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Very volatile organic compounds: an understudied class of indoor air pollutants

Abstract Very volatile organic compounds (VVOCs), as categorized by the WHO, are an important subgroup of indoor pollutants and cover a wide spectrum of chemical substances. Some VVOCs are components of products commonly used indoors, some result from chemical reactions and some are reactive precursors of secondary products. Nevertheless, there is still no clear and internationally accepted definition of VVOCs. Current approaches are based on the boiling point, and the saturation vapor pressure or refer to analytical procedures. A significant problem is that many airborne VVOCs cannot be routinely analyzed by the usually applied technique of sampling on Tenax TA[®] followed by thermal desorption GC/MS or by DNPH-sampling/HPLC/UV. Some VVOCs are therefore often neglected in indoor-related studies. However, VVOCs are of high significance for indoor air quality assessment and there is need for their broader consideration in measurement campaigns and material emission testing.

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Practical Implications

So far, many very volatile organic compounds (VVOCs) are insufficiently considered, although they are of importance for the evaluation of indoor air quality and building product emissions. Moreover, an appropriate definition of VVOCs does not exist. Therefore, it is the purpose of this publication to shift VVOCs more into the focus of indoor-related research. Potential VVOCs, their sources, indoor air concentrations, and analytical procedures are critically discussed.

Introduction

The investigation of volatile organic compounds (VOCs) in ambient air is a relatively young field of research. Based on observations concerning Los Angeles' smog, the first systematic work regarding damage to plants through reactions in organic trace elements was carried out by Haagen-Smit (1952). Several years

later, it was Went (1960) who reported on the significance of the release of volatile substances from certain species of trees for the atmosphere. As a wide spectrum of compounds was involved (Koppmann, 2007), pragmatic classifications for the investigated species had to be found. Classically, this is based on their role in atmospheric chemistry rather than volatility. Organic substances in the atmosphere were therefore initially

measured as NMHC (non-methane hydrocarbons). Later, other designations developed, such as ROG (reactive organic gases), NMOC (non-methane organic compounds), and, in particular, VOC (volatile organic compounds) (Finlayson-Pitts and Pitts, 2000).

As indoor air research slowly established itself following the Second World War, it was focused initially on defined substances and substance classes in connection with outdoor air (Andersen, 1972); only from the middle of the 70s did an independent research field develop (Salthammer, 2011). In 1979, the World Health Organization (WHO) published a document which also took into account substances which are generated directly in indoor air. However, a further 10 years went by before the WHO (1989) established classifications for organic indoor pollutants according to their boiling points and the term VVOC (very volatile organic compounds) was introduced. However, with a few exceptions (Rothweiler et al., 1992), research activity was not focused upon VVOCs in the following years.

One reason for this is that in 1997, an analytical method for the determination of VOCs in indoor air and of the TVOC value was published (Mølhavé et al., 1997). Based on this work, the ISO 16000-6 (2011) was developed, which provides a sharp, analytically based definition of VOCs and enables their determination through the collection of samples on Tenax TA[®] and their subsequent thermal desorption using a standard gas chromatographic method (Woolfenden, 2010a,b). Other analytical standard procedures such as TO-15 and TO-17 (US EPA, 1999a,b) suggest sorbent combinations to extend the analytical range and do not distinguish between VOCs and VVOCs. Even today, there is no clear definition as to exactly what the term VVOCs covers. Furthermore, VVOCs cannot be determined in accordance with a uniform analytical procedure.

In his review on changes in indoor pollutants since the 1950s, Weschler (2009) mentions only five classical VVOCs: formaldehyde, acetaldehyde, acrolein, 1, 3-butadiene, and isoprene, all with decreasing or undetermined trend. In recent years, however, it has become clear that VVOCs play a significant role in indoor air research and must also be taken into account during the evaluation of indoor air quality. For many VVOCs, reference exposure limits (REL) are already available (<http://oehha.ca.gov/air/allrels.html>). Germany has also started to include VVOCs into their guideline concept with acetaldehyde being the latest example (Ad hoc AG, 2013). In Table 1, organic compounds have been summarized which can be identified in indoor air and which can be classed as VVOCs in accordance with various criteria. However, many of these compounds are still underrepresented in systematic and health-related environmental national surveys such as GerES (Umweltbundesamt, 2008) and RIOPA (Weisel et al.,

2005). The comprehensive review by Logue et al. (2011) considers only 27 of the 79 compounds listed in Table 1. In the following, these 79 compounds will be classified more precisely and discussed as regards their significance for indoor air quality. The most well-known VVOC by far is formaldehyde. However, this substance has always played a special role in indoor air analytics (Salthammer, 2013; Salthammer et al., 2010) and will not be examined in detail here.

What are VVOCs?

The original classification of the WHO (1989) for VVOCs covers boiling points from <0 to 50–100 °C and intentionally draws no sharp distinction between VVOCs and VOCs. The US EPA does not differentiate between VOCs and VVOCs and uses various definitions (<http://www.epa.gov/iaq/voc.html>):

volatile organic compounds (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, except those designated by EPA as having negligible photochemical reactivity

volatile organic compounds, or VOCs, are organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure

The latter is, according to US EPA, the general definition of VOCs that is used in the scientific literature, and is consistent with the definition used for indoor air quality. In a report by the Committee on the Effect of Climate Change on Indoor Air Quality and Public Health (2011), VOCs are defined as organic compounds with a vapor pressure of >10 Pa.

In the ISO 16000-6 (2011), there is also no clear definition for VVOCs. The determination of VOCs as "...volatile organic compounds, sampled on Tenax TA, which elute from a non-polar or slightly polar gas chromatographic separation column between and including n-hexane and n-hexadecane (C6–C16)..." allows, however, the converse argument that VVOCs can be classed as organic compounds which elute before n-hexane under the chromatographic conditions stated in ISO 16000-6. The California Specification 01350 describes a "...standard method for the testing and evaluation of volatile organic chemical emissions from indoor sources using environmental chambers..." and defines as VOCs all organic compounds which, following a specified sampling and analysis procedure, elute gas chromatographically between n-pentane and n-heptadecane (C5–C17) (California Department of Public Health, 2010). Haphazard definitions can also be found for VVOCs. Sometimes, with inadmissible

Table 1 List of organic compounds with relevance for the indoor environment which might be considered as VVOCs due to different criteria: (i) boiling point; (ii) number of carbon atoms; (iii) ISO 16000-6 (2011); (iv) vapor pressure. Boiling points (1013 mbar) and vapor pressures (298.15 K, 1013 mbar) were taken from Mackay et al. (2006) or calculated from the EPI Suite 4.1 Software (<http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>)

