139	166	152	63	83	80	427	560	541
Acetone	36	44	42	21	26	27	139	179	183
Butanal	13	17	18	8	9	10	41	50	67
Pentanal	29	61	65	14	31	35	93	211	236
Hexanal	211	502	548	98	254	294	664	1718	1984
Benzaldehyde	-	-	-	2	3	3	13	21	22
2-Butanone	7	6	7	3	3	4	21	22	24
Sum DNPH tube	487	835	872	238	437	482	1608	2952	3259
Total VOC sum	2777	3398	2577	1290	1727	1391	8714	11671	9397

*: Emission measured from test sample of 37.7 g. The printed matter weighed 148 g.
-: below the detection limit or less than the background concentration in the laboratory

The release of the volatile organic compounds measured over 1 hour for printed matter no. 17 is presented in the table below. It is observed that the release rate of some of the compounds decreases with time while others need time before the release takes place (time lag). In this printed matter it is also observed that several volatile organics increase their emissions during the first week (measuring period). It means that for this printed matter the total VOC emission increases, peaks on day 2 and then decreases at the final measuring period. The exact peak time can not be estimated from the measuring points. For printed matter no. 17, the half-life of emission is 15.5 days if exponential decrease after day 2 is assumed. However, as the estimate is based on two measuring points the estimate should be used with reservation.

Table 3.12 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
0	1,290	8,714
2	1,727	11,671
7	1,391	9,397

Subjective evaluation of the odour

The printed matter has a weak odour of oil (hydrocarbons). The odour intensity decreases with time.

3.1.4.6 *Printed matter no. 19 (offset))*

Measured concentrations and calculated values are presented in the table below.

Table 3.13 Results of emission measurement of printed matter no. 19

Compound	µg/m³ *			µg/printed matter			µg/kg printed matter		
Day	0	5	7	0	5	7	0	5	7
Toluene	14	33	9	2	8	1	27	131	22
Xylenes	21	14	17	2	3	3	38	55	45
C_8-C_{12}, aliph. hydrocarbons	11282	15897	13077	1240	3695	1971	21019	62626	33406
C_{13}-C_{19}, aliph. Hydrocarbons	12436	19744	15385	1367	4589	2319	23169	77778	39301
Sum: charcoal/tenax	23753	35688	28488	2611	8295	4294	44253	140590	72774
Formaldehyde	<0.1	3	4	1.3	3	2	17	54	38
Acetaldehyde	12	23	67	1.8	7	11	30	110	182
Acroleine	<0.03								
Propanal	2	110	283	0.01	25	42	1	427	719
Acetone	17	52	123	3	14	20	48	238	337
Butanal	-	37	92	-	9	14	-	147	236
Pentanal	7	179	596	0.9	42	90	15	708	1525
Hexanal	2	127	408	0.6	30	62	9	513	1049
Benzaldehyde	<0.1	<0.1	2	0.3	1.1	1.5	5	19	25
2-Butanone	156	191	123	17	44	19	290	752	315
Sum DNPH tube	196	722	1699	25	175	261	416	2968	4428
Total VOC sum	23949	36410	30186	2635	8470	4555	44669	143559	77202

*: Emission measured from test sample of 62.8 g. The printed matter weighed 59 g.
-: below the detection limit or less than the background concentration in the laboratory

The release of the volatile organic compounds measured over 1 hour for printed matter no. 19 is presented in the table below. It is observed as in the previous mentioned offset printed matters an increase in the release of some of the compounds. Especially the aldehydes are noted to increase during the measuring period. The total VOC emission has a peak at day 5. The exact peak time can not be estimated from the measuring points. The half-life of the total VOC emission is estimated to be 2.5 days assuming an exponential decrease after the second measurement. However, as the estimate is based on two measuring points the estimate should be used with reservation.

Table 3.14 Emission of VOC per hour at the three measuring times

Day	µg/ printed matter/ h	µg/kg printed matter/ h
1	2,635	44,669
5	8,470	143,558
7	4,555	77,202

The total amount of released VOC's is considerably higher than from printed matter no. 8 (approx. 4 times higher). This relationship is attributed to a significantly higher ink covering.

The ink covering is thus an essential factor for the emissions.

Subjective evaluation of the odour

The printed matter has a strong odour of oils (hydrocarbons). The odour intensity decreases with time.

4 Exposure and health evaluation

The human health evaluation is based on the dosis and thereby the exposure leading to a certain response. Dosis is an expression of the amount of chemical compound brought into the organism. Humans and animals are not always masters of the exposure they incur. This applies especially to chemical compounds exposed to either by inhalation or dermal contact. These two exposure routes are the most common in the working environment and to consumers. It is possible by measuring blood concentrations, urinary concentrations or the metabolism/elimination to get an impression of the exposure and uptake of the chemical compound. However, the concentration in air may also be used as a measure of the exposure. It is an approximate value because there is a certain proportionality between the concentration in the inhaled air and the amount of compound taken up by the lungs. Dosis may be expressed as the product of the concentration in air and the exposure time.

The exposure from volatile chemical compounds in printed matter is complicated by the fact that it is a mixed exposure and not exposure to single compounds. In the report it is attempted to use the same effect (irritation) and to assume that the effects from single chemical compounds are additive, i.e. the sum of the effect from single compounds are equal to the effects of the mixture.

Information has been available that certain printed matter release odour. Odour is an olfactory sensation (impression) that after affecting the olfactory epithelium in the nasal cavity is registered in the brain. Two receptor systems exist in the nasal cavity. One type is attached to special cells in the olfactory epithelium which send information to the brain via the brain nerve *Nervus olfactorius*. This receptor type is assumed to register common senses of odour, especially weak odours or odours of a pleasant character. Another type of receptors are attached to the nervous system *Nervus trigeminus* where the receptors react among others to pain, i.e. the strong irritating or burning odour characters. These receptors are reacting to the strong mucous membrane irritating substances as e.g. formaldehyde and acroleine (Mølhave 1980). The two receptor types contributes a variety of information, depending on the properties of the substance. The odour is an expression of the total impression. The perception vary strongly between individuals as strong, weak, unpleasant, pleasant etc. Even if odours sometimes may be used as warning signals reflecting the existence of a hazardous substance in the inhaled air, no general correlation between odour threshold and hazardous effects from chemical compounds has been proved (Hille 1977).

For some chemical compounds, a linear correlation exists between the logarithm to the intensity of the odour and the logarithm to the size of stimulus ("the psycho-physical law"):

$$I = k \times (C_i)^n \Rightarrow \log I = k \times \log C_i$$

where I is the intensity, C is a stimulus and n and k are constants describing a given stimulus-effect relationship.

The function will present a straight line when related values are placed in a double logarithmic co-ordinate system. This applies to e.g. the alcohols npropanol, n-butanol, n-hexanol and n-octanol (Cain 1969, Moskowitz *et al.* 1974). It means that a stronger odour often is correlated with a higher air concentration. Thus, the olfactory sensation is not entirely unimportant even it does not always tell you anything about potential health hazards.

Therefore, odour threshold values have been used in the assessment as a subjective evaluation whether it was likely that the substance could be sensed by odour. The threshold limit values have been used as basis for the evaluations. Primarily the threshold limit values for the working environment as set in Denmark by the National Labour Inspection (Arbejdstilsynet 2002). In a few cases limit values from other sources has been used, e.g. from Sweden (Arbetsskyddsstyrelsen 2002) or Germany (MAK 2000). Besides LCI-values are included in the evaluation. LCI ("Lowest Concentration of Interest") values were developed especially for the indoor environment and mainly based on irritation effects (EU 1997, Jensen *et al.*1999, Larsen *et al.* 1999). The methodology is described in section 4.2.

The air concentration and threshold limit values of a single compound is often expressed in ppm or mg/m^3 air. The correlation between the two abbreviations is (Arbejdstilsynet 2002):

$$mg / m^3 = \frac{Molecular\ weight}{24.45} \times ppm$$

In this report only mg/m^3 or µg/m^3 is used to avoid confusion.

4.1 Exposure scenarios

4.1.1 Method

The exposure varies according to consumption of printed matter, the room (size, etc) in which they are located, ventilation and the time of exposure (duration). For the evaluation of the exposure in a standardised matter, theoretical exposure scenarios have been developed to illustrate a reasonable worst case scenario.

4.1.2 Scenarios

For the evaluation of exposure during distribution (to distributors in shops and delivery persons, etc.) and handling by the consumers the below mentioned scenarios have been developed:

1. Direct exposure of distributors
The direct exposure during sorting and distribution in retail, to distributors, etc. is assumed to be analogous to the direct exposure when leafing through the printed matter, based on the larger amount of printed matter handled. The exposure is equivalent to the 2nd measurement (1 to 5 days after printing, however, for foreign printed matter approx. 10 days).

2. Direct exposure of the consumer
The direct exposure of the consumer is assumed to take place when the printed matter reaches the consumer and the consumer leaf through the printed matter.

The exposure is assumed to be equivalent to the 3rd measurement (2 to 15 days after printing).

3. "Indirect" exposure
The indirect exposure of the consumer is imagined as a hall scenario where the printed matter is located in an entrance hall. The exposure is estimated as the concentrations reached in a room of 10 m^3 with a ventilation of 0.5 times an hour. The concentration has been calculated for each compound and as a total VOC arising from each printed matter.

The potential concentrations is also estimated when the printed matter is leafed through in the living room. In the estimations are assumed a standard room of 50 m^3, i.e. 20 m^2 and 2.5 m to the ceiling and with an air shift of 0.5 times an hour.

Finally a scenario is used where the estimated concentrations that may be reached when the printed matter is laying untouched by the consumer in the entrance hall or living room is calculated.

4.2 Assessment method

4.2.1 Assessment method

For the chemical compounds observed to evaporate, it is evaluated which compounds that appeared to be the most serious by the Danish EPA. Data for each compound in relation to health hazard evaluation were searched in Danish and foreign monographs, databases etc. The retrieved data were compared to the estimated concentrations released from the printed matter in the scenarios.

The methodology used is approximately the same as recommended in connection to risk assessment in the European Union (EU) i.e. Technical Guidance Document (TGD 1996) and the revised version of TGD (Final draft, May 2002). In the TGD the potential risk is estimated as the ratio between the predicted environmental concentration (PEC) and the predicted no-effect concentration. The potential risk to humans is estimated as the ratio between PEC and the no-adverse-effect level (NOAEL), i.e. PEC/NOAEL. NOAEL is usually based on mammalian data other than human: typically rats, mice and rabbits. Therefore, safety factors are introduced to cover differences going from other animals to humans. This is expressed either by attaching a fixed safety factor (SF) or by expressing the margin of safety (MOS) which represents the distance of the estimated / measured concentration to the NOAEL. Typically MOS is preferred to be above 100.

The safety factor is interpreted as being a margin of safety applied to a no-observed-effect level to produce a value below which exposures are presumed to be safe. The SF is traditionally composed of a factor 10 for extrapolation between species (animal to human), a factor 10 to protect the most sensitive individuals of the population (e.g. children) and a third factor depending on the data and which may vary. For instance it is 10 if LOAEL (lowest observed adverse effect level) is used instead of NOAEL. The total safety factor is a result from multiplication of the three factors.

In environmental assessment is used an assessment factor (AF). They are applied to acute or chronic values based on the type and quality of data available. It is used to arrive at a concentration that, if equalled or exceeded, could cause adverse effects to the environment.

The effect level divided with the safety factors or the assessment factor are used in conjunction with the hazard assessment to derive concentrations of concern (concern level) and to provide a basis for further data retrieval.

Thus, one can choose to express concern level based on the ratio of the estimated concentration divided by the safe level (which is effect level divided by SF or AF) or MOS (humans).

In modern society many chemical compounds are used. It can be difficult for each consumer to keep track of them all. The management of chemical compounds are therefore regulated by an extensive chemical legislation. In relation to this project, no safe levels of chemicals have been developed if established threshold limit values developed by national or international experts existed.

The classification authorised in Denmark (Miljøministeriet 2002), which is an implementation of EU classification (28th amendment to EU directive 67/548/EEC), is used in the evaluation. For the evaluation of each compound is used the threshold limit values obligatory for the working environment in Denmark (Arbejdstilsynet 2002) applied with a safety factor of 100. The safety factor is derived by recalculating threshold limit value from the working environment based on 8 hours per day for 5 days a week to indoor values at 24 hours a day for 7 days a week (24/8×7/5=4.2), applying an extra safety factor of 10 for sensitive individuals and an extra factor of 2: a total of 100. This means that a safety margin of 100 is used.

In the tables below is mentioned a value as TLV/100 where TLV ("Threshold Limit Value") is the threshold limit value adopted by the National Labour Inspection: NLI (Arbejdstilsynet) or equivalent from other countries when no Danish value existed. TLV from the NLI is only applicable to facilities where the chemical compound is used in production (e.g. printing houses and -works). The threshold limit values are based on 8 hour time weighted average (TWA). For a shorter period these values may be exceeded at a maximum of a factor 2 (Arbejdstilsynet 2002). For distributors, a value of 1/10 of TLV may be used. However, as distributors also may include children it was decided to use the same evaluation value, i.e.TLV/100, as for consumers in this report.

Another concept of health assessment included was LCI. Volatile concentrations calculated from concentrations in the glass container to estimated exposure indoor concentrations were compared to the toxicologically derived Lowest Concentration of Interest (LCI).

LCI is defined as the lowest concentration of a certain substance, which according to our present knowledge at continued exposure in the indoor air will not cause damaging impact on humans (EU 1997, Larsen *et al.* 1999). *It should be noted that LCI-values are weighing factors indicating the relative hazard of substances and not a criteria for indoor air quality or a fixed threshold limit value.*

For most of the chemical substances the LCI values are based on irritation. Deviations are mentioned in the substance assessment. More serious effects may appear for most substances at concentrations considerably higher than the level of irritation.

Irritation was the most frequently met toxicological effect for the observed volatile compounds from printed matter.

The derivation of LCI values were difficult due to a lack of toxicological data on some of the volatile organic compounds observed at low concentrations. Therefore, the LCI values used are the values derived in Jensen *et al.* (1999) and EU (1997).

4.2.2 Procedure for assessments

Evaluations have been performed for the selected organic chemicals and printed matter. The evaluations of printed matter are based on measured and calculated concentrations of each substance in air and in the printed matter.

Effect level

The effect level for each printed matter is based on the evaluation of each compound. The established Danish threshold limit values are used if existing. If no Danish values are found, values from similar projects are used (Larsen *et al.* 1999, Jensen *et al.* 1999a, 1999b) or other national/international recommended values.

The used threshold limit values for the measured substances are presented in Appendix 3 together with the classification.

The indoor air quality depends of several factors (ventilation, temperature, etc.) and other sources. In this report only the contribution from printed matter is considered but it should be noted that other sources to the same chemical compound may exist in the consumers resident (e.g. volatiles from paint, lacquers, carpets, etc.).

The exposure of the consumer in the home is besides the concentration in the indoor air also dependent on the exposure duration. Because the exposure duration may vary considerably, a maximal exposure of 24 hours is assumed. However, the ventilation is included using an assumed air change in the indoor scenarios of 0.5 times per hour, i.e. 50% of the air is exchanged every hour.

Observed compounds groups

The major groups of compounds have been aldehydes, aliphatic and aromatic hydrocarbons, and terpenes.

Aldehydes are volatile organic compounds characterised by their irritative properties. Aldehydes irritate skin, eyes and upper respiratory system. Especially the lower aliphatic aldehydes and unsaturated aldehydes are irritants (Jensen *et al.* 1999, Larsen *et al.* 1999a, b).

5 Evaluation of individual compounds

A number of compounds were selected for further study. Included are:

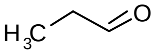
Aldehydes	Propanal
	Pentanal
	Hexanal
	Heptanal
Aliphatic alcohols	2-Ethyl-1-hexanol
Ketone	2-Heptanone
Ester	Propanoic acid butylester
Furan	Pentylfuran
Aromatic hydrocarbons	Toluene
	Xylenes, ethylbenzene
Terpenes	*alpha*-Pinene
	Camphene
	D-limonene
	decahydro-(1,5,5,8a)-tetramethyl-1,2,4-methanoazulene

5.1 Aldehydes

Aldehydes are typically volatile organic compounds characterised by their irritative properties. Aldehydes irritate skin, eyes and the upper respiratory tract. The low molecular weight aldehydes, the halogenated aliphatic aldehydes, and the unsaturated aldehydes are particularly irritating. The mucous membranes of the nasal and oral passages and the upper respiratory tract are affected, producing a burning sensation, an increased ventilation rate, bronchial constriction, choking, and coughing. The eyes tear, and a burning sensation is noted on the skin of the face. During low exposures, the initial discomfort may abate after 5 to 10 minutes but will recur if exposure is resumed after an interruption (Clayton and Clayton 1981)

5.1.1 Propanal

Identification:

Name	Propanal
CAS no.	123-38-6
EINECS no.	204-623-0
Molecular formula	$C_3 H_6 O$
Molecular structure	
Molecular weight	58.08 g/mol
Synonyms	propionic aldehyde methylacetaldehyde

The melting point is -81°C. The boiling point is 49°C. The vapour pressure is 42256 Pa at 25°C (317 mmHg) (Budavari 1996). The water solubility is 306 g/l (Riddick *et al.* 1985). The octanol/water distribution coefficient log Kow is experimentally determined to 0.59 (Hansch *et al.* 1995).

Environment
With a high vapour pressure propanal is expected to evaporate from printed matter.

The potential of propanal to bioaccumulate is estimated to be low based on a bioaccumulation factor (BCF) 3.1 for fish estimated from log Kow.

Propanal is considered ready biodegradable in sewage treatment plants. Propanal is degraded by photochemical degradation in the atmosphere at an estimated half-life of 20 hours.

Health
Propanal irritates the respiratory system, eyes and the skin (Larsen *et al.* 1999). Selected effect concentrations are mentioned below.

Acute toxicity:

Acute oral, rat	LD_{50}	800-1600 mg/kg	Verschueren 1983
	LD_{lo}	3400 mg/kg	Larsen *et al.* 1999
Acute dermal, rabbit	LD_{50}	5040 mg/kg	Lewis 1996
	LD_{lo}	3400 mg/kg	Larsen *et al.* 1999
Acute inhalation, rat	LC_{50} (½ h)	61800 mg/m^3 (26000 ppm)	Verschueren 1983
Acute inhalation, mouse	LC_{50} (2 h)	21800 mg/m^3	Lewis 1996
Respiratory irritation, mouse	RD_{50}	5730 mg/m^3	VOCBASE 1996
Eye irritation, rabbit	severe effect	41 mg/eye	NIEHS

Classification
Propanal is adopted on the List of dangerous substances and classified under EU index no. 605-018-00-8 (List of dangerous substances, Miljøministeriet 2002):

F;R11	Highly flammable
Xi;R36/37/38	Irritant. Irritating to eyes, respiratory system and skin

Threshold limit values
A Danish threshold level value was not found and, therefore, an American value is used instead: TLV (TWA): 20 ppm corresponding to 47.5 mg/m^3 (ACGIH 2001).
LCI value 4.3 mg/m^3 is based on respiratory irritation in mouse (RD_{50}×0.03/40) (Larsen *et al.* 1999).
Odour threshold: 14 µg/m^3 (Larsen *et al.* 1999)

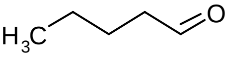
Conclusion
The odour threshold is low and propanal is a substance that may be sensed at low concentrations. At measured emissions up to 719 µg/kg printed matter and estimated consumer exposure concentrations up to 21 µg/m^3 propanal may be smelled at direct exposure (leaf through) of printed matter. The highest exposure concentrations were measured from offset printed matter (40 µg/m^3 in no. 17 and 21 µg/m^3 in no. 19, cf. table 6.5 and 6.6, respectively). The TLV/100 and LCI were not exceeded and thus propanal is not considered likely to cause health problems at the measured concentrations. The odour

however may be considered unpleasant to some consumers even though the irritation threshold value is 4300 µg/m^3 (LCI value, Larsen *et al.* 1999).

For exposure in rooms the largest estimated value was 3.8 µg/m^3 in the "worst case" entrance hall. Based on the two room scenarios the estimated concentrations varied between 0.3 and 3.8 µg/m^3 (Table 6.7) leafing through the printed matters is not considered a potential health problem and the values to be below the odour threshold.

5.1.2 Pentanal

Identification

Name	Pentanal
CAS no.	110-62-3
EINECS no.	203-784-4
Molecular formula	$C_5 H_{10} O$
Molecular structure	
Molecular weight	86.13 g/mol
Synonyms	*n*-Pentanal Valeral *n*-Valeraldehyd

The melting point is -91,5°C. The boiling point is 103°C (Budavari 1996). The vapour pressure is 3466 Pa at 20°C (26 mmHg) (ACGIH 1991). The water solubility is 11700 mg/l at 20°C (Yalkowsky and Dannenfelser 1992). The octanol/water distribution coefficient log Kow is estimated to 1.31 (QSAR).

Environment

Pentanal is ready biodegradable. Pentanal has a low estimated BCF and is not expected to bioaccumulate. Pentanal has a high vapour pressure and a low adsorption coefficient. Thus pentanal is expected to evaporate. Pentanal may undergo photochemical degradation in the atmosphere at an estimated half-life of 13.5 hours.

Ecotoxicity data:

Fish	*Pimephales promelas* (fathead minnow)	LD_{50} (96 h)	12.4 mg/l	(Geiger *et al.*1985)

Health

Pentanal is an irritant. Pentanal irritates skin, eyes and the respiratory system. Pentanal is characterised in Larsen *et al.* (1999) as a moderately skin irritant, however, severe eye irritation was observed in rabbits. Selected data presented below.

Acute toxicity:

Acute oral, rat	LD_{50}	3200 mg/kg	Sax 1984
Acute dermal, rabbit	LD_{50}	4857 mg/kg	Lewis 1992
Acute inhalation rat	LC_{lo} (4 h)	14090 mg/m^3 (4000 ppm)	ACGIH 1991
Irritation, mouse	RD_{50} (10 min)	4140 mg/m^3 (1120 ppm)	Steinhagen and Barros 1984
Eye irritation	severe effect	1 drop, 100%, 24 h obs.	NIOSH

Classification

Pentanal is not classified.

