



Cite this: *Environ. Sci.: Atmos.*, 2023, **3**, 474

Acetaldehyde in the indoor environment

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Acetaldehyde is a very volatile carbonyl compound with a boiling point of 20.1 °C. The industrial importance of acetaldehyde is comparatively small and tends to decrease. Nevertheless, the substance is ubiquitous in the environment, because acetaldehyde occurs in many chemical and biological processes as an intermediate and byproduct. Acetaldehyde plays an important role in atmospheric chemistry, it is formed during combustion and from the oxidation of fats and oils. Acetaldehyde primarily occurs in the metabolism of plant and animal organisms. Due to the diverse chemical reactions, there are a large number of potential sources, which means that acetaldehyde is also important for the indoor environment. Building products are often rich in fatty acids, which slowly decompose under the formation of aldehydes. Sources from human activities include the preparation of food, burning of candles, wood, and ethanol, as well as the consumption of cigarettes and e-cigarettes. Many other products and devices can release acetaldehyde, the human respiratory gas must not be disregarded, and acetaldehyde is present in outdoor air. Several organizations and institutions regard acetaldehyde as a priority indoor pollutant. This is due to its acute and chronic effects, but also to its classification as a carcinogenic substance. There are sufficient data for acetaldehyde in the atmosphere, as the substance is easily accessible analytically using the DNPH method and is thus often recorded in measurements. Nevertheless, to date, there has been no scientific work that comprehensively characterizes and evaluates acetaldehyde indoors. From the point of view of the necessity of such a summary, an overview of the properties of acetaldehyde and the most important reaction mechanisms is given, followed by a discussion of potential sources and indoor air concentrations. Finally, a health-related assessment of the substance is provided on the basis of indoor guide values.

Received 1st November 2022

Accepted 1st December 2022

DOI: 10.1039/d2ea00146b

rsc.li/esatmospheres



Environmental significance

Acetaldehyde is a substance that is of great importance in environmentally relevant processes in both living and non-living nature. At the same time, the occurrence and thus the health effects of acetaldehyde on humans are difficult to evaluate, since it is an intermediate and byproduct whose formation and release depends on many factors. On average, exposure to acetaldehyde indoors is significantly higher than outdoors. It therefore seems appropriate and necessary to carry out an assessment of acetaldehyde for the indoor environment.

1 Introduction

A large number of organic indoor air pollutants have been identified up to the present day. However, the scientific and public interest in specific substances and substance groups changes over certain periods of time. There are many reasons for this, including their use, substitution and bans in industrial products, new toxicological classifications, and the introduction or updating of guide values.¹ For many years, acetaldehyde was only considered in classical atmospheric chemistry because it is a byproduct from the oxidation of ethane and a precursor to the formation of peroxyacetyl nitrate (PAN).² Interest in acetaldehyde as an indoor pollutant began with a WHO report from 1989,³ which states cigarette smoke as the main source. In the

early 1990s, it was shown that there are a number of other sources of acetaldehyde indoors. The substance is easily accessible analytically *via* the DNPH method and has therefore often been measured. However, it mostly went under the radar, since at that time the interest in very volatile and volatile organic compounds (V VOCs and VOCs) was dominated by formaldehyde, solvents, terpenes, and higher aldehydes. The acetaldehyde concentrations measured indoors are often inconspicuous and are pushed into the background by other carbonyl compounds.

In 2001, an expert group of the European Union classified acetaldehyde as one of the 14 indoor pollutants, which need a detailed assessment.⁴ Logue *et al.*⁵ evaluated the results from 77 published studies reporting measurements of chemical pollutants in residences in the United States. Acetaldehyde was one of the 9 substances that were identified as priority hazards based on the robustness of measured concentration data and

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the fraction of residences that appeared to be impacted. This assessment of Logue *et al.*⁵ is essentially based on the U.S. EPA's Reference Concentration for Chronic Inhalation Exposure (RfC) of 0.009 mg m^{-3} . In his 2009 publication on changes in indoor pollutants since the 1950s, Weschler⁴ names acetaldehyde as one of the five VVOCs, but states that the trend regarding its importance for the indoor environment is undetermined. On the basis of pending reassessments by IARC and the EU with regard to carcinogenicity, Salthammer⁶ later came to the conclusion that in the future, acetaldehyde will receive a lot more attention in indoor air studies.