Group	Compound	Formula	CAS-no.	M (g/mol)	b.p. (°C)	log(P _s) (Pa)	
C1	(Methane) ^a	(CH ₄)	(74-82-8)	(16.0)	(−164.0)	(7.45)	
	Methanol	CH ₃ OH	67-56-1	32.0	64.6	4.22	
	Formaldehyde	HCHO	50-00-0	30.0	−21.0	5.72	
	Formic acid	HCOOH	64-18-6	46.0	101	3.75	
	Chloromethane	ClCH ₃	74-87-3	50.5	−24.1	5.73	
	Dichloromethane	CH ₂ Cl ₂	75-09-2	84.9	40.1	4.76	
	Trichloromethane	CHCl ₃	67-66-3	119.4	61.1	4.42	
	Trichlorofluoromethane	CCl ₃ F	75-69-4	137.4	23.8	5.03	
	Dichlorodifluoromethane	CCl ₂ F ₂	75-81-8	120.9	−29.8	5.75	
	Dichlorofluoromethane	CHCl ₂ F	75-43-4	102.9	8.9	5.26	
	Chlorodifluoromethane	CHClF ₂	75-45-6	86.5	−40.7	5.99	
	Methyl bromide	CH ₃ Br	74-83-9	94.9	3.6	5.33	
	Phosgene	COCl ₂	75-44-5	98.9	7.4	5.28	
	C2	Ethane	C ₂ H ₆	74-84-0	30.1	−88.6	6.61
Ethanol		C ₂ H ₅ OH	64-17-5	46.1	78.3	3.90	
Acetaldehyde		CH ₃ CHO	75-07-0	44.1	20.8	5.08	
Acetic acid ^b		CH ₃ COOH	64-19-7	60.1	117.9	3.32	
Chloroethane		C ₂ H ₅ Cl	75-00-3	64.5	12.3	5.13	
1,1-Dichloroethane ^b		Cl ₂ CHCH ₃	75-34-3	99.0	57.4	4.46	
1,1-Dichloroethene		Cl ₂ CCH ₂	75-35-4	97.0	31.6	4.90	
cis-1,2-Dichloroethene ^b		ClCHCHCl	156-59-2	97.0	60.1	4.43	
1,2-Dichloroethane ^b		ClCH ₂ CH ₂ Cl	107-06-2	99.0	83.6	4.05	
Trichloroethene ^b		C ₂ HCl ₃	79-01-6	131.4	87.2	3.96	
2-Chloroethanol ^b		CH ₂ ClCH ₂ OH	107-07-3	80.5	128.6	2.98	
Vinyl chloride		C ₂ H ₃ Cl	75-01-4	62.5	−13.3	5.60	
Glyoxal		CHOCHO	107-22-2	58.0	50.4	4.53	
Ethylene oxide		C ₂ H ₄ O	75-21-8	44.1	10.5	5.24	
C3		Propane	C ₃ H ₈	74-98-6	44.1	−42.1	5.98
		1-Propanol	CH ₃ (CH ₂) ₂ OH	71-23-8	60.1	97.2	3.45
	2-Propanol	CH ₃ CH(OH)CH ₃	67-63-0	60.1	82.3	3.78	
	Propanal	C ₃ H ₆ O	123-38-6	58.1	48.0	4.63	
	2-Propenal (Acrolein)	CH ₂ CHCHO	107-02-8	56.1	52.6	4.56	
	2-Propanone (Acetone)	CO(CH ₃) ₂	67-64-1	58.1	56.1	4.50	
	Propanoic acid ^b	C ₂ H ₅ COOH	79-09-4	74.1	141.1	2.70	
	Dimethoxymethane	CH ₂ (OCH ₃) ₂	109-87-5	76.1	42.0	4.73	
	Methylacetate	CH ₃ COOCH ₃	79-20-9	74.1	56.8	4.46	
	Methylglyoxal	CHOCOCOCH ₃	78-98-8	72.1	72.0	4.21	
	2-Chloropropane	CH ₃ CHClCH ₃	75-29-6	78.5	35.0	4.84	
	1-Chloro-2-propanol ^b	ClCH ₂ CH(OH)CH ₃	127-00-4	94.5	126.8	2.81	
	1,2-Dichloropropane ^b	CH ₂ ClCHClCH ₃	78-87-5	113.0	95.7	3.85	
	C4	n-Butane	C ₄ H ₁₀	106-97-8	58.1	−0.5	5.40
2-Methylpropane		CH ₃ CH(CH ₃)CH ₃	75-28-5	58.1	−11.7	5.54	
1,3-Butadiene		CH ₂ CH=CHCH ₂	106-99-0	54.1	−4.4	5.45	
1-Butanol ^b		CH ₃ (CH ₂) ₃ OH	71-36-3	74.1	118.4	2.95	
2-Butanol ^b		CH ₃ CH(OH)C ₂ H ₅	78-92-2	74.2	98.9	3.39	
Butanal		C ₄ H ₈ O	123-72-8	72.1	74.8	4.19	
2-Methylpropanal		CH ₃ CH(CH ₃)CHO	78-84-2	72.1	63.5	4.36	
2-Methyl-2-propanol		CH ₃ C(CH ₃)(OH)CH ₃	75-65-0	74.1	82.9	3.73	
Methacrolein		CH ₂ C(CH ₃)CHO	78-85-3	70.1	72.9	4.32	
2-Butanone		CH ₃ COCH ₂ CH ₃	78-93-3	72.1	79.5	4.08	
Methyl vinyl ketone		CH ₃ C(O)CHCH ₂	78-94-4	70.1	81.4	4.09	
2,3-Butanedione		CH ₃ C(O)C(O)CH ₃	431-03-8	86.1	88.2	3.88	
Vinyl acetate		CH ₃ C(O)OCHCH ₂	108-05-4	86.1	71.6	4.08	
Furan		C ₄ H ₄ O	110-00-9	68.1	31.5	4.90	
Tetrahydrofuran ^b		C ₄ H ₈ O	109-99-9	72.1	65.0	4.33	
2-Chloro-1,3-butadiene		CH ₂ CHCClCH ₂	126-99-8	88.5	59.4	4.46	
C5	n-Pentane	C ₅ H ₁₂	109-66-0	72.2	36.1	4.83	
	Cyclopentane	C ₅ H ₁₀	287-92-3	70.1	49.2	4.63	
	2-Methylbutane	CH ₃ CH(CH ₃)C ₂ H ₅	78-78-4	72.2	27.9	4.90	
	Isoprene	CH ₂ C(CH ₃)CHCH ₂	78-79-5	68.1	34.0	4.86	
	Pentanal ^b	C ₅ H ₁₀ O	110-62-3	86.1	103.1	3.54	