Threshold limit values

TLV: 50 ppm corresponding to 175 mg/m^3 (Arbejdstilsynet 2002).

TLV: 8 hr Time Weighted Average (TWA) 50 ppm corresponding to 175 mg/m^3. (ACGIH 1991, 2002).

LCI value is 3100 µg/m^3 based on on respiratory irritation in mouse (RD_{50}×0.03/40) (Larsen *et al.* 1999).

Odour threshold limit is 22 µg/m^3 (Larsen *et al.* 1999).

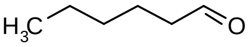
Conclusion

The odour threshold is low and pentanal may be sensed at low concentrations. At measured emissions up to 1525 µg/kg printed matter, pentanal can be smelled at direct exposure during leaf through of printed matter. The highest exposure concentrations were found from offset printed matter (45 µg/m^3 in no. 19 and 17.5 µg/m^3 in no. 17, cf. table 6.6 and 6.5, respectively) after 7 days when the printed matter reaches the consumer. It is noted that the concentrations increased during the study period in two offset printed matter No. 17 and 19, respectively (cf. table 3.11 and 3.13), indicating that the substance had been adsorbed into the paper and released later in the use phase. The TLV/100 and LCI were not exceeded and pentanal is therefore not considered to pose any health problem at the measured concentration.

For exposure in rooms the largest estimated value was 1.1 µg/m^3 in the "worst case" entrance hall. Based on the two room scenarios the estimated concentrations vary between 0.2 and 1.1 µg/m^3 (Table 6.7), leafing through the printed matters is not considered a potential health problem and the values to be below the odour threshold.

5.1.3 Hexanal

Identification

Name	Hexanal
CAS no.	66-25-1
EINECS no.	200-624-5
Molecular formula	$C_6\,H_{12}\,O$
Molecular structure	
Molecular weight	100.18 g/mol
Synonyms	Hexaldehyd Hexylaldehyd Caproaldehyd Caproic aldehyde

The melting point is -56°C. The boiling point is 131°C (Budavari 1996). The vapour pressure is 1506 Pa at 25°C (11.3 mmHg) (Daubert and Danner 1989). The water solubility is 5640 mg/l at 20°C (Davis 1968, Ullmann A1 1985). The octanol/water distribution coefficient log Kow is experimentally measured to 1.78 (Hansch *et al.* 1995).

Environment

Hexanal has a high vapour pressure and is expected to evaporate from dry surfaces. Hexanal has an experimental Henry's Law constant (H) of 2.13 x 10^{-4} atm m^3/mol and is therefore expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 221 indicating that a moderate adsorption to suspended matter (dust) may be expected. Hexanal can undergo photochemical degradation in the atmosphere at an estimated half-life of 13 hours.

Hexanal is expected to be ready biodegradable, which is based on analogous substances with linear carbon chain. Based on a low BCF of 13, bioaccumulation is not expected.

Health
Hexanal irritates respiratory system, skin and eyes (Grant 1986, Larsen *et al.* 1999), cf. selected values below.

Acute toxicity:

Acute oral, rat	LD_{50}	3200 mg/kg	Lewis 1992
Acute dermal, rabbit	LD_{50}	10 mg/kg	Lewis 1992
Acute inhalation, rat	LC_{lo} (4 h)	2000 ppm (8200 mg/m^3)	Clayton and Clayton 1981
Irritation, mouse	RD_{50} (10 min)	4470 mg/m^3	Steinhagen and Barros 1984

Classification
Hexanal is not classified.

Threshold limit values
TLV (TWA): 50 ppm corresponding to 175 mg/m^3 (NIOSH 1997).
LCI value is calculated to 3.4 mg/m^3 based on on respiratory irritation in mouse (RD_{50}×0.03/40) (Larsen *et al.* 1999).
Odour threshold is 58 µg/m^3 (Larsen *et al.* 1999).

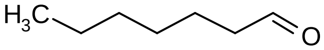
Conclusion
The odour threshold is low and hexanal may be sensed at low concentrations. At measured emissions up to 1984 µg/kg printed matter, hexanal may be smelled at direct exposure during leaf through. The two highest exposure concentrations of hexanal were found from offset printed matter (147 µg/m^3 in no. 17 and 31 µg/m^3 in no. 19, cf. table 6.5 and 6.6, respectively) after 7 days, i.e. when the printed matter reach the consumer. It is noted that concentrations increased during the study period (cf. printed matter no. 17 and 19, table 3.11 and 3.13, respectively) indicating that the substances may have been adsorbed into the paper and released later in the use phase. The TLV/100 and LCI were not exceeded and hexanal is considered not to be a health problem at the measured concentrations.

For exposure in rooms the highest estimated value was 10.5 µg/m^3 in the "worst case" entrance hall. Based on the two room scenarios the estimated concentrations vary between 1 and 10 µg/m^3 (Table 6.7), leafing through the printed matters is not considered a potential health problem and the values to be below the odour threshold.

5.1.4 Heptanal

Identification

Name	Heptanal
CAS no.	111-71-7
EINECS no.	203-898-4

Molecular formula	$C_7 H_{14} O$
Molecular structure	
Molecular weight	114.19 g/mol
Synonyms	Heptaldehyd Heptylaldehyd Enanthaldehyd Oenanthaldehyde

The melting point is -53,3°C. The boiling point is 152,8°C (Budavari 1996). The vapour pressure is 469 Pa at 25°C (3.52 mmHg) (Daubert and Danner 1989). The water solubility is 1250 mg/l at 25°C. The octanol/water distribution coefficient log Kow is estimated to 2.29 (Hansch *et al*. 1995).

Environment

Heptanal has a high vapour pressure and can be expected to evaporate from dry surfaces. Heptanal has an experimental Henry's Law constant (H) of 2.7×10^{-4} atm m^3/mol and therefore expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 32 indicating a low adsorption to suspended matter. Heptanal can degrade photochemically in the atmosphere with an estimated half-life of 13 hours.

Based on analogous substances, heptanal is expected to be ready biodegradable. Hexanal is not expected to bioaccumulated based on an estimated BCF of 32.

Health

Heptanal irritates skin, eyes and respiratory system as most aldehydes (Clayton and Clayton 1981). In a dermal sensitisation test on 18 rabbits using 0.1 ml applied on skin, 4 animals showed positive response after 24 hours and 3 animals a positive response after 48 hours (HSDB 2002).

Acute toxicity:

Acute oral, rat	LD_{50}	14000 mg/kg	Lewis 1992
Acute oral, mouse	LD_{50}	25000 mg/kg	Clayton and Clayton 1981

Classification

Heptanal is not classified.

Threshold limit values

TLV has not been found but based on analogous substances estimated to be 175 mg/m^3.

LCI is 3100 µg/m^3. The LCI value refers to the sensory irritation of saturated aldehydes and corresponds to the value of pentanal (cf. 5.1.2). (Larsen *et al.* 1999).

Odour threshold is 23 µg/m^3 (Larsen *et al.* 1999).

Conclusion

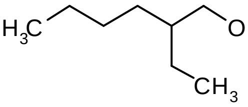
The odour threshold is low and heptanal may be possible to be smelled at low concentrations. Heptanal was found in the screening analysis but not in the quantitative analysis. Thus, the contribution to VOC can not be evaluated.

5.2 Alcohols

Alcohols are generally organic compounds characterised by rather low acute toxicity in single-dose oral toxicity experiments. Repeated or prolonged exposure to alcohols may lead to depression of the central nervous system (narcotic action). Alcohol vapours are characterised by their irritative properties to the eyes and mucous membranes in the respiratory tract (Larsen *et al.* 1999).

5.2.1 2-Ethyl-1-hexanol

Identification

Name	2-Ethyl-1-hexanol
CAS no.	104-76-7
EINECS no.	203-234-3
Molecular formula	$C_8 H_{18} O$
Molecular structure	
Molecular weight	130.23 g/mol
Synonyms	2-ethylhexan-1-ol Ethylhexanol

The melting point is -70°C. The boiling point is 184.6°C (Budavari 1996). The vapour pressure is 18.13 Pa at 25°C (0.136 mmHg) (Daubert and Danner 1989). The water solubility is 880 mg/l at 25°C (HSDB 2002). The octanol/water distribution coefficient log Kow is estimated to 2.73 (Hansch *et al*. 1995).

Environment

Ethyl-1-hexanol has a high vapour pressure and, thus, is expected to evaporate from dry surfaces. Ethylhexanol has an estimated Henry's Law constant (H) of 2.7×10^{-5} atm m^3/mol and is therefore expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 105 indicating some adsorption to suspended matter. Ethylhexanol can undergo photochemical degradation in the atmosphere at an estimated half-life of 1.2 days.

Ethylhexanol is ready biodegradable in screening tests (MITI). Bioaccumulation is not expected based on a low BCF of 13.

Health

Ethylhexanol is moderately skin irritant and slightly toxic at oral administration. Irritation of eyes and upper respiratory tract is also observed (Gosselin *et al.* 1976, Grant 1986, Wolkoff and Nielsen 1996). Selected effect data presented below.

Acute toxicity:

Acute oral, rat	LD_{50}	1246 ml/kg	Budavari 1996
Acute dermal, rabbit	LD_{50}	1986 mg/kg	WHO 1993
Acute inhalation, rat	LC_{50} (6 t)	>227 ppm (>1210 mg/m^3)	WHO 1993
Eye irritation, rabbit	severe effect	4.16 mg	HSDB 2002
Mucous irritation, mouse	RD_{50}	240 mg/m^3	VOCBASE 1996

Classification

2-Ethylhexanol is not classified.

Threshold limit values

No Danish TLV was found. Therefore, a German equivalent value was used: MAK 50 ppm corresponding to 270 mg/m^3 (Maksimaler Arbeitsplatz Konzentration, MAK 2000)
LCI value is 1000 µg/m^3 based on expert evaluation (EU 1997).
An indoor comfort value at 1750 µg/m^3 was found with the notion that the compound is an irritant to the mucous membrane (Wolkoff and Nielsen 1996).

Conclusion

2-Ethylhexanol is used as a solvent in inks, resin and oils. 2-Ethylhexanol is one of many alcohols observed in the volatilised compounds from flexographic printing.

The odour threshold has not been found but estimated to be about 14-20 µg/m^3 as for analogous alcohols: Ethylhexanol may therefore be sensed at low concentrations. At measured emissions up to 491 and 105 µg/kg printed matter after 5 and 7 days, respectively. The exposure concentrations were estimated to 0.2 µg/m^3 after day 5 from printed matter no. 4 (table 3.7). 2-Ethylhexanol may be smelled by the distributor but hardly by the consumer. 2-Ethylhexanol will probably be inseparable from most alcohols to most humans. The measured concentrations were below MAK/100 (assumed equal to TLV/100) and the LCI value (cf. table 6.3). 2-Ethylhexanol is therefore not considered to be a health problem at the measured concentrations.

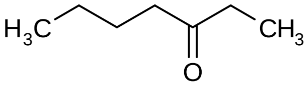
2-Ethylhexanol was not included in the hall and living room scenario but considering the dilution the compound is unlikely to be smelled or present any nuisance.

5.3 Ketones

Ketones can act on the central and peripheral nervous system, respiratory system, and kidney and liver function. Some ketones are neurotoxic, e.g. methylethylketone. Ketones are generally irritating to the eyes and respiratory system.

5.3.1 Heptanone

Identification

Name	3-Heptanone
CAS no.	106-35-4
EINECS no.	203-388-1
Molecular formula	$C_7 H_{14} O$
Molecular structure	
Molecular weight	114.19 g/mol
Synonyms	Heptan-3-one Butyl ethyl ketone Ethylbutylketone

The melting point is -39°C. The boiling point is 147°C (Budavari 1996). The vapour pressure is 347 Pa at 25°C (2.6 mmHg) (Daubert and Danner 1993). The water solubility is 4300 mg/l at 20°C (HSDB 2002). The octanol/water distribution coefficient log Kow is estimated to 1.73 (Hansch *et al*. 1995).

Environment

3-Heptanone has a high vapour pressure and can be expected to evaporate from dry surfaces. Heptanone has an experimental Henry's Law constant (H) of 9.08 x10^{-5} atm m^3/mol (Daubert and Danner 1993) and is therefore expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to be 25 and a low adsorption to suspended matter is expected. Heptanone may undergo photochemical degradation in the atmosphere at an estimated half-life of 16 hours.

3-Heptanone is ready biodegradable in aerobic screening tests (MITI). Bioaccumulation is not expected based on a BCF of 4.

Health

3-Heptanone is a moderate skin irritant and slightly toxic by oral administration (Clayton and Clayton 1981). Irritation of eyes and respiratory tract is also noted (Gosselin *et al.* 1976, Grant 1986), cf. effect levels below.

Acute toxicity:

Acute oral, rat	LD_{50}	2760 mg/kg	ACGIH 1986
Acute dermal, rabbit	LD_{50}	> 20 ml/kg	ACGIH 1986
Acute inhalation, rat	LC_{50} (6 t)	2000 ppm: none died 4000 ppm: all died	ACGIH 1986
Eye irritation, rabbit	mild, 3*	1 drop, 100%	ACGIH 1986
Skin irritation, rabbit	mild	applied undiluted on skin	Clayton and Clayton 1981

*: rate 3 out of 10 where 10 indicate most severe injuries

Classification

3-Heptanone is adopted on the List of dangerous substances and classified under EU index no. 606-003-00-9 (Miljøministeriet 2002):

R10	Flammable
Xn;R20	Harmful. Harmful by inhalation
Xi;R36	Irritant. Irritating to eyes

Threshold limit values

TLV: 50 ppm corresponding to 238 mg/m^3 (Arbejdstilsynet 2002).
LCI value: 2300 µg/m^3. The LCI value is based on the assumption that the effects of 2-hexanone is comparable to those of 3-heptanone, i.e. sensory irritation RD_{50}×0.03/40 (Larsen *et al.* 1999).
Odour threshold: no value found. The odour threshold is 680 µg/m^3 for 2-heptanone.

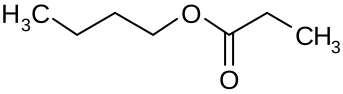
Conclusion

3-Heptanone is used as solvent in lacquers and resins. 3-Heptanone was observed in the screening analysis but not in the quantitative analysis. By comparison of the area percentages from the chromatograms in the screening analysis with area percentages and concentration of other compounds there is no indications that the TLV/100 and LCI value would be exceeded.

5.4 Esters

5.4.1 Propanoic acid, butylester

Identification

Name	Propanoic acid, butylester
CAS no.	590-01-2
EINECS no.	209-669-5
Molecular formula	$C_7 H_{14} O_2$
Molecular structure	
Molecular weight	130.19 g/mol
Synonyms	n-Butyl propionat

The melting point is -89°C. The boiling point is 146.8°C (Budavari 1996). The vapour pressure is measured to 589 Pa at 25°C (4.42 mmHg) (Yaws 1994). The water solubility is 1500 mg/l at 25°C (Yalkowsky and Dannenfelser 1992). The octanol/water distribution coefficient log Kow is estimated to 2.3.

Environment
Propanoic acid butylester has an estimated vapour pressure high enough to indicate that the compound may evaporate from dry surfaces. Propanoic acid butylester has an estimated Henry's Law constant (H) of 5 x 10^{-4} atm m^3/mol at 25°C (Syracuse) and may therefore be expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 40 indicating a low adsorption to suspended matter. Propanoic acid butylester may undergo photochemical degradation in the atmosphere with a half-life of 2 days.

Propanoic acid butylester is ready biodegradable based on model estimates (BIOWIN and MITI). The bioaccumulation is estimated to be low based on an estimated BCF of 12.

QSAR estimates indicate that the compound is toxic to aquatic organisms with estimated EC_{50} values between 1 and 50 mg/l.

Health
Propanoic acid butylester is adopted on the list of dangerous substances but further information has not been available. From the safety data sheet is noted that ”Butyl propionate can affect you when breathed in. Butyl propionate can irritate the eyes and skin on contact. Breathing butyl propionate can irritate the nose and throat. No information on exposure concentrations is presented. The substance is flammable but not else classified.

Classification
Propanoic acid butylester is adopted on the List of dangerous substances and classified under EU index no. 607-029-00-3 (Miljøministeriet 2002):

R10	Flammable

The EU index number 607-029-00-3 covers the group "Butylpropionate" which covers both linear butylester and branched C_4 compounds (Miljøministeriet 2002).

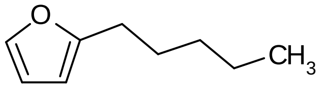
Conclusion

Propanoic acid butylester was observed in printed matter no. 4 but the concentration was below the background concentration. The contribution to VOC could not be evaluated.

5.5 Furan

5.5.1 2-Pentylfuran

Identification

Name	2-Pentylfuran
CAS no.	3777-69-3
EINECS no.	223-234-7
Molecular formula	$C_9 H_{14} O$
Molecular structure	
Molecular weight	138.21 g/mol
Synonyms	2-Amylfuran

The melting point is estimated to -19°C. The boiling point is estimated to 175°C (QSAR). The vapour pressure is estimated to 160 Pa at 25°C (1.2 mmHg) (QSAR). The water solubility is estimated to 42 mg/l at 25°C (QSAR). The octanol/water distribution coefficient log Kow is estimated to 3.87 (QSAR).

Environment

Pentylfuran has an estimated vapour pressure that is high enough to indicate that evaporation from dry surfaces can be expected. Pentylfuran has an estimated Henry's Law constant (H) of 0.02 atm m^3/mol at 25°C (Syracuse) and can be expected to evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 1760 indicating a high adsorption to suspended matter. Pentylfuran can be photochemically biodegraded in the atmosphere at an estimated half-life of <1 day.

Pentylfuran is estimated to be ready biodegradable based on model estimations (QSAR). The bioaccumulation is expected low based on an estimated BCF of 192.

QSAR estimates indicate that the compound is toxic to aquatic organisms with estimated EC_{50} values between 1 and 10 mg/l (QSAR)

Health

No relevant information on pentylfuran has been found.

If assuming furan (CAS. No.: 110-00-9) is the most reactive part of the molecule a relevant data on mouse may be used:

Acute inhalation, mouse LC_{50} (1 h) 120 mg/m^3 (Lewis 1996).

Using the method applied in Larsen *et al.* (1999) this would result in a LCI (RD_{50} x 0.03/40=) 0.09 mg/m^3.

Furan is toxic by inhalation and may penetrate skin.

For furfural (furanaldehyd) CAS. no.: 98-01-1, comparative studies have been found with higher values (i.e. less toxic than furan):

Acute inhalation, rat	LC_{50} (4 h)	601 mg/m^3 (153 ppm)	Lewis 1996
Acute inhalation, mouse	LC_{lo}	1454 mg/m^3 (370 ppm)	Lewis 1996

Classification

Pentylfuran is not classified. 2-Pentylfuran is adopted on the Danish EPA self-classification list and suggested classified:

N;R50/53	Dangerous for the environment. Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Conclusion

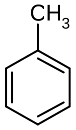
Pentylfuran was observed in the screening analysis but not in the quantitative analyses. An evaluation of the VOC contribution could therefore not be performed.

5.6 Aromatic hydrocarbons

The aromatic hydrocarbons are primary skin irritants and repeated or prolonged skin contact may cause dermatitis. Eye contact may cause lacrymation and irritation.

5.6.1 Toluene

Identification

Name	Toluene
CAS no.	108-88-3
EINECS no.	203-625-9
Molecular formula	$C_7 H_8$
Molecular structure	
Molecular weight	92.15 g/mol
Synonyms	methylbenzene phenylmethane

The melting point is -95°C. The boiling point is 111°C. The vapour pressure is 3800 Pa at 25°C. The water solubility is 515 mg/l (ECB 2001). The octanol/water distribution coefficient log Kow is measured to 2.65.

The adsorption of toluene is estimated to be moderate based on measured adsorption coefficient Koc from 37 to 160. Based on the high vapour pressure, toluene is estimated to evaporate from dry surfaces.

Environment

Toluene is toxic to aquatic organisms, ready biodegradable and not bioaccumulating.

Below is presented the lowest data on acute toxicity to aquatic organisms (ECB 2001).

	Species	Effect	Concentration (mg/l)	Reference
Acute data				
Fish	Oncorhynchus kisutch (Coho laks)	LC_{50} (96 h)	5.5	Moles et al. 1981
Dafnia	Ceriodaphnia dubia	LC_{50} (48 h)	3.8	Niederlehner et al. 1998
Algae	Clamydomonas angulosa	E_bC_{50} (96 h)	134	Hutchinson et al. 1980
Chronic data				
Fish	Oncorhynchus mykiss (regnbueørred)	NOEC	1.4	WRc 1998
Dafnia	Ceriodaphnia dubia	NOEC (21 d)	0.74	Niederlehner et al. 1998
Algae	Skeletonema capricornutum	NOEC (72 h)	10	Heijden et al. 1988

After production, i.e. during use and disposal, the most significant emission of toluene to the environment from printed matter is to the air. However, it is considered that the contribution from printed matter during these life-cycle phases is small compared to the contribution of toluene from other sources such as combustion of oil and gasoline. The contribution to the total load can not be estimated because of lack of data..

Health

Toluene is a skin irritant and harmful. Toluene is under suspicion of being repro-toxic, i.e. with a possible risk of harm to the unborn child.

Acute toxicity (several acute data are available, only a few is mentioned):

Acute oral, rat	LD_{50}	5500 mg/kg	Kimura *et al.* 1971
Acute dermal, rabbit	LD_{50}	12400 mg/kg	Smyth *et al.* 1969
Acute inhalation, rat	LC_{50} (6 h)	22 mg/l (22 g/m^3)	Bonnet *et al.* 1982
Acute inhalation, mouse	LC_0 (6 h)	24 mg/l (24 g/m^3)	Bonnet *et al.* 1982

The acute oral toxicity is 5500-7500 mg/kg based on LD_{50} values.
The acute dermal toxicity is low and above 12000 mg/kg. The values indicate that skin contact to printed matter is not considered to be significantly acute harmful.

