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CONCENTRATION OF SOLVENTS IN VARIOUS INDUSTRIAL ENVIRONMENTS

18.1 MEASUREMENT AND ESTIMATION OF SOLVENTS EMISSION AND ODOR

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18.1.1 DEFINITION "SOLVENT" AND "VOLATILE ORGANIC COMPOUNDS" (VOC)

Solvents are generally understood to be substances that can physically dissolve other substances, more narrowly they are inorganic and organic liquids able to dissolve other gaseous, liquid, or solid substances. A qualifier for the suitability as a solvent is that, during the solution, neither the solvent nor the dissolved substance undergoes chemical change, i.e., the components of the solution may be recovered in their original form by physical separation processes, such as distillation, crystallization, sublimation, evaporation, adsorption.

From a chemical point of view, solvents or volatile organic compounds, VOCs, vary widely. They are often classified using their boiling point, and vapor pressure. These properties do not define their suitability as solvents.

In the context of VOCs, only organic solvents are of relevance. Therefore, in the following discussion, only organic solvents will be discussed.

Definition of solvent according to Council Directive 1999/13/EC of 11 March 1999[1]

Organic solvent shall mean any VOC which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, or a plasticizer, or as a preservative.

Definition of solvent according to ISO/DIS 4618-4: 1999[2]

Paints and varnishes - terms and definition for coating materials: Solvent: A single liquid or blends of liquids, volatile under specified drying conditions, and in which the binder is completely soluble.

For certain application purposes, solvents are defined more specifically:

Technische Regeln für Gefahrstoffe TRGS 610 (Technical Regulations for Hazardous Substances) as applied to high solvent-containing primers and flooring glues the definition is:

Solvents are volatile organic compounds as well as mixtures thereof at a boiling point < 200°C, which under normal conditions (20°C and 1013 hPa) are liquid and are applied for dissolving and diluting other substances without undergoing chemical change.[3]

As can be seen, there are clear differences in the way VOCs are defined.[4] The most general, and hence least disputable, one is:

Definition of volatile organic compounds according to DIN ISO 11890/1,2,[5,6]

Solvent is generally any organic liquid and/or any organic solid substance, which evaporates by itself under prevailing conditions (temperature and pressure).

Definition of VOC according to Council Directive 1999/13/EC[1]

Volatile organic compound, VOC, shall mean any organic compound having at 293.15 K a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use. For the purpose of this Directive, the fraction of creosote, which exceeds this value of vapor pressure at 293.15 K shall be considered as a VOC.

In the **Lösemittelverordnung Österreichs (Austrian Regulations on Solvents)** of 1995,[7] which on this issue corresponds to the **österreichische Lackieranlagen-Verordnung (Austrian Regulation on Varnishing Plants)** of 1995,[8] VOCs have a maximum boiling point of 200°C. Hence, the volatile compounds at a boiling point > 200°C are not included. These comprise, e.g., some film forming media, such as butyldiglycol, butyldiglycolacetate, and texanol. Similarly, reactive solvents are excluded from this regulation.

Definitions of VOCs in the USA according to ASTM D 3960-1[9]

Volatile Organic Compound (VOC), means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity: Methane; ethane; methylene chloride (dichloromethane); 1.1.1-trichloroethane (methyl chloroform); 1.1.1-trichloro-2.2.2-trifluorethane (CFC-113), furthermore cyclic, branched or linear completely methylated siloxanes: acetone: and perfluorocarbon compounds.

The regulatory definition under the control of the U.S. EPA may change.

Certain organic compounds that may be released under the specified bake conditions are not classified as VOC as they do not participate in atmospheric photochemical reactions. Such non-photochemically active compounds are referred to as exempt volatile compounds in the practice.

An example of an exempt compound in the USA according to the EPA is tertiary-butyl-acetate (TBA, B.p. of 98 °C). It is described as a substance not harmful in air.[10]

Substances contained in air are differentiated in their mixtures according to their volatility:[11]

Abbreviation	Compound class	Range of boiling point in °C
VVOC	very volatile organic compounds	< 0 up to 50 ÷ 100
VOC	volatile organic compounds	50 ÷ 100 up to 250 ÷ 260
SVOC	semi-volatile organic compounds	250 ÷ 260 up to 380 ÷ 500

TVOC means “total volatile organic compounds”.

18.1.2 REVIEW OF SOURCES OF SOLVENT EMISSIONS

18.1.2.1 Causes for emissions

The basic human needs include: eating, drinking and breathing. In a 60-year lifetime, human being takes up about 30 t of food, 60 t of drink and 300 t of air.[12] Thus air pollution may have a large influence on human health. In comparison with outside air and the ambient air within public transportation vehicles and terminals, room air quality is of the greatest interest, since the population in North American cities stays indoors more than 93% time according to findings by Szalai[13] and more than 91% according to Chapin,[14] of this time > 67 % is spent in living space and about 4-5 % in the workplace.

Sources for volatile substances in indoor air are diverse and originate, apart from that brought in with outside air and produced by the living occupants (people, pets) and their activities (e.g., smoking), from the materials themselves which have been applied for building and furnishing the room. These include:

- building materials
- glues
- floor covering
- wallpaper
- internal decorative textiles
- paints
- furniture, upholstered furniture, etc.

These materials may contain volatile organic, but also inorganic, compounds, which are evaporated during use. The emission of these volatile compounds is influenced by a large number of factors, such as:

- chemical/physical structure of the material (thickness, surface structure)
- volatility, polarity of the volatile compounds
- room temperature and humidity
- room load, i.e., the ratio of the area of emitting surface and the volume of room air
- ventilation, rate of air flow
- load of the external air entering (dust, substances)

The residual monomers from plastics, reactive products (e.g., formaldehyde), degradation products, flame protection media, softeners etc. may be emitted from building materials.

18.1.2.2 Emissions of VOCs from varnishes and paints

A substantial part of emitted materials are solvents. They preferably originate from varnishes, paints and glues. Table 18.1.1 shows a survey of the main types of varnishes referring to their average solvent content.

Table 18.1.1. Solvent share in various types of varnishes

Material	Solvent content, wt%
Stain	~95
Cellulose nitrate varnish	~75
PUR varnish	35-70
Polyester varnish	35
UV roller varnish based on acrylate	2-10

Despite the introduction of water based and powder varnishes, cellulose nitrate varnishes with their high solvent content, are still widely used due to their easy application and their low prices. The current varnish application still requires the use of solvents. The chosen coating procedure determines the necessary processing viscosity, which may be adjusted in different ways:

- Thinning the binding agent/varnish with a solvent consisting of one or more organic compounds without altering the binding agent chemically. Nowadays, the solvent can partly or almost totally be replaced by water.
- Thinning the binding agent with a reactive thinner, i.e., one or more monomers/oligomers included in the system, which react with the binding agent during the hardening process and is built into a molecule. According to definitions, they do not have characteristics of solvents. They partly take over the solvent function while they remain in the liquid state.
- Temperature increase of the coating system, which limits the required amount of solvents.
- Liquid application of a melted solid system

Profiled construction components form parts of complicated shapes, which must rely on the spraying of coatings for decorative and protective purposes. The spraying requires low-viscosity material. Viscosity reduction is usually achieved by adding solvents but sometimes by increasing the material temperature. Parts with large flat surfaces however, may be coated by roller-coating, which tolerates higher viscosity materials. After fulfilling their function as solvents, they are expected to completely evaporate from the varnish system.

Emission of solvents from a varnish system occurs in the course of the “life-cycle” of a varnish in several different locations as the following survey shows (Figure 18.1.1). As early as in the production stage of the varnish system, solvent emissions contaminate the ambient air of the factory. About 90 % of the solvents contained in the varnish system evaporates during its application which affects the air quality in the workplaces. These emissions are in the milligram per cubic meter of air range. The thinning effect decreases the solvent concentration in the ambient air at the varnisher’s workplace into the microgram to nanogram per cubic meter.

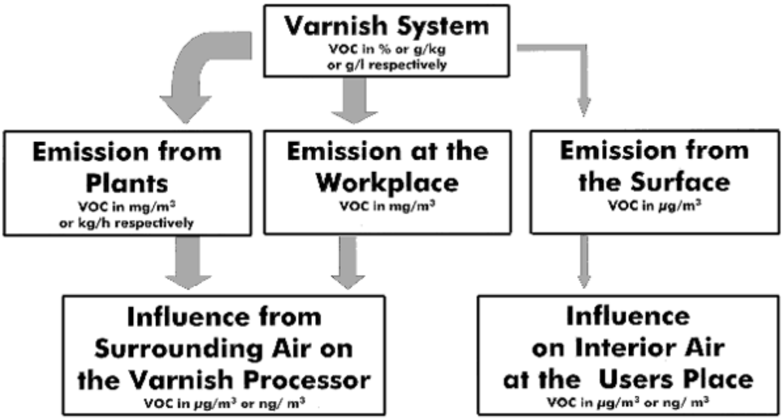


Figure 18.1.1. Emission of VOCs in the life-cycle of a varnish.

About 10 % of the solvent remains in the varnish and it is emitted, depending on the type of solvent and varnish, with variable rate on their way to the consumers and in their living spaces.

According to the European Commission, the furniture industry alone used more than 185,000 tons of solvents/year in 1994.[15]

Not all the VOCs enter the air, however, since remedial efforts, such as absorption and solvent reclaim, after-burning of solvents, the use of bio-filters, result in emission reduction.

Nevertheless, it is still evident that limitation of solvents, VOCs, reduction in varnishes and coatings may help in reducing emissions.

18.1.2.3 VOC emissions from emulsion paints

Although emulsion paints and plasters contain less than 2% VOCs these are produced in such large quantities (3.5 Million t in 1995)[16] and applied over such an extensive surface that 100,000 t of VOCs are emitted from these materials per year. These enter the environment in an uncontrolled way.

Prior to an interior application of the coating, there is no VOC in room atmosphere, unless sources already exist in the room. Then the load - from the beginning of the application - increases very rapidly. After the application, the VOC concentration in the ambient air decreases exponentially. If these emissions are to be monitored it is desirable to have methods available to record VOC concentrations typical of emitting stages.[17]

18.1.3 MEASURING OF VOC-CONTENT IN PAINTS AND VARNISHES

18.1.3.1 Definition of low-emissive coating materials

In order to limit the sources of solvent emission in ambient air in the most effective manner, primary goal must be to reduce the VOC content in coating materials. In Germany, there is a draft for the Varnishing Plant Regulation[18] - regulating the application of low-emissive varnishes, which will require that coating materials must initially not contain more than 420 g/l VOC. Four years after the introduction of the regulation this is reduced to 250 g/l VOC.

The "Jury Umweltzeichen" (Environmental Trade Mark), which, since 1999, rewards certain products with the environmental trade mark goes even further: For flat, plain materials (e.g., interior doors, panels, floors with varnished surfaces, pre-fabricated parquet) the coating systems applied must not exceed the VOC content = max. 250 g/l.[19]

Varnishing plants are exempt if they employ waste gas purification facilities corresponding to the EU VOC Guideline.[20]

The draft of the Varnishing Plant Regulation follows the US method according to ASTM D 3960-121 in determining the VOC content.

18.1.3.2 Determination of the VOC content according to ASTM D 3960-1

ASTM D 3960-1 is the method used in the US to determine the VOC content of coating materials. The VOC value is calculated as follows:

$$\mathit{VOC\ value}\,[g/l] = \frac{\mathit{mass\ of\ volatile\ components}\,[g] - \mathit{mass\ of\ water}\,[g]}{\mathit{volume\ of\ varnish}\,[l] - \mathit{volume\ of\ water}\,[l]} \quad [18.1.1]$$

For varnishes exclusively containing solvents, this formula results in high values. This calculation is, however, of dubious value for water-containing varnishes. The unit g/l does not refer to 1 liter of an actual varnish, but to a hypothetical product, which only expresses the binding agent in liters.

This is demonstrated in Example 1, which will then also be calculated according to other methods.

Example 1:

Water spray varnish: 30% solid matter content (binding agent and pigments)
10% solvent content
60% water content
varnish density: 1.0 g/cm^3
VOC (g/l) = (700 g - 600 g)/(1 l - 0.6 l) = 250 g/l

18.1.3.3 Determination of the VOC content according to ISO/DIS 11 890/1[5] and 2[6]

18.1.3.3.1 VOC content > 15%

The calculation according to ISO/DIS 11 890/1 gives a more logical result. VOCs are given here as a mass share in % of the ready-to-use varnish. At a VOC content > 15 % (of the mass share), the determination is made by the differential approach:

$$VOC\ [\%\ of\ the\ mass\ share] = 100 - nfA - m_w \qquad [18.1.2]$$

where:

nfA non-volatile parts determined by ISO 3251[22] (1 h/110°C)
m_w mass as water in % of the mass parts, determined according to ISO 760[23] (after Karl-Fischer)

Many more recently available techniques for water determination are not sufficiently common and thus are not considered.

Example 2:

Water solvent stain: 5% solid matter content = non-volatile parts
25% solvent
70% water share

VOC (mass %) = 100 - 5 - 70 = 25 %

For density ≠ 1

$$VOC\ [g/l] = 10(100 - nfA - m_w)\,\rho_s \qquad [18.1.3]$$

where:

ρ_s varnish density in g/ml at 23°C

In this case, the VOC content refers to 1 l of actual varnish.

Example 3:

Solvent stain: 5% solid matter content
95% solvent share
VOC (g/l) = (100 - 5 - 0) × 0.9 = 855 g/l

Example 4:

Solvent/water stain: 5% solid matter content
70% solvent
25% water share

Density: 0.9 g/cm^3
VOC (g/l) = (100 - 5 - 25) × 0.9 × 10 = 630 g/l

DIN ISO 11 890 also allows the calculation to be made using the method prescribed by ASTM D 3960:

$$VOC_{lw}\,[g/l] = 1000\frac{100 - nfA\,m_w}{100 - \rho_s\dfrac{m_w}{\rho_w}}\rho_s \qquad [18.1.4]$$

where:

ρ_s	varnish density in g/ml at 23°C
nfA	non-volatile parts determined by ISO 3251[22] (1 h/110°C)
m_w	mass as water in % mass parts, determined acc. to ISO 760[23] (after Karl-Fischer)
ρ_w	density, in g/ml, of water at 23°C (ρ_w = 0.997537 g/ml at 23°C)

Example 1

Water spray varnish: 30% solid matter content
10% solvent
60% water content
varnish density 1.0 g/cm^3
water density 1.0 g/cm^3
VOC_{lw} = [(100 - 30 - 60)/(100 - 1.0 × 60)] × 1.0 × 1000 = 250 g/l

Example 1:

Water spray varnish but with a density of 0.9 g/cm^3
VOC_{lw} = [(100 - 3 - 60)/(100 - 0.9 × 60)] × 0.9 × 1000 = 196 g/l

Or another example:

Example 5:

Water varnish primer: 15% solid matter content
10% solvent
75% water
varnish density 1.0 g/cm^3
VOC_{lw} = [(100 - 15 -75)/(100 - 1.0 × 75)] × 1.0 × 1000 = 400 g/l

The calculation permits the deduction of exempt compounds, which are defined as organic compounds which do not participate in photochemical reactions in the atmosphere.

$$VOC_{lwe}\,[g/l] = 1000\frac{100 - nfA - m_w\sum_{i=1}^{i=n} m_{eci}}{100 - \rho_s\dfrac{m_w}{\rho_w} - \rho_s\sum_{i=1}^{i=n}\dfrac{m_{eci}}{\rho_{eci}}}\rho_s \qquad [18.1.5]$$

where:

VOC_{lwe}	VOC content, in g/l, contained in the product in its ready-to-use condition minus water and minus exempt compounds
nfA	content of non-solvent parts, as a mass share in %
m_w	water content, as mass share in %
m_{eci}	content, as mass share in %, of the exempt compound i
ρ_s	density, in g/ml, of sample at 23°C

ρ_w	density, in g/ml, of water at 23°C (ρ_w = 0.997537 g/ml at 23°C);
ρ_{eci}	density, in g/ml, of the exempt compound i
1000	conversion factor × 1000 in g/l

Example 4:

Exempt compounds are propanol and ethanol
Solvent water stain 5% solid matter content
(density 0.9 cm^3) 20% propanol (density 0.8 g/cm^3)
10% ethanol (density 0.79 g/cm^3)
40% other solvent
25% water

$$VOC_{lwe} = [(100-5-25-(10))/\{100-0.9(25/1.0)-0.9[(20/0.8)+(10/0.79)]\}]\times 0.9\times 1000=825\ g/l$$

Calculated according to DIN ISO 11 890-1, for the same water stain applies (example 4)
after approach 1: 70%
after approach 2: 630 g/l
(propanol and ethanol are treated as VOC)

18.1.3.3.2 VOC content > 0.1 and < 15 %

For VOC content > 0,1 (by mass) and < 15 % the determination is made using gas chromatography (ISO/DIS 11 890-2).[6] A hot or the cold injection is used depending on the sample properties.

After assessing the peak areas, the quantitative assessment and evaluation of the VOC content in the product in its ready-to-use condition, the calculation is made in the simplest case according to:

$$VOC[g/l]=\sum_{i=1}^{i=n} m_i \rho_s 1000 \qquad [18.1.6]$$

where:

VOC	VOC content, in g/l, of the ready-to-use product;
m_i	mass, in g, of compound i in 1 g of the sample
ρ_s	density, in g/ml, of the sample at 23°C
1000	conversion factor × 1000 in g/l.

Table 18.1.2 shows how the application of the various formulae affects the result of calculation. The VOC contents, calculated after ISO/DIS 11 890, are credible for Examples 2, 3, 4. Values calculated according to ASTM, using ratio solvent - water in Examples 2 and 4, are almost the same as VOC contents calculated according to ISO/DIS.

Only by increasing the solid matter content, the VOC content can be reduced in examples calculated according to ASTM (cf. Examples 5 and 1), while an increase in the water content, in spite of the same solvent share, leads to an increase of the ASTM value, because a higher water content increases the sum of the denominator and consequently increases the VOC content.

18.1.3.4 Determination of VOC-content in water-thinnable emulsion paints (in-can VOC)

DIN 55 649[24] describes an approach, which, via the so-called total evaporation method, assesses the content of volatile organic compounds in water-thinnable emulsion paints (in-can VOC).

Table 18.1.2. Examples for the VOC content calculated by various methods

Example	Coating material wt%	Non-volatile parts wt%	Solvent fraction wt%	Water fraction wt%	Density g/cm^3	VOC content according to		
						ASTM D 3960	DIN ISO 11 890/1	
						g/l	%	g/l
1	Water spray varnish	30	10	60	1.000 0.900	250 196	10 10	100 90
2	Water/solvent stain	5	25	70	1.000	833	25	250
3	Solvent stain	5	95	0	0.900	855	95	855
4	Solvent/water stain	5	70	25	0.900	839	70	630
5	Water varnish primer	15	10	75	1.000	400	10	100

Measuring principle:

The VOCs are totally evaporated from a very small amount (a few milliliters) of the thinned original sample by means of a head-space injector and subsequent gas chromatographic analysis.

All components, whose retention time is lower than the retention time of tetradecane (boiling point 252.6°C) are included as VOCs.