Table 1 Continued

Group	Compound	Formula	CAS-no.	M (g/mol)	b.p. (°C)	log(P _s) (Pa)
	2-Methylfuran	(C ₄ H ₈ O)CH ₃	534-22-5	82.1	64.7	4.32
	<i>2-Methyl-3-buten-1-ol</i> ^b	(CH ₃) ₂ C(OH)CHCH ₂	115-18-4	86.1	97.0	3.49
	<i>Furfural</i> ^b	(C ₄ H ₃ O)CHO	98-01-1	96.1	161.8	2.47
C6	<i>n-Hexane</i> ^b	C ₆ H ₁₄	110-54-3	86.2	69.0	4.30
	2-Methylpentane	CH ₃ CH(CH ₃)C ₃ H ₇	107-83-5	86.2	60.2	4.45
	3-Methylpentane	C ₂ H ₅ CH(CH ₃)C ₂ H ₅	96-14-0	86.2	63.3	4.40
	<i>Diisopropylether</i> ^b	(CH ₃) ₂ CHOCH(CH ₃) ₂	108-20-3	102.2	68.4	4.30
Other	Carbon disulfide	CS ₂	75-15-0	76.1	46.0	4.68
	Methylsulfide	HSCH ₃	74-93-1	48.1	5.9	5.30
	Dimethylsulfide	S(CH ₃) ₂	75-18-3	62.1	37.3	4.83
	Trimethylsilanol	Si(CH ₃) ₃ OH	1066-40-6	90.2	97.8	3.27
	Acrylonitrile	CH ₂ CHCN	107-13-1	53.1	77.3	4.16
	Acetonitrile	CH ₃ CN	75-05-8	41.1	81.7	4.07
	Dimethylamine	HN(CH ₃) ₂	124-40-3	45.1	7.4	5.55
	Trimethylamine	N(CH ₃) ₃	75-50-3	59.1	2.9	5.33
	Diethylamine	HN(C ₂ H ₅) ₂	109-89-7	73.1	56.1	4.50
	<i>Triethylamine</i> ^b	N(C ₂ H ₅) ₃	121-44-8	101.2	89.3	3.88
	<i>Dimethylformamide</i> ^b	N(CH ₃) ₂ CHO	68-12-2	73.1	153.0	2.71

^aUsually not considered in VVOC analysis (see text).

^bCompounds printed in *italic* are no VVOCs per definition by ISO-16000-6.

reference to ISO 16000-6, all the substances which have a boiling point of <69 °C (n-hexane) or substances with fewer than six carbon atoms (<C6) are designated as VVOCs.

Analysis of VVOCs in indoor air

The great advantage of VOC analytics in accordance with ISO 16000-6 (2011) is that, with a few exceptions, all relevant substances can be covered using one single method. For the full spectrum of VVOCs, however, alternative methods must be applied but a standardized protocol for VVOC sampling and analysis is still missing. In the European Collaborative Action (2013) Report no. 29, it is stated that “Besides the VOCs that have already been accommodated in the EU-LCI harmonisation framework... there is a need to consider the inclusion and development of protocols for assessing... VVOCs for which European harmonised test methods are not yet available”. Several analytical methods are presented below, where they are discussed regarding their suitability for VVOC analytics.

Gas chromatographic methods

The most commonly used method by far for the determination of volatile organic compounds in air is gas chromatography/mass spectrometry after thermal desorption (TD-GC/MS). A defined volume of sample gas (typically 1–6 l) is drawn from the air and fed through a sorption tube which is filled with an adsorbent or a combination of multiple adsorbents. Subsequently, the collected compounds are thermally desorbed by the sorption tube and injected via a cold

trap by means of an inert carrier-gas stream into the GC, which is fitted with a capillary column. As an alternative to MS, a flame ionization detector (FID) can be used for detection. Different standard methods are currently available. Although the ISO 16000-6, which uses a non- or slightly polar capillary column, has been designed for the retention range of the substances eluting between n-hexane (C6) and n-hexadecane (C16), many VVOCs can also be quantitatively detected (see Table 2). Very polar compounds such as formic acid and acetic acid are, however, characterized by a strong peak broadening. The California Specification 01350 explains that an extension of the retention range from C5 to C17 can result in lower readings for highly volatile compounds. As an alternative to Tenax TA[®], carbonized molecular sieves (Carbosive[™], Carboxen[™], SulfiCarb[™]) and graphitized carbon (Carbopack[™], Carbograph[™]) are conceivable for VVOCs from C2 onwards and derivatives of methane (Markes, 2013; Woolfenden, 2010a,b). A disadvantage of these adsorbents is, however, their high water-retention capability, due to which only small sampling volumes are possible. Therefore, TO-17 (US EPA, 1999b) suggests a dry purge procedure at humidities above 65% and temperatures above 30 °C. As the sensitivity of GC/MS and GC/FID devices has increased, sufficient detection limits well below 1 µg/m³ can be achieved even with small sampling volumes of <2 l. The analytical step might require modification of the cooling trap in commercial thermal desorption systems and the application of thick-film capillary columns.

TO-17 has been defined for specific target compounds and does not discriminate between VOCs and VVOCs. In this document, a sorbent tube TD-GC method is described. For compounds ranging in vola-

Table 2 Analytical methods for VOCs and references dealing with specific compounds

Group	Compound	Analytical method	Source	References	
C1	(Methane) ^a	(Canister sampling, GC/FID)	(Biotic, domestic gas)	Lofffield et al. (1997)	
	Methanol	CMS ^c , TD-GC/MS	Wood products, exhaled breath, photocatalytic degradation	Mo et al. (2009)	
	Formaldehyde	ISO 16000-3	Miscellaneous	Salthammer et al. (2010)	
	Formic acid	ISO 16000-6; IC ^e	Reaction product	Zhang et al. (1994a)	
	Chloromethane	CMS ^c , TD-GC/MS		Logue et al. (2011) ^d	
	Dichloromethane	ISO 16000-6	Solvent	Logue et al. (2011) ^d	
	Trichloromethane	ISO 16000-6	Tap water	Kerger et al. (2000)	
	Trichlorofluoromethane	CMS ^c , TD-GC/MS	Freon 11 (former propellant)	Logue et al. (2011) ^d	
	Dichlorodifluoromethane	CMS ^c , TD-GC/MS	Freon 12 (former propellant)	Logue et al. (2011) ^d	
	Dichlorofluoromethane	CMS ^c , TD-GC/MS	Freon 21 (former propellant)	Logue et al. (2011) ^d	
	Chlorodifluoromethane	CMS ^c , TD-GC/MS	Freon 22 (former propellant)	Logue et al. (2011) ^d	
	Methyl bromide	CMS ^c , TD-GC/MS	Fumigant	Corsi et al. (2007)	
	Phosgene	Derivatization, GC/MS/ECD	Reaction product	Coleman et al. (2010)	
	C2	Ethane	Carbosieve TM , TD-GC/MS	Biotic, domestic gas	
		Ethanol	ISO 16000-6	Solvent	Logue et al. (2011) ^d
		Acetaldehyde	ISO 16000-3	Reaction product, plant material	Sarigiannis et al. (2011)
Acetic acid ^b		ISO 16000-6; IC ^e	Plant material, household products	Gibson and Watt (2010)	
Chloroethane		CMS ^c , TD-GC/MS	Foam	Logue et al. (2011) ^d	
1,1-Dichloroethane ^b		ISO 16000-6		Logue et al. (2011) ^d	
1,1-Dichloroethene		CMS ^c , TD-GC/MS		Logue et al. (2011) ^d	
cis-1,2-Dichloroethene ^b		ISO 16000-6			
1,2-Dichloroethane ^b		ISO 16000-6		Logue et al. (2011) ^d	
Trichloroethene ^b		ISO 16000-6	Foam	Logue et al. (2011) ^d	
2-Chloroethanol ^b		ISO 16000-6	Reaction product		
Vinyl chloride		CMS ^c , TD-GC/MS	Monomer (PVC)	Logue et al. (2011) ^d	
Glyoxal		ISO 16000-3		Liu et al. (2006)	
Ethylene oxide		TO-17	Fumigant		
C3		Propane	CMS ^c , TD-GC/MS	Liquid gas, propellant	
		1-Propanol	ISO 16000-6	Solvent, cleanser	
	2-Propanol	ISO 16000-6	Solvent, cleanser	Logue et al. (2011) ^d	
	Propanal	ISO 16000-3	Degradation product fatty acids	Zhang et al. (1994b)	
	2-Propenal (Acrolein)	ISO 16000-3; ISO 16000-6	Cooking, building products	Seaman et al. (2007)	
	2-Propanone (Acetone)	ISO 16000-3; ISO 16000-6	Solvent, exhaled breath		
	Propanoic acid ^b	ISO 16000-6	Degradation product fatty acids		
	Dimethoxymethane	ISO 16000-6	Solvent		
	Methylacetate	ISO 16000-6	Solvent		
	Methylglyoxal	ISO 16000-6		Liu et al. (2006)	
	2-Chloropropane	ISO 16000-6	Foaming agent		
	1-Chloro-2-propanol ^b	ISO 16000-6	Degradation product (foam)	Salthammer et al. (2003)	
	1,2-Dichloropropane ^b	ISO 16000-6	Degradation product (foam)	Salthammer et al. (2003)	
	C4	n-Butane	CMS ^c , TD-GC/MS	Liquid gas, propellant	
		2-Methylpropane	CMS ^c , TD-GC/MS	Propellant, refrigerating agent	
		1,3-Butadiene	CMS ^c , TD-GC/MS	Monomer (SBR)	Logue et al. (2011) ^d
1-Butanol ^b		ISO 16000-6	Solvent, hydrolysis	Logue et al. (2011) ^d	
2-Butanol ^b		ISO 16000-6	Solvent, hydrolysis		
Butanal		ISO 16000-3; ISO 16000-6	Degradation product fatty acids		
2-Methylpropanal		ISO 16000-6			
2-Methyl-2-propanol		ISO 16000-6			
Methacrolein		ISO 16000-6	Reaction product	Logue et al. (2011) ^d	
2-Butanone		ISO 16000-6	Solvent	Logue et al. (2011) ^d	
Methyl vinyl ketone		ISO 16000-6			
2,3-Butanedione		ISO 16000-6	Food (Popcorn)	Zhang et al. (2014)	
Vinyl acetate		ISO 16000-6	Monomer		
Furan		ISO 16000-6	Food		
Tetrahydrofuran ^b		ISO 16000-6	Solvent	Logue et al. (2011) ^d	
C5		2-Chloro-1.3-butadiene	ISO 16000-6	Monomer	
	n-Pentane	ISO 16000-6	Foaming agent		
	Cyclopentane	ISO 16000-6	Foaming agent (insulation materials)		
	2-Methylbutane	ISO 16000-6	Foaming agent		
	Isoprene	ISO 16000-6	Exhaled breath, plants	Riess et al. (2010)	
	Pentanal ^b	ISO 16000-3; ISO 16000-6	Degradation product fatty acids		
	2-Methylfuran	ISO 16000-6			