Data on acute toxicity by inhalation is 22 - 24 g/m^3, which is highly above the exposure concentration measured from printed matter and therefore indicate no cause for concern. On the other hand it is noted that toluene at low concentrations, from 285 mg/m^3, may cause headaches, dizziness, irritation and sleepiness.

An inhalation value for human with a TC_{lo} 25 mg/m^3 has been found (Lewis and Sweet 1984, US-NTP 2002).

Long-term effects

Toluene is recommended classified as reprotoxic category 3 (29th ATP, cf. below), i.e. indications have been observed of possible risk of harm to the unborn child. Indication on repeated contact may cause allergic contact dermatitis has also been observed.

Absorption via gastro-intestinal tract is quick and almost complete. In rabbits orally exposed, the absorption was 100% (EU-RAR 2001).

In studies on dermal exposure the fraction of penetration was low. However dermal uptake may take place. For instance, the workers in the rotogravure industry are recommended to wear gloves at where potential exposure to toluene exists. Dermal uptake from exposure to toluene vapours is measured to approx. 1% of the inhaled toluene by exposure to the same concentrations (Riihimäki and Pfäffli 1978, Piotrowski 1967).

Uptake via inhalation is studied in humans. The uptake after 3 hours of exposure when at rest was approx. 50% of the inhaled amount of toluene. During work the uptake may be significantly higher. It was concluded that toluene is fast taken up by inhalation and that the amount depended on the respiration rate.

A 90-day rat oral NOAEL of 625 mg/kg/day, and a two-year rat inhalatory NOAEC of 300 ppm (1125 mg/m^3) is found (EU-RAR 2001).

In humans experimentally exposed to toluene, concentrations at and above 75 ppm (285 mg/m^3) caused headache, dizziness, and feeling of intoxication, irritation and sleepiness. A NOAEC of 40 ppm (150 mg/m^3) for these effects has been identified (EU-RAR 2001).

Classification

Toluene is adopted on the list of dangerous substances and classified under EU index no. 601-021-00-3 (Miljøministeriet 2002):

F;R11	Highly flammable
Xn;R20	Harmful. Harmful by inhalation

The classification is more severe after the risk assessment (ECB). Toluene has been adopted on the 29. revised list, i.e. not notified until published in the Official Journal as an official amendment to the directive on classification of dangerous substances:

F; R11	*Highly flammable*
Repr.Cat.3; R63	*Possible risk of harm to the unborn child*
Xn; R48/20-65	*Harmful. Danger of serious damage to health by prolonged exposure through inhalation. May cause lung damage if swallowed*
Xi; R38	*Irritant. Irritating to skin*
R67	*Vapours may cause drowsiness and dizziness*

Threshold limit values

TLV: 94 mg/m^3 corresponding to 25 ppm (Arbejdstilsynet 2002).
LCI: 400 µg/m^3 based on C-value (Larsen *et al.* 1999).
Odour threshold: 7.6 mg/m^3 (Matzke 1993).

Conclusion

In the printing ink industry, toluene is used primarily as solvent during the use and production of printing inks. Toluene was found in all printed matter. The emission to the air during reading/leaf through the printed matter was measured to vary between 73 and 272 mg/kg printed matter when the printed matter reaches the consumer. The highest concentration was observed in rotogravure printed matter where toluene was the dominant VOC.

The odour threshold is relatively high: 7.6 mg/m^3. Toluene can therefore not be smelled at low concentrations. However, at estimated concentrations up to 23 mg/m^3 toluene can be smelled at direct exposure when leaf through of printed matter occur. The two highest concentrations evaporated from rotogravure printed matter (23 mg/m^3 from no. 2 and 6 mg/m^3 from no. 3) after 2 and 15 days, respectively, or when the printed matter has reached the consumer. It is noted that the concentrations decrease during the measuring period (table 3.3 and 3.5). It indicates that the lower concentration from the foreign printed matter is due to the longer period available for evaporation. The measured concentrations indicate that the consumer by handling/leaf through of the printed matter will be able to smell the toluene for a period in the home.

The TLV/100 and LCI were exceeded in the leaf through scenario (table 6.1. and 6.2. The toluene exposure is therefore assessed by comparison to the NOAEC value 150 mg/m^3. The margin of safety (MOS) varied between 2 and 6 which is considered low but acceptable as the exposure is assumed of short duration for the average consumer and only taking place by direct exposure from leaf through or handling the printed matter.

By exposures in rooms the highest concentration was estimated in the "worst case" entrance hall scenario: 3648 µg/m^3. Based on the two room scenarios the estimated concentrations (0.3-3.6 mg/m^3, table 6.7) may be potentially harmful when handling the printed matter took place. The concentration was not above the odour threshold. The highest values were above the LCI value and indicate that irritation is possible.

Based on the box model estimations, the VOC concentration from average amount of printed matter is estimated to reach an equilibrium concentration of 3 mg/m^3 (cf. figure 6.1). In the "worst case" scenario which is considered not uncommon the equilibrium VOC concentration was approx. 6 mg/m^3 (cf. figure 6.2).
It should be noted that toluene in air also receives contributions from other sources than printed matter. The actual indoor concentration of toluene may therefore be higher than the estimated concentrations.

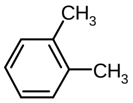
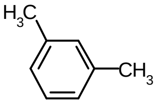
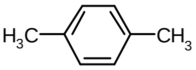
5.6.2 Xylenes

Xylene is used as solvent and in the production of printing inks. Xylene is a mixture of three isomers: o-, m-, and p-xylene where m- xylene is dominating (ratio approx. 20:40:20, respectively).

Identification

Name	Xylene
CAS no.	1330-20-7
EINECS no.	205-535-7
Molecular formula	$C8 H10$
Molecular structure	$C_6 H_4 (CH_3)_2$
Molecular weight	106.16 g/mol
Synonyms	Dimethylbenzene, (isomers o-, m-, and p-xylene) Methyltoluene Xylol

Identification of the three isomers:

Name	CAS no.	EINECS no.	Structure
ortho-xylene (1,2-dimethylbenzene)	95-47-6	202-422-2	
meta-xylene (1,3-dimethylbenzene)	108-38-3	203-576-3	
para-xylene (1,4-dimethylbenzene)	106-42-3	203-396-5	

The boiling point of the mixture is 138.5°C. The vapour pressure is 1065 Pa at 25°C (7.99 mmHg) (Daubert and Danner 1985). The water solubility is 106 mg/l at 25°C (Yalkowski and Dannenfelser 1992). The octanol/water distribution coefficient log Kow is measured to 3.12 (Hansch *et al.* 1995). Henrys Law constant is 6.63 atm m^3/mol at 25°C (Sanemasa *et al.* 1982). Koc is estimated to 434.

m-Xylene's melting point is –47,8°C. The boiling point is 139.1°C. The vapour pressure is 1105 Pa at 25°C (8.29 mmHg) (Chau *et al.* 1983). The water solubility is 161 mg/l at 25°C (Sanemasa *et al.* 1982). The octanol/water distribution coefficient log Kow is measured to 3.20 (Hansch *et al.* 1995). Henrys Law constant is 7.18 x 10^{-3} atm m^3/mol at 25°C (Sanemasa *et al.* 1982). Koc is estimated to 434. BCF is 58.

o-Xylene's melting point is –25,2°C. The boiling point is 144.5°C. The vapour pressure is 881 Pa at 25°C (6,61 mmHg) (Daubert and Danner 1989). The water solubility is 178 mg/l at 25°C (Sanemasa *et al.* 1982). The octanol/water distribution coefficient log Kow is measured to 3.12 (Hansch *et al.* 1995). Henrys Law constant is 5.18 x 10^{-3} atm m^3/mol at 25°C (Sanemasa *et al*. 1982). Koc is estimated to 443. BCF is 50.4.

p-Xylene's melting point is 13.2°C. The boiling point is 138.3°C. The vapour pressure is 1178 Pa at 25°C (8.84 mmHg) (Chau *et al.* 1983). The water solubility is 162 mg/l at 25°C (Sanemasa *et al.* 1982). The octanol/water distribution coefficient log Kow is measured to 3.15 (Hansch *et al.* 1995). Henrys Law constant is 6.90 x 10^{-3} atm m^3/mol at 25°C (Sanemasa *et al*. 1982). Koc is estimated to 434. BCF is 53.

Environment

The ecotoxicity of xylenes is presented below using the lowest measured values:

Organism	Species	Effect	Concentration	Reference
Fish	Oncorhynchus mykiss rainbow trout	EC$_{50}$ (96 h)	7.6 mg/l (o-xylene) 8.4 mg/l (m-xylene) 2.6 mg/l (p-xylene)	Galassi et al. 1988
Daphnia	Daphnia magna	EC$_{50}$ (24 h)	1.0 mg/l (o-xylene) 4.7 mg/l (m-xylene) 3.6 mg/l (p-xylene)	Galassi et al. 1988
Algae	Selenastrum capricornutum	EC$_{50}$ (72 h)	4.7 mg/l (o-xylene) 4.9 mg/l (m-xylene) 3.2 mg/l (p-xylene)	Galassi et al. 1988

The large amount of data found in literature is reduced severely by the fact that most data were based on nominal values disregarding the volatile capacity of the compounds. Therefore only results based on measured concentrations are reliable. Only a few chronic results were available and they were unreliable.

Absurd results with values high above the water solubility indicate that studies performed with volatile compounds are difficult to perform.

Health

Acute toxicity:

A recommended threshold limit value of 0.87 mg/m^3 (0.2 ppm) is calculated from an inhalation study using reprotoxicity as endpoint. The result of the study was 870 mg/m^3 (200 ppm) (Haas and Jacobsen 1993, IPCS 1997)

Acute and chronic toxicity:

Acute oral, rat	LD_{50}	3608 mg/kg (o-xylene) 5011 mg/kg (m-xylene) 4029 mg/kg (p-xylene)	IPCS 1997
Acute dermal, rabbit	LD_{50}	12180 mg/kg	IPCS 1997
Acute inhalation, rat	LC_{50} (6 h)	4330 ppm (o-xylene) 5796 ppm (m-xylene) 4591 ppm (p-xylene)	IPCS 1997
Chronic tests			
Oral, rat	NOEL	250 mg/kg	2 år, IPCS 1997
Inhalation, rat	LOAEL (6 h/d, 20 d	870 mg/m^3 (200ppm)	Hass and Jacobsen 1993

Classification

Xylenes (incl. isomers) are adopted on the list of dangerous substances and classified under EU index no. 601-022-00-9 (Miljøministeriet 2002):

R10	Flammable
Xn;R20/21	Harmful. Harmful by inhalation and in contact with skin
Xi;R38	Irritant. Irritating to

Threshold limit values

TDI (tolerable daily intake): 150 µg/kg bw/day

TCA (tolerable concentration in air): 870 µg/m^3 (Baars *et al.* 2001)

TLV: 25 ppm corresponding to 109 mg/m^3 with remark H (can penetrate skin) (Arbejdstilsynet 2002)

Odour threshold: 4000 µg/m^3 (IPCS 1997)

The tolerable concentration in air, TCA is based on LOAEL 870 mg/m^3 from Hass and Jakobsen (1993) using a safety factor of 1000 (IPCS 1997).

LCI-value 100 µg/m^3 is based on a NOEL for teratogenic effects in animals of 10 mg/m^3 where LCI= NOEL/10×10×1 (Larsen *et al.*1999).

Prolonged exposure to organic solvents may cause brain damages. Generally concentrations around 100 ppm is observed to be the NOEL for brain damages. 10 mg/m^3 is observed to be NOEL for teratogenic effects in animal studies (IPCS 1997).

The uptake of xylene after inhalation is observed to be approx. 60% (ATSDR 1995, IPCS 1997). ATSDR (1995) points out that both animal and human data indicate that the mixture of xylenes xylener, m-, o- and p-xylene all result in similar effects but each isomer is not necessarily equal potent when considering a specific effect.

Conclusion
The odour threshold is relatively high (4 mg/m^3). Xylene was measured in both rotogravure and in offset printed matter (printed matter no. 3, 17 and 19, section 3.1.4). Xylene was measured at the highest concentration in rotogravure printed matter. At emissions measured up to 600 mg/kg printed matter (incl. ethylbenzene, table 3.5) and an estimated exposure concentration of 49 µg/m^3 (table 6.2), xylene is not likely to be smelled at direct exposure from leaf through of printed matter by the consumer.

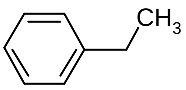
The TVL/100 was not exceeded. LCI was exceeded to a minor extent with a factor of approx. 2 (table 6.2). Xylene is therefore not considered representing a significant health problem at the measured concentrations.

At exposures in rooms the highest VOC concentration was observed in the "worst case" entrance hall scenario: 30 µg/m^3. Based on the two room scenarios the estimated concentrations (2 to30 µg/m^3, table 6.7) is considered to be non-harmful and below the odour threshold.

5.6.3 Ethylbenzene

Ethylbenzene is used as solvent of resins in printing inks and lacquers. Ethylbenzene is a component of oil products.

Identification

Name	Ethylbenzene
CAS no.	100-41-4
EINECS no.	202-849-4
Molecular formula	$C_8 H_{10}$
Molecular structure	
Molecular weight	106.17 g/mol

The melting point is –95°C. The boiling point is 136.2°C (Weast). The vapour pressure is 1280 Pa at 25°C (9.6 mmHg) (Daubert and Danner 1985). The water solubility is 169 mg/l at 25°C (Sanemase *et al.* 1982). The octanol/water distribution coefficient log Kow is measured to 3.15 (Hansch *et al.* 1995).

Environment
Ethylbenzene has an estimated vapour pressure that indicates it may evaporate from dry surfaces. Ethylbenzene has an estimated Henry's Law constant (H) of 8 x 10^{-3} atm m^3/mol at 25°C (Syracuse) indicating that it may evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 518 indicating a high adsorption potential to suspended matter. Ethylbenzene can be photochemically degraded in the atmosphere at an estimated half-life of <2 days.

Ethylbenzene is ready biodegradable based on model estimates (QSAR). The potential for bioaccumulation is expected to be low based on an estimated BCF of 53.

Ecotoxicity:

Fish	*Oncorhynchus mykiss* (Rainbow trout)	EC50 (96 h)	4.2 mg/l	Galassi *et al.* 1986
Daphni	*Daphnia magna*	EC50 (48 h)	1.8 mg/l	Viganò 1993

a

Algae	*Selenastrum capricornutum*	E_rC50 (72 h)	4.6 mg/l	Galassi *et al.* 1988

Health
Ethylbenzene is an irritant to skin, eyes and mucous membranes and may affect the central nervous system (Budavari 1996, IPCS 1996). Examples of effect levels are presented below and under the section Threshold limit values.

Ethylbenzene has been evaluated by IARC who concluded that there was insufficient evidence of ethylbenzene being carcinogenic to humans but sufficient evidence for test animals. Ethylbenzene was therefore classified in group 2B: "possibly carcinogenic to humans" (IARC 2000).

The main part of toxicity studies on ethylbenzene is inhalation studies. Based on a 13 weeks inhalation study a NOAEL of 430 mg/m^3 (100 ppm) has been derived (IPCS 1996, ATSDR 1999). The NOAEL 430 mg/m^3 is based on 6 hours/day, 5 days a week. A back-calculation based on continuous exposure 24 hours/day and 7 days/week results in a concentration of 77 mg/m^3. Using an uncertainty factor of 100 (10 for interspecies and 10 for intraspecies extrapolation) resulted in the TCA 770 µg/m^3 (Baars *et al.* 2001).

A recommended threshold limit value 22 mg/m^3 (5 ppm) is calculated from a 13 week inhalation study: 2150/(10×5×2) (IPCS 1996).

The most common exposure is inhalation where 44-64% is taken up by the lungs (IPCS1996).

Ethylbenzene has a low acute and chronic toxicity. The acute threshold values are 430-860 mg/m^3 (100-200 ppm) (IPCS 1996). Ethylbenzene is moderately toxic by oral administration (Lewis 1992).

Acute toxicity:			
Acute oral, rat	LD_{50}	3500 mg/kg	IPCS 1996
Acute dermal, rabbit	LD_{50}	77400 mg/kg	IPCS 1996
Acute inhalation, rat	LCL_0	9370 mg/m^3 (2180 ppm)	IPCS 1996
Chronic			
Oral, rat	NOAEL	136 mg/kg/d	Vermeire *et al.* 1996
Inhalation, rat	NOAEL	430 mg/m^3	Vermeire *et al.* 1996
Inhalation, rat	NOEL	2150 mg/m^3 (500 ppm)	IPCS 1996

Classification
Ethylbenzene is adopted on the list of dangerous substances and classified under EU index no. 601-023-00-4 (Miljøministeriet 2002):

F;R11	Highly flammable
Xn;R20	Harmful. Harmful by inhalation

Threshold limit values
TDI (tolerable daily intake): 100 µg/kg bw/day.
TLV: 50 ppm corresponding to 217 mg/m^3 (Arbejdstilsynet 2002).
TCA (tolerable concentration in air): 770 µg/m^3 (Baars *et al.* 2001).
LCI: 4300 µg/m^3, based on LOEL 434 mg/m^3, human irritation of nose and eyes (434/1×10×10=4.34 mg/m^3) (Larsen *et al.* 1999).

Conclusion

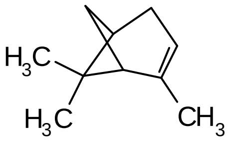
Ethylbenzene was observed in the screening analysis. In the quantitative analyses it was quantified together with xylenes. Ethylbenzene is therefore included in the evaluation of xylene concentration.

5.7 Terpenes

Terpenes exist in ethereal oils. Terpenes may arise from the use of vegetable oils and resins as solvent in the printing process and/or inks. The terpenes are generally irritants to the mucous membranes. Turpentine from coniferous trees are skin sensibilisers. The sensibilisation, however, is not confirmed for the individual terpenes with the exception of 3-carene, CAS no. 13466-78-9 (ASS 2000).

5.7.1 alpha-Pinene

Identification

Name	*alpha*-Pinene
CAS no.	7785-26-4, 80-56-8
EINECS no.	232-077-3
Molecular formula	C_{10} H_{16}
Molecular structure	
Molecular weight	136.24 g/mol
Synonyms	2,6,6-trimethyl-bicyclo[3.1.1]hept-2-ene 2,6,6-trimethyl-bicyclo[3.1.1]-2-heptene Pinene 2-Pinene

The melting point is -62,5°C. The boiling point is 156°C (Furia and Bellanca 1975). The vapour pressure is 633 Pa at 25°C (4.75 mmHg) (Daubert and Danner 1989). The water solubility is 0.65 mg/l at 250°C (FFHPVC 2002). The octanol/water distribution coefficient log Kow is measured to 4.83 (Li and Perdue 1995).

Environment

Pinene has a high vapour pressure indicating that pinene can evaporate from dry surfaces. Pinene has am estimated Henry's Law constant (H) of 0.107 atm m^3/mol (Syracuse) indicating it can evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 1200 indicating a high adsorption to suspended matter. Pinene is estimated to undergo photochemical degradation in the atmosphere with a half-life of 4 hours.

Pinene is not ready biodegradable in aerobic sludge tests (FFHPVC 2002). The potential for bioaccumulation is estimated to be high with an estimated BCF of 1045.

Terpenes are toxic to aquatic organisms. Most studies present effect results far above the water solubility and are therefore considered unreliable. Model estimations using ECOSAR (QSAR) resulted in EC_{50} levels below 1 mg/l. This is supported by the only two studies found reliable:

Ecotoxicity:

Fish	*Pimephales promelas* (Fathead minnow)	LC_{50}, 96 h	0.28 mg/l	FFHPVC 2002
Dafnia	*Daphnia magna*	LC_{50}, 48 h	1.44 mg/l	FFHPVC 2002

Health
alpha-Pinene is moderately oral toxic but very toxic by inhalation (Lewis 1992) and strongly irritating to skin, eyes and mucous membranes (Budavari 1996, Lewis 1992). Examples on effect levels are presented below. *alpha*-Pinene is known as contact allergen (Thomsen 1990).

Acute toxicity:

Acute oral, rat	LD_{50}	3700 mg/kg	Lewis 1992
Acute inhalation, rat	LC_{lo} (6 t)	0.625 mg/m^3	Lewis 1992
Acute inhalation, mouse	LC_{lo}	0.364 mg/m^3	Lewis 1992

Classification
alpha-Pinen is not classified under its own name or CAS no. If pinene is considered analogues to mineral turpentine under EU index no. 649-345-00-4 (Miljøministeriet 2002) the classification is:

Carc2;R45	May cause cancer

Threshold limit values
TLV: 25 ppm corresponding to 140 mg/m^3 the same as high boiling aromatic hydrocarbons (terpenes, turpentine) (Arbejdstilsynet 2002).
LCI is 250 µg/m^3 for most terpenes. The LCI value is based on an inhalation study on humans with a NOEL for lung symptoms on 25 mg/m3. Thus LCI = NOEL/1×10×10 (Larsen *et al.* 1999).
Odour threshold: 3900 µg/m^3 (Larsen *et al.* 1999).

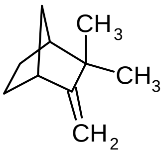
Conclusion
alpha-Pinene was observed in rotogravure printed matter. The odour threshold is moderate and *alpha*-pinene may be smelled at low concentrations. At measured emissions up to 1478 µg/kg printed matter the compound is not likely to be identifiable by its odour alone at direct exposure by handling or leaf through of the printed matter. However, together with other terpenes the concentration in the direct scenario reached the odour level and will be identifiable as a characteristic odour of terpenes. For instance the sum of terpenes in rotogravure printed matter no. 3 was approx. 14 mg/kg printed matter (table 3.5).

The two highest concentrations evaporated from printed matter were estimated to 122 µg/m^3 from no. 3 and 26 µg/m^3 from no. 2 after 15 and 2 days, respectively, when the printed matter reaches the consumer (cf. table 6.1 and 6.2). It is noted that the concentrations decreased during the measuring period for printed matter no. 3 while it was slow increase for no. 2 (table 3.3 and 3.5). LCI was not exceeded for printed matter no. 3 and *alpha*-pinene could not be considered a potential health problem by prolonged handling/leaf through of printed matter. However, it is noted that *alpha*-pinene is recognised as an allergenic that may cause contact dermatitis (Thomsen 1990).