VOC content calculation:

$$VOC[mg/kg] = 1000\frac{m_{VOC}}{E_\rho} \quad [18.1.7]$$

where:

m_{VOC}	mass in mg VOC, related to originally weighted-in quantity of the original sample E_ρ
E_ρ	originally weighted-in quantity in g of the original sample

$$VOC[g/l] = \frac{VOC_{[mg/kg]}\rho_{df}}{100} \quad [18.1.8]$$

where:

ρ_{df}	density in g/ml of the original sample (emulsion paint)

18.1.4 MEASUREMENT OF SOLVENT EMISSIONS IN INDUSTRIAL PLANTS

18.1.4.1 Plant requirements

In spite of considerable reductions in the use of organic solvents, the worldwide-adopted ozone values in the troposphere are not being attained. It is crucial to apply consistent measures worldwide to reduce solvent emissions.

In Europe, for example, the Council Directive 1999/13/EG[1] "On limiting emissions of volatile organic compounds, due to the use of organic solvents in certain activities and installations" [EU-VOC-Richtlinie] came into force on March 11, 1999. It has to be transferred into national laws within two years. The application area refers to activities in applying solvents, as enlisted in Appendix IIA of the EU-VOC-Richtlinie (Table 18.1.3).

Table 18.1.3 Threshold and emission controls

[a]Activity	[b]Threshold	[c]Emission limit, mgC/Nm^3	[d]Fugitive emission values, %		[e]Total emission		Special provisions
			New	Exist.	New	Exist.	
Web offset printing (>15)	15-25 >25	100 20	30(1) 30(1)				(1)Solvent residue in finished product is not to be considered as part of fugitive emissions
Publication rotogravure (>25)		75	10	15			
Other rotogravure, flexography, rotary screen, printing, laminating or varnishing units (>15) rotary screen printing on textile/cardboard (>30)	15-25 >25 >30(1)	100 100 100	25 20 20				(1)Threshold for rotary screen printing on textile and on cardboard
Surface cleaning(1) (>1)	1-5 >5	20(2) 20(2)	15 10				(1)Using compounds specified in Article 5(6) and (8); (2)Limit refers to mass of compounds in mg/Nm^3, and not to total carbon
Other surface cleaning (>2)	2-10 >10	75(1) 75(1)	20(1) 15(1)				(1)Installations which demonstrate to the competent authority that the average organic solvent content of all cleaning materials used does not exceed 30 wt% are exempt from application of these values
Vehicle coating (<15) and vehicle refinishing	>0,5	50(1)	25				(1)Compliance in accordance with Article 9(3) should be demonstrated based on 15 minute average measurements
Coil coating (>25)		50(1)	5	10			(1)For installations which use techniques which allow reuse of recovered solvents, the emission limit shall be 150

[a]Activity	[b]Threshold	[c]Emission limit, mgC/Nm³	[d]Fugitive emission values, % New Exist.	[e]Total emission New Exist.	Special provisions
Other coating, including metal, plastic, textile(5), fabric, film and paper coating (>5)	5-15 >15	100(1)(4) 50/75(2)(3)(4)	20(4) 20(4)		(1)Emission limit value applies to coating application and drying processes operated under contained conditions. (2)The first emission limit value applies to drying processes, the second to coating application processes. (3)For textile coating installations which use techniques which allow reuse of recovered solvents, the emission limit applied to coating application and drying processes taken together shall be 150. (4)Coating activities which cannot be applied under contained conditions (such as shipbuilding, aircraft painting) may be exempted from these values, in accordance with Article 5(3)(b). (5)Rotary screen printing on textile is covered by activity No 3
Winding wire coating (>5)				10 g/kg(1) 5 g/kg(2)	(1)Applies to installations where average diameter of wire ≤0.1mm. (2)Applies to all other installations
Coating of wooden surfaces (>15)	15-25 >25	100(1) 50/70(2)	25 20		(1)Emission limit applies to coating application and drying processes operated under contained conditions. (2)The first value applies to drying processes, the second to coating application processes

[a]Activity	[b]Threshold	[c]Emission limit, mgC/Nm^3	[d]Fugitive emission values, %		[e]Total emission		Special provisions
			New	Exist.	New	Exist.	
Dry cleaning					20 g/kg(1)(2)(3)		(1)Expressed in mass of solvent emitted per kilogram of product cleaned and dried. (2)The emission limit in Article 5(8) does not apply to this sector. (3)The following exemption refers only to Greece: the total emission limit value does not apply, for a period of 12 years after the date on which this Directive is brought into effect, to existing installations located in remote areas and/or islands, with a population of no more than 2000 permanent inhabitants where the use of advanced technology equipment is not economically feasible
Wood impregnations (>25)		100(1)	45		11 kg/m^3		(1)Does not apply to impregnation with creosote
Coating of leather (>10)	10-25 >25 (>10)(1)				85 g/m^2 75 g/m^2 150 g/m^2		Emission limits are expressed in grams of solvent emitted per m^2 of product produced. (1)For leather coating activities in furnishing and particular leather goods used as small consumer goods like bags, belts, wallets, etc.
Footwear manufacture (>5)					25 g per pair		Total emission limit values are expressed in grams of solvent emitted per pair of complete footwear produced
Wood and plastic lamination (>5)					30 g/m^2		
Adhesive coating (>5)	5-15 >15	50(1) 50(1)	25 20				(1)If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150

[a]Activity	[b]Threshold	[c]Emission limit, mgC/Nm^3	[d]Fugitive emission values, %		[e]Total emission		Special provisions
			New	Exist.	New	Exist.	
Manufacture of coating preparations, varnishes, inks and adhesives (>100)	100-1000 >1000	150 150	5 3		5% of solvent input		The fugitive emission value does not include solvent sold as part of a coatings preparation in a sealed container
Rubber conversion (>15)		20(1)	25(2)		25% of solvent input		(1)If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150. (2)The fugitive emission value does not include solvent sold as part of products or preparations in a sealed container
Vegetable oil and animal fat extraction and vegetable oil refining activities (>10)					[f]see below the table		(1)Total emission limit values for installations processing individual batches of seeds and other vegetable matter should be set by the competent authority on a case-by-case basis, applying the best available techniques. (2)Applies to all fractionation processes excluding de-gumming (the removal of gums from the oil). (3)Applies to de-gumming
Manufacturing of pharmaceutical products (>50)		20(1)	5(2)	15(2)	5% of solvent input	15% of solvent input	(1)If techniques are used which allow reuse of recovered solvent, the emission limit value in waste gases shall be 150. (2)The fugitive emission limit value does not include solvent sold as part of products or preparations in a sealed container

[a](solvent consumption threshold in tonnes/year); [b](solvent consumption threshold in tonnes/year); [c]values in waste gases; [d](percentage of solvent input); [e]limit values; [f]Animal fat: 1.5 kg/tonne, Castor: 3 kg/tonne, Rape seed: 1 kg/tonne, Sunflower seed: 1 kg/tonne, Soya beans (normal crush): 0.8 kg/tonne, Soya beans (white flakes): 1.2 kg/tonne, Other seeds and other vegetable matter: 3 kg/tonne(1) 1.5 kg/tonne(2) 4 kg/tonne(3)

The quoted threshold levels for the solvent consumption in tonnes/year is of decisive importance as to whether a plant falls under this directive. This value changes depending on the technical feasibility within the industry.

For example, the threshold level for solvent consumption is for illustration-gravure-printing > 25 tonnes/year, for wood coating > 15 tonnes/year.

An analysis of the activity requires data on solvent consumption as calculated from the amount of solvent purchased both as pure solvent and included in solvent containing materials less the amount of solvent retained and/or contained in waste. The calculated difference includes all emissions including diffuse emissions such as the solvent loss from drying racks or solvent initially retained by pained, varnished, printed or dry cleaned articles. These measurements are essential if the statutes are to be enforced and emissions are to be effectively reduced.

Emissive limit values are stipulated for plants covered under this directive for exhaust-gases in mgC/Nm³ as well as limits for diffuse emissions in % solvents input. If these data are not available, total emission limit values are used.

Definition of "Emission Limit Value": The "Emission Limit Value" is understood as the mass of volatile organic compounds, the concentration, the percentage and/or the amount of emission - ascertained under normal conditions - expressed in certain specific parameters, which in one or several time periods must not be exceeded [EU-VOC-Richtlinie].[1]

Plant measurement must be made to provide data for analyzing the actual situation as well as for being able to prove the emission reduction which business must attain.

18.1.4.2 The determination of the total carbon content in mg C/Nm³

18.1.4.2.1 Flame ionization detector (FID)

The total C/Nm³ is assessed according to the Guideline VDI 3481/page 3[25] by means of a flame ionization detector (FID). This device is the component of a mobile device for random sample tests or a continuously measuring device for total carbon concentration measurement in an exhaust-gas flow. This approach measures the total organic substance in an exhaust gas. Should the composition of the solvents contained in the exhaust air not be known, their concentration may be quoted in carbon equivalents as mgC/m³.

Measuring principle:

An FID detects ionized organically compounded C atoms in a hydrogen flame. The ion flow developed in the induced electrical field is electrically amplified and measured. The ion flow arising when burning carbon compounds is proportional to the mass of carbon atoms exposed to the flame per time unit.

The detection of organic compounds with heteroatoms, e.g., N, O, S, Cl, is generally less sensitive. The calibration of the device is done in most cases with propane as the test gas. Procedural data (measuring ranges, proof limits, etc.) by FIDs of various types are compiled in a table in the Guidelines VDI. Figure 18.1.2 shows a measuring arrangement for assessing emissions from a drying plant by means of an FID.

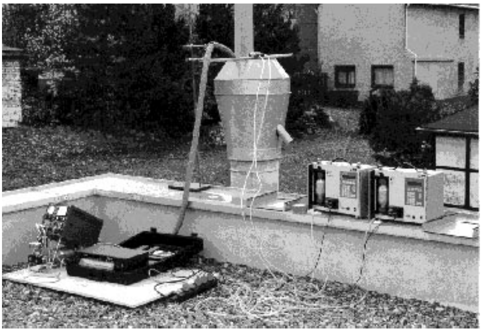


Figure 18.1.2. Emission measurement by FID.

18.1.4.2.2 Silica gel approach

The determination of the total carbon concentration in an exhaust gas by means of the silica gel approach is effected according to the Guideline VDI 3481, p. 2.[26] A partial flow of the exhaust air to be tested is guided through a sorption pipe filled with silica gel. The organic compounds are absorbed by the silica gel. Subsequently, the organic compounds are desorbed in an oxygen flow at an increased temperature and burnt to carbon dioxide (CO_2), which is determined quantitatively. This is a discontinuous method. The data reflect concentration in the measured time intervals and the causes of deviations are difficult to ascertain.

18.1.4.3 Qualitative and quantitative assessment of individual components in the exhaust-gas

While the methods mentioned under 18.1.4.2 reflect the total carbon concentration as a summary parameter, it is still necessary to know concentrations of the individual solvents to assess the plant emission.

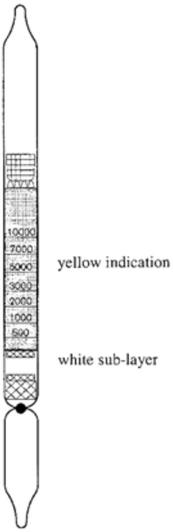


Figure 18.1.3. Indication tube for ethyl acetate 500/a-D.

18.1.4.3.1 Indicator tubes

For many solvents and other substances directly indicating detector tubes are available.[27] They are used for rapid assessment of emission. Since they often do not react specifically with a certain compound alone, errors have to be considered due to cross-sensitivity.

Detector tubes contain sorption-active agents. A gas flow of a defined rate is fed through and the substance in the gas flow produces a color reaction with the agent in the tube. The color intensity is checked against the scale on the test tube and the ppm value can be registered.

Figure 18.1.3 shows such a tube for determining ethyl acetate.[27] The color change in this case is from yellow to light green.

Reaction principle:

$CH_3\text{-}COOC_2H_5 + Cr^{VI} \rightarrow Cr^{III} +$ various oxidation products

This reaction is not substance-specific. Other alcohols, at varying cross-sensitivity as well as methyl ethyl ketone, are reactive as well.

18.1.4.3.2 Quantitative solvent determination in exhaust gas of plants by means of gas-chromatography

A defined amount of exhaust gas is fed into an adsorption medium (activated carbon, thenax, etc.) and its concentration is enriched. There is a subsequent extraction by means of a solvent. The mixture is then injected into a gas chromatograph. The individual components are determined according to Guideline VDI 34 82, page 1.[28]

Measuring principle:

A heatable capillary coated on the inside with various materials (polyester or silicon resins, silica gel) is used as a separating unit. The gaseous substance mixture is transported by means of an inert gas (nitrogen, argon, etc.). The individual solvents remain in the column for different time periods depending on their polarity. After leaving the column solvent is detected by sensitive physical methods. By combining the highly resolving capillary gas chromatography with a mass spectrometer even unknown substances may be identified in the mixtures. The quantitative evaluation of the gas chromatograms is automatically done with appropriate software.

1st Example: Emission measurement in an industrial varnishing plant

The measurement was done in a furniture company, which applies different varnish systems on several varnishing lines.[29]

For preliminary investigations, four chimneys were selected for the measurement as typical sources of emission.

Based on the analysis of the varnish materials and measurements performed over extended period of time, it is certain that the materials and concentrations processed during the measuring gave a representative cross-section of the production activity. Table 18.1.4 shows a summary of the varnish and solvent amounts processed per day, which were emitted from chimneys 1 to 4.

Table 18.1.4. Summary of the varnish and solvent amounts processed in the 1st example

Measuring point chimney	Varnish	Solvent share, %	Varnish processed, l/day	Total solvent, l/day
1	1	34	10 - 15	~40 - 45
	2	76		
	3	80	30 - 35	
	3	80	5	
	4	80	5	
2	5	56	50 - 60	37
	6	34	10	
3	7	38	30	12.5
	6	34	3	
4	1	34	~240	~170
	8	52.88	120-130	
	6	34	50	

At the chimneys, the following exhaust air parameters were established:

Chimney diameter	mm
Exhaust air flow rate	m/s
Exhaust air temperature	°C
Humidity	%
Volume flow (operation)	m^3/h
Volume flow	Nm^3/h
Heat flow	MW

Table 18.1.5 contains a summary of the established emission values expressed in mg C total/Nm^3 as well as the mass flow g C/h.

Table 18.1.5. Measuring results for total carbon concentration at different measuring points

Measuring point chimney	Time	Volume flow, Nm^3/h	Carbon concentration, mgC/Nm^3	Mass flow, gC/h	Odorant concentration(1), GE/m^3	Mass flow, TGE/m^3
1	10.35 - 11.20	35 200	112.6	3 964	93	3 519
	11.45 - 12.00		96.5	3 397	87	3 292
	13.45 - 14.35		128.6	4 527		

Measuring point chimney	Time	Volume flow, Nm^3/h	Carbon concentration, mgC/Nm^3	Mass flow, gC/h	Odorant concentration(1), GE/m^3	Mass flow, TGE/m^3
2	11.25 - 12.00	39 240	72.4	2 841	91	4 151
	12.45 - 13.10		56.3	2 209	87	3 969
	13.10 - 14.30		56.3	2 209	93	4 242
3	13.50 - 14.40	33 900	48.2	1 634	100	3 747
	09.25 - 09.55		56.3	1 908	115	4 309
	09.55 - 10.25		64.3	2 180		
4	09.15 - 09.45	108 650	112.5	12 223	98	12 837
	09.45 - 10.15		152.8	16 602	213	27 900
	10.15 - 10.45		160.8	17 471		

(1) The odorant concentration does not refer to the times stated.

The EU VOC Directive for plants for wood coating with a solvent consumption of 15 - 25 t/year requires an emission limit of 100 mg C/Nm^3.

In the example, this is only met at chimneys 2 and 3.

As a parallel to these measurements, using activated carbon tubes and subsequent gas chromatographic evaluation it was determined that the main components of VOCs were acetone, ethyl acetate, toluene, butyl acetate, xylene, ethylbenzene (Table 18.1.6). Butyl acetate and ethyl acetate were the main components in the respective solvent mixtures.

Table 18.1.6. Measured results for individual components at different measuring points

MPC*	Acetone		Ethyl acetate		Toluene		Butyl acetate		Ethyl benzene		Xylene	
	Conc[a]	MF[b]	Conc[a]	MF[b]	Conc[a]	MF[b]	Conc[a]	MF[b]	Conc[a]	MF[b]	Conc[a]	MF[b]
1	6.5	229	15.5	546	9.0	317	15.5	545	1.0	352	4.2	158
	4.5	158	11.0	387	5.5	194	11.0	387	1.0	352	2.5	88
2	11.0	432	24.5	961	14.5	569	24.5	961	1.0	39	6.5	255
	4.5	176	9.0	353	6.5	255	14.5	569	-	-	-	-
3	-	-	4.5	152	2.0	68	3.5	118	0.5	17	2.0	68
	-	-	15.5	525	5.5	186	8.0	271	1.0	34	5.5	186
4	9.0	978	20.0	2 173	9.0	978	17.0	1 847	2.0	217	8.0	869
	5.5	597	27.0	2 933	18.0	1 956	37.0	4 020	3.5	380	17.0	1 847

*MPC = Measuring point chimney; [a]concentration in mg/Nm^3; [b]MF = mass flow in g/h

2nd Example: Emissions measured in a spray-room

The usual technique of measuring VOC emissions in plants by means of the FID according to VDI 3481/page 3 has the shortcoming that individual components in the gas mixture cannot be measured separately, but only determined as total carbon. Also the device needs to be placed in the immediate vicinity of the measuring point and requires frequent calibration.

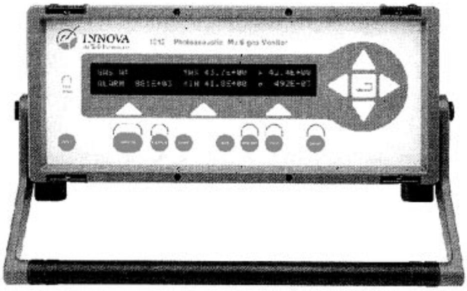


Figure 18.1.4. Photoacoustic Multigas Monitor 1312.

A portable multi-gas monitor 1312 [Bruel & Kjaer][30] weighing 9 kg (Figure 18.1.4) enables sampling in six places up to 50 m away from the monitor. It can determine at each measuring point the concentration of up to a maximum 5 components as well as the humidity. This is done by a multi-point sampler with a dosing apparatus controlled by system software. The device needs calibration only four times a year. Beyond that, the device may also be used for determining the total C concentration.

Measuring principle (Figure 18.1.5)

1. The "new" air sample is hermetically sealed in the analysis cell by closing the inlet and outlet valves.

2. Light from an infrared light source is reflected by a mirror, passed through a mechanical chopper, which pulsates it, and then passes through one of the optical filters in the filter carousel.

3. The light transmitted by the optical filter is selectively absorbed by the gas monitored, causing the temperature of the gas to increase. Because the light is pulsating, the gas temperature increases and decreases, causing an equivalent increase and decrease in the pressure of the gas (an acoustic signal) in the closed cell.

4. Two microphones mounted in the cell wall measure this acoustic signal, which is directly proportional to the concentration of the monitored gas present in the cell.

5. The filter carousel turns so that light is transmitted through the next optical filter, and the new signal is measured. The number of times this step is repeated depends on the number of gases being measured.