Table 2 Continued

Group	Compound	Analytical method	Source	References
C6	<i>2-Methyl-3-buten-1-ol</i> ^b	ISO 16000-6		
	<i>Furfural</i> ^b	ISO 16000-6	Wood, wood-based products, cooking	Horn et al. (1998)
	<i>n-Hexane</i> ^b	ISO 16000-6	Solvent	Logue et al. (2011) ^d
	2-Methylpentane	ISO 16000-6	Solvent, cleanser	
	3-Methylpentane	ISO 16000-6	Solvent, cleanser	
Other	<i>Diisopropylether</i> ^b	ISO 16000-6		
	Carbon disulfide	ISO 16000-6	Reaction product	Uhde and Salthammer (2007)
	Methylsulfide	CMS ^c , TD-GC/MS	Reaction product	
	Dimethylsulfide	ISO 16000-6	Reaction product	
	Trimethylsilanol	ISO 16000-6		
	Acrylonitrile	ISO 16000-6	Monomer (ABS - acrylonitrile/butadiene/styrene)	Logue et al. (2011) ^d
	Acetonitrile	CMS ^c , TD-GC/MS	Solvent	
	Dimethylamine	CMS ^c , TD-GC/MS		
	Trimethylamine	CMS ^c , TD-GC/MS		
	Diethylamine	ISO 16000-6	Reaction product	Uhde and Salthammer (2007)
	<i>Triethylamine</i> ^b	ISO 16000-6	Additive in lacquer and paint	Schripp et al. (2014)
<i>Dimethylformamide</i> ^b	ISO 16000-6	Solvent, leather products		

ISO 16000-3 is defined for selected carbonyls, including formaldehyde, acetaldehyde, propanal, butanal, and acetone. ISO 16000-6 is defined for compounds eluting between n-hexane and n-hexadecane under defined chromatographic conditions. In this table, assignment of an ISO standard to a specific compound does not automatically mean that measurement of this compound is recommended in the standard. The standards TO-17 (US EPA, 1999b) and ASTM D6196-03 (2009) provide criteria for the selection of sorbent tubes and sorbent tube combinations for volatile organic compounds in ambient air. Assignment of a compound to ISO 16000-6 does not exclude the applicability of TO-17 and ASTM D6196-03.

^aUsually not considered in VVOC analysis (see text).

^bCompounds printed in *italic* are no VVOCs per definition by ISO-16000-6.

^cCMS = carbonized molecular sieve (see Markes (2013), Woolfenden (2010a,b), TO-17 (US EPA, 1999b), and ASTM D6196-03 (2009) for more details).

^dThe publication by Logue et al. (2011) summarizes the results of at least 77 international studies (see also references therein).

^eIC, ion chromatography.

tivity from C₃ to C₁₂, a multisorbent tube of CarbosieveTM B plus CarbosieveTM SIII or CarboxenTM is recommended for air samples of 2 l. An alternative for compounds ranging in volatility from C₃ to C₁₆ is a multisorbent tube of CarboxenTM C plus CarboxenTM B plus CarbosieveTM SIII or CarboxenTM 1000 for air volumes of 2 l. TO-17 offers sorbent tubes or tube combinations for a number of specific compounds, including polar substances such as alcohols and nitriles. The standard ASTM D6196-03 (2009) also deals with the selection of sorbent tubes and tube combinations for the determination of organic compounds in the volatility range between C₃ and C₁₆. For polar and non-polar so-called very and ultra volatile compounds, this standard recommends UniCarbTM (replaced by SulfiCarbTM), Porapak N, and CarbosieveTM SIII.

Sorbent combinations are successfully applied for the analysis of indoor air. In their study on gas-phase organics in environmental tobacco smoke, Singer et al. (2002) used a combination of Tenax TA[®] and CarbosieveTM SIII to monitor interalia 1,3-butadiene, isoprene, acrolein, acrylonitrile, acetonitrile, and 2-butanone. Dodson et al. (2008) report the application of a CarboxenTM B, CarboxenTM X, and CarboxenTM 1001 triple bed tube for measuring interalia dichloromethane, trichloroethane, and 1,3-butadiene.