By exposures i rooms the highest value was estimated in the "worst case" entrance hall scenario: 74 µg/m^3. Based on the two room scenarios with estimated concentrations of 6 to 74 µg/m^3 (table 6.7) , *alpha*-pinene is not considered harmful or above the odour threshold during leaf through or laying untouched in the hall or living room.

5.7.2 Camphene

Identification

Name	Camphene
CAS no.	79-92-5
EINECS no.	201-234-8
Molecular formula	$C_{10} H_{16}$
Molecular structure	
Molecular weight	136.24 g/mol
Synonyms	2,2-dimethyl-3-methylene-bicyclo[2.2.1]heptane 2,2-dimethyl-3-methylene-norbonane 3,3-dimethyl-2-methylenenorcamphane

The melting point is 52°C. The boiling point is 160°C (Clayton and Clayton 1981). The vapour pressure is 333 Pa at 25°C (2.5 mmHg) (Daubert and Danner 1989). The water solubility is 4.6 mg/l at 20°C (CITI 1992). The octanol/water distribution coefficient log Kow is estimeret to 4.35 (LOGKOW).

Environment
Camphene has a high vapour pressure indicating camphene can be expected to evaporate from dry surfaces. Camphene has an estimated Henry's Law constant (H) of 0.16 atm m^3/mol (Syracuse) indicating it can evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 1200 indicating a high adsorption to suspended matter. Camphene is estimated to degrade photochemically in the atmosphere with an estimated half-life of 6.6 hours.

Camphene is not ready biodegradable in aerobic screening tests (CITI 1992) where a biodegradation of 4% over 28 days was observed. The potential for bioaccumulation is estimated to be high based on a measured BCF of 432-1290 in 8-weeks carp fish study (CITI 1992).

The terpenes are toxic to aquatic organisms. Most studies present effect results far above the water solubility and are therefore considered unreliable. Model estimations using ECOSAR (QSAR) resulted in EC_{50} levels below 1 mg/l. This is supported by the only two studies found reliable:

Ecotoxicity:

Fisk	Sheepshead minnow	LD_{50}, 96 h	1.9 mg/l	Heitmüller 1981
	Brachydanio rerio (zebra fish)	LC_{50}, 96 h	0.72 mg/l	FFHPVC 2002

Health
Camphene is moderate to slightly irritating to the skin and has a low oral toxicity (Clayton and Clayton 1981). Irritation of eye and upper respiratory tract is also noted, i.e. the compound is n irritant to the mucous membrane (Gosselin *et al.* 1976, Grant 1986).

Acute toxicity:

Acute oral, rat	LD_{50}	>5000 mg/kg	Clayton and Clayton 1981

Classification
Camphene is not classified.

Threshold limit values
TLV: 25 ppm corresponding to 140 mg/m^3, equivalent to high boiling aromatic hydrocarbons (terpenes, turpentine) (Arbejdstilsynet 2002)
LCI is 250 mg/m^3 for most terpenes, cf. section 5.7.1 (Larsen *et al.* 1999)
Odour threshold: 28000 µg/m^3 (Larsen *et al.* 1999)

Conclusion
Camphene was observed in rotogravure printed matter. The odour threshold is high and camphene is not likely to be smelled at low concentrations. The measurements showed emissions up to 473 µg/kg printed matter and camphene is unlikely to present any odour identifiable by direct exposure during handling or leaf through the printed matter.

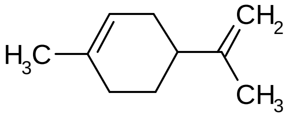
The two highest consumer exposure concentrations of evaporated camphene from rotogravure printed matter were 40 µg/m^3 from no. 3 and 35 µg/m^3 from no. 2 after 15 and 2 days, respectively when the printed matter has reached the consumer (table 6.2 and 6.1). It is noted that the concentrations decreased during the measuring period for printed matter no. 3 but increased no. 2 (table 3.3 and 3.5). The TLV/100 and LCI were not exceeded and camphene is not considered to represent a health problem at the measured concentrations.

By exposure to rooms the highest concentration was estimated in the "worst case" entrance hall scenario: 24 µg/m^3. Based on the two room scenarios the concentrations estimated (2 to 24 µg/m^3, table 6.7) is not considered to represent any health hazard or being above the odour threshold.

5.7.3 Limonene

Limonene is used as solvent, in the production of resins and as wetting and dispersing agent.

Identification

Name	d-Limonene
CAS no.	5989-27-5
EINECS no.	227-813-5
Molecular formula	C_{10} H_{16}
Molecular structure	
Molecular weight	136.24 g/mol
Synonyms	(R)-1-methyl-4-(1-methylethenyl)-cyclohexene 4-Isopropenyl-1-methylcyclohexene p-Mentha-1,8-diene Citrene Cinene

The melting point is –74.35°C (Lide 1992). The boiling point is 176°C (Budavari 1996). The vapour pressure is 192 Pa at 25°C (1.44 mmHg)

(Nadais and Bernardo 1993, Riddick *et al.* 1986). The water solubility is 13.8 mg/l at 25°C (Massaldi and King 1973). The octanol/water distribution coefficient log Kow is measured to 4.57 (Li and Perdue 1995).

Environment

d-Limonene has a high vapour pressure indicating that limonene can evaporate from dry surfaces. Limonene has a measured Henry's Law constant (H) of 2.57 x 10^{-2} atm m^3/mol at 25°C (Syracuse) indicating it can evaporate from wet surfaces. The adsorption coefficient (Koc) is estimeret to 1324 indicating a strong adsorption to suspended matter. Limonene is estimated to undergo photochemical degradation in the atmosphere at a half-life of 1 hour.

d-Limonene is not ready biodegradable in aerobic screening tests (HSDB). The potential of bioaccumulating is high based on an estimated BCF of 659.

d-Limonene is very toxic to aquatic organisms.

Ecotoxicity:

Fish	*Pimephales promelas* (Fathead minnows)	LC_{50}, 96 h	0.7 mg/l	US-EPA 1990
Dafnia	*Daphnia magna*	EC_{50}, 48 h	0.42 mg/l	US-EPA 1990
Algae	*Selenastrum capricornutum*	NOEC, 96 h	4.08 mg/l	US-EPA 1990

Health

d-Limonene is irritating to the skin and may be a sensitizer (Budavari 1996, Karlberg and Lindell 1993). d-Limonene is a moderate oral toxicant (Lewis 1992). Examples of effect levels are presented below.

d-Limonene is easily taken up from the lungs after inhalation. Short-time exposure studies shows 58 to 70% absorbed after 2 hours of exposure (Karlberg and Lindell 1993, Falk-Filipsson *et al.* 1993, 1998).

d-Limonene is readily oxidised by the air oxygen. Experimental studies shows that limonene in itself is not allergenic but allergenic compounds are formed from limonene by autooxidation (Karlberg *et al.* 1992, Karlberg and Lindell 1993).

Acute toxicity:

Acute oral, rat	LD_{50}	4400 mg/kg	Lewis 1992
Acute oral, mouse	LD_{50}	5600 ml/kg (4710 mg/kg)	HSDB 2002
Acute dermal, rabbit	LD_{50}	>5000 mg/kg	Karlberg and Lindell 1993
Oral rat, 13 weeks	NOEL	10 mg/kg/d	Falk-Filipsson 1998

Classification

d-Limonene is adopted on the list of dangerous substances and classified under EU index no. 601-029-00-7 (Miljøministeriet 2002):

R10	Flammable
Xi;R38 R43	Irritant. Irritating to skin. May cause sensitization by skin contact
N;R50/53	Dangerous for the environment. Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

Threshold limit values

TDI: 0.1 mg/kg bw/d based on 13 weeks oral rat (Falk-Filipsson 1998).
TLV: 25 ppm corresponding to 140 mg/m^3, equivalent to terpenes, turpentine (Arbejdstilsynet 2002).
Sverige: NGV (niveaugränsvärde) 150 mg/m^3 (25 ppm) with the remark skin sensitizer (Karlberg and Lindell 1993).
LCI: 300 µg/m^3. The LCI is based on an inhalation study on animals with a LOEL of 75 mg/kg and conversion from oral exposure to inhalation: LCI = 75 mg/kg × 70 kg × 20 m^3 / 10×10×10 (Larsen *et al.* 1999).
Odour threshold: 2500 µg/m^3 (Larsen *et al.* 1999).

Limonen is on the list of undesirable substances because it is suspected to be allergenic (Miljøstyrelsen 2000).

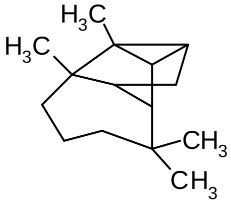
Conclusion

d-Limonene was measured in rotogravure printed matter. The odour threshold is low and limonene can be smelled at low concentrations. The measurements showed evaporated amounts of limonene up to 554 µg/kg printed matter where the compound is not likely to be to give any noticeable odour by itself during handling or leaf through of printed matter. However, together with other terpenes it may contribute to a characteristic odour of terpenes. Limonene is naturally present in citrus fruits. The two highest concentrations of limonene evaporated from printed matter were estimated to 46 µg/m^3 from no. 3 and 15 µg/m^3 from no. 2 after 15 and 2 days, respectively, when the printed matter reached the consumer. It is noted that the concentrations were increasing in the measuring period for both printed matters. The LCI was not exceeded and d-limonene is not considered to present a health problem during handling or leaf through of the printed matter. However, d-limonene is known to oxidise to allergenic compounds.

By exposure in rooms the highest concentration was estimated in the "worst case" entrance hall scenario: 28 µg/m^3. Based on the two room scenarios and the estimated concentrations that vary between 2 and 28 µg/m^3 (table 6.7) d-limonene is not considered to present a health problem or getting above the odour threshold when laying untouched in the hall or living room.

5.7.4 Tetramethyl methenoazulene

Identification

Name	decahydro-1,5,5,8a-tetramethyl-1,2,4-methenoazulene, [1S-(1.*alpha*.,2.*alpha*.,3a.*beta*.,4.*alpha*.,8a.*beta*.,9R*)]-
CAS no.	1137-12-8
EINECS no.	214-504-5
Molecular formula	$C_{15}H_{24}$
Molecular structure	
Molecular weight	204.36 g/mol

The melting point is estimeret to 44°C (QSAR). The boiling point is estimeret to 227°C (QSAR). The vapour pressure is estimated to 12 Pa at 25°C (0.09

mmHg) (QSAR). The water solubility is estimated to 0.2 mg/l at 25°C (QSAR). The octanol/water distribution coefficient log Kow is estimated to 5.6 (QSAR).

Environment
Metenoazulene has an estimated vapour pressure high enough to indicated that methenoazulene evaporates from dry surfaces. Metenoazulene has an estimated Henry's Law constant (H) of 0.28 atm m^3/mol at 25°C (Syracuse) indicating it may evaporate from wet surfaces. The adsorption coefficient (Koc) is estimated to 20300 indication a strong adsorption to suspended matter is expected. Metenoazulene is estimated to be photochemical degraded in the atmosphere at a half-life of 13 hours.

Metenoazulene is not ready biodegradable based on model estimates (QSAR). The potential of bioaccumulation is estimated to be high, based on an estimated BCF of 4000.

QSAR estimates indicate that the compound is acute very toxic to aquatic organisms with EC_{50} values below 1 mg/l (ECOSAR).

Health
No relevant information was found on the compound. Methenoazulene is therefore evaluated as the analogous terpenes.

Classification
Tetramethyl methenoazulene is not classified but reminds in structure of other terpenes and is assumed to have the same properties.

Threshold limit values
No threshold limit values found for the specific compound. Methenoazulene assumed to have the same levels as the analogous terpenes:
TLV: 25 ppm corresponding to 140 mg/m^3 as for terpenes and turpentine (Arbejdstilsynet 2002)
LCI: 250 µg/m^3 based on its terpenoid structure and an assumed comparable effect level (Larsen *et al.* 1999)

Conclusion
Methenoazulene is considered terpenoid based on structure, which however is tricyclic. Methenoazulene was observed in the screenings test but not in the quantitative analyses.

5.8 Aliphatic hydrocarbons

The aliphatic hydrocarbons may have a linear or branched carbon structure. The alkanes C_{9-19} (nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane) is grouped in the analyses. A division between C_{9-12} and C_{13-19} is performed.

Health
For many of the aliphatic hydrocarbons dermatitis, irritation, central nervous system depressions and anaesthesia have been noted. The effect of the aliphatic carbons increases with the molecular weight. In general, aliphatic mixtures have a neurotoxic effect on the level about 100 ppm corresponding to 200-600 mg/m^3 (Larsen *et al.*1999).

The lowest toxic dose for tetradecane on mouse exposed for 20 weeks is: TD_{lo} 9600 mg/kg according to Clayton and Clayton (1981) who also states that C_{13}-C_{16} alkanes at inhalation have the same effects as C_6-C_{10} but with a slower mortality rate.

Classification
Alkanes, C_{12-26}- linear and branched is included on the "list of dangerous substances" (Miljøministeriet 2002) under CAS no.: 90622-53-0, EINECS no.: 292-454-3.

Carc2;R45	May cause cancer

Threshold limit values
TLV (C9-C13): 180 mg/m^3 (Arbejdstilsynet)

Suggested LCI for C_{7-12} based on the general neurotoxic effect at 200 to 600 mg/m^3 in humans: LCI = NOEL/1×10 = 20 - 60 mg/m^3 (Larsen *et al.*1999)

Of other threshold limit values found for alkanes:

Substance	TLV/100 µg/m^3	LCI, µg/m^3	C-value, µg/m^3
Heptane	8200	8000	
Octane	9350		
Nonane	1800	10000	
Decane	1800	2000	
Undecane	1800		1000
Dodecane	1800		
Tridecane	1800		1000

The odour threshold values reported are (Larsen *et al.* 1999):

Heptane	40.7 mg/m^3
Octane	27.5 mg/m^3
Nonane	6.8 mg/m^3
Decane	4.4 mg/m^3
Undecane	3.5 mg/m^3
Dodecane	37.0 mg/m^3

Conclusion
The aliphatic hydrocarbons could not be separated by the used analytical method and is considered as a group. The odour threshold is unknown for all included substances. The few known threshold values are mentioned above. Based on the subjective evaluation performed as the measurements were initiated their presence was recognised by their characteristic odour. From the printed matter an oily odour typical for hydrocarbons of the kerosene type was registered. A comparison with later measurements, showed that the odour could be classified in this study. The subjective evaluation at a concentration later measured to approx. 5 mg/kg printed matter was "weak odour", at 15 mg/kg "smells" and at 44 mg/kg "strong smell". Thus, the aliphatic hydrocarbons could be smelled at direct exposure from handling the printed matter. The highest amount evaporated from offset printed matter no. 19 (C_{8-12}: 33 mg/kg printed matter and for C_{13-18}: 39 mg/kg printed matter) (13 mg/m^3 C_{8-12} and 15 mg/m^3 C_{13-18}) after 7 days, i.e. when the printed matter had reached the consumer (table 3.13). The equivalent estimated exposure concentrations were 986 µg/m^3 and 1160 µg/m^3 (table 6.6)

The measured concentrations from each group do not exceed the 200 mg/m^3 that could cause neurotoxic damage according to Larsen *et al.* (1999).

The database is considered too weak to conclude the evaluation. If the mentioned classification is correct, at least the long chained alkanes may cause cancer.

By exposure in rooms the highest concentration was estimated in the "worst case" entrance hall scenario: 1.8 mg/m^3. Based on the two room scenarios the estimated concentrations (0.2 to 1.8 µg/m^3, table 6.7) are below the odour threshold.

6 Evaluation of printed matter

6.1 Health assessment of selected printed matter

The assessment is performed for each individual printed matter. The individual selected substances are evaluated in previous section 5. For the evaluation is used threshold limit values (Arbejdstilsynet 2002). However, because the theshold limit values are aimed at the working environment and do not apply to the home, values that are 1/100 of the TLV is used. As supplement, the LCI-values are included in the evaluation. LCI values are developed especially for the indoor environment.

Based on TGD (TGD 1996) for short-term local exposure, the value for air volume is set to 2 m^3 to represent the volume of air immediately sourrounding the user. The emission was measured during 1 hour which was assumed to be the exposure period in the leaf through scenario. It should be noticed that the concentration estimated for the short-tem local exposure is a worst case situation of the concentration in the air around the reader in the reading/leafing situation within one hour. The real average concentration around the reader will be lower than the estimated concentrations in table 6.1 to 6.6, because the air will be mixed with the surrounding air in the room.

Based on the measured concentrations from volatile organic compounds (presented in $\mu g/m^3$) the ratio between the estimated concentration in air and TLV/100 (C air / $C_{TLV/100}$) and LCI (C air / LCI) is calculated. Table values above 1 thus indicate an exceeding of the applied theshold value and indicates a potential health problem.

6.1.1 Printed matter no. 2 (rotogravure)

The evaluation of printed matter no. 2 (rotogravure) is based on the calculated values presented in the table below. The measured values are from table 3.3.

Table 6.1 Exposure and risk characterisation at direct exposure of distributor, day 1 and consumer, day 2 from printed matter no. 2 (rotogravure)

Compound	CAS no.	TLV/100 µg/m^3	LCI µg/m^3	Distributor			Consumer		
				µg/m^3	C air / $C_{TLV/100}$	Cair / LCI	µg/m^3	C air / $C_{TLV/100}$	Cair / LCI
Day				1			2		
Toluene	108-88-3	940	400	36410	38.7	91.0	22980	24.4	57.5
Octane	111-65-9	935		22.5	0.024		20	0.021	
Naphthalene	91-20-3	500	40 (C)	11.5	0.023	0.288	11.5	0.023	0.288
C9 H12, arom hydrocarbon	98-82-8	1000	1750	11	0.011	0.006	13	0.013	0.007
alfa-Pinene	7785-26-4	1400	250	24	0.017	0.096	26	0.019	0.104
Camphene	79-92-5	1400	250	31.5	0.023	0.126	35	0.025	0.140
beta-Pinene	127-91-3	1400	250	<0.2			<0.2		
d-Limonene	5989-27-5	1400	300	11.5	0.008	0.038	14.5	0.010	0.048
2-Propenylbenzene *	300-57-2	1000		11.5	0.012		14.5	0.015	
2,3-Dimethylphenol	526-75-0			6			5		
1-Methylindane	767-58-8			13.5			13.5		
Other terpenes		1400	250	185.5	0.13	0.74	251.5	0.18	1.006
Formaldehyde	50-00-0	4	100	9	2.25	0.09	8.5	2.13	0.085
Acetaldehyde	75-07-0	450	5200	32	0.071	0.006	21	0.047	0.004
Acrolein	107-02-8	1.20	3	<0.03			<0.03		
Propanal	123-38-6	475 (US)	4300	12	0.025	0.003	6	0.013	0.001
Acetone	67-64-1	6000	400	23	0.004	0.058	16	0.003	0.040
Butanal	123-72-8	1000(B)	2800	1	0.001	0.0004	1	0.001	0.0004
Pentanal	110-62-3	1750	3100	1	0.001	0.0003	0.5	0.0003	0.0002
Hexanal	66-25-1	1750 (US)	3400	4	0.002	0.001	3	0.002	0.001
Benzaldehyde	100-52-7		1200	31.5		0.026	22		0.018
2-Butanone	78-93-3	1450	1000(C)	1	0.001	0.001	1	0.001	0.001
Total VOC sum				36855	41.3	92.5	23466	26.9	59.2

*: For propenylbenzene is used the same TLV as for the analogous 2-propylbenzene (CAS.: 98-82-8). (C): i.e. based on C-value (Miljøstyrelsen 2002). (US): American TLV used

For printed matter no. 2, it is obvious that toluene is the major VOC component. Toluene has been evaluated in section 5. The emitted amount of 272 mg/kg printed matter results an estimated concentration of 23 mg/m^3. This is estimated from a worst case reading/leafing situation, and the air around the reader in a reading/leafing situation will be lower than the estimated concentration because the air will be mixed with the surrounding air in the room. It should be noted that toluene is a harmfull substance and may pose risk to the unborn child.

The TLV/100 and LCI were exceeded in the leaf through scenario (table 6.1). The toluene exposure is therefore assessed by comparison to the NOAEC value 150 mg/m^3. The margin of safety (MOS) for the consumer was 6 which is considered low but acceptable as the value is based on human effekt data. Besides, the exposure is assumed of short duration for the average consumer and only taking place by direct exposure from leaf through or handling the printed matter.

Of other hazardous substances having a concentration exceeding the used threshold values (i.e. TLV/100 or LCI) are formaldehyde and "other terpenes". However, the exceedings are small and insignificant.

For some of the compounds evaporated from the printed matter, no threshold values were found. However, even without the contribution from these compounds the high values in the summing up of the exceedings from each compound clearly indicate which compound that represents the largest contribution of VOC.

Based on the total sum of VOC there are indications of health hazards irrespective of which threshold value (TLV/100 or LCI) is used. This applies to both scenarios for the distributor and the consumer. The sum of exceeding indicates that the consumer is exposed to approx. 2/3 of the level of the distributor.

The effect of the total VOC exposure is unknown and therefore not evaluated.

6.1.2 Printed matter no. 3 (rotogravure)

The evaluation of printed matter no. 3 (rotogravure) is based on the calculated values presented in the table below. The measured concentrations are from table 3.5.