With the exception of formaldehyde, the group of VVOCs, which includes acetaldehyde, was not considered in the first approaches for the assessment of building materials.⁷ It took until 2013 that acetaldehyde was recognized as a priority pollutant in the harmonization framework for health-based evaluation of indoor emissions from construction products in the European Union and an LCI (lowest concentration of interest) value was derived.⁸ Despite the growing interest in indoor exposure to acetaldehyde, there is still no comprehensive overview of this substance. This may also be due to the fact that acetaldehyde is difficult to classify as a typical intermediate and reaction product. There is only vague information on the respective sources and emission levels, the same applies to the room air concentrations. In the present work, the physical and health-related properties of acetaldehyde are first described. After an outline of the analytical methods, the second part focuses on the emission sources and indoor air concentrations with reference to guide values. The cited literature was chosen to be representative for the respective topic. With the information presented, the reader has the opportunity to better assess the emission of and exposure to acetaldehyde indoors.

2 Properties of acetaldehyde

2.1 Molecular properties

The mesomeric boundary structures of the aprotic compound acetaldehyde are shown in Fig. 1. Its tautomer vinyl alcohol ($\text{CH}_2 = \text{CH-OH}$) is not stable at room temperature. The



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absorption maximum at 290 nm results from an $n \rightarrow \pi^*$ transition, and the absorption cross section at this wavelength is $\sigma(298 \text{ K}) = 4.86 \times 10^{-20} \text{ cm}^2$ per molecule.⁹ In the atmosphere, acetaldehyde is an important precursor for peroxyacetyl nitrate (PAN). In the first step (see eqn (1)), the main reaction with the OH radical leads to the acetyl radical. PAN is then formed in the well-known subsequent reactions with oxygen and nitrogen dioxide.²

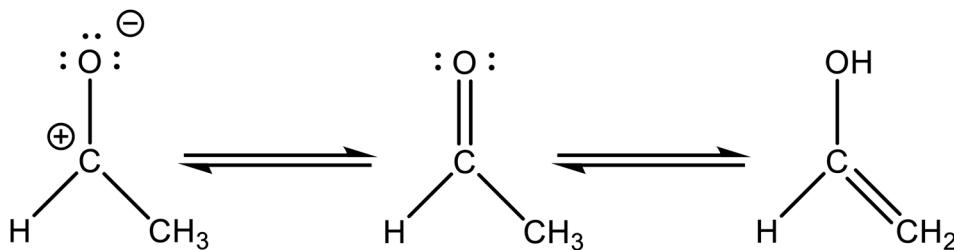


At 20 °C, acetaldehyde is a low-viscosity, flammable and colorless liquid. The substance is completely miscible with water, at low concentrations it causes a sharp and fruity odor. According to Ruth,¹⁰ the odor thresholds are between 0.0002 mg m^{-3} and 4.14 mg m^{-3} . Amoore and Hautala¹¹ state an odor threshold in air of 0.050 ppm. Devos *et al.*¹² evaluated various studies and arrived at an odor threshold of 0.19 ppm (0.34 mg m^{-3}). Because of its fruity aroma, acetaldehyde is used as a flavoring agent.¹³ The molecular properties of acetaldehyde are summarized in Table 1. The LFER (linear free energy relationship) parameters are Abraham coefficients. They allow kinetic and thermodynamic molecular properties to be calculated using QSAR approaches.¹⁴ Acetaldehyde is a reactive compound. At room temperature, the trimeric molecule paraldehyde is formed by cyclization in the presence of acids. Furthermore, acetaldehyde tends to undergo aldol addition and aldol condensation. Acetaldehyde also forms hydrates in aqueous solution.

2.2 Health-related properties

According to the Globally Harmonized System of Classification and Labeling of Chemicals, acetaldehyde is flammable (GHS02), harmful (GHS07), and a health hazard (GHS08). The European Chemicals Agency (ECHA) classifies acetaldehyde as carcinogenic (category 1B) and suspected to be mutagenic (category 2). The International Agency for Research on Cancer (IARC) has listed acetaldehyde as a Group 2B (possibly carcinogenic to humans) carcinogen on the basis of inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in experimental animals. However, if associated with the consumption of alcoholic beverages, the classification is Group 1 (carcinogenic to humans). In 2019, IARC concluded that there were sufficient data for a reassessment. Acetaldehyde is acutely irritating to the eyes and respiratory tract and has central nervous system effects. The occupational exposure limit (OEL) in the European Union is 91 mg m^{-3} (50 ppm). The agreed EU-LCI value (with status 2022) is $300 \mu\text{g m}^{-3}$.²⁵ The previous value as derived in 2013 is $1200 \mu\text{g m}^{-3}$.⁸ EU-LCI values are health-based reference concentrations of volatile organic compounds for inhalation exposure used to assess emissions after 28 days from a single product during a laboratory test chamber procedure as defined in the EN 16516.²⁶

The most comprehensive study on the toxicology of acetaldehyde with reference to the indoor environment was presented by the *ad hoc* working group of the German Federal



Mesomeric structures

Tautomer

Fig. 1 Mesomeric and tautomeric structures of acetaldehyde.