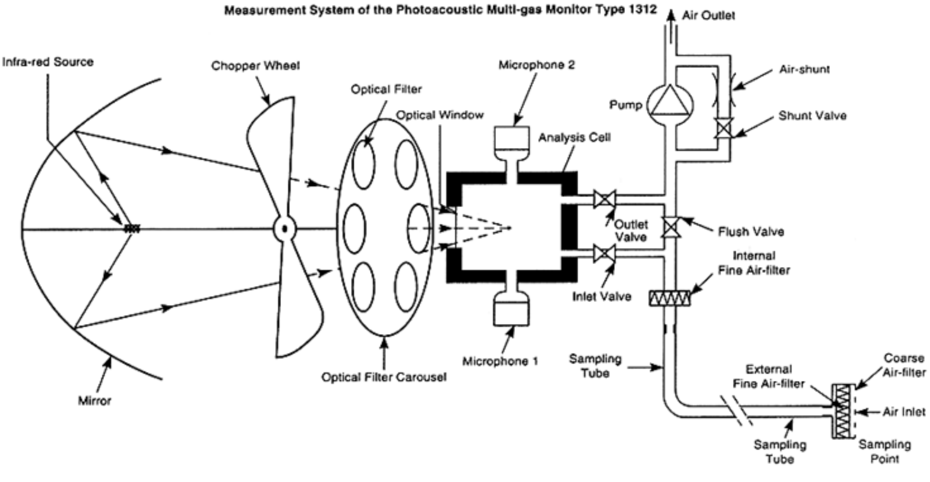
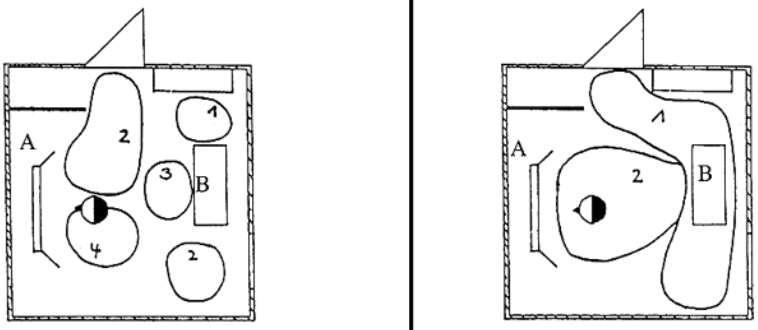


Figure 18.1.5. Measurement principle of Photoacoustic Multigas Monitor Type 1312.


Natural Ventilation

Technical Ventilation

Natural Ventilation

area	mg/m^3
1	3650
2	4430
	4910
	4530
3	5580
4	6690

Technical Ventilation

area	mg/m^3
1	489
	483
	499
2	662
	614
	564

Figure 18.1.6. Maximum concentration of n-butyl acetate in the spray-room of a joiner's with windows and door closed. A - Spray wall, B - Rack track for shelving the varnished parts.

The response time is only 13 s for a single gas or water-vapor, or approx. 40 s if 5 gases and water-vapor are measured.

The measurements are quasi-continuous. When measuring a single gas, the measuring value is updated every 30 s, with five gases and humidity the update time is 105 s. The measured values are stored, statistically evaluated and numerical or graphical output can be obtained either immediately or on demand. Such devices make the emission measurement effort much easier than with the older, less automated equipment.

Figure 18.1.6 shows the results of emission investigations in the spray-room of a joiner's with and without ventilation.[31] Windows and doors were closed. The varnisher was standing in front of a spray-wall, opposite to him was placed a platform rack truck for shelving the varnished parts. Those areas in the joiner's, which showed roughly the same emission values of n-butyl acetate, are marked on each drawing.

The emission load in the room was decreased by the technical ventilation to about a tenth of the values.

18.1.5 "ODOR" DEFINITION

One of the senses of the living organism is the sense of smell. Smell is caused by a substance whose effect is largely dependent on its chemical structure.

The odorous substances perceived by human are suspended in the air as volatile substances. The degree of response to a substance depends on its vapor pressure, thus, in turn on its concentration in the air and its molecular weight. An odorant also has to be sufficiently water and fat-soluble, which enables it to interact with the olfactory receptors.

Whether an odorous impression is considered pleasant or unpleasant is largely determined by the functional groups of the chemical compounds (Table 18.1.7).

Table 18.1.7. Scent qualities of various chemical compounds in relation to their functional groups[33,34]

Odorous impression	Functional group	Substance group
Pleasant	-OH -OR -CHO -COR -COOR -CN -NO_2	Alcohols Ethers Aldehydes Ketones Esters Cyanogen compounds Nitro compounds
Unpleasant	-SH -SR -CSR -NC -NH_2	Merkaptanes Thioethers Thioketones Nitriles Amines

This division should be, however, only regarded as a rough guideline, since the so-called "pleasant" odor, at higher concentrations, can easily be perceived as very "unpleasant".

Almost all solvents, such as, ketones, esters, glycols, alcohols, aromatic and aliphatic hydrocarbons, contribute to a more or less intensive smell.

"Odor" is not a parameter of substance, but a summarized parameter of effects. Its determination is based on the fact that the sense of a smell can be used subjectively to evaluate certain substances (odorants). The concentration of those substances suspended in the air can be determined, which is called odorant concentration.

Odor threshold or perception threshold[35-38]

The odor threshold is a concentration of the odorant in the air, given in mg/m³. The odor threshold corresponds to an odor unit (GE). It is the amount of odorous substance, which - distributed in 1 m³ of scent-neutral synthetic air - initiates in just 50% of the evaluators a perception of smell and in the other 50%, no response.

The odor threshold is very specific to substance. It is determined in several measuring series and the results form a Gaussian distribution curve. Since this is ultimately a subjective evaluation, one should not be surprised to find more as well as, less, reliable data in literature. Examples are shown in Table 18.1.8.

Odorant concentration

The odorant concentration of a sample is the multiple of the odor threshold and it is determined in odor units (GE) per 1 m³ neutral air.

Odor intensity[39]

Since the odor threshold alone is an insufficient evaluation criterion for an odorant, the increase in response with increasing odorant concentration may additionally be taken into account as a scale of reference.

The increase in response is mainly material and/or mixture dependent for a given odorant concentration and is called odor intensity. [Schön, p. 68][32]

Table 18.1.8. Odor thresholds of selected compounds from literature [Geruchs-Immissions-Richtlinie][34]

Compound	Odor threshold, mg/m³	Compound	Odor threshold, mg/m³
Butyl acetate	0.03	Ethanol	19.1
Ethyl acetate	22	1-butanol	0.4
Benzene	16.2	Acetone	48
Toluene	7.6	Ethyl acrylate	0.002
Xylene	0.35	Dichloromethane	706

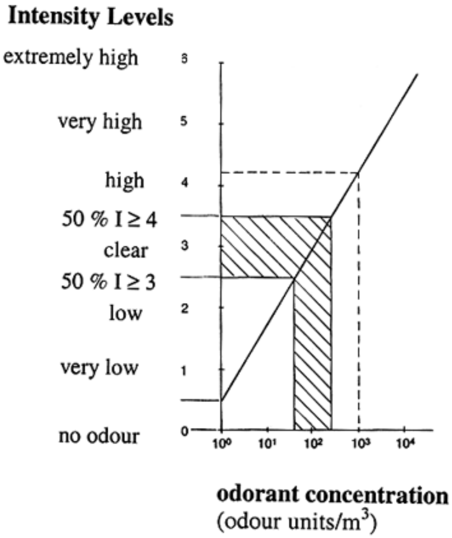


Figure 18.1.7. Interdependence of odorant concentration and odor intensity in an artificial example.

Figure 18.1.7 shows the interaction between odorant concentration and odor intensity in an artificial example.[41]

Odor intensity is assessed by means of a scale from 1 to 6 [VDI 3882/1][39] (Table 18.1.9).

Table 18.1.9. Correlation of odor with an intensity level

Odor	Intensity level
Extremely high	6
Very high	5
High	4
Moderate	3
Low	2
Very low	1
No scent	0

Hedonic odor tone

An odor may be quantified by determining the odor concentration, the character of the odor (pleasant or unpleasant) is not considered. Unpleasant odors may result in deteriorating health and should therefore be avoided.

By determining the hedonic odor effect, the emotional reaction initiated by an irritation to the sense of smell may be included. It should not be confused with the kind of smell (it smells like ...) or with the odor intensity (it smells “strong” to “weak”). It may be determined not only for

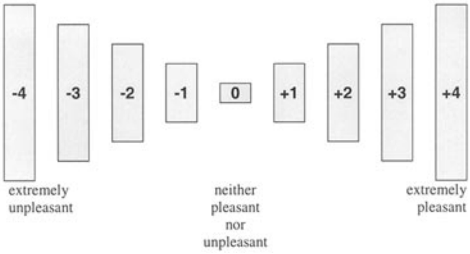


Figure 18.1.8. Evaluation of the hedonic effect of an odor sample [VDI 3882/2].[40]

a single odorant, but also for an odorant mixture. Odor samples of an odorant concentration above the odor threshold are ranked by evaluators according to the odorants' position in the following response range between "extremely unpleasant" to "extremely pleasant".

In many cases of odor evaluation, there are big differences between the results among the individual evaluators, since they have a widely varied background of experience.

18.1.6 MEASUREMENT OF ODOR IN MATERIALS AND INDUSTRIAL PLANTS

18.1.6.1 Introduction

Various methods are known for determining odors. One of particular interest is pupil dilatation. This is based on the fact, that pupils dilatate when a strong odor is sensed, as may be caused by concentrated ammonia.

A simple sampling of odors is based on the Öko-Tex Standard 200.[42] The samples are conditioned in a desiccator and their odor is subsequently judged by 6 evaluators according to a five-point scale:

1 odorless
2 low odor
3 bearable odor
4 annoying odor
5 unbearable odor

Such a scale also serves the "Deutsche Gütegemeinschaft Möbel" (German Quality Association of Furniture Manufacturers) as a methodical approach for evaluation of odors of furniture, cover fabric, leather, etc.

Level 3, however, is defined as "commodity typical". It needs to be achieved in order for the respective product to have the attribute "tested for noxious substances".

In principle, odors may be determined by means of sample recognition with the help of arrays of gas sensors, so-called electronic noses. Unknown samples are compared with known samples. Hence, olfactometric investigations need to precede. Such a measuring device is applicable only in a specific case and has to be trained prior to use. Odor can become a controllable quality feature of a product. Samples of good quality can be made distinguishable from samples of bad quality.

In practice, odor determination by means of the olfactometer has been widely applied and generally adopted.

18.1.6.2 Odor determination by means of the "electronic nose"

The principle of odor determination in different fields of application has been discussed in detail by Moy and Collins[43] and Schulz.[44]

Measuring principle:

The substance mixture in question, which causes the odor, undergoes an overall investigation by means of a sensor array. In doing so, the device makes use of the semi-conductive properties of various metal oxides, which are on the surface of 12 sensors which react to the gaseous substances which come in contact with them. The response also depends on the temperature, humidity and flow rate of the gas. Each sensor issues its own reply signal as soon as the sample of air touches its surface.

The measurement is done within about two minutes, readjustment of the sensors takes about 4 minutes. The measuring device is linked to a computer with relevant software.

Each odor is, according to the twelve sensors, represented by 12 graphs showing a characteristic "profile" ("fingerprint"). These sensor-specific, time-dependent, series of electric conductivity data, which are produced by the presence of the odorous substances provide the data for the evaluation. They are processed by means of neuronal networks.

The available odor samples can be shown as two or three-dimensional. Comparative or referential samples are treated in the same way. By means of sample series, they may serve the purposes of the identification of new samples.

It remains an issue, that odor-relevant compounds exist in much lower concentration in most cases than the less odorous compounds, thus they are also less influential on the sensor signal. Much research effort has yet to be undertaken to apply the electronic nose in the future.

18.1.6.3 Odor determination by means of the olfactometer

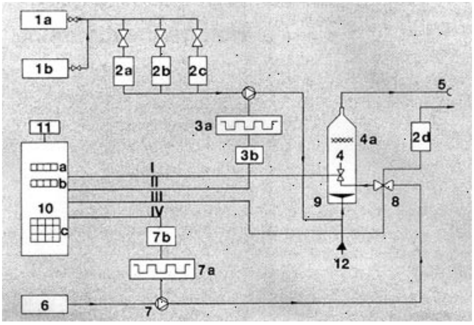


Figure 18.1.9. Principle of an olfactometer. 1 diluent air a) outer air, b) synthetic air (bottle); 2 acitvated charcoal filter air from 2d to rinse by-pass, 3 glass bulb pump with electronically controlled drive (a,b); 4 mix chamber (with installation a); 5 evaluator's mask; 6 sample air (if necessary pre-mixed); 7 glass bulb pump with electronically controlled drive (a,b); 8 by-pass valve; 9 mix chamber valve; 10 control terminal, a) display (programme step), b) display, c) terminal keyboard; 11 printer: I - IV control line; 12 additional pump (24 l x min-1).

The method of odor determination by means of the olfactometer is based on the guidelines Richtlinien VDI 3881, pages 1 to 4[35-38] and VDI 3882, pages 1 and 2.[39,40]

Measuring principle:

An odorant sample is diluted in a defined way with neutral air in an olfactometer and offered to test persons as an odor sample. The test persons are exposed to several dilution levels. Should an odor be perceived, it shall be confirmed by pressing a button. An olfactometric determination requires at least 5, and preferably 8 evaluators. These evaluators need to pass a suitability test in accordance with Guideline VDI 3882, p. 2.[40] The principle of an olfactometer[45] is shown in Figure 18.1.9.

The results are presented in odor units/m^3 of neutral air and they are automatically displayed as the averaged data of the panel's evaluation.

18.1.6.4 Example for odor determination for selected materials: Determination of odorant concentration in varnished furniture surfaces

The odor potential of furniture is determined primarily by the applied varnishes although adhesives also play a minor role. Furniture varnishes may contain up to 80% solvents. The residual solvents remaining in the varnish thus determine the VOC and odorant concentration of furniture surfaces.

A specific test method has been developed for determining the VOC and odorant concentration of coated surfaces,[46-48] as shown schematically in Figure 18.1.10. Similar to formaldehyde determination,[49] sample testing is done using a test chamber approach. After some atmospheric conditioning, of the varnished furniture, the samples are stored in a test chamber (typically 1 m^3) under the following conditions: 23°C±0.5; 45±3% relative humidity; charged with 1 = 1 m^2 of emitting sample surface per 1 m^3 test chamber volume air flow rate at sample surface: between 0.1 and 0.3 m/s. The samples remain in the test chamber for an initial 48 hours without an air exchange in the test chamber, in order to simulate a “worst case scenario”, i.e., that, for instance, the new furniture is sealed off air-tight during transport, so that residual solvents accumulate.

After 48 h of storage time without an air exchange, air samples are taken in parallel for the determination of VOC emission by means of gas chromatograph and for determination of odor by the olfactometer. Subsequently, there is an air exchange of one air change per hour, and the slow-down curve of VOC and odorant concentration is determined.

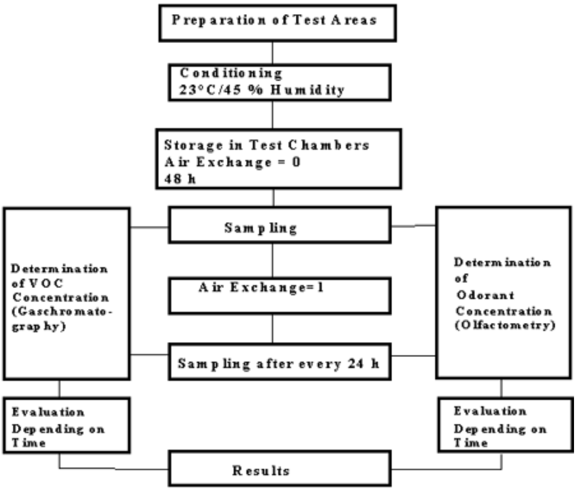


Figure 18.1.10. Test approach for the determination of VOC and odorant concentration in coated surfaces.

Figure 18.1.11 shows the decreasing VOC concentration depending on the storage time in the test chamber with an air exchange 1,[50,46] and Figure 18.1.12 shows the decreasing odorant under the same test conditions.[50,46]

The curves for VOC and the odorant concentration follow a similar pattern, they are, however, not identical. While the VOC concentration in water varnish is the lowest after 11 days, the odorant concentration after this time is equally high with both DD-varnish and water varnish. This, however, does not generally apply to these types of varnish. Also DD-varnishes of different origins may differ greatly in emitting residual solvents.

In single-solvent systems, it is easy to see the interdependence between VOC and odorant concentration. This does not necessarily apply to solvent mixtures. This is due to the large variations in odor thresholds and the different evaporating behavior of the various solvents.

Acrylate varnishes, for example, need contain only a few µg of ethyl acrylate in order to produce odor, since odor threshold level is at 0.002 mg/m^3. Thus the determination of the

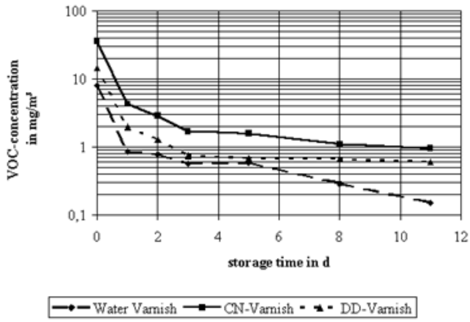


Figure 18.1.11. VOC concentration depending on the storage time in the test chamber with air exchange 1.

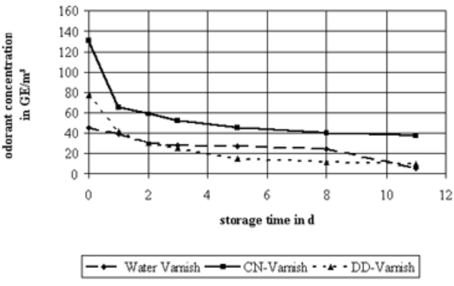


Figure 18.1.12. Decreasing odorant concentration depending on the storage time in the test chamber with air exchange 1.

VOC concentration alone is not sufficient for determining the quality of coated surfaces must also be evaluated.

18.1.6.5 Example of odor determination in industrial plants: Odor measurement in an industrial varnishing plant

In a study parallel to the measurements of the VOC emission at the varnishing lines of a furniture company, as described in Section 18.1.4.3.2, 1st Example, odorant concentrations were sampled in the exhaust air from the individual chimneys by means of olfactometry.[29] All conditions of measurement described in Section 18.1.4.3.2 also apply to the determination of the odorant concentration.

The results are contained in Table 18.1.5 as odorant concentration in GE (odorant units)/m^3 and in the mass flow in TGE/h (one thousand odorant units per hour). The evaluation of the analytical determination of individual components resulted in the main components being butyl acetate and ethyl acetate. Due to the very low odorant threshold of butyl acetate (0.03 mg/m^3), as compared to other available substances, (ethyl acetate 22 mg/m^3), butyl acetate may be assumed to be responsible for for the bulk of detectable odor.