Table 6.2 Results of emission measurements of printed matter no. 3 (rotogravure)

Compound	CAS no.	TLV/100 µg/m^3	LCI µg/m^3	Distributor			Consumer		
				µg/m^3	C air / $C_{TLV/100}$	Cair / LCI	µg/m^3	C air / $C_{TLV/100}$	Cair / LCI
Day				11			15		
Toluene	108-88-3	940	400	11097	11.8	27.7	6072	6.5	15.2
Xylenes		1090	100(B)	83	0.08	0.830	49.5	0.05	0.5
Naphthalene	91-20-3	500	40 (B)	-			-		
C_9H_{12}, arom. hydrocarbon	98-82-8	1000	1750	17.5	0.02	0.01	17	0.02	0.01
alpha-Pinene	7785-26-4	1400	250	166.5	0.12	0.666	122.5	0.09	0.49
Camphene	79-92-5	1400	250	53.5	0.04	0.214	39.5	0.03	0.16
beta-Pinene	127-91-3	1400	250	27.5	0.02	0.110	23.5	0.02	0.09
d-Limonene	5989-27-5	1400	300	50.5	0.04	0.168	46	0.03	0.15
$C_{10}H_{14}$ arom hydrocarbon				53.5			49		
Other terpenes		1400	250	992	0.71	3.968	914	0.65	3.66
Formaldehyde	50-00-0	4	100	-			-		
Acetaldehyde	75-07-0	450	5200	22.5	0.05	0.004	17	0.04	0.003
Acroleine	107-02-8	1.20	3	-			-		
Propanal	123-38-6	475 (US)	4300	7.5	0.016	0.002	6.5	0.014	0.002
Acetone	67-64-1	6000	400	40.5	0.007	0.101	45	0.008	0.113
Butanal	123-72-8	1000	2800	1	0.001	0.0004	1.5	0.002	0.001
Pentanal	110-62-3	1750	3100	1	0.001	0.0003	1	0.001	0.000
Hexanal	66-25-1	1750 (US)	3400	11.5	0.007	0.003	13.5	0.008	0.004
Benzaldehyde	100-52-7		1200	12.5		0.010	8		0.007
2-Butanone	78-93-3	1450	1000	0.15	0.0001	0.0002	0.35	0.0002	0.0004
Total VOC sum				12638	13	34	7425	7	20

-: below detection limit. B: based on C-values. (US): American TLV used

For printed matter no. 3, rotogravure, it is obvious that toluene is the major VOC compound. Toluene is discussed in detail in section 5. The measured emission of 73 mg/kg printed matter results in an estimated concentration of 6 mg/m^3. This is estimated from a worst case reading/leafing situation, and the air around the reader in a reading/leafing situation will be lower than the estimated concentration because the air will be mixed with the surrounding air in the room. It should be noted that toluene is a harmfull substance and may pose risk to the unborn child.

The TLV/100 and LCI were exceeded in the leaf through scenario (table 6.2). The toluene exposure is therefore assessed by comparison to the NOAEC value 150 mg/m^3. The margin of safety (MOS) to the consumer was 25 which is considered low but acceptable as the value is based on human effect data. Besides, the exposure is assumed of short duration for the average consumer and only taking place by direct exposure from leaf through or handling the printed matter.

Of the remaining compounds exceeding the threshold limit values are "other terpenes”. However, the exceeding is small.

For some of the compounds evaporated from the printed matter, no threshold values were found. However, even without the contribution from these compounds the high values in the summing up of the exceedings from each compound clearly indicate which compound that represents the largest contribution of VOC.

Based on the total sum of VOC, there are indications of health hazards irrespective of which limit value is used. This applies to both scenarios for the distributor and the consumer. The sum of exceeding indicates that the consumer is exposed to approx. 1/4 of the level of the distributor.

The effect of the total VOC sum is unknown and therefore not assessed.

6.1.3 Printed matter no. 4 (flexographic)

The evaluation of printed matter no. 4 (flexographic) is based on the calculated values presented in the table below. The measured values are from table 3.7.

Table 6.3 Results of emission measurement of printed matter no. 4 (Flexographic)

Compound	CAS	TLV/100 µg/m³	LCI µg/m³	Distributor			Consumer		
				µg/m³	C air / $C_{TLV/100}$	Cair / LCI	µg/m³	C air / $C_{TLV/100}$	Cair / LCI
Day				5			7		
1-Butanol	71-36-3	1500	200	-			-		
2-Hexanol	626-93-7	-	1000				-		
Toluene	108-88-3	940	400 (B)	0,04	<0,001	0,0001	0,0295	<0,001	<0,001
Butylacetate	123-86-4	7100	2700		<0,001	<0,001			
Cyclohexanone	108-94-1	400	2300	0,01	<0,001	<0,001		<0,001	<0,001
n-Butylether	142-96-1								
Propanoic acid butylester	590-01-2	-	-						
3-Methyl-4-heptanone	15726-15-5	-	1900	0,04		<0,001			<0,001
C_9H_{12} arom. Hydrocarbon (n=6)		1000	30(B)	0,24	<0,001	0,008		<0,001	<0,001
2-Ethyl-1-hexanol	104-76-7	2700 (D)	1000	0,21	<0,001	<0,001	0,0445	<0,001	<0,001
C9H10				0,06					
C10H16 (terpene)*	6004-38-2	1400	250						
Acetic acid, 2-ethylhexylester	103-09-3		1100	0,14		<0,001	0,060		<0,001
Naphthalene	91-20-3	500	40 (B)	0,06	<0,001	0,002	0,052	<0,001	0,001
C8H16	3404-80-6			0,08			0,030		
Terpenes		1400	250	1,02	0,001	<0,001	0,519	<0,001	0,002
Formaldehyde	50-00-0	4	100	0,04	0,010	<0,001	0,149	0,037	0,001
Acetaldehyde	75-07-0	450	5200	0,03	<0,001	<0,001	0,034	<0,001	<0,001
Acroleine	107-02-8	1.20	3						
Propanal	123-38-6	475 (US)	4300						
Acetone	67-64-1	6000	400	0,032	<0,001	<0,001	0,073	<0,001	<0,001
Butanal	123-72-8	1000	2800	0,003	<0,001	<0,001	0,002	<0,001	<0,001
Pentanal	110-62-3	1750	3100	0,025	<0,001	<0,001	0,012	<0,001	<0,001
Hexanal	66-25-1	1750 (US)	3400	0,004	<0,001	<0,001	0,008	<0,001	<0,001
Benzaldehyde	100-52-7		1200	0,020		<0,001	0,015		<0,001
2-Butanone	78-93-3	1450	1000 (B)	0,003	<0,001	<0,001	0,002	<0,001	<0,001
Total VOC sum				2,1	0,011	0,014	1,0	0,038	0,005

*: octahydro-4,7-Methano-1H-indene.
-: below detection limit.
(B): based on C values (Miljøstyrelsen 2002).
(D): based on German MAK value (MAK 2000).
(US): American TLV used

In printed matter no. 4, no exceedings of the threshold values are observed. For evaluation of the individual compounds refer to section 5.

The total VOC sum is exceeded if assumed that the values can be added. Because the printed matter is a label the exposure period is assumed to be short and the number of labels presented to most consumer small. Therefore it is concluded that this specific printed matter does not pose a potential health problem to most consumers.

No residue monomers of acrylates were observed which indicate that the printed matter is cured sufficiently. If the UV-curing had not been complete monomers of acrylates might have been present. Residual monomers could have caused contact dermatitis if exposed to skin.

6.1.4 Printed matter no. 8 (offset, heatset)

The evaluation of printed matter no. 8 (offset, heatset) is based on the calculated values presented in the table below. The measured values are from table 3.9.

Table 6.4 Results of emission measurements of printed matter no. 8

Compound	CAS	TLV/100 µg/m^3	LCI µg/m^3	Distributor			Consumer		
				µg/m^3	C air / $C_{TLV/100}$	Cair / LCI	µg/m^3	C air / $C_{TLV/100}$	Cair / LCI
Day				4			5		
Toluene	108-88-3	940	400(B)	5.5	0.006	0.014	9.0	0.0096	0.023
Xylenes	1330-20-7	1090	100(B)	-			-		
C9-C12 aliph. Hydrocarbons		(1000)	2000	331.5	0.332	0.166	176.0	0.1760	0.088
C13-C19 aliph. Hydrocarbons				2698.5			1917.5		
Formaldehyde	50-00-0	4	100	2.5	0.625	0.025	2.5	0.6250	0.025
Acetaldehyde	75-07-0	450	5200	6.5	0.014	0.001	4.5	0.0100	0.001
Acrolein	107-02-8	1.20	3	-			-		
Propanal	123-38-6	475 (US)	4300	3.5	0.007	0.001	-		
Acetone	67-64-1	6000	400	10.5	0.002	0.026	5.50	0.0009	0.014
Butanal	123-72-8	1000 (B)	2800	1.5	0.002	0.001	0.75	0.0008	0.0003
Pentanal	110-62-3	1750	3100	2.5	0.001	0.001	0.80	0.0005	0.0003
Hexanal	66-25-1	1750 (US)	3400	33.0	0.019	0.010	5.00	0.0029	0.001
Benzaldehyde	100-52-7		1200	0.8		0.001	0.15		0.0001
2-Butanone	78-93-3	1450	1000 (B)	0.6	0.0004	0.001	-		
Total VOC sum				3097	1.0	0.2	2122	0.8	0.2

-: below detection limit.
(B): based on C-value
(US): American TLV used

For printed matter no. 8, no exceeding of the threshold values were observed. However, theoretically there might be exceedings of the aliphatic hydrocarbons.

For the total VOC sum also the only exceeding was observed to distributors from aliphatic hydrocarbons. It is concluded that a minor potential health problem may exist in the retail. To the consumer no indications of health hazards exist.

6.1.5 Printed matter no. 17 (offset)

The evaluation of printed matter no. 17 (offset) is based on the calculated values presented in the table below. The measured values are from table 3.11.

Table 6.5 Results of emission measurements of printed matter no. 17

Compound	CAS	TLV/100 µg/m^3	LCI µg/m^3	Distributor			Consumer		
				µg/m^3	C air / $C_{TLV/100}$	Cair / LCI	µg/m^3	C air / $C_{TLV/100}$	Cair / LCI
Day				2			7		
Toluene	108-88-3	940	400 (B)	4	0.004	0.010	5	0.005	0.013
Xylenes	1330-20-7	1090	100 (B)	6	0.005	0.055	5	0.005	0.050
Styrene	100-42-5	1050	200 (B)						
C_9H_{12}, arom. Hydrocarbon			17,5	16		0.91	13		0.74
C_9H_{12}, arom. Hydrocarbon				7			7		
C_8-C_{12}, aliph. Hydrocarbon		(1000)	2000	226	0.23	0.11	143.5	0.14	0.07
C_{13}-C_{19}, aliph. Hydrocarbon				323			225.5		
Terpenes		1400	250	42	0.03	0.17	34	0.02	0.14
C10 H12 O2 *	3602-55-9			23			21		
Formaldehyde	50-00-0	4	100	4	0.88	0.04	4.5	1.13	0.05
Acetaldehyde	75-07-0	450	5200	10	0.02	0.002	10.5	0.02	0.002
Acrolein	107-02-8	1,20	3						
Propanal	123-38-6	475 (US)	4300	42	0.087	0.010	40	0.084	0.009
Acetone	67-64-1	6000	400	13	0.002	0.033	13.5	0.002	0.034
Butanal	123-72-8	1000 (B)	2800	5	0.005	0.002	5	0.005	0.002
Pentanal	110-62-3	1750	3100	16	0.009	0.005	17.5	0.010	0.006
Hexanal	66-25-1	1750 (US)	3400	127	0.073	0.037	147	0.084	0.043
Benzaldehyde	100-52-7		1200	2		0.001	1.5		0.001
2-Butanone	78-93-3	1450	1000 (B)	2	0.001	0.002	2	0.001	0.002
Total VOC sum				863	1.3	1.4	696	1.5	1.2

*: 2-(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione (= 2-tert-butyl-1,4-benzoquinone). Structure formula: $(CH_3)_3CC_6H_3(=O)_2$
-: below detection limit
(B): based on C-value.
(US): American TLV used

For printed matter no. 17 (offset) exceeding of the threshold values were only observed for formaldehyde. It should be noted that formaldehyde is a suspected carcinogen.

The LCI value for C_9H_{12} aromatic hydrocarbon is based on isopropylbenzene, which has a LCI value of 1.75 mg/m^3 and propylbenzene, which has a LCI value of 5.8 mg/m^3. The lowest value is selected to be on the safe side.

Relating to the total VOC sum minor exceedings are observed to the distributor and consumer. However, the exceedings are small and not considered of any serious health hazard.

6.1.6 Printed matter no. 19 (offset))

The evaluation of printed matter no. 19 (heatset) is based on the calculated values presented in the table below. The measured values are from table 3.13.

Table 6.6 Results of emission measurements of printed matter no. 19

Compound	CAS	TLV/100 µg/m^3	LCI µg/m^3	Distributor			Consumer		
				µg/m^3	C air / $C_{TLV/100}$	Cair / LCI	µg/m^3	C air / $C_{TLV/100}$	Cair / LCI
Day				5			7		
Toluene	108-88-3	940	400 (B)	4	0,004	0,010	0,5	0,001	0,001
Xylenes	1330-20-7	1090	100 (B)	2	0,001	0,015	1,5	0,001	0,015
C_8-C_{12}, aliph. Hydrocarbon		(1000)	2000	1848	1,848	0,924	985,5	0,986	0,493
C_{13}-C_{19}, aliph. Hydrocarbon				2295			1159,5		
Formaldehyde	50-00-0	4	100	2	0,375	0,015	1	0,250	0,010
Acetaldehyde	75-07-0	450	5200	4	0,008	0,001	5,5	0,012	0,001
Acrolein	107-02-8	1.20	3						
Propanal	123-38-6	475 (US)	4300	13	0,026	0,003	21	0,044	0,005
Acetone	67-64-1	6000	400	7	0,001	0,018	10	0,002	0,025
Butanal	123-72-8	1000 (B)	2800	5	0,005	0,002	7	0,007	0,003
Pentanal	110-62-3	1750	3100	21	0,012	0,007	45	0,026	0,015
Hexanal	66-25-1	1750 (US)	3400	15	0,009	0,004	31	0,018	0,009
Benzaldehyde	100-52-7		1200	1		0,0005	0,75		0,001
2-Butanone	78-93-3	1450	1000 (B)	22	0,02	0,022	9,5	0,007	0,010
Total VOC sum				4235	2,3	1,0	2278	1,4	0,6

-: below detection limit
(B): based on C-value
(US): American TLV used

For printed matter no. 19 exceeding of the threshold values were observed in aliphatic hydrocarbons to both distributor and consumer. The aliphatic carbons are not present at a concentration that may cause neurotoxicity, but may cause slight irritation. However the database was too weak for a conclusion (cf. section 5.8).

The total VOC sum exceeds 1, which may indicate a potential health risk. However, if the exposure time is included, the risk would be insignificant. A reading period of e.g. 1 hour means that the exposure time would be approx. 1/24 of the above table value.

6.1.7 Entrance hall and living room scenarios

6.1.7.1 Printed matter leaf through in hall or living room

In the entrance hall scenario is presumed that the room is 10 m^3 with an air change of 0.5 times per hour. To the exposure assessment as a representative for the rotogravure printed matters is used printed matter no. 3 and for offset selected printed matter no. 8. They are only selected as representatives of printed matter. Two estimates are performed:

1) An average scenario based on 61.1 kg printed matter per household per year, of which 18% is assumed to be rotogravure (cf. section 2.5). On a weekly basis the amount corresponds to 963 g offset (no. 8) + 212 g rotogravure (no.3) printed matter, or a total of 1.175 kg printed matter/week.

2) A "worst case" scenario where three rotogravure printed matter (e.g. sale catalogue) arrive to the home at the same time, i.e. 498 g rotogravure and 677 g offset, a total of 1.175 kg printed matter.

Each contribution to the emission is calculated as emissions measured in µg/kg printed matter (data from section 3.1.4: day 15 in table 3.5 rotogravure and day 5 in table 3.9 offset).

Table 6.7 Estimated concentrations in entrance hall and living room at average and "worst case" load

	Printed matter		P.M contributions		Concentrations		"worst case"	
Compound	P.M. 3 µg/kg	P.M. 8 µg/kg	Contribution 3 (x 0.212)	Contribution 8 (x 0.963)	C air hall 10 m^3	C air l. room, 50 m^3	Worst case, hall	Worst case, l. room
	Day 15	Day 5	µg	µg	µg/m^3	µg/m^3	µg/m^3	µg/m^3
Toluene	73153	80	15508.4	77.0	1558.5	311.71	3648.2	729.64
Xylenes, ethylbenzen	599		127.0		12.7	2.54	29.8	5.97
C_9H_{12}, arom hydrocarbon	207		43.9		4.4	0.88	10.3	2.06
alpha-Pinene	1478		313.3		31.3	6.27	73.6	14.72
Camphene	473		100.3		10.0	2.01	23.6	4.71
beta-Pinene	281		59.6		6.0	1.19	14.0	2.80
d-Limonene	554		117.4		11.7	2.35	27.6	5.52
$C_{10}H_{14}$ arom hydrocarbon	591		125.3		12.5	2.51	29.4	5.89
Other terpenes	11010		2334.1		233.4	46.68	548.3	109.66
C9-C13 aliph. Hydrocarbons		1598		1538.9	153.9	30.78	107.9	21.57
C13-C19 aliph. Hydrocarbons		17433		16788.0	1678.8	335.76	1176.7	235.35
Formaldehyde	-	25		24.1	2.4	0.48	1.7	0.34
Acetaldehyde	206	40	43.7	38.5	8.2	1.64	13.0	2.59
Propanal	77	-	16.3		1.6	0.33	3.8	0.75
Acetone	540	48	114.5	46.2	16.1	3.21	30.1	6.03
Butanal	16	7	3.4	6.7	1.0	0.20	1.3	0.25
Pentanal	13	7	2.8	6.7	0.9	0.19	1.1	0.22
Hexanal	152	43	32.2	41.4	7.4	1.47	10.5	2.09
Benzaldehyde	96	2	20.4	1.9	2.2	0.45	4.9	0.98
2-Butanone	4	-	0.8		0.1	0.02	0.1	0.03
Total VOC sum	89449	19282	18963	18569	3753.2	751	5756	1151

-: below detection limit or below the background concentration
P.M.: printed matter. l. room: living room

The changes in the air concentrations in entrance hall and living room scenario are estimated by a box-model.

Box-model
For the evaluation of the concentrations that may arise in a room where printed matter are located and leafed through, a simple theoretical box model can be used. A room with a known volume and a known air change is used.

In the estimations in this study, the following assumptions are used.

Room volume:	10 and 50 m^3
Air change:	0.5 times per hour

It is a further condition that only printed matter is used and leafed through in the room, other sources are not included, and that the air is completely mixed.

The concentration of VOC increases gradually until an equilibrium concentration is reached typically after a few hours. The equilibrium in concentration mean that the amount of VOC's released from the printed matter equals the amount ventilated out of the room.

Assuming a constant emission of VOC's over 8 hours and an air change of 0.5 times per hour, would result in the evolution of the air concentration shown in figure 6.1.

In figure 6.1, an approximated equilibrium is reached within 8 hours. The equilibrium concentration of total VOC is about 8 mg/m^3 of which toluene is approx. 3 mg/m^3.

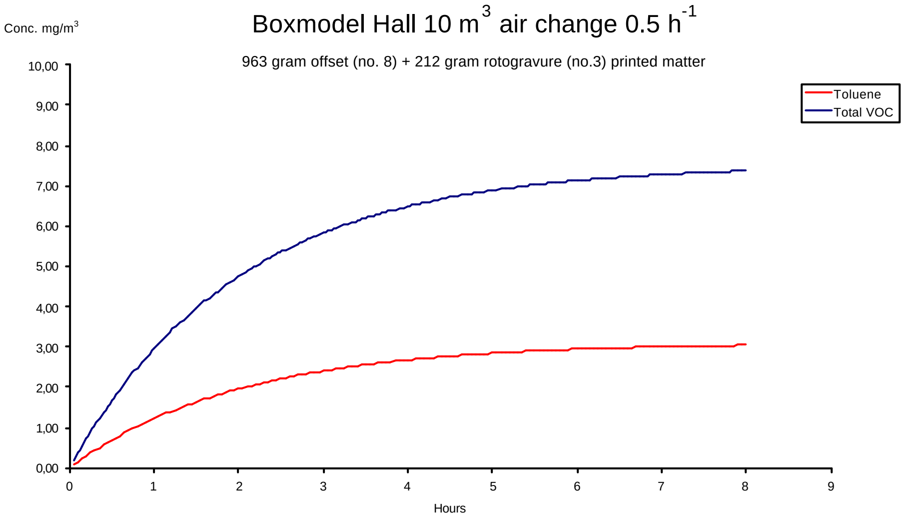


Figure 6.1 Estimated concentration of VOC in hall using the average consumption of printed matter

Toluene from rotogravure is observed to account for an essential part of the average load not only in the average scenario but even more in the "worst case" scenario (cf. below). It should be noted that the "worst case" scenario includes three rotogravure printed matters which is not unrealistic if the home is located near larger stores or malls or near larger cities.

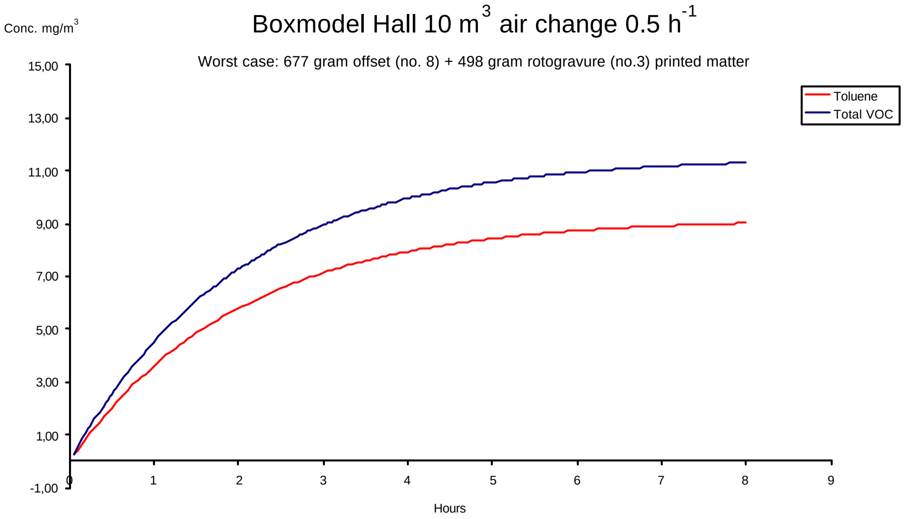


Figure 6.2 Estimated concentrations in hall using "worst case" consumption of printed matter

From figure 6.2, an approximated equilibrium is reached within 8 hours. The VOC equilibrium concentration is approx. 11 mg/m^3 of which toluene accounts for approx. 7 mg/m^3.