Methane itself cannot be analyzed using TD-GC/MS. It is usually sampled into a flask or canister and analyzed by GC-FID (Loftfield et al., 1997). The adsorption on activated carbon with subsequent sol-

vent desorption is rarely used these days for active sampling. This is mainly due to the long sampling period and, compared with thermal desorption techniques, significantly higher detection and determination limits (Uhde, 2009). Hippelein (2006) deployed solid-phase micro-extraction (SPME) in combination with GC for VVOC analytics. However, the method has not been established in ambient air analytics due to the calibration effort required. For special compounds, such as phosgene, elaborate derivatization, and analysis procedures are necessary (Coleman et al., 2010).

The US EPA (1999a) published the TO-15 method as an alternative to the specified collection phases. Here, the air which is to be analyzed is collected into a stainless steel container. The sampling volume is between 400 ml and 6 l. For analysis, an air sample, typically 250–500 ml, is withdrawn from the canister and passed over a suitable adsorbent for concentration. Subsequently, analysis is carried out using GC/MS following thermal desorption. Canisters are difficult to handle and their cleaning is quite extensive, but this technique also offers a number of advantages. The sampling time is short (seconds to minutes), and the storage time is up to 30 days. The method provides low detection limits (usually <1 µg/m³), and it is very suitable for organic compounds of high volatility and for odorous substances. TO-15 is applied in IAQ studies, usually in combination with other sampling procedures (Nirlo et al., 2014).

Liquid chromatographic methods

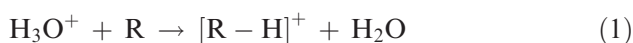
For the determination of volatile carbonyl compounds in air, derivatization with 2,4-dinitrophenylhydrazine (DNPH), separation by HPLC after extraction with acetonitrile, and subsequent UV/VIS detection is described in the ISO 16000-3 (2011). The reaction to hydrazone occurs during sampling through DNPH-impregnated cartridges of silica gel. It should be noted that during sampling, acetonitrile can be released from the cartridges into the room air. The method is excellently suited for VVOCs such as formaldehyde, acetaldehyde, propanal, butanal, and acetone; however, compared to the gas chromatographic thermal desorption method, low readings were found for the higher aldehydes pentanal and hexanal (Salthammer and Mentese, 2008). Additionally, the DNPH method cannot be readily applied for unsaturated carbonyl compounds such as acrolein (Ho et al., 2011). An alternative to DNPH is derivatization with 1-dimethylaminonaphthalene-5-sulfonyl hydrazine (DNSH) which, due to the naphthalene chromophore, enables sensitive fluorimetric detection after HPLC separation (Vogel et al., 2000; Zhang et al., 2000).

For organic acids, for example, formic acid and acetic acid, ion chromatography (IC) is suitable. Air is thereby drawn through pre-treated silica gel cartridges. After elution with sodium carbonate solution, separation is carried out via an exchange column with subsequent conductivity detection (E. Uhde, C. Apel, A. Schieweck, D. Varol, and T. Salthammer, unpublished results).

Online methods

Most of the available online methods are unsuitable for a specific VVOC analysis. Photoacoustic spectroscopy (PAS) uses broadband light sources and narrow-band IR filters. Thereby, all the molecules which absorb within the selected wave number range are recorded. With the photoionization detector (PID), several substances with a similar ionization potential are also generally detected. Nevertheless, Corsi et al. (2007) successfully applied a specially calibrated PID for the analysis of methyl bromide.

A method now commonly used in indoor air analytics is the proton transfer reaction mass spectrometry (PTR-MS). This is based on the detection of $[M + 1]^+$ ions after reaction in accordance with Equation (1).



In principle, all molecules with a higher proton affinity than water (691.7 kJ/mol) can be detected with this technique. For indoor air investigations, PTR-MS is possibly suitable for VVOCs with rare $[M + 1]^+$ ions such as methanol (m/z 33), acetaldehyde (m/z 45), acetonitrile (m/z 42), ethanol (m/z 42), and acetic acid (m/z 42). Fur-

thermore, there are many potential applications for the determination of VVOCs in test chambers (Schripp et al., 2014). In respiratory gas analytics, PTR-MS today counts as one of the standard methods (Kushch et al., 2008; Riess et al., 2010). The PTR-MS technique has also been used for the monitoring of acetone as a reaction product of skin lipid/ozone chemistry (Wisthaler and Weschler, 2010) and for the detection of VVOCs such as acrolein, acetone, formaldehyde, acetaldehyde, formic acid, methanol, ethanol, and isoprene in a simulated aircraft cabin (Weschler et al., 2007; Wisthaler et al., 2007).

Sources of VVOCs

Similar to the VOCs, an unambiguous designation of VVOC sources is generally difficult, as there are normally several development and input possibilities. In the following, an attempt is made to roughly characterize the fundamental paths. Table 2 shows, where possible, potential sources and relevant references for relevant compounds.

VVOCs from indoor chemistry

The reactions of unsaturated organic compounds with ozone and other reactivated components are analogous in indoor and outdoor air. The main differences relate primarily to the mixing ratio of the components (the concentrations of unsaturated compounds are generally higher indoors than outdoors, but the ozone concentrations are lower) and the lack of daylight chemistry and night chemistry in interior areas. Monoterpenes such as α -pinene, β -pinene, 3-carene, and limonene can reach concentrations of several hundred $\mu\text{g}/\text{m}^3$ in indoor areas. VVOCs such as methanol, formaldehyde, formic acid, ethanol, acetaldehyde, and acetone can be proven to be products of the terpene-ozone chemistry (Finlayson-Pitts and Pitts, 2000) or as direct biogenic emissions (Kirstine et al., 1998).

Weschler et al. (1992) first recognized the importance of ozone chemistry in indoor areas when, during test chamber experiments using textile floor coverings, in the presence of ozone formaldehyde, acetaldehyde, and other oxidation products of unsaturated precursor compounds were determined. In analog studies, Morrison and Nazaroff (2002) found a significantly larger range of saturated and unsaturated aldehydes. Reiss et al. (1995) were also able to identify a series of VVOCs (formaldehyde, acetaldehyde, propanal, butanal, acrolein, butanal, acetone, 2-butanone) during the exposure of latex paint to ozone.

Gas-phase reactions were investigated on the basis of the styrene/ozone and limonene/ozone systems by Zhang et al. (1994a) whereby, in addition to formaldehyde, particularly formic acid and acetic acid occurred as the main products. Also, noteworthy is the detection of phosgene (COCl_2) through the reaction of the insect-

ticide permethrin, which is commonly used in indoor areas, with ozone (Coleman et al., 2010).