An immediate comparison of samples taken at the same point in time resulted in the following data:

concentration of butyl acetate:	8 mg/m^3
odorant concentration:	115 GE(odorant units)/m^3

Adopting the value quoted in the literature for the odorous threshold of butyl acetate at 0.03 mg/m^3, which equals one odorant unit, the odorant concentration estimates a butyl acetate concentration of about 4 mg/m^3. This value is in the same range as the value established for butyl acetate by gas chromatography. In these comparisons one has to consider that odorant thresholds may deviate by one to two exponents to even ten, according to literature sources.[51]

Measurements taken in the housing area about 300 m away from the chimneys of the varnishing plants could not establish any solvent-typical components in the gas analysis. The maximum concentration value for TVOC was at 0.004 mg/m^3.

Also the spreading calculation, which was carried out on the basis of the determined solvent concentration, showed that there should be no significant odor annoyance in the vicinity of the emission source. The results of the spreading calculation on the basis of measured solvent concentrations are considerably more precise, since solvent concentrations may be determined more exactly than odorant concentrations.

The spreading calculation was done using the software package "IMMPROG-P" by AIRINFO AG, Switzerland, and carried out according to a method of the Odor Emission Guideline of the German State of Northrhine-Westfalia/Geruchsimmissions-Richtlinie des deutschen Bundeslandes Nordrhein-Westfalen.[34]

REFERENCES

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18.2 PREDICTION OF ORGANIC SOLVENTS EMISSION DURING TECHNOLOGICAL PROCESSES

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18.2.1 INTRODUCTION

The concentration of toxic substances in air during technological process is very important factor for occupational safety. Typical examples of processes, which have the potential to harm workers, are metal degreasing, painting, and wood impregnation.

If metal processing involves several steps some of which may be done in more than one manufacturing facility, the semi-processed metal parts must be protected during transportation and storage. Such protective coatings of grease and rust preventatives must be removed in degreasing operation. For many processes (e.g., painting, galvanic metal deposition), clean surface is an important requirement. The cleaning process may be done in automated and enclosed equipment or it may be done manually in the open. The degreasing agent may be an organic solvent, a solvent blend, or a water solution, usually alkaline in nature.

Depending on the process used the operation may pose no risk to the worker or be a serious occupational hazard. Similarly environmental emissions may be negligible or of serious concern.

We present a method of evaluating the quantities of emissions from such processes which involve solvents. The method may be applied to such diverse operations as painting, wood preservation, impregnation of porous materials, gluing, cleaning, filing open tanks, general solvent handling operations, and many others.

We have selected metal degreasing as a representative example to demonstrate how the method may be applied.

18.2.2 METHODS OF DEGREASING

Six methods can be identified which differ in the degreasing agent used:

- degreasing in liquid organic solvents, such as naphtha, petroleum, chlorinated aliphatic hydrocarbons, etc.
- degreasing in hot vapors of halogenated solvents such as, trichloroethylene, perchloroethylene, fluorochloroethane and so on
- degreasing in alkaline water solutions of hydroxides, phosphates, surfactants, emulsifiers, common inhibitors, etc.
- degreasing in an emulsion of organic solvents in water
- degreasing in water steam
- supersonic degreasing in stabilized chlorinated hydrocarbons.

Degreasing process can be conducted automatically in different ways by:

- dipping
- spraying
- using high pressure
- supersonic
- pulsating washing

Process can be conducted in open or enclosed equipment. Manual degreasing is still very popular but it is very time and labor consuming, expensive, and large amounts of solvents are lost.

18.2.3 SOLVENTS

In metal degreasing these solvents are most frequently used:

- naphtha solvent,
- naphtha anti-corrosive
- 1-butanol,
- 1,1,2-trichloroethylene,
- 1,1,1- trichloroethane,
- extraction naphtha,
- petroleum(mineral) spirits.

18.2.4 IDENTIFICATION OF THE EMITTED COMPOUNDS

In many cases, solvent mixtures are used. Their composition must be identified. Rodofos is one example of such solvent used in Poland. Its composition was determined by gas chromatography. Analyses were performed using a Hewlett-Packard gas chromatograph model 5890 coupled with computerized mass spectrometer instrument, model 5970.

Capillary column 50 m x 0.32 mm i.d., d.f.= 0.52 μm FFAP and helium as a carrier gas was used at temperature of 40°C. Ions from 20 to 400 amu were counted, delay time was 3.5 min.

Samples were collected by drawing a known volume of air through a bubbler containing 1 ml of carbon disulfide. Volume of the injected sample was 1-5 μl.

Chromatograms are presented in Figure 18.2.1.

18.2.5 EMISSION OF ORGANIC SOLVENTS DURING TECHNOLOGICAL PROCESSES

The concentration of substances emitted to the air during the degreasing processes reached the steady-state constant value:

$$C = E/q \qquad [18.2.1]$$

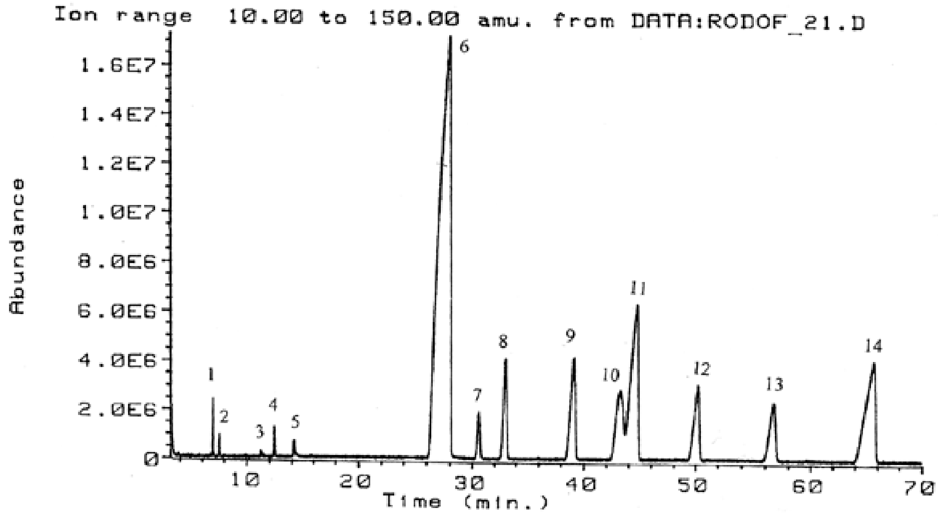

Figure 18.2.1. Chromatogram of substances emitted during degreasing. Oven temperature 40ºC. 1 - benzene, 2 - 2,2-dichloromethylpropane, 3 - butyl ester of formic acid, 4 - methylbenzene, 5 - water, 6 - 1-butanol, 7, 8, 10, 11, 12, 13, 14 - derivatives of methyl ethyl benzene, 9 - propyl benzene.

where:

C	concentration, mg/m^3
q	sum of ventilation flow rates, m^3/min
E	emission, mg/min.

Thus,

$$E = C \times q \qquad [18.2.2]$$

The value C can be measured, but a value for q is difficult to estimate, because it includes mechanical and gravitational ventilation (central air conditioning, influence of open doors, windows, fans and natural ventilation).

When the process of degreasing ends, the decay of concentration can be described by:

$$C_t = C_e \times \exp(-t \times q/V) \qquad [18.2.3]$$

where:

C_e	concentration of the emission at the termination of the process, mg/m^3,
t	duration of process, min,
V	room volume, m^3.

After a transformation:

$$q = (\ln C_e - \ln C_t) \times V/t \qquad [18.2.4]$$

The quantity emitted to a room of known volume depends only on the changes of concentration at time (t).

18.2.6 VERIFICATION OF THE METHOD

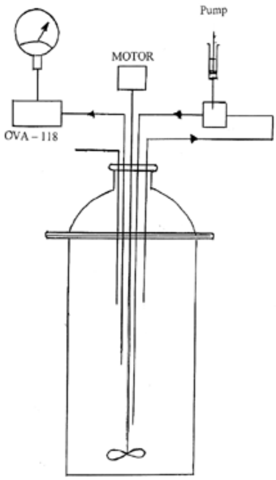

Figure 18.2.2. Emission measuring setup.

Emission measuring setup is given in Figure 18.2.2. Cyclohexane was pumped (with E=6.123 mg/min) into glass bottle (V=44.5 l) equipped with a fan. The air in the bottle was analyzed by gas chromatography using a flame ionization detector - OVA 118. After 20 min., when the concentration reached 2.250 mg/l, the pump was stopped and the decay of concentration with time was measured.

Results are given in Tables 18.2.1 and 18.2.2 (value E from the equation [18.2.2], q from the equation [18.2.4]).

The standard deviation of the sample was 0.0106, of the method - 0.0102 and bias was 0.08 mg/min (1.3%).

Tests were then performed in the macro-scale - emission of cyclohexane in a room, when the emission ended when the process stopped. The estimate is precise when the room volume and ventilation flow rate are known.

The method was verified in the industrial environment in automotive plant. Here, the hazardous substances continue to be emitted to the air after the process had stopped. The concentration measured near the outlet of exhaust was 620 mg/m^3, and because the exhaust flow rate was known to be 50 m^3/min, the emission was precisely estimated according equation [18.2.2] as 31 g/min or 312.48 kg/week. This value was comparable with the average solvent loss - 326.22 kg/week.

Table 18.2.1. Emission of cyclohexane

t, min	C_t, mg/l	E, mg/min
1	0.138	6.210
2	0.273	6.212
3	0.405	6.213
4	0.533	6.201
5	0.659	6.201
6	0.780	6.184
8	1.020	6.200
10	1.250	6.212
12	1.465	6.200
15	1.770	6.188
20	2.250	6.218
E ave. - 6.203, σ_n= 0.0102, σ_{n-1}= 0.0106		

Table 18.2.2. Ventilation flow rate

t, min	C_t, mg/l	Q, l/min
1	2.200	1.000
2	2.215	1.011
3	2.100	1.024
4	2.055	1.008
5	2.010	1.004
6	1.965	0.993
8	1.880	0.999
10	1.800	0.992
12	1.720	0.996
15	1.605	1.002
20	1.435	1.000
q ave. = 1.0026, σ_n = 8.7103×10^{-3}, σ_{n-1} = 9.1354×10^{-3}		

18.2.7 RELATIONSHIPS BETWEEN EMISSION AND TECHNOLOGICAL PARAMETERS

Emission of solvents depends on the evaporation rate of the solvent in the process. The evaporation rate from the surface depends on the concentration in the layer on the surface and the coefficient of mass transfer on the air-side. This relation is approximately true for degreasing operations using both liquid and vapors of organic solvents.

The concentration of solvent in a saturated vapor layer depends on temperature and vapor pressure. The coefficient of mass transfer on the air-side depends on the air velocity in the layer on the surface and Schmidt's number (includes dynamic vapor viscosity, vapor density, and diffusion coefficient). Emissions are measured in mass unit per unit of time and the amount depends on surface area and the rate of evaporation, which, in turn, depends on temperature, air velocity over the surface of solvent and the mass of solvent carried out on the wetted parts which have been degreased.

18.2.7.1 Laboratory test stand

A thin-metal, flat dish 6 cm in diameter was filled with solvent up to 2-3 mm from the upper edge and placed on a laboratory balance (Figure 18.2.3). The amount of evaporated solvent was measured with (precision 0.1 mg) as the difference between the mass of the dish and solvent at the start of the test and the mass of the dish with solvent after pre-determined period of time. The test was repeated under different conditions of temperature and air velocity near the surface of the solvent. The results were reported as the evaporated mass per 1 minute.

18.2.7.2 The influence of temperature on emission

Temperature was measured with a mercury thermometer with a range from 0 to 30°C. Air velocity was 0.3 to 0.4 m/s in this temperature region. The relationship is linear and the equations expressing emission [g/m^3/h] relative to temperature [°C] for different solvents are:

trichloroethylene	$E= 63.6\times t + 699.6$
naphtha solvent	$E= 9.3\times t + 4.9$
naphtha anti-corrosive	$E= 0.55\times t + 5.65$
1-butanol	$E= 6.29\times t + 16.9$
1,1,1- trichloroethane	$E= 94.7\times t + 805.6$
extraction naphtha	$E= 49.5\times t + 1147$
petroleum(mineral) spirits	$E= 11.9\times t + 76.7$
wood preservatives	$E= 2.0\times t + 42$

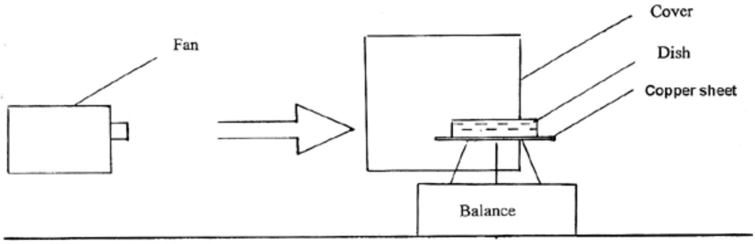

Figure 18.2.3. Test laboratory stand.

18.2.7.3 The influence of air velocity on emission

Air velocity was measured with a TSI air velocity meter in range 0.2- 1.5 m/s. Temperature was 20°C. The relationship has linear character and the equations expressing emissions $[g/m^3/h]$ relative to air velocity [m/s] for different solvents are:

trichloroethylene	$E= 657 \times v + 1766$
naphtha solvent	$E= 109 \times v + 159$
naphtha anti-corrosive	$E= 9.1 \times v + 14.53$
1-butanol	$E= 72 \times v + 121$
1,1,1- trichloroethane	$E= 1403 \times v + 2120$
extraction naphtha	$E= 632 \times v + 830$
petroleum(mineral) spirits	$E= 160 \times v + 242$
wood preservatives	$E = 516 \times v$

18.2.7.4 The relationship between the mass of solvent on wet parts and emissions

The amount of solvent carried out on a degreased part depends on its surface, shape and roughness and on the viscosity and density of the solvent. The amount of solvent carried out on a degreased surface was measured by gravimetric method. Tests show that the amount of solvent retained on 1 m^2 of flat surface is:

trichloroethylene	34.7 g
naphtha solvent	26.0 g
naphtha anti-corrosive	34.5 g
1-butanol	31.3 g
1,1,1- trichloroethane	38.5 g
extraction naphtha	19.0 g
petroleum(mineral) spirits	19.2 g

18.2.8 EMISSION OF SOLVENTS

Combining these factors, the final equations for the evaluated solvents are:

trichloroethylene	$E= (657v + 63.6t + 699.6) \times P_r + 34.7P$	[18.2.5]
naphtha solvent	$E= (109v + 9.3t + 4.9) \times P_r + 26P$	[18.2.6]
naphtha anti-corrosive	$E= (9.1v + 0.55t + 5.65) \times P_r + 34.5P$	[18.2.7]
1-butanol	$E= (72v + 6.3t + 17) \times P_r + 31.3P$	[18.2.8]
1,1,1- trichloroethane	$E= (1403v + 94.7t + 805.6) \times P_r + 38.5P$	[18.2.9]
extraction naphtha	$E= (632v + 49.5t + 1147) \times P_r + 19P$	[18.2.10]
petroleum(mineral) spirits	$E= (160v + 12t + 76.7) \times P_r + 19.2P$	[18.2.11]
wood preservatives	$E= (516v + 2t + 42) \times P_r$	[18.2.12]

where:

E	emission of the solvent, g/h
v	air velocity near the surface of solvent (in still air it is 0.3 m/s)
t	temperature, °C
P_r	the surface of solvent, m^2
P	the surface of elements degreased in one hour, m^2/h.

18.2.9 VERIFICATION IN INDUSTRIAL CONDITIONS

Research was conducted in an industrial hall where an ALDI machine was used for degreasing with trichloroethylene vapor. The volume of the solvent was 1000 dm^3, the surface area was 0.825 m^2 (110 cm by 75 cm). A metal basket with degreased parts was introduced into the degreasing compartment and vapors of trichloroethylene condensed on surface of the parts. After 30 s, the basket was removed from the machine. The average temperature at the surface was 24°C. There was an exhaust in the hall with a flow rate of 50 m^3/min. The solvent loss was 30 l/day and it was independent of the number of degreased elements. The solvent loss of 30 l/day equals 1.25 l/h or 1.825 kg/h with density of trichloroethylene equal 1.46 g/cm^3.

The average concentration of trichloroethylene measured near the exhaust by portable IR spectrophotometer-Miran was 680 mg/m^3. Calculation (equation [18.2.2]) with q=50 m^3/min gives emission of 34 g/min or 2040 g/h.

According to equation [18.2.5] for trichloroethylene:

$E= (657v + 63.6t + 699.6)\times P_r + 34.7P$

v=0.3 m/s (still air near the surface)

t=24°C

P_r=0.825 m^2

In vapor degreasing, the coefficient of mass carried out on wet details ready to ship P=0. Then

$E= (657\times 0.3 + 63.6\times 24 + 699.6)\times 0{,}825 = 1999$ g/h

The measured value of 2040 g/h and the calculated value of 1999 g/h are in good agreement, meaning that the equations can be successfully applied to predict the organic solvents emission during process of automatic degreasing.

Process of manual degreasing was verified for washing motor parts in a metal dish - 0.72 m^2 filled with 500 l of extraction naphtha. The surface of parts was 0.227 m^2. This process took place in an open garage at temperature 14°C. Air velocity in vicinity of parts was 0.48 m/s. The residual solvent volume after degreasing was 4.58 l. The process lasted 7 minutes. Emission estimated according the loss of the solvent during the process was 420 ml. Taking into account the weight density of naphtha - 0.72 g/cm^3, emission was equal 302.4 g/7 min or 2592 g/h.

Applying the equation [18.2.10] for extraction naphtha

$E= (632v + 49.5t + 1147)\times P_r + 19P$

and:

v = 0.48 m/s

t = 14°C

$P_r = 0.72 + 0.227 = 0.947$ m^2, surface of the dish and details

P = 0.947 m^2/7min [8.12 m^2/h], solvent carried out on the details and on the surface of the dish after pouring out extraction naphtha

Thus:

$E= (632\times 0.48 + 49.5\times 14 + 1147)\times 0.947 + 19\times 8.12 = 2184$ g/h

Again measured value of 2592 g/h and the calculated value of 2184 g/h were in good agreement thus the equation can be applied for predicting the organic solvents emission during the processes of manual degreasing.

18.3 INDOOR AIR POLLUTION BY SOLVENTS CONTAINED IN PAINTS AND VARNISHES

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18.3.1 COMPOSITION - SOLVENTS IN PAINTS AND VARNISHES. THEORETICAL ASPECTS

Solvents are normally defined as fluids having a maximum b.p. of 250°C, which are able to dissolve other components of paints, especially binders. They evaporate under drying conditions when paint films are formed.[1,2,3,4] Solvents must not react with the painted or varnished product.

The composition of paints and varnishes is determined by application requirements, drying temperature, and drying time.[2,5] Depending on the properties of paints and varnishes, different mixtures of solvents are added.