In the living room the equilibrium concentrations is approximately 1/5 of the entrance hall scenarios. It is not expected that the printed matter will be in the entrance hall for more than three hours on a weekly basis.

6.1.7.2 Printed matter laying in hall and living room

An estimate of the concentration of total volatile organic compounds (TVOC) is performed assuming the printed matter is laying untouched in an entrance hall of 10 m^3 and a living room of 50 m^3, respectively, both with an air change rate of 0.5 per hour. The results of the estimations are presented in the table below. The results are based on the estimated half-lives of the VOC emissions assuming exponential decrease.

Table 6.8 Hall and living room scenarios, TVOC contribution from single printed matter laying untouched

Printed matter no.	Days after printing	Half-lives, hours	Hall, µg/m^3	Living room, µg/m^3
2, Rotogravure, weekly magazine	2	48	96	19
3, Rotogravure, advertising printed matter	15	132	11	2
8, Offset, monthly journal	5	48	9	2
17, Offset, monthly journal	7	360	< 1	< 1
19, Offset, advertising printed matter	7	60	8	2

Remarks: In printed matter:

No. 2	Toluene constitutes:	98,8 %
No. 3	Toluene constitutes:	81,8 %
No. 8	$C_9 - C_{19}$ constitutes:	98,7 %
No. 17	$C_9 - C_{19}$ constitutes:	53,0 %
No. 19	$C_9 - C_{19}$ constitutes:	94,2 %

The emission of VOC's is considerably reduced when the printed matter is lying untouched.

It is noted that the contributions from the single printed matters are added to the sum of volatile organic compounds (TVOC) and that single compounds or groups of compounds may form a considerable contribution (cf. remarks below table 4.8). The contribution from each printed matter may be small but some consumers may have significant amounts of printed matter in their homes for one or another reason. The effect of this depends on the number, ventilation, temperature and the kind of printed matter.

The results demonstrate that even if the contribution from each printed matter is small printed matter will increase the VOC concentration in the home. Normal concentrations measured in Danish average homes vary between 100 and 1000 µg/m^3 (Eggert 2001).

7 Conclusion

The purpose of the study was to survey the volatile organic compounds which the consumer is exposed to from printed matter.

The volume of printed matter that the consumer receives either by purpose, by purchase or as unaddressed mail is slowly increasing if the estimated consumption is based on the consumed amount of paper and printing inks. The consumption for the average household of paper and cardboard in the year 2000 was approximately 432 tonnes for the country in total, corresponding to 177 kg per year for the average household. Based on weekly and monthly magazines, journals, periodicals and unaddressed mail the consumption was estimated to approx. 61 kg per household. This corresponds to approx. 1.2 kg per week for the average household. Of this rotogravure printed matter made up approx. 18%, Thus the average weekly consumption was 0.2 kg rotogravure printed matter and approx. 1 kg offset printed matter.

During the screening phase, 21 printed matters were analysed for their release of volatile organic compounds. The differences observed is assumed related to the printing method and the difference in used printing inks, raw materials etc. A potential contribution fran e.g. paper types could not be differentiated by the used measuring method.

Rotogravure printed matter (catalogues, advertisement printed matter etc.) released large amounts of volatile substance of which toluene was the major component and to a lesser extent terpenes and aldehydes. In offset especially long-chained aliphatic hydrocarbons (C9 to C19) dominated followed by aldehydes. Monocyclic aromatic hydrocarbons like toluene and xylenes were also present but in small amounts. Flexographic printed matter was also included and the main release of volatile compounds were alcohols and terpenes but to a much lesser extent than from the previous printing techniques. The reason was probably the use of UV-curing printing inks and lacquers which means that the printing inks composed of monomeric acrylates polymerises to solid ink layers. No monomere acrylates were observed in the volatile compounds analysed.

Six types of printed matter were selected for quantitative analysis. The sampling and measuring method were based on the situation representing the largest exposure to consumers from released volatile organic compounds, i.e. during reading or leaf through the printed matter. The situation was modelled by fast shredding of the printed matter, placing it in a closed glass container and sampling of the volatile organic compounds that evaporated from the printed matter. The tests were performed as the printed matter left the printing house or arrived at the country if printed abroad. The measuring was repeated 1 to 5 days after printing to represent the stage of sorting, distribution etc. and again 2 to 15 days after printing when the printed matter is assumed to reach the consumer.

It was observed that some compounds decreased with time, e.g. toluene and alcohols, other compounds peaked during the measurement period, e.g. aliphatic hydrocarbons. Finally some compounds increased their emissions during the measurement period. The latter was observed especially for aldehydes, indicating that aldehydes in offset printed matter may be strongly adsorbed into the paper or the printing ink during printing and released at a later time. It means that a first measurement is not sufficient to realise the emissions, the air concentrations and the volatile organic compounds the consumer is exposed to from printed matter.

The primary situation modelled is the situation where the highest exposure is expected, i.e. during handling, reading or leaf through of the printed matter (magazine or advertising printed matter). Therefore the last measuring was performed as representative for the inhalation concentration which the consumer is exposed to during leaf through the printed matter.

As safe level, 1/100 of the threshold limit value (TLV) was used. The TLV is a value set by the authorities as a value that should not be exceeded in the working environment where the compound is used. Thus, because the TLV is intended for the working environment and not valid for residential homes, 1/100 of the value was used in the assessment.

The LCI (lowest concentration of interest) value was included in the evaluation as the derived values are related to indoor air, and developed in connection with assessment of volatile organic compounds emitted from furniture. It should be noted that LCI-values are weighing factors indicating the relative hazard of substances and not a criteria for indoor air quality or a fixed threshold limit value. The LCI-values is usually derived from irritation data.

Odour threshold values were included to evaluate the possibility of the compound at the measured concentrations be smelled by the consumer. The perceptions of odour vary among consumers but the odour threshold value compared to the measured concentrations indicated the potential of the compounds to be smelled by the consumer.

For rotogravure printed matter toluene was the primary constituent of the emitted concentrations measured. Toluene is a harmful compound and the emitted concentrations exceeded TLV/100 and the LCI value in the leaf through situation. Because the highest measured emission of 272 mg/kg printed matter resulting in an exposure concentration of 23 mg/m^3 was considered acute the evaluation is refined. The leaf through situation is a worst case situation, because it was not taken into account that the air will be mixed in more than 2 m^3 air within one hour. The real concentration around the reader is therefore expected to be lower than the estimated concentration. Considering that the highest value did not exceed the NOAEC 150 mg/m^3 it was concluded that toluene was not a health problem to the average consumer.

For flexographic printed matter only low concentrations of VOC's were measured. No monomers of acrylates were identified and therefore no health problems for the consumer were anticipated.

For offset, the sum of aliphatic hydrocarbons may have exceeded the TLV/100. However, no total or group value exists. The individual substances may not cause problems but some may cause cancer and thus would be without a limit value. Based on individual substances where data existed no indications were available that significant health problems could arise by the measured concentrations of aliphatic hydrocarbons. However, the data were too weak for a conclusion to be made.

The results indicate that the identified VOCs do not exceed the TLVs. A few exceed TLV/100 of which toluene was the most noticeable. A few of the aldehydes also exceed TLV/100 e.g. formaldehyde which is also a harmful substance. A few exceed the LCI.

The terpenes that combined resulted in odour exceeding i.e. could potentially be smelled as a group but hardly individually. Pinene and limonene were observed as potential problematic substances as they are allergenic.

Generally it was observed that only a few compounds exceeded the odour threshold. It can be concluded that only very few compounds are identifiable by the consumer from odour released from printed matter, e.g. toluene. However, the sum of contributions into groups could exceed odour threshold and be identifiable by the consumer as oil, terpenes or a general sense of smell.

Room scenarios were included in the study in order to evaluate the effect of dilution. The estimated individual and total VOC concentrations in the rooms during handling the printed matter included in an amount corresponding the average week load and a "worst case" with a higher percentage of rotogravure are presented. The used evaluation values were not exceeded (except toluene in hall). In general, no health problems would be expected except for sensitive or allergic persons in situation were the "worst case" scenario take place or even is exceeded. Thus, toluen is assessed not to present a health problem to the average consumer.

The emission from each printed matter when lying untouched was estimated. When the printed matter is untouched the emission of volatile organic compounds was significantly reduced. The contribution from each printed matter based on the total volatile organic compounds (TVOC) was small. However, even if the contributions from each single printed matter may be small some consumers may have significant amounts of printed matter in their homes. The effect of this depends on the number, ventilation, temperature and the kind of printed matter. Thus even untouched printed matter may contribute to the total VOC load of the home.

The main fraction of emissions to the environment from printed matter (after production but during use and disposal) is to the atmosphere. However it is concluded that the contribution from printed matter in these "life-cycle" phases are minimal compared to the contribution from other sources such as combustion of oil and gasoline. The total volume of VOC emitted to the atmosphere could not be estimated due to lack of valid data.

The overall conclusion is that no health risks exist to the consumer of printed matter. However, it can not be excluded that allergic reactions may be observed by sensitive consumers.

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Appendix 1 List of printed matter in the screening study

For the screening the following printing houses applied the mentioned printed matter at disposition to the study

Table B.1 List of printed matter used in the screening study

Printing house	Printed matter name	Type	Printing
Aller Tryk A/S	Femina	Weekly magazine	Offset, heatset
Aller Tryk A/S	Kryds journalen	Weekly magazine	Offset, heatset
Berger Plus A/S	Kvickly	Advertising matter	Rotogravure
Berger Plus A/S	BR Legetøj	Advertising matter	Offset, heatset
Berger PlusA/S	Føtex	Advertising matter	Rotogravure
Egmont Magasiner A/S	Her & Nu	Weekly magazine	Rotogravure
Graphx A/S	Bo Concept	Advertising matter	Offset, heatset
Graphx A/S	Silvan	Advertising matter	Offset, heatset
Graphx A/S	Illustreret Videnskab	Monthly magazine	Offset, heatset
Graphx A/S	PC Planet	Monthly magazine	Offset, heatset
Graphx A/S	SID Bladet	Association journal	Offset, heatset
IWACO A/S	Medicin etiket	Label	Flexographics
IWACO A/S	Grå etiket	Label	Flexographics
K. Larsen & Søn A/S	Månedsmagasinet	Advertising matter	Offset, sheet
K. Larsen & Søn A/S	Natur og Miljø	Membership journal	Offset, sheet
K. Larsen & Søn A/S	Handicap Nyt	Membership journal	Offset, sheet
Luna Tryk	Ingen navn	Advertising matter	Offset, sheet
Paritas A/S	IN-FOA-TION	Membership journal	Offset, sheet
Paritas A/S	CVU	Advertising matter	Offset, sheet
Paritas A/S	Tråden	Advertising matter	Offset, sheet
Paritas A/S	Prisliste	Advertising matter	Offset, sheet

Appendix 2 List of volatile organic compounds found in the screening of printed matter

Results from the screening of volatile organic compounds in 21 printed matter. Values presented in area percentages of the chromatograms. If the substance is closely located to another it is marked "in +ID nn." and colored yellow

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
	Syrer																						
1	p-tert-butyl-benzoic acid	98-73-7			0.5																		
	Alcohols																						
2	1-Ethylcyclopropanol	57872-31-8													in 6								
3	2-propyl-1-pentanol	58175-57-8															in 10	in 10				in 10	
4	1,3-butane-diol (=1,3-butylene glycol)	107-88-0																	7				
5	1-Butanol	71-36-3		1.3	1.7	7.1	1.2			<0.1			0.4	0.9			0.5	0.5	0.4	0.3	0.2	0.3	0.5
6	1-Penten-3-ol	616-25-1								0.1	0.3		0.1	0.5	0.4	<0.1	0.2	0.4	0.4	0.5	0.5	0.5	0.3
7	1-Propanol	71-23-8																					<0.1
8	1-Propoxy-2-propanol	1569-01-3															0.3						
9	2-butanol	78-92-2														<0.1							
10	2-Ethyl-1-hexanol	104-76-7				13.4					7		6.3				2.8	2.5				1	0.4
11	2-Hexanol	626-93-7				4.6																	
12	2-Methyl-2-propanol	75-65-0				1	0.8											0.3					0.1
13	2-Propanol (isopropyl alcohol)	67-63-0				2.5	0.9	0.2	0.1	0.2	0.3	0.1			5	0.6				0.4			0.3
14	4-Methyl-2-pentanol	108-11-2					0.2																
15	Ethanol	64-17-5															0.2	0.2	0.4	0.1		1.6	<0.1
16	Pentanol	71-41-0		0.5						<0.1			1.1	0.4	1		0.6	0.7	0.6	0.3	0.3	0.4	0.6
17	1,1-Methylethoxy-2-propanol [=1-Isopropoxy-2-propanol]	3944-36-3																				0.3	
18	1-Octen-3-ol	3391-86-4													0.5								
19	butyleret hydroxytoluen (= 2,6-di-tert-butyl-p-cresol)	128-37-0					0.9																
	Aldehydes																						
20	2-butenal (=crotonaldehyde)	4170-30-3																					<0.1
21	2-Methylpropanal	78-84-2											0.7				0.3	0.6	in 25	in 25			0.3
22	3-Methylbutanal	590-86-3	1.2																				
23	4-Methylhexanal	41065-97-8													0.9								
24	2-n-Butylacrolein	1070-66-2										0.3											
25	Butanal	123-72-8		0.9												<0.1			0.6	0.5	0.9	0.3	
26	Heptanal	111-71-7	0.7	0.6					<0.1	<0.1		0.4	1	0.7	1.7	<0.1	0.7	0.9		0.5		0.4	0.5
27	Hexanal	66-25-1	11.8	12.3	1.2	0.9		0.9	0.2	2.2	2.2	3.5	18	8.5	<0.1	0.6	5	8.3	10.7	4.2	2.6	4.4	4
28	Nonanal	124-19-6	0.8	0.8											1.8								
29	Octanal	124-13-0																in 80					1
30	Pentanal	110-62-3	in 22	1.9				0.1				0.1	3.8				0.9	2.4	2.5	4.1	4.5		2.6
31	Propanal	123-38-6																		1.5	1.3		
32	(E)-2-Butenal	123-73-9																		0.1			
33	2-Heptenal	57266-86-1											0.4		1						0.5		0.3

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
34	2-Hexenal	505-57-7																		0.2			0.1
35	2-Octenal	2548-87-0													2.4								
36	2-Pentenal	1576-87-0											0.3							0.2	0.2	0.2	0.2
37	2-Propenal (= Acrolein)	107-02-8																					<0.1
38	Benzaldehyde	100-52-7			2.4	0.7	1.5						2.8							0.2	0.9		0.3
	Esters																						
39	2-Ethylhexyl-2-ethylhexanoat	7425-14-1											6.2										
40	2-Methyl-propanois acid, 2-methyl-propylester (=isobutylisobutyrate)	97-85-8				2.3																	
41	Butylacetate	123-86-4				5	0.3																
42	Dodecanoic acid, 1-methyl-ethyl-ester	10233-13-3												7.2									
43	Acetic acid, 2-ethylhexylester (= 2-Ethylhexyl acetate)	103-09-3				9.8	24.5																
44	Ethylacetate	141-78-6					0.2																
45	Oktanoic acid, methylester	111-11-5	0.4	0.5																			
46	Propanoic aic butylester (=butylpropionat)	590-01-2				5.7	0.6																
47	Benzoic acid methylester	93-58-3					1.9																
48	Dibutylphthalate	84-74-2							<0.1														
49	2-Propenoic acid, 6-methylheptylester	54774-91-3				0.6																	
50	Di-n-butylether	142-96-1				11.6	0.8																
51	2-Butoxyethanol (=butylglycol)	111-76-2									1												
	Aliphatic hydrocarbons, saturated, unsaturated and cyclic																						
52	C8 - C12 aliphatic hydrocarbons							40		52	42	37	55	36			75	32	70	41	27	68	25
53	C11 - C18 aliphatic hydrocarbons								98.8														
54	C11 - C20 aliphatic hydrocarbons													41		68							60
55	C12 - C18 aliphatic hydrocarbons							56		41	46	57											
56	C12 - C19 aliphatic hydrocarbons																12	49	6	43	58	14	
57	C13 - C18 aliphatic hydrocarbons														70								
58	Dimethylphenol (not in screening)	526-75-0																					
59	2-Hexenal (E)	6728-26-3											0.2								0.2		
60	3-Ethyl-2-methyl-1,3-hexadiene	61142-36-7													0.2								
61	3-Methylen-heptane	1632-16-2					6.7																
62	C8 H16, Ethylcyclohexane	1678-91-7			0.5																		
63	Decane	124-18-5		0.3	0.7		0.8																
64	Dodecane	112-40-3			0.8																	1	
65	Heptane	142-82-5			0.6								0.2							<0.1			<0.1
67	Hexadecane	544-76-3												<0.1									
68	Hexylcyclopentane	4457-00-5					0.2																
69	Nonane	111-84-2			0.4		0.3																

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
70	Octane	111-65-9		<0.1	1.3								0.1							0.1			0.1
71	Pentadecane	629-62-9											1	<0.1									
72	Pentane	109-66-0																	0.3				
73	Tetradecane	629-59-4											0.8	<0.1									
74	Tridecane	629-50-5											0.6										
75	Undecane	1120-21-4		0.4	1.3																		
76	C12 H18, fx 1,2-bis(ethylmethyl)-benzene 577-55-9 / 1441-56-4	577-55-9			0.4																		
77	1,1-Dimethyl-2-propylcyclohexan	81983-71-3											1.4										
78	1-Butoxy-2-ethylhexane	1000139-90-4					1																
79	2-Ethylfuran	3208-16-0								<0.1	0.4		0.3		0.2		0.2	0.3	5.3	0.4		0.4	
80	2-Pentylfuran	3777-69-3	0.7	1.1					<0.1				1.8		3.2		0.1	1.3					in 29
81	2-Propenylbenzene	300-57-2		in84																			
82	C15 H24, Cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-	515-13-9	1.5	2.2																			
83	C8H16:1,3-Dimethylcyclohexane	638-04-0			in 84																		
84	1,4-Dimethylcyclohexane	589-90-2			2.5																		
85	C8 H16, Dimethylcyclohexane (589-90-2 / 638-04-0 / 591-21-9)	591-21-9			1.1																		
86	C9 H18, 1,1,3-Trimethylcyclohexane	3073-66-3			0.7																		
87	Cyclohexanmethanol	5114-00-1	0.7	0.8																			
88	2,3-Dimethyl-1-pentene	3404-72-6																	0.3				
89	2-methyl-2,4-hexadiene	28823-41-8												in103									
90	3-Methyl-2,4-hexadiene	28823-42-9									in 79					<0.1							
91	3-methyl-4-decene	62338-47-0				0.8	35																
92	3-propoxy-1-propene	1471-03-0								0.1				0.7	4.8							1	
93	4,7-Methano-1H-indene, octahydro	6004-38-2				1																	
94	4-ethyl-3-octene	53966-51-1						<0.1															
95	4-methyl-1,4-hexadien e	1116-90-1												in103									
96	6-Dodecene	7206-17-9				1.2																	
97	C12 H24 2 stk, fx 4-dodecen 2030-84-4, or 7206-28-2, 7206-15-7	2030-84-4					1																
98	Decene, fx	7433-56-9						<0.1															
99	Nonene	124-11-8														<0.1							
100	2,4,4-Trimethyl-1-pentene	107-39-1																					<0.1
101	Methylcyclohexane	108-87-2				0.3																	
102	Tetramethylcyclohexane	1000144-07-3			0.5																		
103	4-Methylcyclohexene	591-47-9												0.5							0.3		0.3
104	4-trimethyl-3-Cyclohexen-1-methanol (S) (alfa-terpineol)	10482-56-1	in 144	in 144																			
109	Methylethylcyclohexene	3983-08-2																			0.4		
	Aromatic hydrocarbons																						
110	1-Methyl-indan	767-58-8			1.6																		

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
111	Benzene	71-43-2									0.2												
112	C10 H14 aromatic hydrocarbons (3 pcs) fx 535-77-3, 99-87-6 methylisopropylbenzine)				2.6																		
113	C15 H24, fx: Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	483-76-1	<0.1	0.7																			
114	C15 H24, Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-	39029-41-9	0.7	0.8																			
115	C9 H12 aromatic hydrocarbons				3.1		9.4																
116	C9 H12 aromatic hydrocarbons			0.7		9.2																	
117	C9 H12, fx 98828 isopropylbenzene (cumene)	98-82-8																	0.5				
118	Cyclopropylbenzene	873-49-4				1.1	0.9																
119	Ethylbenzene	100-41-4																					
120	Naphthalene	91-20-3			0.1	0.5	1																
121	Styrene	100-42-5			0.5			0.1			0.2								0.9				
122	Toluene	108-88-3	29.8	17.6	25	1.7	1.3	0.2	<0.1	<0.1	0.1	0.3				0.1							<0.1
123	Xylenes	1330-20-7	2.1	3.2	12.6											<0.1							
124	1-Ethyl-2-methylbenzen (= 2-methylstyren)	611-15-4			1																		
125	Dichloromethane	75-09-2																	1.8				
126	Pyrazin	290-37-9									<0.1												
127	C15 H24, 2H-2,4a-Methanonaphthalene, 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-, (2S)-	1135-66-6	1	1.2	2.4		1.3																
	Ketones																						
128	3-Methyl-4-heptanone	15726-15-5				1.2	0.2																
129	1-Methoxy-2-propanone (methoxyacetone)	5878-19-3												0.3				0.5	0.7		0.4		
130	1-Penten-3-one	1629-58-9																		0.1			<0.1
131	2,6-dimethylcyclohexanone	2816-57-1							<0.1														
132	2-heptanone	110-43-0															0.5		0.5			0.2	0.2
133	2-Hexanone	591-78-6											0.2	0.2			0.1			0.1			0.1
134	2-Propanone (Acetone)	67-64-1	4.8	3.9	1			0.4	0.1			0.4	1		4	0.4	1.1	1.7	2.2			2	1
135	3-Buten-2-one	78-94-4																					<0.1
136	3-Heptanone	106-35-4											0.2							0.2			0.1
137	4-Heptanone	123-19-3				0.5																	
138	Butanone	78-93-3									0.1					<0.1				0.4		0.2	0.4
139	cyclohexanone	108-94-1								0.1				0.6									
	Terpenes, terpenoids																						