VVOCs can be formed by many other reactions and released into the air. Commonly known is the hydrolytic decomposition of esters to alcohols and acids. As an example, 1-butanol and acetic acid are formed through hydrolysis of n-butyl acetate in this way. The degradation products 1-chloro-2-propanol, 2-chloro-1-propanol, and 1,3-dichloro-2-propanol are formed through hydrolysis of the flame retardants tri(chloropropyl)phosphate (TCPP) and tri(di-chloropropyl)phosphate (TDCPP) (Salthammer et al., 2003). From the thermal decomposition of various organophosphorus flame retardants, 1,2-dichloroethane and 1,2-dichloropropane can be detected (Salthammer et al., 2003). The formation of diethylamine and carbon disulfide through the vulcanization accelerator Zn-diethyldithiocarbamate is also a thermal reaction (Uhde and Salthammer, 2007). Photoreactions are also possible. Salthammer and Fuhrmann (2007) as well as Auvinen and Wirtanen (2008) determined the formation of formaldehyde, acetaldehyde, and acetone from photocatalytic wall paints. Air cleaning devices which operate in accordance with the photocatalytic principle are also sources of highly volatile carbonyl compounds (Geiss et al., 2014; Mo et al., 2009). The use of methyl bromide for insect control leads to the formation of methyl sulfide and dimethyl sulfide through its reaction with hydrogen sulfide in walls which contain gypsum. Odorous VVOCs, especially mercaptans and thioethers, are also known as metabolites from mold (Wilkins, 1996) and can be found in damp buildings (Wilkins and Larsen, 1995). Comprehensive statements concerning the formation of VVOCs and other compounds are offered by Uhde and Salthammer (2007), Morrison (2010), and Weschler (2011).

VVOCs from materials, products, and household activities

Many of the products used in indoor areas contain VVOCs as inherent constituents. This applies particularly to natural-based materials. Various deciduous and coniferous trees are known to be strong emission sources for acetic acid (Gibson and Watt, 2010). Methanol, acetaldehyde, and isoprene are also released from wood, wood composites, and paper. Aliphatic and isaliphatic hydrocarbons serve as propellants and foaming agents. Butane and 2-methylpropane are favored for use in spray cans, while pentane, 2-methylbutane, and cyclopentane are deployed for the foaming of plastics such as PVC and EPS (expanded polystyrene). Chlorofluorocarbons, which have been prohibited for many years, are today still detectable in the air of indoor areas. 2-chloropropane is sporadically used for the foaming of phenolic resin rigid foam boards. Methane, ethane, and propane are components of fuel gases and heating gases.

A significant source for VVOCs is human activities in the household, especially the use of cleaning products and cooking, frying, and baking. Acrolein, a VVOC, which is particularly undesirable due to its hazardous properties, is formed by the intensive heating of food which contains glycerin. Furan is also formed through heating food. In recent years, special attention has been gained by the formation of 2,3-butanedione (diacetyl) from microwave popcorn (Zhang et al., 2014). Saturated and unsaturated aldehydes from C3 onwards are formed by the thermal decomposition of linolenic acid (Belitz et al., 2009). Open burning processes are among the strongest sources of emissions for VVOCs in indoor areas (Manoukian et al., 2013). During test chamber investigations on the fire behavior of incense sticks, Lee and Wang (2004) were able to prove the presence of the VVOCs formaldehyde, acetaldehyde, acetone, acrolein, propanal, methacrolein, butanal, methyl chloride, dimethyl chloride, 1,2-dichloroethene, and chloroform. Metabolic processes must also be considered as emission sources in indoor areas. Several authors were able to prove the presence of VVOCs such as methanol, formaldehyde, ethanol, acetaldehyde, acetone, propanol, and isoprene in human breath (Riess et al., 2010; Smith et al., 2007).

A large number of VVOCs cannot be attributed to a particular source. This applies for typical solvents such as dichloromethane, 1- and 2-propanol, methyl acetate, 1- and 2-butanol, 2-butanone, tetrahydrofuran, 2 and 3-methyl pentane, acetonitrile, and dimethylformamide. The substances can be found in diverse chemical products such as paints, waxes, adhesives, sprays, and cleaning materials (Ayoko, 2009). Table 2 shows, where possible, potential sources and references for the individual substances. Outdoor air is also a significant source of biogenic and anthropogenic-generated VVOCs. A very good overview of the different substance classes is provided by Koppmann (2007).

VVOC indoor concentrations and guidelines

In contrast to VOCs, VVOCs have, until now, been insufficiently considered in representative indoor air investigations such as the German Environmental Survey (Umweltbundesamt, 2008) or the RIOPA study (Weisel et al., 2005). This is mainly due to the complex analysis required for a number of VVOCs. The most comprehensive compilation is provided by Logue et al. (2011) whereby, however, different measurement concepts were statistically summarized together. Also, hardly, any reference values for VVOCs have been derived as yet. Based on their statistical evaluation, Logue et al. (2011) have identified a total of nine priority chemical pollutants, including four VVOCs: acetaldehyde, acrolein, 1,3-butadiene, and formaldehyde. In Table 3, indoor air concentrations for a number of

Table 3 VVOCs being frequently measured in the indoor environment, typical concentration ranges, indoor guideline values, and inhalation reference exposure limits (REL)

Compound	C ($\mu\text{g}/\text{m}^3$)	Remarks, References	Guideline (mg/m^3)		Inhalation REL ($\mu\text{g}/\text{m}^3$) ^e chronic (acute)
Chloromethane	1.40	Median (Weisel et al., 2008)			
Dichloromethane	0.84	Median (Weisel et al., 2005)	RW I = 0.2 ^b	RW II = 2 ^b	400
Trichloromethane	0.92	Median (Weisel et al., 2005)			300
	2.40	Median (Weisel et al., 2008)			
Methyl bromide	0.33	Mean (Logue et al., 2011) ^a			5
Formic acid	18–68	Range (Reiss et al., 1995)	0.6 ^c		
	52–100	Range (Schieweck et al., 2005)			
Ethanol	160	Median (Logue et al., 2011) ^a			
Acetaldehyde	0.3–38.3	Range (Lovreglio et al., 2009)	RW I = 0.1 ^b	RW II = 1 ^b	140
	15.5	Median (Umweltbundesamt, 2008)			
	18.9	Median (Weisel et al., 2005)			
1,1-Dichloroethene	5×10^{-4}	Mean (Logue et al., 2011) ^a			70
Acetic acid	25–236	Range (Reiss et al., 1995)	1 ^c		
	<5–174	Range (Schieweck et al., 2005)			
Glyoxal	2.6	Median (Weisel et al., 2005)			
Propanal	2.5	Median (Umweltbundesamt, 2008)			
	1.8	Median (Weisel et al., 2005)			
Acetone	21	Mean (Logue et al., 2011) ^a			
Acrolein	0.62	Median (Weisel et al., 2005)			0.35
	0.9	Median (Gilbert et al., 2005)			
2-Chloropropane	See text	Nix (2012)	RW I = 0.8 ^{b,d}	RW II = 8 ^{b,d}	
Butanal ^f	2.4	Median (Umweltbundesamt, 2008)	RW I = 0.1 ^b	RW II = 2 ^b	
1,3-Butadiene	0.16	Median (Logue et al., 2011) ^a			2
2-Butanone	<7.5	Median (Umweltbundesamt, 2008)			13,000 (Acute)
	3.5	Median Weisel et al., 2008)			
Isoprene	3.6–21.6	Range (Zuraimi et al., 2006)			
	1.6–26.6	Range (Zuraimi et al., 2006)			
Vinyl chloride	0.16	Mean (Logue et al., 2011) ^a			200
Acrylonitrile	0.06	Median (Logue et al., 2011) ^a			5
Carbon disulfide	<1.6	Median (Weisel et al., 2008)			800

^aIn Logue et al. (2011) data from different studies were applied to calculate mean and median values.

^b<http://www.umweltbundesamt.de/themen/gesundheit/kommissionen-arbeitsgruppen/ad-hoc-arbeitsgruppe-innenraumrichtwerte>.