Functions and properties of solvents in paints and varnishes:[2,5]

- Dissolve several components, especially binders
- Influence and control paint viscosity
- Wet pigments (influence on solubility, hydrogen bonding by solvents, prevent the separation of pigment)
- Influence and control flow properties (e.g., butyl acetate, butanol, glycol ethers)
- Influence skin formation.[6] The aim is to produce a homogeneous cure when the paint or varnish film hardens without the formation of a stable surface film during the drying period. The correct composition of the solvent will avoid trapping solvents under the surface film.
- Influence drying process. Acceleration by low boilers, production of a flawless surface by medium and high boilers (chemical and physical drying processes)
- Influence surface tension (e.g., increase by rapid evaporation of solvents)
- Influence mechanical properties of paints (e.g., adhesion properties)
- Influence blushing or blooming of paints by preventing the absorption of condensed water by various solvents, e.g., ethanol and glycol ether
- Influence gloss (e.g., improvement with high boilers)
- Prevent defects particularly in varnish coating (e.g., background wetting)
- Influence electrostatic properties (spray painting)
- Influence defined surface properties (structural change)
- Influence durability of paints and varnishes
- Influence product suitability, e.g., spraying and dipping lacquers which need to dry at room temperature

In addition to their effect on performance and properties solvents interact with other components in paints and varnishes in significant ways.

Interactions between binders and solvents in paints and varnishes are very important.[2,5] With the aid of solubility parameters solvents or mixtures of solvents which produce the required properties may be selected. The influence extends to dissolving of binders, reduction of paint viscosity, pigment wetting, etc. Optimized dissolving of binders can be achieved by selecting the appropriate solvent mixtures, in which the density approaches that of the binder solubility range. Nevertheless the selection of an optimized solvent mixtures is difficult because there are conflicting requirements and outcomes.[2,5] On one hand, the chemical nature of the solvents should be similar to those of the binder to improve the flow but on the other hand, the solubility and hydrogen-bonding abilities of the solvents should be at the edge of the binder solubility range, because this results in rapid drying with low retention of solvents.

18.3.2 OCCURRENCE OF SOLVENTS IN PAINTS AND VARNISHES

18.3.2.1 Solvents in products

Classification

Authorized commissions in Germany describe various groups of solvents in paints and varnishes:

The Association of Varnish Industry VdL (Verband der Lackindustrie) classifies solvents generally used in paints and varnishes in the following groups:[4] Aliphatics, alcohols, aromatic hydrocarbons, esters, glycols, glycol ethers, ketones, terpenes, gasoline, water.

The commission of Hygiene, Health and Environmental Protection (Hygiene, Gesundheit und Umweltschutz) which belongs to the German Standards Commission DIN (Deutsches Institut für Normung e.V.) also describes solvents which may be present in paints as follows:[10]

- Aliphatics (white spirit, turpentine substitutes, cyclohexane)
- Aromatic hydrocarbons (toluene, xylenes, naphtha, styrene)
- Alcohols (methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, glycols)
- Ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone)
- Esters (methyl acetate, ethyl acetate, butyl acetate)
- Others: methylpyrrolidone, oils of turpentine

Chlorinated hydrocarbons are not contained in the above list. Benzene is not included as it is obsolete, although it is sometimes found in some petroleum solvent-based paints.

Shortcomings

The description of paints and varnishes is usually neither complete nor reliable:

- Instructions and comments from manufacturers and suppliers differ in quantity and quality. Usually manufacturers or suppliers are not committed to indicate the exact details of their product’s composition. They often omit information (e.g., information concerning product components, additives or by-products).
- Lack of standards. In Europe there are some mandatory standards concerning products used in construction (e.g., asbestos, formaldehyde in particle board, organic solvents in certain activities and installations are prohibited).
- Solvents or other organic compounds may be present, in low concentrations, in some products (even in water-based paints), e.g., as additives or by-products although there is no reference to them.
- Additives (e.g., low molecular compounds such as esters or glycol ethers with high boiling points) serve as aids for the formation of films, in repelling water, in assisting plasticization or for other functions. In solvent-based paints, additives or diluting agents are often intentionally mixed in.

Table 18.3.1. Systematology of paint and varnish products (after reference 10)

- 1. Paint coatings
  - 1.1 Coloring agents
    - 1.1.1 soluble pigments
      - 1.1.1.1 natural pigments
      - 1.1.1.2 synthetic pigments
    - 1.1.2 insoluble pigments
      - 1.1.2.1 inorganic pigments
      - 1.1.2.2 organic pigments
        - 1.1.2.2.1 animal and vegetable pigments
        - 1.1.2.2.2 synthetic pigments
  - 1.2 Binders
    - 1.2.1 water dilutable binders
      - 1.2.1.1 slaked lime (lime colors)
      - 1.2.1.2 standard cement (cement colors)
      - 1.2.1.3 sodium silicate (colors of 1 or 2 components)
      - 1.2.1.4 vegetable glues (limewash)
      - 1.2.1.5 casein (lime-casein products, alkali-lime products)
      - 1.2.1.6 dispersions
        - 1.2.1.6.1 natural resin emulsion paints
        - 1.2.1.6.2 plastomer emulsion paints (PVAC (homopolymers, copolymers), PVP, polyacrylates (PMMA, styrol-acetate))
        - 1.2.1.6.3 water emulsifiable varnish systems (aqueous acrylate systems, aqueous polyurethane systems)
    - 1.2.2 solvent dilutable binders
      - 1.2.2.1 oil paints
      - 1.2.2.2 varnishes
        - 1.2.2.2.1 products drying by air oxidation (nitrocellulose varnishes, aldehyde resin varnishes, oil varnishes)
        - 1.2.2.2.2 physical drying products (polymer resin varnishes, polyvinyl chloride varnishes, polyvinyl acetate varnishes, polyacrylate varnishes, chlorinated rubber varnishes)
        - 1.2.2.2.3 chemical curing products (phenolic varnishes, aminoplast varnishes, melamine resin varnishes)
        - 1.2.2.2.4 acid-curing varnishes
        - 1.2.2.2.5 epoxy resin varnishes
        - 1.2.2.2.6 polyurethane varnishes
        - 1.2.2.2.7 unsaturated polyester varnishes

- Residuals or by-products can result from various processes (e.g., residual monomers in a polymerization processes).
- Substances which can be classified as solvents are not always exactly defined, e.g., substances in paints with maximum boiling point above 250ºC. Plasticizers and solvents cannot often be strictly separated (e.g., various SVOCs).
- Analytical problems and difficulties in assessment (e.g., mixtures of substances, very low concentrations).
- Even new products are often not well documented (e.g., concerning composition, see above).

18.3.2.2 Paints and varnishes

Definitions and systematology of paints and varnishes are given by various authorized commissions, e.g., European Committee for Standardization (CEN)[1] and DIN-Commissions[9] (see also Table 18.3.1).

Various databases list the paint and varnish products and their composition generally applied in Europe, see Table 18.3.2).

Table 18.3.2. Types of paints and varnishes mainly used in Europe - product groups, important compounds, applications (after references 2,5,11,23,25)

Product groups	Compounds	Application
Silicate paints/products, emulsion paints DIN 18363 (M-SK01)	potash-waterglass (binder), inorganic/organic pigments, mineral fillers, synthetic resins (dispersions, stabilizers), water (dispersing agent)	wall paints, outside house paints
Silicate paints/products, (M-SK02)	potassium silicate (binder, fixing solution), inorganic pigments, adjuvants	water- and weatherproof painting, interior coating (resistant to chemicals)
Emulsion paints (M-DF02)	synthetic resins (dispersions), mineral fillers, inorganic/organic pigments, water (dispersing agent), additives (film-forming agents < 3 %: e.g., glycol-ethers, esters, glycols, hydrocarbons), formaldehyde < 0,1 %	outside house paints, interior coating (wall paints)
Emulsion paints, solvent-free (M-DF01)	synthetic resins (dispersions), mineral fillers, inorganic/organic pigments, water (dispersing agent), additives (film-forming agents: no solvents), formaldehyde < 0,1 %	interior coating (wall paint)
Emulsion paints, outside house paint, water dilutable	emulsions of plastic materials (acrylate, vinyl), pigments, water (dispersing agent), organic solvents: < 0,1-4 %, (glycols, glycol-ethers, mineral varnish)	exterior coating
Emulsion paints, varnishes (M-LW01)	synthetic resins, alkyd resins, copolymerizates, polyurethane resins, inorganic/organic pigments, mineral fillers, additives, water (dispersing agents), organic solvents: 5-10 %, glycols, glycol-ethers, esters, mineral varnish	various applications
Aldehyde resin varnishes, aromatic compounds (M-LL03)	aldehyde resins (binders), inorganic/organic pigments, fillers, 30-55 % solvents: mineral varnish (mixture of hydrocarbons), other solvents (< 10 % esters, ethers, alcohols)	covering varnishes, primers
Aldehyde resin varnishes, low levels of aromatic compounds (M-LL02)	aldehyde resins (binders), inorganic/organic pigments, fillers, 30-55 % solvents: mineral varnish (mixture of hydrocarbons), other solvents (< 10 % esters, ethers, alcohols)	covering varnishes, primers
Aldehyde resin no aromatic substances (M-LL01)	aldehyde resins (binders), inorganic/organic pigments, fillers, 30-55 % solvents: mineral varnish (mixture of hydrocarbons), other solvents (< 10 % esters, ethers, alcohols)	covering varnishes, primers

Product groups	Compounds	Application
Polymer resin paints, high levels of aromatic compounds (M-PL03)	copolymers, inorganic/organic pigments, fillers, 35-50 % solvents: mineral varnish (mixtures of hydrocarbons), other solvents (< 10 %, esters, ethers, alcohols)	outside paints (mineral background)
Polymer resin paints, low levels of aromatic compounds (M-PL02)	copolymers, inorganic/organic pigments, fillers, 35-50 % solvents: mineral varnish (mixtures of hydrocarbons), other solvents (< 10 %, esters, ethers, alcohols)	outside paints (mineral background)
Polymer resin paints, no aromatic compounds (M-PL01)	copolymers, inorganic/organic pigments, fillers, 35-50 % solvents: mineral varnish (mixtures of hydrocarbons), other solvents (< 10 %, esters, ethers, alcohols)	outside paints (mineral background)
Polymer resin paints, dilutable with solvents (M-PL04)	copolymers, inorganic/organic pigments, fillers, 35-50 % solvents: mineral varnish (mixtures of hydrocarbons), other solvents (< 10 %, esters, ethers, alcohols)	outside paints (mineral background)
Natural resin paints	natural resins (e.g., shellac) or chemical modified natural resins (e.g., colophonium derivates), additions (e.g., methyl cellulose, natural latex, casein), inorganic, organic pigments (mainly natural origin), mineral fillers, additives (organic solvents: alcohols, terpenes, oil of turpentine, limonenes), essential oils (eucalyptus oil, oil of rosemary, oil of bergamot)	various applications
Natural resin paints, solvent-free	natural resins (e.g., shellac) or chemical modified natural resins (e.g., colophonium derivates), additions (e.g., methyl cellulose, natural latex, casein), inorganic, organic pigments (mainly natural origin), mineral fillers, additives (see above): < 1 %	various applications
Oil paints, terpene products (M-LL04)	oils (linseed oil, wood oil, soya oil), natural resins and modified natural resins, mineral pigments, wetting agent, flow improver, solvents: oils of turpentine, isoaliphatics, terpenes (citrus, orange)	covering varnishes, primers
Oil paints, terpene-free (M-LL05)	oils (linseed oil, wood oil, soya oil), natural resins and modified natural resins, mineral pigments, wetting agents, flow improvers, solvents: isoaliphatics (dearomatized)	covering varnishes, primers
Oil paints solvent-free No. 665	standard oils, calcium carbonate, pigments, siccatives, lemon oil water-soluble	exterior coating (paneling)
Clear lacquers/glazing composition (wood), low levels of aromatic compounds (M-KH03)	alkyd resins, nitro resins, polymer resins, pigments, fillers, 40-50 % solvents: mineral varnish (mixtures of hydrocarbons), other solvents (< 10 %, esters, ethers, alcohols)	interior coating (clear lacquers), exterior and interior coatings (glazing compositions, wood)
Lead chromate enamels, aromatic compounds	synthetic resins (e.g., aldehyde resins, PVC-polymerizates) inorganic/ organic pigments (lead chromate up to 20 %), fillers, 30-55 % solvents (mixtures of mineral varnish, glycol-ethers, aromatic compounds)	priming coat (steel, aluminum, zinc)

Product groups	Compounds	Application
Silicone resin products, water dilutable (M-SF01)	emulsions of silicone resins mineral fillers, inorganic/organic pigments, water (dispersing agent), additives (film forming agents < 3%)	

Solvent composition is an important aspect in classifying paints and varnishes.[5] Main groups are:

- Solvent products. These products contain solvents of various mixtures, types and concentrations depending on the properties desired (e.g., application method, surface film or skin formation, see above 18.3.1, 18.3.2.1, Table 18.3.1 and 18.3.2). Solvents are normally the main components of these products (for example up to 80 % in nitrocellulose varnishes, low solids).
- Solvent reduced products. These contain solvents in lower concentrations compared to conventional products and hence have a higher content of solids.[1,2] The main groups of solvent reduced paints are medium solid contents (solids 55-65 %) and high solid contents (solids 60-80 %).
- Waterborne coatings. This group contains deionized water as a dispersing agent. Normally cosolvents are added (up to 25 %). The term “waterborne coatings” is mainly applied to industrial coating materials, which differ from silicate colors, wood preservative varnishes and emulsion paints.
- Solvent-free products. The products of this group are produced and applied without organic solvents: powder coatings, radiation curing systems, solvent-free water coating (without cosolvents).

The use of paints and varnishes containing high solvent concentrations is becoming less common, solvent-reduced products, waterborne coatings and solvent-free products are applied more often.

Whereas environmental and health-related concerns call for the reduction of solvents in paints and varnish products (see 18.3.3.2 and 18.3.4), qualitative aspects still demand the use of solvents in some fields of application.[12] Solvent-reduced products should achieve the same qualitative properties as solvent-containing products (e.g., application properties, periods of guarantee, limited costs, loading capacities, surface properties). The development of solvent-reduced or solvent-free varnish products with high quality (e.g., durable, good application properties) and limited costs must be encouraged if not mandated. In some fields of application (e.g., waterborne coatings, high solids in varnish coatings of vehicles) a lot of developmental work has already been done. Additionally, other components in varnishes apart from solvents or modifications of application techniques can improve the properties of solvent-reduced paint and varnish products. Nevertheless, a wide rage of quality exists in paints and varnish products which are offered commercially and, in some cases (e.g., concerning film forming processes, processibility, corrosion protection, purification, special applications or wood preservation), solvent-based products are still preferred. In the field of wood preservation especially, solvent-based products (alkyd resins) are used because of some technical advantages (e.g., more solid surfaces) but alternative high solid systems are available.[12]

18.3.3 EMISSION OF SOLVENTS

18.3.3.1 Emission

Solvents are usually the most significant emission products coming from building materials and interior furnishings.[2,5,6,13] All painted products are potential sources of emission. Even the so-called "bio" paints or natural paints emit various substances,[5] e.g., mineral varnishes, natural oils and even synthetic terpene-like compounds.

Depending on the products and the components which make them up, the various parameters listed below can determine the emission and behavior of solvents in ambient air from paints and varnishes:[2,5,6]

- Film formation. During the film formation stage solvents are emitted. The emission rate is directly proportional to the VOC concentrations in the product and inversely proportional to the film thickness (first order of kinetics). When the film has completely formed, the emission is controlled by diffusion processes, the emission rate is now inversely proportional to the square of the film thickness.
- Application of the paints and varnishes, methods of application of the paint or varnish, e.g. speed of application of the paint.
- Characteristics of solvents in paints and varnishes, e.g., volatility (boiling point), dynamic characteristics of evaporation and concentrations. Substances having a low boiling point evaporate fast, mostly during application and cause a rapid skin formation. Thus the risk of exposure is mainly with the painters. Medium boilers allow the surface to remain open for a while (evaporation of volatile products). The evaporation of substances with a high boiling point is slow, taking several weeks or months after application, resulting in exposure to the building occupants.
- Characteristics of other compounds in paints and varnishes (e.g., relationship of binders to solvents, possible reactions between solvents and other compounds).
- Characteristics of surfaces which have been painted (e.g., area, structure of surface).
- Characteristics of emission processes, e.g., type of emissions (e.g., diffusion), dynamics of emissions (constant of evaporation), interrelations (e.g., diffusion and back diffusion).

The quantitative assessment of emission processes can be described with various models. The usefulness of these models differs. Some models describe these processes very well, as proven by various experiments or measurements (e.g., test chambers). Basic equations which describe emission processes are shown in Table 18.3.3.

The emission processes of solvents from paints and varnishes can be divided into two phases:[2,5,6]

1. Emissions during application of paints. This deals with complex interrelations dependent on various parameters.

2. Emissions after application process. Here the course is governed by complex emission processes dependent on various parameters (e.g., film formation, surface area).

Most solvent products, especially organic solvents and some additives, emitted from paints and varnishes are VOCs. The largest components of VOCs are solvents, e.g., aliphatic and aromatic hydrocarbons, alcohols, amines, acids, aldehydes, esters, ketones, terpenes. The definition of the term VOC varies, a standard definition is published by CEN (European Committee for Standardization):[1] VOCs are any organic liquids and/or solids that evaporate spontaneously at the prevailing temperature and pressure of the atmosphere.

VOCC (volatile organic compound content) is defined as follows:[1] Mass of the volatile organic compounds in a coating material, as determined under specified conditions.

Table 18.3.3. Example for basic calculations of VOC-emissions during application of emulsion paints (after references 2,5,6,13)

1. At the beginning of the application process (t=0) the mass of VOC changes positively ($v_{ST}d_sc_w$) , on the other hand VOC evaporates (first order of kinetics).
   $dm_w/dt = v_{ST}d_sc_w - k_1m_w/d_s$ [18.3.1]
2. In the ambient air the mass of VOC increases because of the evaporation out of the wall and decreases according to the ventilation rates.
   $dm_L/dt = k_1m_w/d_s - k_2m_L$ [18.3.2]
3. If the connected differential equations are solved and integrated (from t=0 until the end of application $t=A/v_{ST}$), the following equations are received:
   $m_w(t) = v_{ST}d_s^2c_w/k_1(1-\exp(-k_1t/d_s))$ [18.3.3]
   and
   $m_L(t) = ((1-\exp(Bt)/B - (1-\exp(k_2t)/k_2)v_{ST}d_sc_w\exp(-k_2t))$ [18.3.4]
   with
   $B = k_2 - k_1/d_2$ [18.3.5]
4. After finishing application only evaporation is relevant (equation [18.3.1] is simplified):
   $dm_w/dt = - k_1m_W/d_s$ [18.3.6]
5. The course of VOC in the ambient air does not change (equation [18.3.2] corresponds to equation [18.3.7]):
   $dm_L/dt = k_1m_w/d_s - k_2m_L$ [18.3.7]
6. The solution of these differential equations describes the quantities of VOC in the wall (equation [18.3.8] and the course of VOC in the ambient air [18.3.9]:
   $m_w(t) = m_{w,AE}\exp(-k_1(t-t_{AE})/d_s)$ [18.3.8]
   $m_L(t) = ((k_1m_{w,AE}/d_s)(\exp(B(t- t_{AE}))-1)/B + m_{L,AE}) \exp(-k_2(t-t_{AE}))$ [18.3.9]
   with
   $B = k_2 - k_1/d_s$ [18.3.5]

where:

A	area of the wall
a	coating thickness
B	fraction of binder
c_W	VOC-concentration in the wall
c_L	VOC-concentration in the ambient air
D	density
d_s	thickness of the layer of the paint application (=a/D)
k_1	constant of evaporation
k_2	ventilation rate of the indoor air
m_L	mass of VOC in the indoor air
$m_{L,AE}$	m_L at the end of the application
m_w	mass of VOC in the wall
$m_{W,AE}$	m_W at the end of the application
R_M	VOC-content in the dispersion
t	time
V	volume of the indoor air
v_{ST}	spreading velocity

In VOCs, especially these emitted from coating materials, the evaporation temperature is specified by European regulations: b.p. max. 250°C (according to DIN ISO 11890-1,-2 or 96/13/EC)[14] or b.p. max. 260°C (according to VDI Guidelines 4300-6).[15] In some US governmental legislation VOCs are defined solely as those compounds that are photochemically active in the atmosphere (ASTM D 3960).[1]

Regulations and assessment of VOCs are under discussion in Germany, e.g., discussion of various threshold limit values of TVOC (total volatile organic compounds): < 200 μg/m^3 according studies of Molhave[16] and 300 μg/m^3 according to BGA.[17]

The percentage of VOC emissions caused by solvents has increased recently mainly because of the reduction of VOC coming from vehicular traffic, e.g., in Germany the estimated anthropogenic VOC emissions (without methane) caused by solvents in 1994 was about 51% compared to 37% in 1988.[12] The solvent VOC emissions are mainly connected with coating materials which are responsible for more than 50% of solvent-based VOC emissions in Germany in 1995 (about 38% caused by varnishes, 4 % by building materials, 19% by other processes such as metal cutting).[12] The main source of emissions of solvents during varnish processing are from equipment without licence requirements (about 60%) and from trade and paint work (about 15%); equipment which has licence requirements (manufacturing plants) contributes only 10% of VOC emissions.[12]

Therefore, solvents released during the application processes of paints and varnishes must be reduced. New EC regulations concerning reduction of solvents in special industrial plants or working processes (e.g., varnish coating of vehicles) have already been formulated.[8] Similar regulations concerning other working fields (e.g., the use of solvent-based paints in home workshops) have been prepared throughout Europe and are already in force in some countries.