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
140	4-trimethyl-Cyclohexanemethanol, ,alpha,,,alpha,,	498-81-7		in 87																			
141	C15 H24, 1,4-Methanoazulene, decahydro-4,8,8-trimethyl-9-methylene- [Longifolene:terpene]	475-20-7	17	23.7	5.8	8.5	8.1																
142	C15 H24, alfa-Caryophyllen	6753-98-6	0.5	0.7																			
143	Terpen, C10 H16, fx:	508-32-7	<0.1	0.5												28							
144	4-trimethyl-3-cyclohexen-1-methanol (=alpha-Terpineol)	98-55-5	0.6	0.9																			
145	1,4-cyclohexadien, 1-methyl-4-(1-methylethyl)- [=gamma-terpinene]	99-85-4							<0.1														
146	beta-Pinene	127-91-3	0.7	0.9																			
147	Borneol	507-70-0		0.2			0.4																
148	Camphene	79-92-5	1.5	2.1	2.6																		
149	D-limonene	5989-27-5	1.3	1.9	0.9																		
150	l-alfa-Pinene	7785-26-4	4.8	6.7	1.9																		
105	C15 H24, 1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-,	1137-12-8	2.4	3.3	3.3	5.4	7.9																
106	C15 H24, 1,4-methano-1H-indene, Octahydro-4-methyl-8-methylen-7-(1-methylethyl)-	3650-28-0	0.5	0.6																			
107	C15 H24, Copaen [Tricyclo(4.4.0.02.7)dec-3-ene, 1,3-dimethyl-8-(1-methylethyl)-]	3856-25-5	1.9	2.6																			
108	C15 H24, Tricyclo(5.4.0.02.8)undec-9-en, 2,6,6,9-tetramethyl	5989-08-2	1.2	1.6																			
	Other																						
151	C10 H14 (fx:Benzene, 1-ethyl-3,5-dimethyl-)	934-74-7					0.2																
152	C10 H14 (4 komponenter)			2.9																			
153	C10 H14 + C12 H22				1																		
154	C10 H20									0.8													
155	C10 H20 / Indan fx 86869-76-3 / 95-13-6				0.4																		
156	C11 H22, fx 81983-71-3	81983-71-3			0.6																		
157	C12 H18, fx 1,3-bis(methylethyl)-benzene 99-62-7 / 98-19-1	99-62-7			0.5																		
158	C12 H24 5 compounds												6										
159	C15 H24,	30021-74-0	in114	in114																			
160	C15 H24, fx 1000109-88-1 / 88-84-6				0.4																		
161	C15 H24, alfa-Cubebene	17699-14-8	in107	in107																			
162	C9 H12 / C10 H14 (3 komp)		1.5																				

ID	Component		1	3	2	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
nr,:		CAS no.:																					
163	C9 H18				0.4																		
164	Cycloisosativene	1000109-88-1				0.8																	
165	Methoxyphenyloxime	1000222-86-6																			0.2		
166	N-methylthioformamide	1000196-87-7						<0.1															
	SUM		56.4	54.7	66.4	86.4	99.3	97.5	99.1	95.6	99.7	98.7	102.5	96.4	93.1	69.3	98.8	99.4	107.7	97.6	97.8	93.8	96.9
	NUMBER		18	25	26	22	24	9	7	11	13	8	22	15	16	11	15	16	18	20	15	16	27

Appendix 3 Alphabetical list of found chemical substances

The table contains the chemical substances found in the study. The identified compounds appear in *alpha*alfabetical order. At the end of the table unidentified groups or uncertain compounds with suggested CAS nos.

Total list of volatile organic compounds,
Type: chemical group,
classification: according to Danish classification (Miljøministeriet 2002),
TLV: threshold limit value, unspecified Danish values (Arbejdstilsynet 2002), t: temporary values, in brackets other countries e.g. D=MAK and US = NIOSH or ACGIH values, EU = Dir. 2000/39/EC
LCI: lowest concentration of interest ,
C-value: Contribution value according to Miljøstyrelsen 2002
odour: Odour threshold value (VOCBASE 1996)
M-form: molecular formula,
MW: molecular weight
VP: vapour pressure (VP).
Italics: Indicates that the value is estimated by QSAR

Compound	CAS no.:	Type	Classification	TLV mg/ m^3	LCI µg/ m^3	C-value mg/ m^3	Odour µg/ m^3	M_form	MW g/mol	VP Pa
Acetaldehyde	75-07-0	aldehyde sat	Fx;R12 Xi;R36/37 Carc3;R40	45	5200	0.02	340	C2 H4 O	44.05	120236
Benzaldehyde	100-52-7	aldehyde unsat	Xn;R22		1200		190	C7 H6 O	106.12	71
Benzene	71-43-2	HC arom	Carc1;R45 F;R11 T;R48/23/24/25 (29.ATP: F;R11 Carc1;R45 Mut1;R46 T;R48/23/24/25 Xn;R65 Xi;R36/38	1.6		0.005	32500	C6 H6	78.11	12637
Benzooic acid methylester	93-58-3	ester					600	C8 H8 O2	136.15	50.65
Borneol	507-70-0	terpene mono-					14	C10 H18 O	154.25	0.06
Butanal	123-72-8	aldehyde sat	F;R11		2800	0.001	28	C4 H8 O	72.11	14796
1,3-butan-diol (1,3-butylene glycol)	107-88-0	alcohol ali.						C4 H10 O2	90.12	2.67
1-Butanol	71-36-3	alcohol, ali.	R10 Xn;R22 Xi;R37/38/41 R67	150	200	0.2	90	C4 H10 O	74.12	893
2-Butanol	78-92-2	alcohol ali.	R10 Xi;R36/37 R67	150		0.7	3300	C4 H10 O	74.12	893
Butanone	78-93-3	ketone	F;R11 Xi;R36 R66 R67	145		1	870	C4 H8 O	72.11	12076
2-Butenal (=crotonaldehyde)	4170-30-3	aldehyde	F;R11 T;R24/25 Tx;R26 Xi:R37/38-41 Xn;R48/22 Mut3;R68 N;R50	6		0.02	390	C4 H6 O	70.09	3999
(E)-2-Butenal	123-73-9	aldehyde unsat	F;R11 T;R24/25 Tx;R26 Xi:R37/38-41 Xn;R48/22 Mut3;R68 N;R50	6		0.02	390	C4 H6 O	70.09	3999
3-Buten-2-one	78-94-4	ketone					570	C4 H6 O	70.09	
2-Butoxyethanol (=butylglycol)	111-76-2	glycol, -ether,-ester	Xn;R20/21/22 Xi;R36/38	98		0.04	5	C6 H14 O2	118.18	117
1-Butoxy-2-ethylhexane	1000139-90-4	HC ali. sat/cyclic								
Butylacetate	123-86-4	ester	R10 R66 R67	710	2700	0.1	47	C6 H12 O2	116.16	1070
2-n-Butylacrolein	1070-66-2	aldehyde sat						C7 H12 O	112.17	928

Compound	CAS no.:	Type	Classification	TLV mg/ m³	LCI µg/ m³	C-value mg/ m³	Odour µg/ m³	M_form	MW g/mol	VP Pa
p-tert-Butyl-benzoic acid	98-73-7	acid						C11 H14 O2	178.28	0.01
Butyleret hydroxytoluene (= 2,6-di-tert-butyl-p-cresol)	128-37-0	alcohol arom		10		0.01		C15 H24 O	220.36	0.69
Camphene	79-92-5	terpene mono-		140	250		28000	C10 H16	136.24	333
1,4-cyclohexadiene, 1-methyl-4-(1-methylethyl) [=gamma-terpinene]	99-85-4	terpen mono-		140	250		1500	C10 H16	136.24	145
Cyclohexanmethanol	5114-00-1	HC ali. sat/cyclic						C10 H20 O	156.27	
cyclohexanone	108-94-1	ketone	R10 Xn:R20	40	2300	0.1	83	C6 H10 O	98.15	577
Cycloisosativene (99%) or cycloisosative (1000157-67-1 (98%), 88-84-6 (90%))	1000109-88-1							C15 H24	204.36	
Cyclopropylbenzene	873-49-4	HC arom						C9 H10	118.18	174
Decane	124-18-5	HC ali. sat		250	2000		4400	C10 H22	142.29	190
Decene, fx	7433-56-9	HC ali. unsat						C10 H20	140.27	271
Di-n-butylether	142-96-1	ether	R10 Xi;R36/37/38 (+29ATP: R52/53)				30	C8 H18 O	130.23	801
Dibutylphthalate	84-74-2	ester (phthalate)	Rep2;R61 Rep3;R62 N;R50	3		0.01*		C16 H22 O4	278.53	0.003
Dichloromethane	75-09-2	chlor.HC	Carc3;R40	122		0.02	3420	C H2 Cl2	84.93	57985
2,6-Dimethylcyclohexanone	2816-57-1	ketone						C8 H14 O	126.2	221
2,3-Dimethyl-1-pentene	3404-72-6	HC ali. unsat						C7 H14	98.19	10810
Dimethylphenol	526-75-0	HC alif. cyclic	T;R24/25 C;R34 N;R51/53				4	C8 H10 O	122.17	12
1,1-Dimethyl-2-propylcyclohexane	81983-71-3	HC ali. sat/cyclic								
Dodecane	112-40-3	HC ali.sat.				1*	14500	C12 H26	170.34	18
Dodecansyre, 1-methyl-ethyl-ester	10233-13-3	ester						C15 H30 O2	242.41	0.36
6-Dodecene	7206-17-9	HC ali. unsat						C12 H24	168.33	21
Eddikesyre, 2-ethylhexylester (= 2-Ethylhexyl acetate)	103-09-3	ester			1100		2300	C10 H20 O2	172.27	30
Ethanol	64-17-5	alcohol ali.	F; R11	1900		5	280	C2 H6 O	46.07	7904
Ethylacetat	141-78-6	ester	F;R11 Xi;R36 R66 R67	540	5000	1	2400	C4 H8 O2	88.11	12423
Ethylbenzen	100-41-4	HC arom	F;R11 Xn;R20	217	4300	0.5	2000	C8 H10	106.17	1279
1-Ethylcyclopropanol	57872-31-8	alcohol								
2-Ethylfuran	3208-16-0	HC ali. sat/cyclic						C6 H8 O	96.13	7024
2-Ethyl-1-hexanol	104-76-7	alcohol ali.		270 (D)	1000		500	C8 H18 O	130.23	18
2-Ethylhexyl-2-ethylhexanoat	7425-14-1	ester								
1-Ethyl-2-methylbenzen (= 2-methylstyren)	611-15-4	HC arom.	Xn;R20 N;R51/53	120		0.1	49000	C9 H10	118.18	246
3-Ethyl-2-methyl-1,3-hexadien	61142-36-7	HC ali.sat						C9 H16	124.23	
4-Ethyl-3-octen	53966-51-1	HC ali. unsat						C10 H20	140.27	
Formaldehyd (ikke med i screening, men i kvantitativ anallyse)	50-00-0	aldehyde sat	Carc3;R40 R43 C;R34 T;R23/24/25	0.4	100	0.01	1100	C H2 O	30.03	518537
Heptan	142-82-5	HC ali. sat	F;R11 Xi;R38 Xn;R65 R67 N;R50/53	820	8000	1	41000	C7 H16	100.21	6131

Compound	CAS no.:	Type	Classification	TLV mg/ m^3	LCI µg/ m^3	C-value mg/ m^3	Odour µg/ m^3	M_form	MW g/mol	VP Pa
Heptanal	111-71-7	aldehyde sat			3100		23	C7 H14 O	114.19	469
2-Heptanon	110-43-0	ketone	R10 Xn;R20/22	238	2300	0.1	680	C7 H14 O	114.19	513
3-Heptanon	106-35-4	ketone	R10 Xn;R20 Xi;R36	95	2300		Nv	C7 H14 O	114.19	346
4-Heptanon	123-19-3	keton	R10 Xn;R20	230				C7 H14 O	114.19	815
2-Heptenal	57266-86-1	aldehyde unsat			2			C7 H12 O	112.17	
Hexadecan	544-76-3	HC ali.sat						C16 H34	226.45	0.19
Hexanal	66-25-1	aldehyde sat		175(US)	3400		58	C6 H12 O	100.16	1506
2-Hexanol	626-93-7	alcohol ali.					3200	C6 H14 O	102.18	331
2-Hexanon	591-78-6	ketone	R10 T;R48/23 Rep3;R62 R67	4		0.3	700	C6 H12 O	100.16	1546
2-Hexenal	505-57-7	aldehyde unsat						C6 H10 O	98.15	
2-Hexenal (E)	6728-26-3	HC ali.sat					130	C6 H10 O	98.15	
Hexylcyclopentan	4457-00-5	HC ali. sat						C11 H22	154.3	59
d-Limonen	5989-27-5	terpene mono-	R10 Xi;R38 R43 N;R50/53	140	300		2500	C10 H16	136.24	191
4,7-Methano-1H-indene, octahydro	6004-38-2	HC ali. unsat						C10 H16	136.24	
Methoxyphenyloxim	1000222-86-6									
1-Methoxy-2-propanon (methoxyacetone)	5878-19-3	ketone						C4 H8 O2	88.12	
3-Methylbutanal /	590-86-3	aldehyde					2	C5 H10 O	86.13	6665
Methylcyclohexan	108-87-2	HC ali.unsat/cycl	F;R11 Xi;R38 Xn;R65 R67 N;R51/53	805	8000	1	2000000	C7 H14	98.19	6131
4-Methylcyclohexen	591-47-9	HC ali.unsat/cyclic						C7 H12	96.17	5145
3-methyl-4-decen	62338-47-0	HC ali. unsat						C11 H22	154.3	179
3-Methylen-heptan	1632-16-2	HC ali. sat						C8 H16	112.22	2626
1,1-Methylethoxy-2-propanol [=1-Isopropoxy-2-propanol]	3944-36-3	alcohol ali. unsat		480 t				C6 H14 O2	118.18	361
Methylethylcyclohexen	3983-08-2	HC ali. unsat/cyclic								
3-Methyl-4-heptanone	15726-15-5	keton		53 (EU)				C8 H16 O	128.22	573
2-Methyl-2,4-hexadien	28823-41-8	HC ali. unsat						C7 H12	96.17	3572
3-Methyl-2,4-hexadien	28823-42-9	HC ali. unsat						C7 H12	96.17	4798
4-Methyl-1,4-hexadien	1116-90-1	HC ali.unsat						C7 H12	96.17	6998
4-Methylhexanal	41065-97-8	aldehyde						C7 H12 O	114.19	802
1-Methyl-indan	767-58-8	HC arom						C10 H12	132.21	77
4-Methyl-2-pentanol	108-11-2	alcohol ali.	R10 Xi;R37	100			4700	C6 H14 O	102.18	706
2-Methylpropanal	78-84-2	aldehyde					123	C4 H8 O	72.11	23060
2-Methyl-2-propanol	75-65-0	alcohol ali.	F;R11 Xn;R20	150		1	71000	C4 H10 O	74.12	5558
2-Methyl-propansyre, 2-methylpropylester [=isobutylisobutyrat]	97-85-8	ester		590 t			1500	C8 H16 O2	144.22	577
N-methylthioformamid	1000196-87-7							C2 H7 N1 O S	94.14	43
Naphthalen	91-20-3	HC arom	Xn;R22 N;R50/53 (Carc3;R40 i 29ATP)	50		0.04	80	C10 H8	128.18	11
Nonanal	124-19-6	aldehyde sat			3100		14	C9 H18 O	142.24	49.3
Nonane	111-84-2	HC ali.sat.		1050	10000		6800	C9 H20	128.26	593.2
Nonen	124-11-8	HC ali.unsat						C9 H18	126.26	719.8

Compound	CAS no.:	Type	Classification	TLV mg/ m^3	LCI µg/ m^3	C-value mg/ m^3	Odour µg/ m^3	M_form	MW g/mol	VP Pa
Octan	111-65-9	HC ali.sat.	F;R11 Xi;R38 Xn;R65 R67 N;R50/53	935			28	C8 H18	114.23	1879.5
Octanal	124-13-0	aldehyde sat			3100		7	C8 H16 O	128.22	157.3
Oktansyre, methylester	111-11-5	ester						C9 H18 O2	158.24	72
2-Octenal	2548-87-0	aldehyde unsat			2		11	C8 H14 O	126.2	114
1-Octen-3-ol	3391-86-4	alcohol ali.unsat			16		16	C8 H16 O	128.22	31
Pentadecan	629-62-9	HC ali.sat.						C15 H32	212.42	0.45
Pentan	109-66-0	HC ali.sat	Fx;R12 Xn;R65 R66 R67 N;R51/53	1500			96000	C5 H12	72.15	68516
Pentanal	110-62-3	aldehyde sat		175	3100		22	C5 H10 O	86.13	3466
Pentanol	71-41-0	alcohol, ali.	R10 Xn;R20	360	4300		20	C5 H12 O	88.15	293.2
2-Pentenal	1576-87-0	aldehyde unsat			2		690	C5 H8 O	84.12	2466
1-Penten-3-ol	616-25-1	alcohol ali.						C5 H10 O	86.13	1217
1-Penten-3-on	1629-58-9	ketone						C5 H8 O	84.12	5092
2-Pentylfuran	3777-69-3	HC ali. sat/cyclic					91	C9 H14 O	138.21	130
l-alfa-Pinen	7785-26-4	terpen mono-		140	250	0.05	3900	C10 H16	136.24	633.1
beta-Pinen	127-91-3	terpen mono-		140	250		36000	C10 H16	136.24	390.5
Propanal	123-38-6	aldehyde sat	F;R11 Xi;R36/37/38	47.5(US)	4300		14	C3 H6 O	58.08	42256
1-Propanol	71-23-8	alcohol ali.	F;R11 Xi;R41 R67	500		1	6000	C3 H8 O	60.1	2799
2-Propanol (isopropyl alcohol)	67-63-0	alcohol ali.	F;R11 Xi;R36 R67	490		1	1200	C3 H8 O	60.1	6051
2-Propanone (Acetone)	67-64-1	ketone	F;R11 Xi;R36 R66 R67	600	400	0.4	14000	C3 H6 O	58.08	30792
Propansyre butylester (=butylpropionat)	590-01-2	ester	R10					C7 H14 O2	130.19	589
2-Propenal (=Acrylaldehyde, Acrolein)	107-02-8	aldehyde unsat	F;R11 T;R24/25 Tx;R26 C;R34 N;R50	0.12	3	0.001	410	C3 H4 O	56.06	36524
2-Propensyre, 6-methylheptylester	54774-91-3	ester/acrylat						C11 H20 O2	184.28	20
2-Propenylbenzen	300-57-2	HC ali. sat/cyclic						C9 H10	118.18	403
1-Propoxy-2-propanol	1569-01-3	alcohol ali.		480 t				C6 H14 O2	118.18	226.6
3-Propoxy-1-propen	1471-03-0	HC ali. unsat						C6 H12 O	100.6	8104.6
2-Propyl-1-pentanol	58175-57-8	alcohol								
Pyrazin	290-37-9	N-HC arom						C4 H4 N2	80.09	1439.6
Styrene	100-42-5	HC arom	R10 Xn;R20 Xi;R36/38	105		0.2	160	C8 H8	104.15	853
Terpen, C10 H16, fx:	508-32-7	terpene		140				C10 H16	136.24	223
Tetradecan	629-59-4	HC ali. sat						C14 H30	198.4	1.55
Tetramethylcyclohexane	1000144-07-3	HC ali. sat/cycl						C10 H20	140.27	855.7
Toluen	108-88-3	HC arom	F;R11 Xn;R20 (29ATP: F:R11 Rep3;R63 XnR48/20-65 Xi;R38 R67)	94	400	0.4	7600	C7 H8	92.14	3785.7
Tridecan	629-50-5	HC ali. sat				1*	17000	C13 H28	184.37	7.4
4-Trimethyl-cyclohexanemethanol, .alpha.,.alpha.,	498-81-7	terpene		140				C10 H20 O	156.27	6
4-Trimethyl-3-cyclohexen-1-methanol (=alpha Terpineol)	98-55-5	terpene alco.		140	250		12000	C10 H18 O	154.25	5.64