^cNielsen et al. (1998).

^dPreliminary guideline values https://www.umweltbundesamt.de/sites/default/files/medien/1/dokumente/46_kurzprotokoll.pdf.

^e<http://oehha.ca.gov/air/allrels.html>.

^fGuideline defined for the sum of C4-C9 aldehydes.

VVOCs (mean, median, range), reference values and Inhalation reference exposure Limits (REL) have been compiled.

In the future, acetaldehyde in particular will receive a lot more attention in indoor air studies. In European dwellings, the average concentrations lie between 10 and 20 $\mu\text{g}/\text{m}^3$ (Sarigiannis et al., 2011). Lovreglio et al. (2009) found concentrations of up to 39 $\mu\text{g}/\text{m}^3$ in Italian homes. The German Environmental Survey obtained the following data: median = 15.5 $\mu\text{g}/\text{m}^3$, 95-Percentile = 50.3 $\mu\text{g}/\text{m}^3$, max = 863 $\mu\text{g}/\text{m}^3$. The toxicologically derived reference values I (long-term) and II (effect related) (Heinzow and Sagunski, 2009) (see Table 3) are, however, rarely exceeded even with low air exchange (Ad hoc AG, 2013). However, Hult et al. (2015) observed the trend of higher formaldehyde and acetaldehyde concentrations in apartments with lower air exchange rates. Acetaldehyde is a typical reaction product which is formed by ozone reactions (see Gas chromatographic methods) and which is emitted by certain species of wood, wood materials (Suzuki

et al., 2014), and cork. Acetaldehyde often coincides with acetic acid, formaldehyde, and formic acid. Organic acids are not only potentially problematic in residential interiors, but also contain a high corrosion potential. Particularly in museums, formic and acetic acid contribute to the damage of metallic objects through the formation of formates and acetates (Schieweck et al., 2005). Nielsen et al. (1998) derived indoor guideline values of 0.6 and 1 mg/m^3 for formic acid and acetic acid. The concentrations of acetone and isoprene typically lie in the range of 20 $\mu\text{g}/\text{m}^3$. Higher concentrations have been reported for ethanol (Logue et al., 2011) and, in particular, 2-chloropropane. In conjunction with the installation of specific insulation panels, values for 2-chloropropane in the range of 1000 $\mu\text{g}/\text{m}^3$ were measured (Nix, 2012), which recently led to the derivation of guideline values RW I and RW II (see Table 3).

The concentrations of most of the other VVOCs vary within the range of a few $\mu\text{g}/\text{m}^3$ or less (see Table 3). Despite the seemingly low average indoor air

concentrations of $<1 \mu\text{g}/\text{m}^3$, particularly 1,3-butadiene and acrolein must, as identified by Logue et al. (2011), be deemed problematic due to their low inhalation REL of 2 and $0.35 \mu\text{g}/\text{m}^3$, respectively. For methyl bromide, it can also be expected that the inhalation REL of $5 \mu\text{g}/\text{m}^3$ will be exceeded for a period of time following gassing actions, as the substance interacts strongly with construction products (Corsi et al., 2007). The concentrations of aliphatic hydrocarbons, such as ethane and propane, in outdoor air are subject to significant fluctuations depending on the location (Duan et al., 2008; Sarwar et al., 2002) which, in turn, has an impact on indoor air concentrations.

Discussion

In building product evaluation systems such as AFS-SET (2009), AgBB (2012), and ECA (2013), VVOCs are currently not considered, although some organic compounds have already been classified as VVOCs (see Supporting Information). The proportion of VVOCs can be thereby quite substantial. For oriented strand board (OSB), a TVOC value of $1617 \mu\text{g}/\text{m}^3$ following a 28-day testing period was measured in accordance with AgBB (2012). The sum of the VVOCs, measured using TD-GC/MS after adsorption on Tenax TA[®], was $471 \mu\text{g}/\text{m}^3$ with the major components acetone, formic acid, methacrolein, and butanal. This is 23% of the total emissions determined through this method. For a test specimen made of expanded polystyrene (EPS), the following values were determined after 48 h: TVOC = $872 \mu\text{g}/\text{m}^3$ and $\Sigma\text{VVOC} = 4603 \mu\text{g}/\text{m}^3$ with the foaming agents 2-methyl butane, n-pentane and cyclopentane as the main components (E. Uhde, 2014, unpublished results). These results are supported by Figure 1, which summarizes the concentrations of VOCs and VVOCs of 17 arbitrarily selected building product in test chambers after 28 days. In eight cases, the portion of VVOCs was 10% or higher (please note that only organic compounds being accessible by ISO 16000-6 are considered here).

The TVOC value, as introduced by Mølhave et al. (1997) and analytically defined by ISO 16000-6, is frequently used as a hygiene-based indicator for indoor air quality. Neglecting VVOCs, different countries have developed evaluation schemes on the basis of TVOC (Heinzow and Sagunski, 2009; Salthammer, 2011). Other evaluation concepts define all identified compounds as VOCs and do not consider the TVOC value. Instead, the single substances are discussed or the substances are grouped by their chemical classification.

For the reasons stated, there is an urgent need for a sharp definition of VVOCs, for their systematic qualitative and quantitative analytical determination and for better consideration in indoor air quality assessments. In Figure 2, the boiling points for the compounds shown in Table 1 - with the exception of methane and ethane - are

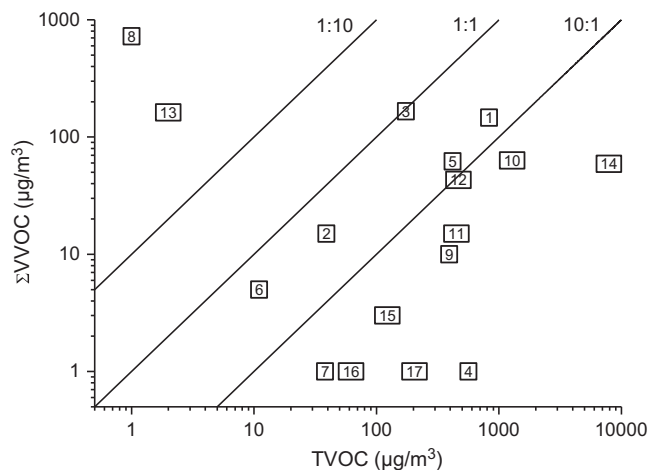


Fig. 1 VOC vs. VVOC concentrations for 17 building products after 28 days in a test chamber at $T = 23 \text{ }^\circ\text{C}$, relative humidity = 50%, and analysis according to ISO 16000-6. Loading rate $q = 1.25 \text{ m}^3/(\text{m}^2 \text{ h})$: 1, 2 (flooring material); 3 (concrete); 4 (parquet coating on glass); 5 (pine board); 6 (melamine resin foam); 7 (flooring adhesive on glass); 8 (insulation material); 9 (laminated); 10 (paint on oak); 11 (oak parquet). Loading rate $q = 0.5 \text{ m}^3/(\text{m}^2 \text{ h})$: 12 (plywood); 13 (insulation material); 14 (MDF board); 15 (fiber board); 16 (wall paint on glass); 17 (wall covering)