18.3.3.2 Immission

In Europe, various regulations and schemes for the assessment of VOCs are in use according to special conditions, e.g.:

- Indoor air: Schemes and values proposed by central environmental institutions (Sachverständigenrat für Umweltfragen),[18,19] commissions of UBA (Umweltbundesamt).[20]
- Place of work: Special values (e.g., TLV-, MAK-, TRK-values) proposed by special institutions, e.g., commissions of ACIGH (American Conference of Governmental Industrial Hygienists)[21] or DFG (Deutsche Forschungsgemeinschaft).[22] TLV (Threshold Limit Values) refer to airborne concentrations of substances. They represent conditions to which workers may be repeatedly exposed during an 8-hour workday in a 40-hour week. MAK-values (Maximale Arbeitsplatzkonzentration) describe maximum concentrations of individual substances allowed in the work place (8 hours per day or 40 hours per week with some exceptions allowed). MAK-values are obligatory limits in Germany but in cases where MAK values cannot be evaluated (e.g., carcinogenic compounds) TRK values (Technische Richtkonzentrationen) are used. These recommendations are based on current technical knowledge.[22]
- Atmosphere, especially the significance of photooxidation. Various measures and regulations (e.g., reduction of VOCs)[8] intend to limit substances which play a part in photooxidizing processes (e.g., ozone formation).

When defining threshold limit values, it is important that prevailing conditions and methods are specified, e.g., ventilation rates, methods of sampling, determination and calculation.[1,17,23]

Immission processes of solvents from paints and varnishes are determined by surrounding conditions: e.g., parameters of the ambient air, indoor air parameters, e.g., ventilation (ventilation rates), air distribution, air movements, composition of ambient air, concentrations of air compounds, humidity, temperature, volume of the indoor air, extreme conditions (e.g., worst case).

18.3.4 EFFECTS ON HEALTH OF SOLVENTS FROM PAINTS AND VARNISHES

Only the effects resulting directly from the exposure to paints and varnish solvent are discussed in this chapter. For the effects of other solvents, see Chapter 20.1.

18.3.4.1 Exposure

Usually the effects of solvents in paints and varnishes on health are dependent on concentration and exposure time. Adverse health effects may follow exposure to paints, varnishes and their solvents at the workplace. The conditions at paint and lacquer manufacturing sites (e.g., manufacturing methods, use of exhaust hoods, etc.) are responsible for the levels of evaporated solvents measured in the air.[24] Adverse health effects depend on how the paint is applied, paint properties and working conditions (e.g., increased risk with spray painting). There is sufficient evidence to substantiate the fact that solvents to which painters have been exposed, are responsible for incidences of cancer. However, within paint manufacturing plants, this evidence is inadequate.[25]

Nevertheless, person working at home, occupants of painted rooms and children of parents which have been exposed are also at risk. Those involved with the abuse of solvents as a psychoactive substance (e.g., aromatic hydrocarbons in spray paints, mainly semi-volatile or nonvolatile components) are at a much higher risk.

The main path of entry of solvents from paints and varnishes to the body is by inhalation. Volatile paint compounds present a particularly high risk as do some forms of paint application (e.g., spray painting with the risk of inhalation of even less volatile and nonvolatile paint components). Other pathways should, however, also be considered as dermal contact.

In addition to solvents, other compounds from paints and varnishes can cause various diseases, often similar to the effects caused by solvents (e.g., asbestos as paint filler or in the construction and shipyard industry, silica, dusts, thermal decomposition products, contaminations of solvents, chromium, iron and lead compounds in paint pigments). It is often difficult to associate a particular components of paints and varnishes with adverse health effects. In most cases, the paint and varnish products were found to be a relevant cause of illness, but their individual compounds were not.

18.3.4.2 Health effects

18.3.4.2.1 Toxic responses of skin and mucose membranes

The following symptoms involving the skin and mucose membranes may occur as a result of using paints and varnishes:

- Irritations of skin and mucose membranes
- Allergic diseases of skin and mucose membranes
- Removal of grease from skin (removal of sebaceous matter, with subsequent adverse skin conditions such as infection)
- Changes in the lens of the eye and corneal changes
- Absorption of solvents through the skin (e.g, benzene, toluene, xylene, methyl alcohol, methyl ethyl ketone, glycol ethers)

Workers in the paint manufacturing industry and painters have experienced occupational diseases, especially dermatosis affecting the hands and arms.[26-28] Whereas several paint components have been shown to cause non-allergic and allergic contact eczema, organic solvents were shown to provoke mainly non-allergic contact eczema and some solvents cause only irritation (e.g., some ketones and esters).

In another study by Mancuso et al.[28] it was shown that the occupational contact dermatitis of workers in shoe factories was probably a result of solvents in varnishes and adhesives. This study was based on interviews, medical examinations and patch test series.

Eye diseases stemmed from both non-allergic and allergic reactions, and in some cases corneal and lens changes were noted.[29]

In a further study,[30] with water based paints there was a significant reduction in eye and skin disease and worker discomfort on the job.

18.3.4.2.2 Neurological disorders

Indoor air immissions of organic solvents from paints and varnishes can cause neurological disorders:

- Neuro-psychological and neuro-behavioral symptoms (e.g., subjective symptoms, multiple chemical sensitivity - MCS)
- Neurophysiological symptoms
- Neurological diseases (e.g., polyneuropathy)
- Neuropsychiatric diseases

Other compounds in paints and varnishes apart from solvents can cause neurological disorders (e.g., lead). However, it is difficult to prove that solvents specifically cause neurological changes.

A study of production plants producing dyes and varnishes,[31] showed that mixtures of organic solvents are responsible for several neurological and neurophysiological symptoms: headache, dizziness, increased emotional excitability, memory and concentration disorders, mood instability, fatigue. Neurological examinations, however, showed no significant changes in the central and peripheral nervous system but EEG and VEP anomalies were seen.

In contrast to the studies mentioned above, a study of shipyard spray painters[32] exposed to xylene and mixed organic solvents described neurophysiological changes, e.g., decreased nerve function and, in addition, neuropsychological symptoms, e.g., mood changes and fatigue. Similar results including reduced nerve conduction were shown by workers exposed to styrene. Other studies found several dose-response relationships between solvent mixtures and neuro-behavioral effects among paint manufacturing employees and painters.[33,34] Significant relationships concerning the total amounts of hydrocarbons, lifetime exposure and lifetime-weighted average were described.

In earlier reviews and cross-sectional studies, various symptoms and neuro-behavioral effects were described for workers in the paint manufacturing industry, house painters, car and industry painters, and shipyard painters.[35] Subjective symptoms (fatigue, loss of concentration, emotional instability, short-term memory disorders, headache) or effects on psychomotoric performance are examples of these symptoms. However, similar former studies did not find symptoms in house painters using mainly water-based paints.[36]

Different results were found concerning neuro-physiological changes and neurological diseases. Electroencephalographic changes and a slight decrease in cerebral blood flow of paint industry workers was noted by Oerbaek et al.[37] and there were occasional cases of clinical polyneuropathy in spray painters exposed mainly to methyl n-butyl ketone as described by Mallov.[38] Furthermore, slight neurological impairments of car and industry painters was noted by Elofsson et al.[29] and Maizlish et al.[39] and in house painters by Askergren et al.[36] Nevertheless, no similar effects were described in other studies.[42,43] In particular, no effects on the peripheral nervous system were reported in workers using water-based paints.[36]

Inconsistent results were reported for severe diseases of the central nervous system (neuropsychiatric diseases, encephalopathy) for painters and other persons exposed to solvents.[42-44,47]

Environmental exposure to organic solvents is supposed to be one cause of multiple chemical sensitivity which characterizes neuropsychological disorders. Organic solvents from paints seem to play a role.[45,46] The relevant exposure characteristics (dose, time, possible dose-response relationship) are also discussed.[45]

18.3.4.2.3 Carcinogenic effects

Various solvents which occur in paints and varnishes exhibit a carcinogenic potential. Benzene and all isomers of dinitrobenzenes are particular examples (see also Chapter 20.1). This was confirmed by several extensive studies of occupational exposures in paint manufacturing plants and in painters.[25] These data show the risk of contracting cancer to be about 20% above the national average.

In many studies, increased risks were described mainly for lung cancer (about 40% above the national average), leukemia, bladder cancer, liver cancer, and childhood cancers where there has been parental exposure.[25]

In a meta-analysis using standardized mortality ratios the relationship between painting exposure[48] and cancer mortality showed the highest risks for leukemia and liver cancer. Elevated risks were also predicted for lung cancer, oesophageal cancer, stomach cancer and bladder cancer. The development of leukemia, especially in the case of benzene mixed with other organic solvents, being most prominent and the development of lung cancer (main risks being lead chromate and asbestos) to a lesser degree.

It should be noted, however, that more critical risk factors such as smoking and alcohol can obscure such correlations.

Although high risks for cancer resulting from occupational exposures were mentioned, no significant information concerning the occupation of painted rooms could be noted. This area has been inadequately studied.

As mentioned above, lung cancer is a major concern. Painters, as opposed to those involved in paint manufacture were shown to be at greatest risk for contracting lung cancer.[25,48] In fact, there was no evidence of increased risk in persons involved in the manufacture of paints.[25,49]

Other cancers of the respiratory tract are documented also, e.g., cancer of the nasal cavity,[50] pleural mesothelioma with high incidences in painters and paper-hangers[51] and cancers of the larynx.[52]

The evidence of several types of leukemia is convincing with regard to occupational exposures to paints and solvents.[25,48] Increased risks for contracting other haematopoietic neoplasmas[25] such as Hodgkin´s disease,[53] non-Hodgkin´s lymphoma,[54] multiple myeloma,[55] reticulum-cell sarcoma and lymphosarcoma[56] were also reported. Probably all neoplasmas were caused mainly by organic solvents. Some former studies, however, included solvents which are rarely used now, especially benzene.[25]

Davico et al.[57] and Crane[58] showed clonal aberrations in chromosome 8 of workers exposed to paints which is correlated with higher risks of acute myelocytic leukemia.

Occupational exposure to dyestuff manufacture, paints, solvents and inks are an important risk factor for cancer development of the urinary tract (especially aromatic amines in bladder cancer).[25,59] A major risk factor responsible for about 50% of bladder cancer cases in western countries is smoking. A second risk factor is occupational exposure (including exposure to paints and solvents).[59] Some studies showed greater risks according to certain exposures: e.g., spray painting,[60,61] lacquering and painting of furniture and cars or sign-post painting.[62]

An increased risk of cancer of the prostate was found for workers in paint manufacturing plants, but no increase in risks could be evaluated for exposure to paints.[63] In one study an increased risk for testicular cancer was shown.[25]

Inconsistent results were noted for cancers of the gastrointestinal tract.[25] Some studies showed higher rates of stomach and intestinal cancers, but other risk factors apart from paints cannot be excluded. Higher risks for liver cancer was found by Chen and Seaton.[48] Norell et al.[64] noted an excess of pancreatic cancers, especially as a result of exposure to paint thinners. No significant risks were described concerning cancer of the biliary tract.[65]

A distinct relation between parental occupational exposure and childhood cancer was shown for solvents and paints. High parental exposure resulted in higher incidences of childhood cancers.[66] In the same study, however, generally more cancers were found as a result of parental use of alcohol and tobacco smoke. Childhood leukemia and nervous system cancers, in particular, are the types suspected to be caused by parental exposure to paints and solvents.[67] Kishi et al.[68] described an elevated risk for acute lymphatic leukemia in children of mothers with prenatal exposures to benzene and to paints. In former studies with small numbers of children these tendencies could also be shown, mainly in male painters whose children showed a higher incidence of childhood leukemia and brain tumors.[25]

18.3.4.2.4 Respiratory effects

The following respiratory symptoms are provoked by solvents:

- Irritations
- Allergic reactions
- Changes in lung function parameters (mainly obstructive ventilation)
- Pathohistological changes

Irritations of the air passages were described in people exposed to fumes in paint factories.[27,69]

VOCs in paints can provoke respiratory symptoms (wheezing, breathlessness) in asthmatics. Conventional water-based paints with only small amounts of VOCs have also been shown to cause such symptoms, but there were no effects using VOC-free paints.[70] No differences were found in the same study looking at lung function and airway responsiveness. Toxic pyrolysis products in paints and polymer films probably evoke asthma-like symptoms similar to PVC pyrolysis.[71]

A decrease in forced vital capacity, expiratory volume in one second and of peak exspiratory flow was observed after exposure to water-based paints.[72] Bronchial obstruction in painters was confirmed by White and Baker,[69] but other studies could not detect changes in lung function parameters in house painters who were exposed to solvent-based and water-based paints.[36] Beving et al.[73] did not find obstructive effects in car painters. An increase in mortality from chronic obstructive bronchitis of painters was recorded by Engholm and Englund,[74] but not confirmed in other studies.[25]

Histological changes in the nasal mucosa of spray painters were also noted in a study of Hellquist et al.[75]

18.3.4.2.5 Toxic responses of the blood

A case-control study of Guiguet et al.[76] observed an increased risk for aplastic anaemia after exposure to paints (effective compounds in the paints are unknown), but no increased risk after exposure to solvents alone. Reduction of blood hemoglobin levels was shown after exposure to gasoline, car spray paint (xylene) and various solvents (house painters).[25,77,78] An increased Hb level was noted, however, in a study of car and industrial spray painters.[29]

Alterations of several blood components (production of auto-antibodies) and of vascular endothelial cells were described for workers exposed to hydrocarbon-based paints or to mixed solvents.[79]

Even a group experiencing low exposure (house painters exposed to alkyd paints) showed hematological changes. Higher platelet counts and higher resistivity calculated from the the impedance of the whole blood were observed.[73]

Some studies showed decreases of thrombocyte counts in car painters and paint industry workers, other studies, however, recorded no changes.[25] Studies concerning effects of paints on the white cell and thrombocyte counts were inconsistent. A decrease of white cells was described in several studies[11] and a lymphocytosis was noted by Angerer and Wulf.[77] Elofsson et al.,[29] however, recorded no changes in white cell counts. Additionally, myelotoxic effects of solvents were shown, especially for benzene.

18.3.4.2.6 Toxic responses of the reproductive system

In interviews with pregnant women, the effects of paints, varnishes and solvents were evaluated. No effects were found concerning congenital heart disease of infants with Down Syndrome (trisomie 21).[80] The maternal risk was associated with smoking.

Maternal toluene sniffing used as an organic solvent in acrylic paints, varnishes and other sources is associated with premature births and, in one case, renal tubular acidosis.[81]

Other studies of female painters showed tendencies towards an increase of spontaneous abortions[82] or infant mortality.[83] Other studies[84] did not confirm these tendencies.

McDowall reported an increase in malformations in children (polydactyly, syndactyly, spina bifida and anencephalus) whose parents were painters, assemblers or had related occupations.[83] A study by Olson[85] showed congenital malformations of the central nervous system for paternal exposure to paints.

18.3.4.2.7 Toxic responses on other organ systems

Contradictory effects of solvents in paints on the kidneys have been described.[25] Lauwerys et al., for example, have described some solvents used in paints as nephrotoxic (e.g., toluene).[88] Minor effects such as slight hematuria and albuminuria or small effects on the glomeruli or even no effects were detected in other studies.[25]

In some studies of spray painters in the automobile and airplane industries and of house painters mortality from liver cirrhosis was increased.[25,87] Another study investigating house painters, however, did not show an increase.[42]

There seem to be no increased risk for cardiovascular diseases according to some studies of paint industry workers.[25,89] Nevertheless, effects of solvents on muscles and vessels could be shown (e.g., increased serum creatinine levels).[25]

18.3.5 METHODS FOR THE EXAMINATION OF SOLVENTS IN PAINTS AND VARNISHES

18.3.5.1 Environmental monitoring

There are several test procedures generally used in Europe. Procedures are still being developed to determine the presence of solvents in paints and varnishes.

18.3.5.1.1 Solvents in products

Officially approved test procedures are:

- Gravimetry: Determination of volatile organic compounds (DIN ISO 11 890-1[7] - VOCs > 15 %).
- Gas chromatography: Determination of volatile organic compounds (DIN ISO 11 890-2[7] - VOCs 0,1 % -15 %).

18.3.5.1.2 Emission of solvents

Test chamber[7,92,93] (volume 1 m^3, defined conditions: temperature, humidity, air changing rates, air velocity). This is usually carried out 3 days after application of paints or varnishes by placing the products into a test chamber. The test series starts with sampling emissions of the products on defined absorption materials (Tenax, charcoal filters, activated charcoal), reconditioning and finally identification and classification of VOCs with gas chromatography. The test methods are repeated after 14 and 28 days. These test criteria permit determination of the behavior of emissions from finished products under defined conditions.

Emission test cells.[7,92,93] The product under investigation is hermetically sealed into the emission test cells. The emitted compounds are sampled by absorption materials and analyzed. This method can be used under laboratory conditions or *in situ*.