Compound	CAS no.:	Type	Classification	TLV mg/ m³	LCI µg/ m³	C-value mg/ m³	Odour µg/ m³	M_form	MW g/mol	VP Pa
4-Trimethyl-3-Cyclohexen-1-methanol (S) (=alpha-terpineol)	10482-56-1	HC ali. unsat/cyclic		140			240	C10 H18 O	154.25	5.6
2,4,4-Trimethyl-1-penten	107-39-1	HC ali. unsat.	F:R11 N;R51/53					C18 H18	112.22	5958.5
Undecan	1120-21-4	HC ali.sat				1*	7800	C11 H24	156.31	54.9
Xylener	1330-20-7	HC arom	R10 Xn;R20/21 Xi;R38 (C afh)	109	100	0.1	4350	C8H10	106.17	1065
C8 - C12 aliphatic hydrocarbons		HC ali.								
C8 H16 (2 komponenter) 1,3-Dimethylcyclohexane	638-04-0	HC ali.sat/cyclic						C8 H16	112.22	2346
C8 H16 (2 komponenter) 1,4-Dimethylcyclohexane	589-90-2	HC ali.sat/cyclic	F;R11 Xi;R38 Xn;R65 R67 N;R51/53					C8 H16	112.22	3025
C8 H16, Dimethylcyclohexane (589-90-2 / 638-04-0 / 591-21-9)	591-21-9	HC ali.sat/cyclic						C8 H16	112.22	234
C8 H16, Ethylcyclohexane	1678-91-7	HC ali. sat						C8 H16	112.22	1706
C9 H12 / C10 H14 (3 komp)										
C9 H12 aromatiske kulbrinter		HC arom								
C9 H12 aromatiske kulbrinter		HC arom								
C9 H12, fx 98828 isopropylbenzene (cumen)	98-82-8	HC arom	CumenR10 Xi;R37 Xn;R65 N;R51/53	100	1750	0.03	120	C9 H12	120.2	600
C9 H18										
C9 H18, 1,1,3-Trimethylcyclohexane	3073-66-3	HC ali. sat/cyclic						C9 H18	126.24	1440
C10 H14 (fx:Benzene, 1-ethyl-3,5-dimethyl-)	934-74-7							C10 H14	134.22	137.3
C10 H14 (4 komponenter)								C10 H14	134.22	
C10 H14 + C12 H22										
C10 H14 aromatiske kulbrinter (3 stk) fx 535-77-3, 99-87-6 methylisopropylbenzin,)		HC arom		135			12	C10 H14	134.22	229
C10 H20										
C10 H20 / Indan fx 86869-76-3 / 95-13-6			indene	45						
C11 - C18 aliphatic hydrocarbons		HC ali.								
C11 - C20 aliphatic hydrocarbons		HC ali.								
C11 H22, fx 81983-71-3	81983-71-3									
C12 - C18 aliphatic hydrocarbons		HC ali.								
C12 - C19 aliphatic hydrocarbons		HC ali.								
C12 H18, fx 1,2-bis(ethylmethyl)-benzene 577-55-9 / 1441-56-4	577-55-9	Hc ali. Sat.cyclic						C12 H18	162.28	34.1
C12 H18, fx 1,3-bis(methylethyl)-benzene 99-62-7 / 98-19-1	99-62-7							C12 H18	162.28	52.4
C12 H24 2 stk, fx 4-dodecen 2030-84-4, or 7206-28-2, 7206-15-7	2030-84-4	HC ali. unsat								
C12 H24 5 komponenter										
C13 - C18 aliphatic hydrocarbons		HC ali.								
C15 H24,	30021-74-0									
C15 H24, fx 1000109-88-1 / 88-84-6				140						
C15 H24, alpha-Caryophyllen	6753-98-6	terpene		140				C15 H24	204.36	2

Compound	CAS no.:	Type	Classification	TLV mg/ m^3	LCI µg/ m^3	C-value mg/ m^3	Odour µg/ m^3	M_form	MW g/mol	VP Pa
C15 H24, alpha-Cubeben	17699-14-8			140				C15 H24	204.36	6
C15 H24, Copaen [Tricyclo(4.4.0.02,7)dec-3-ene, 1,3-dimethyl-8-(1-methylethyl)-]	3856-25-5	terpene		140						
C15 H24, Cyclohexan, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)-	515-13-9	HC ali.sat/cyclic		140				C15 H24	204.36	12
C15 H24, 1,4-Methanoazulene, decahydro-4,8,8-trimethyl-9-methylene- [Longifolene:terpene]	475-20-7	terpene		140				C15 H24	204.36	2.5
C15 H24, 1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-,	1137-12-8	terpene		140				C15 H24	204.36	11.4
C15 H24, 1,4-methano-1H-indene, Octahydro-4-methyl-8-methylen-7-(1-methylethyl)-	3650-28-0	terpene		140				C15 H24	204.36	8.5
C15 H24, 2H-2,4a-Methanonaphthalene, 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-, (2S)-	1135-66-6	HV arom		140				C15 H24	204.36	5.4
C15 H24, fx: Naphthalene, 1,2,3,5,6,8a-hexahydro-4,7-dimethyl-1-(1-methylethyl)-	483-76-1	HC arom		140				C15 H24	204.36	2.5
C15 H24, Naphthalene, 1,2,3,4,4a,5,6,8a-octahydro-7-methyl-4-methylene-1-(1-methylethyl)-	39029-41-9	HC arom		140				C15 H24	204.36	4.8
C15 H24, Tricyclo(5.4.0.02.8)undec-9-en, 2,6,6,9-tetramethyl	5989-08-2	HC ali. unsat/cyclic		140						
ANTAL		124	44	53	38	36	29			

Teknologisk Institut
Miljø- og Affaldsteknik
Att.: Ole Chr. Hansen/Torben Eggert
Gregersensvej
2630 Taastrup

Test report

on chemical analyses performed at Chemical Technology, Danish Technological Institute.

Task:	Project: Survey, emission and evaluation of volatile chemical compounds from printed matter. Analyses af carbon and tenax filters for content of volatile organic compounds. Analyses of DNPH filters for content of selected aldehydes.
Sampling:	The client
Sample received:	14. – 23. October 2002
Analyseperiode:	23. oktober - 11. november 2002
Comments:	The results, test marking(s) and used method(s) are mentioned on the next page(s) and concerns only test samples taken to the analyses. The results have been forwarded on e-mail.

The test results are solely referring to the tested (examined) materials.
Publication of the Test Report in full is allowed. Publication of extracts from the Test Report is allowed, if the testing laboratory has given a written approval.

Chemical Technology, Taastrup

Eva Pedersen	Brian Christiansen	Jakob Mossing
Chemotechnician	Laboratory assistant	M.Sc. Chemistry

Test results of carbon and tenax filters in µg total per filter

Chemical Technology mark: Printed matter no. 2 - Rotogravure

Component	CAS-No.	29936-30 KF. 507	29936-31 KF. 510	29936-32 KF. 516	29936-33 TF. 508	29936-34 TF. 511	29936-35 TF. 517	LOD
1-Butanol	71-36-3	-	-	-	-	N. D.	N. D.	0.2
Toluene	108-88-3	6300	5300	3200	*	N. D.	N. D.	0.2
Oktane	111-65-9	2.4	3.3	2.8	*	N. D.	N. D.	0.2
C9H12 aromatic hydrocarbon	Fx 98-82-8	1.0	1.6	1.8	*	N. D.	N. D.	0.2
Naphthalene	91-20-3	*	-	-	2.3	1.7	1.6	0.2
Benzaldehyde	100-52-7	N. D.	N. D.	N. D.	6.5/1.2	N. D.	N. D.	0.2
α-pinene	7785-26-4	3.2	3.5	3.6	*	N. D.	N. D.	0.2
Camphene	79-92-5	3.4	4.6	4.9	*	N. D.	N. D.	0.2
D-Limonene	5989-27-5	2.2	3.4	3.9	*	N. D.	N. D.	0.2
2-Propenylbenzene	300-57-2				*	N. D.	N. D.	0.2
2.3-Dimethylphenol	526-75-0	-	-	-	1.5	0.9	0.7	0.2
1-Methyl-indane	767-58-8	1.6	2.0	1.9				0.2
C15H24	1000109-88-1	1.8	1.4	2.2	*	N. D.	N. D.	0.2
C15H24	1137-12-8	6.9	5.9	7.4	*	N. D.	N. D.	0.2
C15H24	1135-66-6	5.7	5.4	6.7	*	N. D.	N. D.	0.2
C15H24	475-20-7	13	11	14	*	N. D.	N. D.	0.2
C15H24	511-59-1	1.9	1.6	2.2	*	N. D.	N. D.	0.2
C15H24	1000157-62-7 813-21-4	2.2	1.7	2.6	*	N. D.	N. D.	0.2

”-”: means less than detection limit (LOD)

”*”: means that the component is found, quantification on carbon filter.

Comments

2,3-Dimethylphenol and 1-methyl-indan to close for separation – the amount noted as sum.

C15H24: CAS nos. suggested from analogous substances.

Analyses results of DNPH filters

Chemical Technology mark: Printed matter No. 2 - Rotogravure

Filter No. : Sample mrk.: No. L:	509 Printed matter No. 2 39		512 Printed matter No. 2 39		518 Printed matter No. 2 39		LOD
DTI mrk.:	29936-36		29936-37		29936-38		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	1.7	44	1.5	39	1.4	36	0.03
Acetaldehyde	5.8	150	4.8	120	3.0	78	0.03
Acrolein	-	-	-	-	-	-	0.03
Propanal	2.0	51	1.9	48	1.0	26	0.03
Acetone	13	330	3.5	90	2.4	62	0.1
Butanal	0.49	13	0.15	3.9	0.14	3.7	0.03
Pentanal	1.1	27	0.12	3.1	0.07	1.7	0.03
Hexanal	3.6	92	0.59	15	0.44	11	0.03
Benzaldehyde	7.9	200	4.6	120	3.1	80	0.03
2-Butanone	0.26	6.5	0.15	3.9	0.14	3.7	0.03

"-" means less than detection limit (LOD) or unquantifiable

Analyses results of carbon and tenax filters in µg total per filter

Chemical Technology mrk: Printed matter No. 3 - Rotogravure

Component	CAS-No.	29936-XX KF. 513	29936-22 KF. 522	29936-23 KF. 537	29936-24 TF. 514	LOD
Toluene	108-88-3	2600	1600	990	*	0.2
Xylenes		11	12	8.1	*	0.2
Naphthalene	91-20-3	-	-	-	*	0.2
C_9H_{12} aromatic hydrocarbon	E.g. 98-82-8	2.7	2.5	2.8	*	0.2
α-pinene	7785-26-4	26	24	20	*	0.2
Camphene	79-92-5	7.9	7.7	6.4	*	0.2
β-pinene	127-91-3	3.9	4.0	3.8	*	0.2
D-Limonene	5989-27-5	6.4	7.3	7.5	*	0.2
$C_{10}H_{14}$ aromatic hydrocarbon		6.8	7.7	8.0	*	0.2
$C_{15}H_{24}$		5.6	7.1	7.1	*	0.2
$C_{15}H_{24}$		13	17	17	*	0.2
$C_{15}H_{24}$		10	12	13	*	0.2
$C_{15}H_{24}$		1.7	2.3	2.6	*	0.2
$C_{15}H_{24}$		3.7	4.7	5.0	*	0.2
$C_{15}H_{24}$		75	91	96	50/19	0.2
$C_{15}H_{24}$		2.8	3.7	3.9	*	0.2
$C_{15}H_{24}$		3.5	4.8	4.8	*	0.2

”-”: means less than detection limit (LOD)

”*”: means that the component is found, quantification on carbon filter.

Comments

$C_{15}H_{24}$: Suggested CAS nos. from analogous compounds, cf. 29936-2.

Analyses results of DNPH filters

Chemical Technology mrk: Printed matter No. 3 - Rotogravure

Sample No. : Sample mrk.: Nos. L:	515 Printed matter No. 3 39		524 Printed matter No. 3 39		539 Printed matter No. 3 39		LOD
DTI mrk.:	29936-27		29936-29		29936-28		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	0.59	15	0.27	6.9	0.11	2.9	0.03
Acetaldehyde	3.6	93	3.3	85	2.9	74	0.03
Acrolein	-	-	-	-	-	-	0.03
Propanal	1.1	28	1.2	30	1.2	30.0	0.03
Acetone	5.0	130	6.0	150	7.5	190	0.1
Butanal	0.18	4.6	0.16	4.1	0.23	5.8	0.03
Pentanal	0.06	1.6	0.16	4.1	0.19	4.9	0.03
Hexanal	0.57	15	1.7	44	2.2	57	0.03
Benzaldehydee	0.81	21	1.8	46	1.3	34	0.03
2-Butanone	0.04	1.1	0.03	0.9	0.07	1.7	0.03

"-" means less than detection limit (LOD) or not quantifiable

Analyses results of carbon and tenax filters in µg total per filter

Chemical Technology mrk: Printed matter No. 4 – Flexographic print using UV curing colours

Component	CAS-No.	29936-39 KF. 519	29936-40 KF. 531	29936-41 KF. 543	29936-42 TF. 520	29936-43 TF. 532	29936-44 TF. 544	LOD
1-Butanol	71-36-3	0.6	-	-	-	N. D.	N. D.	0.2
2-Hexanol	626-93-7	0.9	-	-	*	N. D.	N. D.	0.2
Toluene	108-88-3	2.6	0.74	0.4	*	N. D.	N. D.	0.2
Butylacetate	123-86-4	2.2	-	-	2.3	N. D.	N. D.	0.2
Cyclohexanone	108-94-1	N. D.	N. D.	N. D.	3.3	0.2	-	0.2
n-Butyl ether	142-96-1	6.1	-	-	5.2	N. D.	N. D.	0.2
Propanoic acid butyl ester	590-01-2	4.2	-	-	4.7	N. D.	N. D.	0.2
3-Methyl-4-heptanone	15726-15-5	0.8	0.7	-	*	N. D.	N. D.	0.2
Benzaldehyde	100-52-7	1.3	1.3	-	6.0	N. D.	N. D.	0.2
C_9H_{12}; 6 aromatic hydrocarbons		8.5	4.2	-	*	N. D.	N. D.	0.2
2-Ethyl-1-hexanol	104-76-7	9.5	3.7	0.6	*	N. D.	N. D.	0.2
C_9H_{10}	Fx 1000191-13-7	1.5	1.1	-	*	N. D.	N. D.	0.2
$C_{10}H_{16}$	6004-38-2	1.1	-	-	*	N. D.	N. D.	0.2
Acetic acid-2-ethylhexylester	103-09-3	10	2.5	0.8	13	N. D.	N. D.	0.2
Naphthalene	91-20-3	0.9	-	-	3.5	1.1	0.7	0.2
C_8H_{16}	Fx 3404-80-6	3.6	1.5	0.4	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 1000109-88-1	1.2	0.7	-	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 1137-12-8	10	6.5	2.5	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 1135-66-6	1.0	-	-	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 475-20-7	16.5	11	4.4	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 511-59-1	0.4	-	-	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 1000157-62-7	0.4	-	-	*	N. D.	N. D.	0.2

”-”: means less than detection limit (LOD)
”*”: means that the component is found , quantification on carbon filter.

Comments

C_8H_{16} – for example (fx) 3404-80-6: 2-methyl-4-methylen-hexane

Analyses results of DNPH filters

Chemical Technology mrk: Printed matter No. 4 – Flexographic with UV curing colours

Sample No. : Sample mrk.: Nos. L:	521 Printed matter No. 4 39		533 Printed matter No. 4 39		545 Printed matter No. 4 39		LOD
DTI mrk.:	29936-45		29936-46		29936-47		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	1.9	49	0.90	23	2,2	57	0,03
Acetaldehyde	3.1	78	0.63	16	0,54	14	0,03
Acrolein	-	-	-	-	-	-	0,03
Propanal	0.13	3.3	0.06	1.4	0,04	1,1	0,03
Acetone	1.7	43	0.73	19	1,2	29	0,1
Butanal	0.11	2.7	0.05	1.3	0,03	0,8	0,03
Pentanal	6.6	170	0.44	11	0,17	4,4	0,03
Hexanal	0.42	11	0.09	2.3	0,12	3,0	0,03
Benzaldehyde	5.1	130	0.35	8.9	0,21	5,5	0,03
2-Butanone	0.06	1.6	0.05	1.3	0,03	0,8	0,03

"-" means less than detection limit (LOD) or not quantifiable

Analyses results of carbon and tenax filters in µg total per filter

Chemical Technology mrk: Printed matter No. 8 - Offset

Component	CAS-No.	29936-48 KF. 528	29936-49 KF. 549	29936-66 KF. 555	29936-50 TF. 529	L.O.D
Toluene	108-88-3	0.74	0.72	1.1	*	0.2
Xylenes, ethylbenzene		-	-	-	*	0.2
C9 – C13 alifatic hydrocarbons		-	43	22	*	5
C13 – C19 alifatic hydrocarbons		200	350	240	*	5

”-”: means less than detection limit (LOD)

”*”: means that the component is found, quantification on carbon filter.

Analyses results of DNPH filters

Chemical Technology mrk: Printed matter No. 8 - Offset

Sample No. :	530		551		557		LOD
Sample mrk.:	Printed matter No. 8		Printed matter No. 8		Printed matter No. 8		
Nos. L:	39		39		39		
DTI mrk.:	29936-52		29936-53		29936-68		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	0.65	17	0.51	13	0,55	14	0,03
Acetaldehyde	0.61	16	0.96	25	0,64	16	0,03
Acrolein	-	-	-	-	-	-	0,03
Propanal	0.20	5.2	0.57	15	0,12	3,2	0,03
Acetone	1.2	31	1.5	39	0,83	21	0,1
Butanal	0.07	1.9	0.19	4.8	0,10	2,6	0,03
Pentanal	0.11	2.7	0.33	8.4	0,11	2,7	0,03
Hexanal	2.5	63	4.3	110.0	0,62	16	0,03
Benzaldehyde	0.12	3.0	0.11	2.8	0,03	0,9	0,03
2-Butanone	0.04	1.1	0.08	2.1	-	-	0,03

"-" means less than detection limit (LOD) or not quantifiable

Analyses results of carbon and tenax filters in µg total per filter

Chemical Technology mrk: Printed matter No. 17 - Offset

Component	CAS-No.	29936-54 KF. 525	29936-55 KF. 534	29936-56 KF. 540	29936-57 TF. 526	29936-58 TF. 535	29936-59 TF. 541	LOD
Toluene	108-88-3	1.7	0.64	0.76	*	N. D.	N. D.	0.1
Xylenes, ethylbenzene		1.1	0.84	0.74	*	N. D.	N. D.	0.1
Styrene	100-42-5	0.2	-	-	*	N. D.	N. D.	0.2
C_9H_{12}		2.1	2.5	1.9	*	N. D.	N. D.	0.2
C_9H_{12}		1.1	1.1	1.0	*	N. D.	N. D.	0.2
C8 – C12 alifatic hydrocarbons		20	35	21	*	N. D.	N. D.	5
C13 – C19 alifatic hydrocarbons		60	56	38	*	N. D.	N. D.	5
$C_{15}H_{24}$	Fx 1137-12-8	1.5	1.6	1.1	*	N. D.	N. D.	0.2
$C_{15}H_{24}$	Fx 475-20-7	5.4	4.8	3.9	*	N. D.	N. D.	0.2
$C_{10}H_{12}O_2$	3602-55-9	N. D.	N. D.	N. D.	3.2	3.5	3.1	0.2
Hexanal	66-25-1	N. D.	N. D.	N. D.	*	N. D.	N. D.	

”-”: means less than detection limit (LOD)

”*”: means that the component is found, quantification on carbon filter (KF).

Comments

2 components - $C_{15}H_{24}$ – is included in C13-C19 alifatic hydrocarbons

CAS-No. 3602-55-9: 2,5-Cyclohexadien-1,4-dione, 2-(1,1-dimethylethyl).

Analyses results of DNPH filters

Chemical Technology mrk: Printed matter No. 17 - Offset

Sample No. : Sample mrk.: Nos. L:	527 Printed matter No. 17 39		536 Printed matter No. 17 39		542 Printed matter No. 17 39		LOD
DTI mrk.:	29936-60		29936-61		29936-62		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	0.94	24	0.78	20	0,85	22	0,03
Acetaldehyde	2.0	51	1.6	41	1,6	42	0,03
Acrolein	-	-	-	-	-	-	0,03
Propanal	5.5	140	6.6	170	6,0	154	0,03
Acetone	1.9	49	2.2	57	2,2	55	0,1
Butanal	0.53	14	0.68	17	0,73	19	0,03
Pentanal	1.2	30	2.4	62	2,6	66	0,03
Hexanal	8.4	210	20	510	22	550	0,03
Benzaldehyde	0.17	4.4	0.25	6.4	0,25	6,3	0,03
2-Butanone	0.28	7.3	0.29	7.3	0,27	6,9	0,03

"-" means less than detection limit (LOD) or not quantifiable

Analyses results of carbon and tenax filters in µg total per filter

Chemical Technology mrk: Printed matter No. 19 - Offset

Component	CAS-No.	29936-69 KF. 552	29936-70 KF. 559	29936-71 KF. 562	29936-72 TF. 553	LOD
Toluene	108-88-3	0.56	1.3	0.34	*	0.2
Xylenes, ethylbenzene		0.80	0.54	0.68	*	0.2
C9 – C13 alifatic hydrocarbons		440	620	510	*	5
C13 – C19 alifatic hydrocarbons		485	770	600	*	5

”-”: means less than detection limit (LOD)

”*”: means that the component is found , quantification on carbon filter.

Analyseresultater of DNPH-filters

Chemical Technology mrk: Printed matter No. 19 - Offset

Sample No. : Sample mrk.: Nos. L:	554 Printed matter No. 19 39		561 Printed matter No. 19 39		564 Printed matter No. 19 39		LOD
DTI mrk.:	29936-75		29936-76		29936-77		
Component	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample	µg/m^3	µg/sample
Formaldehyde	0.57	15	0.75	19	0,80	20	0,03
Acetaldehyde	0.72	18	1.2	30	2,9	73	0,03
Acrolein	-	-	-	-	-	-	0,03
Propanal	0.15	3.8	4.4	110	11	280	0,03
Acetone	1.2	30	2.5	65	5,3	140	0,1
Butanal	-	-	1.5	37	3,6	93	0,03
Pentanal	0.33	8.4	7.0	180	23	600	0,03
Hexanal	0.22	5.7	5.1	130	16	410	0,03
Benzaldehyde	0.12	3.1	0.20	5.1	0,40	10	0,03
2-Butanone	6.1	160	7.45	190	4,8	120	0,03

"-" means less than detection limit (LOD) or not quantifiable

Background analyses of DNPH filters

Sample No. :	548		LOD
Sample mrk.:	Background, room		
Nos L:	90		
DTI mrk.:	29936-65		
Component	µg/sample	µg/m^3	µg/sample
Formaldehyde	1.47	16.3	0.03
Acetaldehyde	0.61	6.7	0.03
Acrolein	-	-	0.03
Propanal	0.90	9.9	0.03
Acetone	1.16	12.8	0.1
Butanal	0.06	0.7	0.03
Pentanal	0.06	0.7	0.03
Hexanal	0.15	1.7	0.03
Benzaldehyde	0.06	0.7	0.03
2-Butanone	0.07	0.78	0.03

"-" below detection limit or not accountable

Method description

Danish Teknological Institute's method OT 060b – Analysis of carbon filters for content of volatile organic compounds

Extraction using carbon-disulfide with deuterium labelled internal standards followed by analysis by GC-MS-SIM.

Analysis of tenax filters for content of volatile organic compounds

Extraction using diethylether with deuterium labelled internal standards followed by analysis by GC-MS-SIM.

Analysis of DNPH-filters for content of selected aldehydes

Extraction using acetonitril followed by analysis by HPLC-UV.