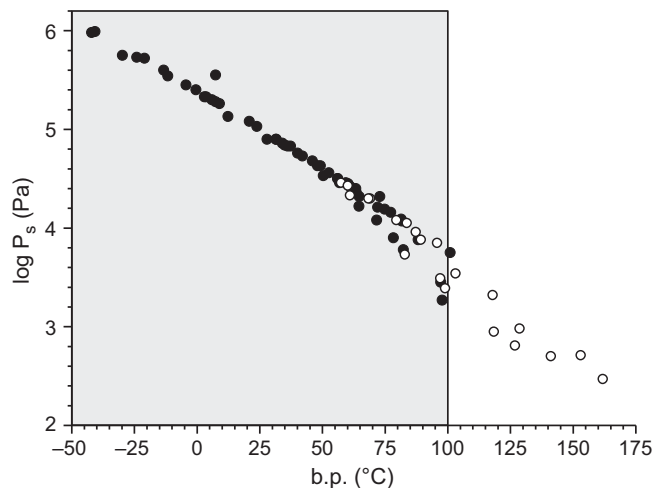


Fig. 2 Logarithmic vapor pressure (Pa) vs. boiling point ($^\circ\text{C}$) for organic compounds with relevance for the indoor environment which might be considered as VVOCs due to different criteria. The filled (●) and open (○) circles denote substances which, according to ISO 16000-6, elute before and after n-hexane, respectively

plotted against the logarithm of the vapor pressure (Pa). The filled circles (●) denote substances which, according to ISO 16000-6, elute before n-hexane. The open circles (○) denote substances which, according to ISO 16000-6, elute after n-hexane; according to this definition, they are therefore deemed to be VOCs. In Figure 3, the boiling point for a number of substances is plotted against the gas chromatographic retention index in accordance with the ISO 16000-6 method.

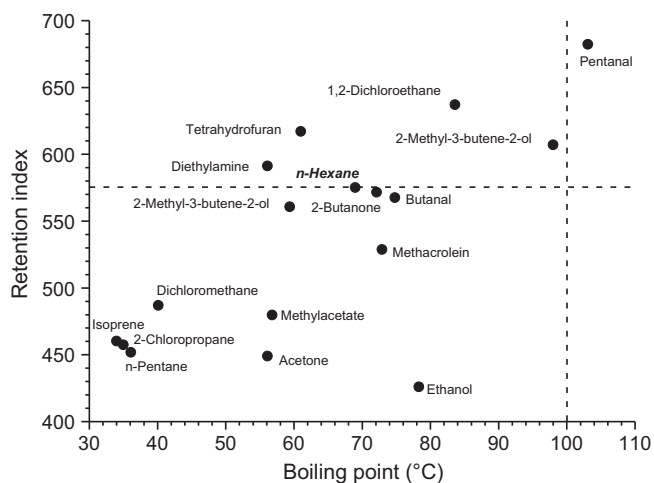


Fig. 3 Boiling point (°C) vs. gas chromatographic retention index (determined in accordance with ISO 16000-6) for selected VVOCs and VOCs. The horizontal dashed line indicates the retention index of n-hexane, and the vertical dashed line indicates a boiling point of 100 °C

From Figure 2, it can initially be seen that all potential VVOCs have a log vapor pressure of >2 (>100 Pa). Moreover, substances which, according to ISO 16000-6, elute before n-hexane have a log vapor pressure of >3 (>1000 Pa). The boiling point is not a strict criterion for distinguishing between VOCs and VVOCs. All organic compounds which have a boiling point of >100 °C, such as acetic acid, 1-butanol, furfural, and dimethylformamide (see Table 1 and Figure 2), are to be attributed to the VOCs. However, many substances with a boiling point of <100 °C can also be classed as VOCs, according to ISO 16000-6. Conversely, there are compounds with a boiling point of >69 °C (n-hexane) which are, according to ISO 16000-6, VVOCs. The number of carbon atoms can also not be used for the classification of VVOCs. As is clearly evident from Figure 3, pentanal, with a boiling point of 103.1 °C and a retention index of 682, is to be classified as a VOC. The same applies to tetrahydrofuran, triethylamine, etc. In contrast, butanal, with a boiling point of 74.8 °C and a retention index of 568, is a VVOC. To summarize, it can be determined that there is no meaningful way of classifying VOCs and VVOCs according to their physical-chemical properties. The definition should therefore be carried out in accordance with analytical criteria.

Methane cannot be analyzed via TD-GC/MS; the concentration in the atmosphere lies in the area of 2 ppm. Therefore, as is the case in atmospheric chemistry, only non-methane compounds should be considered as VVOCs. Expanding the analytical window of the ISO 16000-6 downwards to n-pentane (C5) would also appear to be impracticable. Although diverse VVOCs can be determined with this method, the development of a thermal desorption method for the analyt-

ical window of C2–C6 using multisorbent tubes would, however, appear to be useful. This, complemented by the DNPH method, would analytically cover most of the indoor-relevant VOCs and VVOCs.

Conclusion

So far, the only available definition for VVOCs has been published by the WHO (1989). For practical applications, this definition lacks sufficient precision. However, organic compounds with boiling points of 50–100 °C or below form a subgroup which should be taken more strongly into account when analyzing indoor and test chamber air. This study has shown that molecular properties such as vapor pressure, boiling point, and number of carbon atoms cannot be referred to in order to more strictly differentiate between VOCs and VVOCs. Extending the VOC definition to C5 is also not advisable due to the analytical difficulties. From a pragmatic perspective, only the analytical definition would seem suitable. According to ISO 16000-6 (2011), VVOCs are then defined as organic substances which elute before n-hexane in gas chromatography. A standardized GC/MS method for C2–C6 compounds is currently unavailable, although initial trials have been promising with selected target compounds on molecular sieve and subsequent TD-GC/MS analytics. An analytical method will be nonetheless much more elaborate than with the VOCs, as many of the potential VVOCs are gases at room temperature. For the low molecular weight carbonyls, TD-GC/MS analysis always needs to be complemented by the DNPH method or equivalent techniques.

Moreover, the question arises how VVOCs will be evaluated in the future. ISO 16000-6 in its current form clearly defines the TVOC value and therefore demands, if a sum value for VVOCs is desired, definition of a ‘TVVOC-value’ or ‘SVVOC-value’ (please note that AgBB (2012) has already introduced a ‘SVVOC-value’ for semi-volatile organic compounds). Alternatively, the analytical TVOC window could be extended. Single VVOCs in indoor air can be evaluated on the basis of available guideline values. In case of building product certification, VVOCs will probably be considered in the future by use of the LCI-concept (Lowest Concentration of Interest) (European Collaborative Action, 2013).

In summary, the extension of the standard analysis spectrum for compounds relevant to indoor air is advisable. It is also desirable to take into account compounds such as NH_3 and H_2S , which cannot be assigned to the VVOCs. Looking ahead, attention should also be paid to the other end of the VOC spectrum. AgBB (2012) defines semi-volatile organic compounds (SVOCs) according to ISO 16000-6 for the retention range C16–C22. There is need for discussion on this matter, too.

Acknowledgements

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1 VVOCs as classified by AgBB (2012) and AFSSET (2009).

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