18.3.5.2 Biological monitoring of solvents in human body fluids

18.3.5.2.1 Solvents and metabolites in human body fluids and tissues

The biological monitoring of solvents emitted from paints or varnishes on humans is not well developed. In two studies,[94,95] solvents from paints and varnishes were determined in blood, urine and internal breath. Blood and urine analysis is less sensitive than internal breath measurements. This was carried out in a study on exposure to paints in aircraft maintenance.[94]

Kramer et al.[95] found xylenes during paint production and paint-spraying in ambient air and in the blood and urine of workers. Threshold limit values (TLV) and biological exposure indices (BEI) were not exceeded.[22,23]

18.3.5.2.2 Biomarkers

Even low air concentrations of solvents emitted from paints have an influence on the human organism, e.g. the induction of hepatic enzymes. This effect was shown in workers exposed to butyl glycol from paints in an electrophoresis painting plant where the exposure value was shown to be less than 0.3 times of the average limit. In these cases D-glucaric acid in urine, which reflects the D-glucarid acid enzyme pathway, was increased.[96]

In some studies the genetic effects on paint industry workers could not be detected when chromosomal aberrations and sister chromatid exchanges were studied.[86,87] In other studies[94,95] it was shown that the frequency of micronuclei and sister chromatid exchanges increased.

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18.4 SOLVENT USES WITH EXPOSURE RISKS

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18.4.1 INTRODUCTION

This chapter deals merely with exposure to common organic solvents which are used in large quantities to dissolve fats, resins, and other materials. Very dangerous chemicals, such as benzene, which are no more used as solvents due to their toxic properties, will not be discussed even though they may have had even extensive uses as solvents earlier and even though those may be still important chemicals as petroleum components or as intermediates for other chemicals. Also, solvents with very specialized uses, such as carbon disulfide the use of which is practically limited to viscose rayon industry and laboratories, are only shortly considered. Exposure data presented originate mainly from literature; however, some unpublished data obtained from the Finnish Institute of Occupational Health (FIOH) has been added to indicate the order of magnitude of current exposure levels in industrialized countries (data cover the years 1994-1996).

Exposure to organic solvents should be avoided mainly due to the risk of neurotoxic effects. Acute effects are narcotic resembling those caused by the use of alcohol. Those appear, for example, as a decrease in reaction time and impairment in psychological performance. Chronic neurotoxic effects are often called as the organic psychosyndrome (OPS) including memory disturbances, excessive tiredness, personality changes, irritability and affect lability. Intellectual reduction may occur but it seems that development of real dementia would require simultaneously heavy consumption of alcohol.[1] Increased risk of sleep apnoea has been observed among men exposed occupationally to organic solvents.[2] Exposure to toluene, xylene, and styrene has been found to contribute to the development of noise-induced hearing loss. This interaction has been suggested to be due to neurotoxic injuries caused by solvents in the cochlea.[3]

Long-term exposure to carbon disulfide and n-hexane may result in peripheral neuropathy. It should be noted that n-heptane and n-octane have not been shown to cause the type of peripheral neuropathy (numbness, weakness, and pain in extremities) associated with n-hexane.[4] Otherwise than the other alkanes, n-hexane is metabolized to a reactive, toxic compound (2,5-hexanedione).[5]

Organic solvents are generally skin irritants. Repeated or prolonged contact may cause erythema and dryness of the skin. Defatting may lead to cracked skin. Many solvents also readily absorb through the skin (see 18.4.2). Reactive solvents, such as styrene and vinyltoluene, may cause contact dermatitis.[6] The annual incidence of occupational diseases caused by organic solvents was 20.6 cases/10,000 exposed workers in Finland in the 1980's. More than half of the cases (64%) were dermatoses.[7]

Benzene is a well-known human carcinogen. An association with exposure to benzene and leukemia was detected already in 1920's.[8] There is some evidence that exposure to other organic solvents may constitute a carcinogenic risk. The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of painters' occupational exposure.[9] Epidemiological studies conducted among dry cleaning and metal degreasing workers suggest an increased cancer risk due to exposure to chlorinated solvents.[10] The carcinogenicity of aromatic solvents (styrene, toluene, and xylene) has been investigated in many large epidemiological studies. Although the results have been inconclusive, certain site-specific associations (e.g., for lymphohematopoietic tissues) have appeared in some of the studies.[11] Only styrene has shown to have some genotoxic activity in animal studies.[9]

18.4.2 EXPOSURE ASSESSMENT

Inhalation is usually clearly the most important route for occupational exposure to solvents. Organic solvents also enter the body through the skin.[12] For some solvents, especially for alkoxyalcohols (glycol ethers) and their acetates, this is even the main route of absorption. Even the skin uptake of vapor can be significant for these compounds.[13] Dermal absorption of vapors is, however, usually negligible and contact with liquid is required. Increased workload and heat enhance both inhalation and dermal absorption.[14] Skin contamination may also lead to oral uptake due to eating and smoking but this is of minor importance for volatile solvents.

Most industrial countries have occupational exposure limits (OELs) for airborne concentrations to prevent excessive exposures. The threshold limit values (TLVs) published by the American Conference of Governmental Industrial Hygienists (ACGIH[15]) are unofficial but have had a great impact on OELs in the Western countries. These are updated annually based on new epidemiological and toxicological data. Organic solvents are often used as mixtures. Because the OELs for most solvents base on their neurotoxic properties, their effect is considered to be additive and the combined exposure levels (or hygienic effects) are calculated as the sum of the fraction of the OEL that each solvent represents. If the sum is larger than one, a noncompliance situation exists. Compounds which may be dangerous by uptake through the skin carry a skin notation. However, no quantitative dermal exposure limits are available yet. Methanol, turpentine, glycol ethers, and many chlorinated and aromatic hydrocarbons have the skin notation.

Exposures can also be assessed by analyzing biological specimens, such as blood or urine. Metabolites of compounds are usually analyzed from urine samples. The amount of biological exposure limits or indices (BEIs) is, however, much smaller than that for airborne concentrations. However, biological monitoring may be useful although no BEI has been established to ascertain effectiveness of personal protection or to follow exposure trend. Biological monitoring reflects exposure via all routes. This is beneficial for individual exposure assessment. Biological monitoring also reveals possible accumulation of a compound. This is, however, of minor importance for most solvents because of their short half-lives. The largest disadvantage of biological monitoring is that it does not provide any information on the reasons of exposure. About twenty solvents have an ACGIH BEI (e.g., acetone, carbon disulfide, 2-ethoxyethanol, n-hexane, methanol, methyl ethyl ketone, perchloroethylene, styrene, toluene, trichloroethylene, and xylene).[15]

Airborne concentrations of solvents are most commonly determined by taking samples on adsorbents, such as activated carbon. Sampling can be done with a pump or passively based on diffusion. In industrial working places where airborne concentrations of solvents are on ppm-level, samples are generally extracted with a solvent (carbon disulfide is the most common one). In offices and other nonindustrial environments where concentrations are at ppb-level, samples are taken onto Tenax adsorption tubes which are desorbed thermally. In both cases, gas chromatography is the most common analytical method. Because the sampling time generally varies, it is important to calculate the time-weighted average (TWA) concentration. TWA concentration is obtained by using the sampling times as weights. Sampling and analysis has been reviewed e.g. by Soule.[16] Direct-reading instruments, such as infrared or photoionic analyzers are good if only one solvent is present but interferences may be a problem when solvent mixtures are analyzed.

Monitoring methods for dermal exposure have not been standardized as well as the methods to assess inhalation exposure. Adsorptive pads of activated carbon cloth can be used for monitoring of dermal exposure to organic solvents. Patches are attached on various parts of the body under the clothing and the amounts analyzed are then multiplied with the areas of each body region.[17] Exposure assessment is complicated by the contribution of solvent vapor on the samples. Because the adsorptive surface of activated carbon is much larger than that of the skin, pads will adsorb much more solvents than the skin. However, only exposure to liquid phase is usually significant; therefore, the adsorbed vapor should be subtracted from the total mass analyzed.[18] However, this makes the exposure assessment quite complicated, and if biological monitoring methods are available those usually provide a more practical alternative.

Urine and blood are the most commonly used biological samples. Exhaled air samples can also be used. Sampling is usually carried out at the end of the shift. Because the amount of water consumed affects the concentration of the solvent or its metabolite in urine, creatinine (a normal constituent of urine) correction is often applied (mass analyzed is presented per gram of creatinine). Alternatively, the correction can be made for the relative density of urine. A density of urine of 1.024 is usually applied for this purpose. In principle, collection of 24-hour urine would be an ideal approach for biological monitoring because then the actually excreted amount of the metabolite would be measured. Because this is very difficult to carry out creatinine or density correction is generally chosen as a more practical alternative. Unfortunately, not only several ways of correction for the density of urine are being used but also several different units have been adopted. For example, the ACGIH BEIs are usually given as mg/g creatinine but the values of the FIOH and many other European organizations are presented as µmol/l of urine. In addition, other units, such as µmol/mol of creatinine, are used. The mass units given in mg can be converted to mmol by dividing by the molecular weight of the compound (molecular weight of creatinine is 113). On the other hand, because the concentration of creatinine in urine varies and it is determined separately for each individual sample, values given with and without creatinine correction (or density correction) cannot be compared directly. That is the reason why the BEIs given by different institutions or agencies have not been converted to the same units in the text. As a rule of thumb, the concentration per gram of creatinine can be obtained by multiplying the concentration per liter of urine with a factor of 0.5 - 1.0.

Airborne solvent concentrations usually vary much with time. Although repeated random personal sampling is theoretically the optimal method for inhalation exposure assessment, it is very time-consuming and does not necessarily reveal the reasons for exposure. Often, occupational hygiene surveys are conducted only to make certain that the concentrations of air impurities are in compliance with the OELs. Also, the European standard (EN 689/95) for occupational exposure assessment is primarily issued for this purpose. It would, however, be practical if the measurements conducted would also provide useful information for planning of remedial measures if the measurements reveal those to be necessary. For this purpose, it is important to recognize the difference between manual tasks and process industries.

In manual tasks, emissions are released very close to the worker. Most problematic solvent exposures occur while performing manual tasks, such as painting, gluing, degreasing, and cleaning. Batch processes in paint and printing ink manufacture also contain many manual tasks. Manual lay-up methods are common in the reinforced plastics industry. The workers often perform different tasks with different exposure levels. All major tasks should be investigated under various conditions. Smoke tube tests provide useful information on the spreading of solvent vapor and the efficiency of local exhausts. Good enclosure for the emission source is important for successful exposure control. Detailed instructions for ventilation arrangements in various industries are available (references will be given later).

Rotogravure printing is an example of a process industry with solvent exposures. The process is, in principle, closed but emissions take place from the openings for the paper web. The workers do not need to stay in the immediate vicinity of the emission sources but can often spend most of their time in the clean control room. Thus, the workers' exposure levels depend mainly on their moving pattern during the work shift. In addition, the emission rate depends on the production rate, i.e. on the consumption rate of the solvent (toluene). Stationary sampling can be applied for exposure assessment when it is combined with questionnaire on use of time in various areas. This can be done with a direct-reading instrument because the airborne concentration level remains quite stable.[20]

The possible skin exposure should also be taken into consideration. If skin contamination seems possible adequate protective clothing should be used. Glove selection is an important but difficult issue. Glove materials often tolerate organic solvents poorly. Glove manufacturers have useful information for selecting gloves for individual solvents. Especially difficult is, however, to find gloves protecting efficiently penetration of solvent mixtures. Nitrile (butadiene-acrylonitrile copolymer) gloves are often chosen in such a situation. There is, however, considerable intermanufacturer and even batch lot variability in penetration of solvents through nitrile gloves.[19] The workers should also be instructed not to use thinners for hand and skin cleaning.

Total quality management (TQM) is an effective way to ensure also a high quality of the working environment. The guidance for right and safe working practices should be subjoined to all working instructions. Employee participation is an essential feature of a well working TQM, and also greatly assists the achievement of the hygienic goals set.

18.4.3 PRODUCTION OF PAINTS AND PRINTING INKS

Painting technology has changed over the years. The exposure levels were generally highest between the mid-1950's and mid-1960's when solvent-based paints were used extensively both as construction and industrial paints, and exposure control technology was still undeveloped.[21] Rotogravure and silkscreen printing inks contain organic solvents. Until 1950's benzene was used as the solvent in rotogravure inks and it remained as an impurity in toluene until 1960's.[22] Today, toluene used in rotogravure inks does not contain benzene. Alkoxyalcohols and their acetates are used as silkscreen ink solvents. The development of safer solvents has been started quite recently. First, alkoxyethanols were replaced by their acetates which have lower vapor pressures. This did not, however, improve the safety much because the skin is the main route of absorption for both alkoxyethanols and alkoxyethylacetates, and they are considered to be equally toxic. Their substitution by alkoxypropanols and their acetates is, however, a significant improvement because those do not metabolize to toxic alkoxyacetic acids.[23]

High exposures remained common in paint and printing ink industry still in 1970's; for example, most solvent measurements conducted in these industries in Finland exceeded the present OELs.[24] Water-based paints are today clearly most common in construction painting. Alkyd-based construction paints with white spirit (Stoddard solvent, mineral spirit or solvent naphtha) as a solvent are, however, still produced. Solvent-based paints have remained most common in industrial painting, even though the solventless powder paints are also produced in large quantities.

The main products are nowadays manufactured in automated processes. On the other hand, special products are also usually made in batches and include several manual tasks. In addition to paints and inks, thinners are often canned. When the processes are provided with proper enclosures and local exhausts, the airborne solvent concentrations can be kept well below the OELs. An easy but important control measure is to keep all solvent containing pots covered. Xylene (TLV 100 ppm, the Finnish OEL 100 ppm with skin notation), toluene

(TLV and the Finnish OEL 50 ppm with skin notation), butanol (TLV 50 ppm as ceiling value and with skin notation, the Finnish OEL 50 ppm with skin notation), and white spirit (TLV 100 ppm, the Finnish OEL 770 mg/m^3 or 135 ppm) are usually the main concerns in paint manufacturing plants.[24,25] In the 1980's, the combined solvent exposure levels were generally below the OEL but high exposure levels were detected in pot cleaning.[26] The situation has further improved to some extent in Finland in 1990's. The measurements conducted in a large Finnish paint factory in 1996-7 yielded the following mean combined personal solvent exposure levels: batch production 0.34 (range 0.14 -0.72), automated production lines 0.17, filling 0.41 (range 0.14-1.0), and pot cleaning 1.51 (range 0.28-3.06). Thus, pot cleaning remains as a problematic task. Exposures to xylene and 1-methoxy-2-propanol caused the largest contributions in the hygienic effects. Xylene was the solvent with the highest airborne concentration (mean 26 ppm; range 0.1-359 ppm) compared to the OELs in the Finnish paint manufacturing plants in general in the mid 1990's. It has been reported that no profound changes in exposures have occurred in the Swedish paint industry since the mid-1980's.[21]

In the Finnish printing ink plants, the combined solvent levels were still in the 1980's often out of compliance when compared to the OELs.[26] Significant airborne concentrations were observed for toluene, ethyl acetate (TLV 400 ppm, the Finnish OEL 300 ppm), aromatic solvent naphtha (the Finnish OEL 240 mg/m^3), and acetone (TLV and the Finnish OEL 500 ppm). The cleaning of vessels of barrels was again an especially problematic task. If cleaning is done manually, it is difficult to control the exposure sufficiently well with local ventilation but respiratory protection is also needed.

18.4.4 PAINTING

Painters are probably the largest worker group exposed to solvents. This may also be the reason why much data on occupational health risks due to solvent exposure originate from painting work although the exposure levels have been generally lower than e.g. in paint manufacture. On the other hand, chronic neurotoxic effects and especially cancer require long exposure time (more than 10 years) and thus the patients with solvent-related disorders have been exposed long ago when the exposure levels, especially in construction painting, were considerably higher than nowadays. In addition, a solvent induced mild toxic encephalopathy is often a progressive disease after the cessation of exposure. There is, however, a great individual variability both in susceptibility and prognosis of the disease.[27] Several studies have indicated an interaction between solvent exposure and high alcohol consumption. It has even been suggested that solvent exposure and use of alcohol are acting synergistically.[28]

The changes in paint technology have had a great impact on exposure to solvents in construction painting where the influence has been much more significant than in paint production because of poor ventilation. Period of high solvent exposure lasted from mid-1950's to mid-1970's.[28] At that time, even acute intoxications occurred. Painting and lacquering using epoxyester formulations often caused very high exposure levels.[24] The average exposure level to white spirit was estimated to be 130 ppm for painters when alkyd paints were extensively used. During actual painting situations, the exposure levels could rise to 300 ppm. Levels of about 200 ppm are, however, more typical in conditions of poor ventilation. If doors and windows can be kept open, the airborne white spirit concentration is significantly reduced, about to 40 ppm. In early 1980's, the average exposure levels to white spirit were reduced to about 40 ppm in Finland.[29] Nowadays, water-based paints are also commonly used in repair and maintenance painting and the average exposure levels have become generally low.[28] Occasionally, high peak exposures continue to take place when solvent-based paints are used in poorly ventilated spaces.

When small items are painted industrially, the worker can stay outside the spray booth and exposure to solvents can be effectively controlled. Measurements conducted in the 1970's already indicated that no serious problems existed in that kind of work.[29] Video terminal painting is a modern example of such a situation.[30] On the other hand, when large metal products, such as cars and trailers, are painted, the worker must enter the booth and control is much more difficult. Solvents are not, however, the biggest hygienic problem in car painting but the paint mist (overspray). The measurements carried out in Finland in the 1980's indicated that the combined solvent concentration was usually less than 50% of the OEL.[26] On the other hand, the paint mist concentrations exceeded clearly the standards.[29] If painting is done in a poorly ventilated booth, high solvent concentrations, however, appear.[30] Isocyanate-based urethane paints are nowadays common in car painting. They contain 1,6-hexamethylene diisocyanate (HDI) based polyisocyanates, which have become a major cause of occupational diseases, especially asthma.[31,32] Downdraft spray-painting booths provide the best overspray control. Air velocity, flow direction, and flow homogeneity are the ventilation parameters having the largest effect on booth performance. Spray-painting booths do not, however, completely control exposure to paint mist and isocyanates.[33,34]

In addition to actual painting, the workers may become exposed to solvents during other tasks, such as solvent cleaning. For example, isopropanol (TLV 400 ppm, the Finnish OEL 200 ppm) is used for wiping cars before the application of the primer. If this is performed in a well-ventilated room, the concentrations remain below the OEL. As high concentrations as 130 ppm were, however, measured in a room provided with a ventilation of 50 air changes per hour.[35]

Solvent containing formaldehyde resin paints and lacquers have been used extensively in Nordic furniture and wood product industry. In the early 1980's, combined solvent concentration and especially formaldehyde levels often exceeded the OELs. The OEL violations became rare in the late 1980's.[36] The recent concentrations of other solvents than ethanol (even its mean concentration was only 17 ppm) have been below 10 ppm in Finland. Nowadays, solventless acrylics are mainly used for industrial wood coatings. This substitution has, however, created a new occupational health problem. The new products have caused many cases of dermal sensitization among exposed workers.

18.4.5 PRINTING

The exposure to toluene has often been extensive in the past. As high exposure estimates as 450 ppm have been given for Swedish rotogravure printing workers in the 1950's.[37] A linear correlation has been observed between airborne toluene concentration in the pressroom air and the consumption rate of toluene.[20] Large day-to-day variation in the airborne concentration is, therefore, common. The long-term mean concentrations were 63-186 ppm in two Nordic studies.[24,38] At least in Finland, the exposure to toluene remained rather stable between 1960-1980 because the effect of ventilation improvements was outweighed by increased production. In the early 1980's, the Finnish rotogravure printing plants were modernized and effective ventilation systems were installed. The new presses had better enclosures and the contaminated zones around the presses were separated from the other parts of the pressroom.[39] The mean exposure level of toluene can be less than 20 ppm in a modern rotogravure printing plant.[37]

As stated earlier, toxic alkoxyethanols and their acetates have been used commonly in silkscreen printing inks. Those have no warning odor and are, therefore, easily considered to be safe. Airborne concentrations of 2-ethoxyethanol and 2-ethoxyethyl acetate from 3 to 14 ppm (both have a TLV of 5 ppm, the Finnish OEL 2 ppm) have been detected during printing.[40,41] Because the inhalation exposure consists only a part of the total exposure and absorption through the skin is of equal or greater importance, biological monitoring is the preferred exposure assessment method. The concentration of the toxic metabolite, 2-ethoxyacetic acid, in urine is the most commonly used method. Biomonitoring is also important because, otherwise than most other solvents, 2-ethoxyacetic acid has a long half-life and, therefore, it accumulates in the body during the workweek. Its ACGIH BEI is 100 mg/g creatinine (109 mmol/mol creatinine). A lower value of 30 mmol/mol creatinine has been proposed in Finland.[42] The average urinary 2-ethoxyacetic acid concentrations were found to increase from 40 to near 90 mmol/mol of creatinine during a workweek.[42]

Other alkoxyethanols, especially 2-methoxyethanol and 2-butoxyethanol and their acetates have also been used in silkscreen printing inks. The TLV for 2-methoxyethanol and its acetate is 5 ppm (their Finnish OEL is 0.5 ppm) and 25 ppm for 2-butoxyethanol (the Finnish OEL is 20 ppm for 2-butoxyethanol and its acetate but a value of 5 ppm has been proposed.[42] ACGIH has not set BEIs for these compounds. Limits of 3 mmol methoxyacetic acid/mol creatinine and 60 mmol butoxyacetic acid/mol creatinine has been recommended in Finland for the concentrations of the urinary metabolites.[41] Mean inhalation exposure levels to 2-methoxyethyl acetate from 0.2 to 1.9 ppm have ben reported.[40,42] The urinary methoxyacetic acid concentrations have ranged from 0.1 to 10.7 mmol/mol creatinine.[42] Airborne mean 2-butoxyethanol and 2-butoxyethylacetate concentrations from 0.1 to 3.2 ppm have been observed.[40,42]

The use of safer alkoxypropanols and their acetates is rather new in silkscreen printing inks. Among them, only 1-methoxy-2-propanol has a TLV (100 ppm). Its German MAK value is 50 ppm (also given for its acetate). A German MAK value of 20 ppm have been set for 2-methoxy-1-propanol and its acetate (this is also the Norwegian OEL). These have no BEIs or official biological action limits in any country. A value of 3 mmol 2-methoxypropionic acid/mol creatinine has been found to correspond to inhalation exposure to 1-methoxy-2-propyl acetate at the German MAK level.[42] The corresponding value for 1-ethoxypropionic acid is 40 mmol/mol creatinine.[42] Even though alkoxypropanols are less toxic than alkoxyethanols and their dermal uptakes are lower, they have the disadvantage of having higher vapor pressures. However, if enclosed and automatic machines have been used airborne levels of alkoxypropanols have remained well below the German MAK levels.[42] Screen printing inks also contain other solvents, e.g., toluene, xylene, and cyclohexanone (TLV 25 ppm with skin notation, the Finnish OEL 25 ppm as a ceiling value and with skin notation).

The printers are also exposed to solvents while cleaning the press. The rollers are cleaned regularly. Occasionally, ink stains are also removed from other parts of the presses and floor (see 18.4.6).

18.4.6 DEGREASING, PRESS CLEANING AND PAINT REMOVAL

Chlorinated solvents have traditionally been used as metal degreasing agents. Trichloroethylene (TLV 50 ppm; the Finnish OEL 30 ppm) and 1,1,1-trichloroethane (methyl chloroform; TLV 350 ppm; the Finnish OEL 100 ppm) have been the most common solvents for this purpose. The use of 1,1,1-trichloroethane has, however, recently been restricted in many countries due to environmental reasons. Urinary trichloroacetic acid and trichloroethanol concentrations can be used for biological monitoring for both solvents. The ACGIH BEI for trichloroacetic acid is 100 mg/g creatinine for trichloroethylene exposure and 10 mg/l for 1,1,1-trichloroethane.[15] The BEI given by the Finnish Institute of Occupational Health (FIOH) is 360 µmol/l for trichloroethylene. In Finland, the concentration of 1,1,1-trichloroethane in blood (FIOH BEI 2 µmol/l) is recommended for biological monitoring of 1,1,1-trichloroethane because less than 10% of this solvent is metabolized. The ACGIH BEI for urinary trichloroethanol is 30 mg/l for 1,1,1-trichloroethane. For trichloroethylene, the sum of urinary trichloroethanol and trichloroethanol is used (ACGIH BEI 300 mg/g creatinine; the FIOH BEI 1000 µmol/l). Chlorofluorocarbons (CFCs) are also used but their use is decreasing due to their contribution to the ozone depletion in the stratosphere.[43] 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113; TLV and the Finnish OEL 1000 ppm) is used especially for ultrasonic cleaning of small metal parts. Alternative degreasing methods using either alkaline aqueous solutions or citrus oil (D-limonene) have been developed.[43] Exposure to trichloroethylene and 1,1,1-trichloroethane should be avoided especially due to their neurotoxic properties.[44,45] Some evidence is on the carcinogenicity of trichloroethylene.[9] 1,1,1-Trichloroethane was earlier stabilized with carcinogenic 1,4-dioxane. Nowadays, it has usually been replaced with other stabilizers.[46] 1,1,1-Trichloroethane has the skin notation in the Finnish OEL list.

Metal degreasing is usually performed as vapor phase operation, where solvent is heated and the vapor condenses on the metal part. An extensive occupational hygiene survey on the US vapor degreasing operations has been performed in the 1970's. Typical sample concentrations were 100-400 ppm.[50] Much lower airborne trichloroethylene concentrations were observed in Finland in the 1980's. The mean 8 h concentration was 7 ppm (range <1-30 ppm).[46] The biological monitoring, however, revealed higher exposure levels. The mean concentration of trichloroacetic acid in urine was 153 µmol/l. The highest level was 860 µmol/l.[46] Airborne 1,1,1-trichloroethane levels from 34 to 85 ppm has been detected in Finland during metal degreasing in the 1980's.[46] The mean airborne concentration of trichloroethylene was 22 ppm (range 9-45 ppm) in Finland in the mid 1990's. The level of 1,1,1-trichloroethane has varied from less than 0.1 to 1.8 µmol/l (mean 0.3 µmol/l) in blood.[46] The concentrations of 1,1,2-trichloro-1,2,2-trifluoroethane have been low in Finland. The mean airborne concentration was 25 ppm (range 5-85 ppm) in the 1980's.[46]

Methylene chloride (dichloromethane) is most commonly used for paint removal. The stripping solution contains 55-85% methylene chloride.[47] Ethanol (TLV and the Finnish OEL 1000 ppm), methanol (TLV and the Finnish OEL 200 ppm with skin notation), toluene and formic acid are other common constituents.[46,47] US National Institute of Occupational Safety and Health has recommended that methylene chloride be regarded as a potential carcinogen and that it should be controlled to the lowest feasible limit.[48] Its TLV is 50 ppm (the Finnish OEL 100 ppm).

Very high airborne methylene chloride concentrations have been detected in the USA during furniture stripping. The TWA concentration was above 50 ppm in all five plants investigated. The highest TWA level was as high as 854 ppm. In individual samples, concentrations up to 2160 ppm were detected.[51] In Finland, the 8 h TWA concentration has varied from 26 to 380 ppm. The highest sample concentration was 850 ppm.[46] Local exhaust system based on the ACGIH manual criteria for open surface tanks[51] has been found to be effective for stripping tanks.[47] When different versions of such a hood was installed in an existing stripping tank, considerable improvement in airborne concentrations was achieved. Methylene concentrations were reduced from 600-1150 ppm to 28-34 ppm. By the use of side baffles and larger room area which would allow more even supply of make-up air even lower airborne levels would be possible to achieve.[47]

Toluene is used to clean the rotogravure presses. High exposure levels, up to 700 ppm, may occur during this task.[49] Offset presses are usually cleaned with chlorinated solvents. 1,1,1-Trichloroethane and Freons were earlier commonly used as cleaning solvents.[46] The mean concentration of 1,1,1-trichloroethane has been 23 ppm. The highest concentration observed in Finland has been 117 ppm.[46] Solvent cleaning is a task where exposure is difficult to control with ventilation arrangements but the use of a respirator is needed. Because it usually lasts only for a short time (typically about 1 hour/week) its use is neither too heavy physically.

18.4.7 DRY CLEANING

Carbon tetrachloride was the first solvent used in dry cleaning. It was introduced in the 1920's and used until the 1950's. The use of trichloroethylene started in the 1930's and it is still used to a limited extent. Perchloroethylene (tetrachloroethylene) was introduced in the 1950's and is today by far the most common dry cleaning solvent.[10] Perchloroethylene is neurotoxic and NIOSH considers it as potential human carcinogen.[53] Its TLV is 25 ppm and the Finnish OEL 50 ppm. The concentration of perchloroethylene in blood is used for biological monitoring. The ACGIH BEI is 0.5 mg/l and FIOH BEI 6 mol/l (1 mg/l). Petroleum solvents are a safer alternative for dry cleaning.[53] Emulsion cleaning, where an alkaline mixture of surfactants is used together with a small amount of nonchlorinated organic solvent in water, can be used for textiles that tolerate water.[43]

Dry cleaning machines have developed safer over the time. Five generations of machines have appeared. The first generation machines, where solvent-laden clothing was manually transferred to a separate dryer, were used until the late 1960's. This transfer was eliminated in the machines of the second generation. Residual solvents were still vented to the atmosphere. Condensers were introduced to the non-vented, third generation machines in the late 1970's. The fourth generation machines have in addition to the refrigerated condenser an activated carbon absorber to control solvent vapor at the cylinder outlet at the end of the drying cycle. The fifth generation machines are also provided with a monitor and an interlocking system to ensure that the concentration of perchloroethylene is below 300 ppm when the door is opened.[54] The TWA exposure level was 40-60 ppm when the first generation machines were used. With the second and third generation machines the TWA exposure level was 15-20 ppm. All these machines, however, created short-term peak concentrations up to 1000-4000 ppm. The fourth generation machines reduced the TWA exposure level below 3 ppm, and when the fifth generation machines are used TWA concentration remains below 2 ppm. With the fourth and fifth generation machines, the peak concentrations are 10-300 ppm.[54] Local ventilation hoods can be used above the door as an additional control measure.[55] In addition to the cleaners, pressers, sewers, counters, and maintenance workers may be exposed to some extent.[56]

The mean 8 h TWA concentration of perchloroethylene was 13 ppm (range 3-29 ppm) in Finland. The mean concentration of perchloroethylene in the blood of Finnish dry cleaning workers was 1.3 μmol/l (range <0.1 - 14.0 μmol/l).[46] The average value for maintenance men was 0.3 μmol/l. Their highest value was 1.3 μmol/l.[46]

18.4.8 REINFORCED PLASTICS INDUSTRY

Exposure to styrene is the main occupational hygiene problem in reinforced plastics industry, where it is used as a crosslinking agent and solvent in unsaturated polyester resins. In addition, workers are exposed to acetone which is used as a clean-up solvent. Other solvents, such as methylene chloride, toluene, xylene, heptane (TLV 400 ppm, the Finnish OEL 300 ppm), methylcyclohexane (TLV and the Finnish OEL 400 ppm), and butyl acetate (TLV and the Finnish OEL 150 ppm) may also be used.[57] Styrene is neurotoxic.[58] Styrene is also a suspected carcinogen because it is metabolized via styrene-7,8-oxide.[59] The TLV and the Finnish OEL of styrene is 20 ppm. Urinary mandelic acid concentration is the most common biological monitoring method for styrene. The ACGIH BEI is 800 mg/g creatinine and the FIOH BEI 3.2 mmol/l.

Open mold methods (hand lay-up and spray-up methods) are most commonly used. In addition, the products often have large surface areas and large styrene vapor emissions take place. The emission depends on the type of resin used. While the mean evaporation loss of styrene was 11.6% for conventional resins, it was only 4.4% for the low styrene emission (LSE) resins containing volatilization inhibitors.[60]

The reinforced plastics industry began in 1950's. The airborne concentrations of styrene were typically 100-200 ppm until the 1980's.[61] Styrene concentrations of about 50 ppm were found possible to achieve during the production of small and medium-sized products in the 1980's by using a mobile fan or a set of successive air jets to blow fresh air from behind the worker towards the mold. The prevention of eddy formation over the mold was found to be of crucial importance.[62] When a large occupational hygiene survey was conducted in Finland in the early 1990's, it appeared that styrene concentrations had remained high. As many as 77% of the 8-h TWA concentrations exceeded the Finnish OEL of 20 ppm. The mean TWA concentration was 43 ppm and the highest TWA value 123 ppm.[63] The average concentrations of styrene oxide were low, on an average one pre mil of the styrene concentration (mean concentration was 0.1 ppm).[63] The mean concentration of acetone was 78 ppm (range 3-565 ppm).[63] Airborne levels of styrene were still high in the Finnish boat manufacturing plants in the mid 1990's (mean concentration 51 ppm, range 15-89 ppm). The mean acetone concentration was 25 ppm (range 9-53 ppm). Lower concentrations of about 10 ppm were reported from Sweden.[64] However, no detailed process and ventilation description was given.

The mean urinary mandelic acid concentration was about 5 mmol/l in the late 1970's in Finland. The level was reduced to about 4 mmol/l in mid-1980's and to 35 mmol/l in late 1980's. However, the maximum levels remained above 30 mmol/l throughout the whole period.[65]

Recent studies have indicated that sophisticated ventilation arrangements are needed to reduce the concentration of styrene below 20 ppm. In hand lay-up work, this is possible by the use of a mobile supply ventilation and exhaust ventilation.[66] In the spray-up work, concentrations below 20 ppm can be achieved by using a booth provided with mobile curtains to reduce the open face area and by maintaining a control velocity of 0.35 m/s.[66]

18.4.9 GLUING

Shoe manufacturing is an industry where toxic solvents have been used. Benzene containing glues were used until mid-1960's, at least in Italy.[67] A significant part of the information on the toxic and carcinogenic effects of benzene on the hematopoietic system originates from this industry.[68] After benzene, n-hexane became the most important solvent.[67] Epidemiological evidence on neuropathy caused by exposure to n-hexane comes again largely from shoe manufacturing.[5] The TLV and the Finnish OEL of hexane is 50 ppm. The concentration of the toxic metabolite, 2,5-hexanedione is used for biological monitoring of exposure to n-hexane. The BEI given by the FIOH is 12 μmol/l. The ACGIH BEI is 5 mg/g creatinine. Shoe glues may also contain toluene, methyl ethyl ketone, and acetone.[69]

The mean airborne concentration of n-hexane was 38 ppm (range 4-90 ppm) in the Finnish shoe industry in the 1980's.[26] The mean concentrations of acetone and toluene were 131 ppm and 14 ppm.[26] The mean exposure levels in two US shoe manufacturing plants in the late 1970's were: toluene 22-50 ppm, methyl ethyl ketone 133-153 ppm, acetone 46-223 ppm, and n-hexane 22-55 ppm.[69] The exposure is, however, easy to control by doing the gluing in enclosure hoods.

Contact glues contain usually white spirit with low boiling point range (60-90°C). Its Finnish OEL is 350 mg/m^3. The solvent contains n-hexane, earlier usually 5% or more. In the 1990's, white spirits containing only ca. 2% n-hexane have become available. Contact glues are used to fasten seals and strips e.g., in construction and transportation vehicle industries. Levels have usually been below the OEL in Finland. If contact glues are used for floor coverings, very high exposures may occur. These glues have, however, largely been replaced by ethanol- and water-based glues.[24]

18.4.10 OTHER

In the production of viscose, the workers are exposed to carbon disulfide. In addition to inhalation exposure, absorption through the skin may be important.[70] It is strongly neurotoxic.[71] Its TLV is 10 ppm and the Finnish OEL 5 ppm. Both carry the skin notation. Urinary 2-thiothiazolidine-4-carboxylic acid concentration can be used for biological monitoring of exposure to carbon disulfide. Its ACGIH BEI is 5 mg/g creatinine (4 mmol/mol creatinine) and the BEI given by the FIOH 2.0 mmol/mol creatinine.

Airborne concentrations from less than 0.2 to 65.7 ppm were detected in measurements conducted in a German plant in the 1990's. The urinary 2-thiothiazolidine-4-carboxylic acid levels ranged from less than 0.16 to 11.6 mg/g creatinine.[70] A long time average of about 8 ppm has been reported in a Dutch factory.[72]

In acetate fiber plants, the workers are exposed to acetone. The mean concentration in the air of three Japanese factories was 372 ppm. Some workers' exposure levels exceeded 1000 ppm.[73]

Exposure to various solvents takes place in pharmaceutical industry. The airborne 8-h TWA concentrations of methylene chloride were 16-167 ppm in a Finnish factory in the 1980's.[46]

Even though the active ingredients cause the main health risk while pesticides are used, but the exposure to solvents may also be important. As many as 71 different solvents were used in the 8000 pesticide formulations sold in Italy in the 1990's. Among the solvents, carcinogens such as benzene, carbon tetrachloride, and chloroform were found.[74]

Cyclohexanone is used as a coating solvent in audio and video tape production. Airborne TWA concentrations from 2 to 20 ppm were detected in factory in Singapore.[75] Urinary cyclohexanol level of 54.5 mg/l (23.3 mg/g creatinine) was found to correspond inhalation exposure to 25 ppm of cyclohexanone.[75]

18.4.11 SUMMARY

Even though organic solvents have been increasingly replaced by water-based and solid formulations, they are still widely used. About 3% of the Finnish working population has estimated to have significant solvent exposure.[26] It should also be noted that solventless products may cause new health problems and the knowledge of the health risks of the substitutions is often poor.[43]

An extensive survey of chemical exposure conducted by FIOH in Finland in the 1980's. The highest exposure levels were detected in shoe gluing, painting of furniture and other wood products, silkscreen and rotogravure printing, floor lacquering, reinforced plastics production, paint removing, metal degreasing, and various solvent cleaning operations.[25,45,64]

Mostly, inhalation exposure can be effectively controlled by enclosures and ventilation. Open mold methods in the reinforced plastics industry and paint stripping, however, require sophisticated ventilation arrangements. High exposures often occur during solvent cleaning operations. Exposure levels may be very high while cleaning pots in paint and printing ink industry. The use of a proper respirator is necessary during such a work. The avoidance of high peak exposures is important also to prevent development of addiction. The workers may adopt working habits that cause unnecessary exposure. In extreme causes, even this may lead to solvent sniffing.[24]

Recent studies have revealed that percutaneous absorption is often an important route of solvent exposure. As the control of respiratory exposures develops, the relative importance of dermal exposures increases.

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