Table 1 Molecular properties of acetaldehyde

Parameter	Value	Ref.
Systematic IUPAC name	Ethanal	
Molecular formula	CH ₃ CHO	
CAS	75-07-0	
SMILES	CC=O	
Molecular weight (MW)	44.05 g mol ⁻¹	15
Melting point (m.p.)	-123.4 °C	15
Boiling point (b.p.)	20.8 °C	15
Density (ρ)	0.785 g cm ⁻³ (20 °C)	15
Dipole moment (μ)	2.750 D	15
Polarizability (α)	4.30 × 10 ⁻²⁴ cm ³	16
Refraction index (n_D)	1.3316 (20 °C)	15
Dielectric constant (ϵ)	21.0 (20 °C)	15
$\log K_{OW}$	0.45	17
$\log K_{OA}$	1.98	18
$\log K_{Hda}$ (L)	1.22	18
Henry constant (H)	1.3 × 10 ⁻¹ mol (m ³ Pa) ⁻¹	19
Antoine coefficients (219–313 K)	$A = 61\,814$ $B = 1070.6$ K $C = -37.15$ K	20
$\Delta_{vap}H$	25.8 kJ mol ⁻¹ (293.3 K)	21
LFER parameters	$A = 0.00$ $B = 0.45$ $E = 0.21$ $S = 0.67$ $L = 1.23$ $V = 0.4061$	22
Proton affinity	768.5 kJ mol ⁻¹	23
k (proton transfer)	3.36 × 10 ⁻⁹ cm ³ s ⁻¹	16
k (OH)	14.7 × 10 ⁻¹² cm ³	24
k (O ₃)	per molecule per s (298 K) 3.4 × 10 ⁻²⁰ cm ³ per molecule per s (298 K) 1 ppb = 1.801 µg m ⁻³	24
Conversion factor ($T = 298$ K, $p = 1013$ mbar)		

Environment Agency for the derivation of indoor air guide values.²⁷ The study by Dorman *et al.*²⁸ was used as the starting point for deriving the LOAEC (lowest observed adverse effect concentration). After subchronic inhalation exposure of rats to 270 mg m⁻³ (150 ppm), Dorman *et al.*²⁸ observed degeneration and vacuole formation in the olfactory nasal epithelium with loss of olfactory neurons. Note that despite the carcinogenic

properties of acetaldehyde, guide values are derived. It is assumed that at concentrations below these guide values, no significant contribution to the cancer risk for humans is to be expected. A detailed discussion of indoor guide values is provided in Section 6.

3 Production and formation of acetaldehyde

3.1 Industrial production

Acetaldehyde was first synthesized by Carl Wilhelm Scheele in the 18th century when he was trying to oxidize ethanol. However, it was Justus Liebig who characterized the compound as a dehydrated alcohol and coined the name “aldehyde”. The classic synthesis with ethanol involves the use of strong oxidizing agents such as chromic acid. For large-scale synthesis, acetaldehyde is produced using the Wacker process by catalytic water addition to ethene with simultaneous air oxidation over fixed-bed catalysts. Eqn (2) describes the formal reaction.



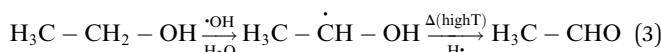
The annual global production of acetaldehyde varies between one and two million tons, depending on its importance and demand for the raw material market. It essentially serves as an intermediate in the production of several industrial chemicals.²⁹

3.2 Formation *via* natural processes

Combustion processes are the main source of acetaldehyde in outdoor air. These include road traffic³⁰ and emissions in the industrial³¹ and private³² sectors. The basic mechanisms of potential indoor sources are explained below. Specific sources are discussed in Section 5.

3.2.1 Ethanol combustion. As a substitute for conventional fuels, ethanol was already being used in Brazil in the mid-1970s. The aim was to become less dependent on oil imports. However, the campaign did not take into account that most of the existing engines were not designed for the combustion of ethanol at all. This caused extreme pollution with carbonyl compounds in Brazilian cities.³³ During the ethanol combustion process, a hydrogen atom is first abstracted, usually by an OH radical.

This leads to the formation of the α -hydroxyethyl radical. At high temperatures, abstraction of another hydrogen atom results in acetaldehyde according to eqn (3).³⁴



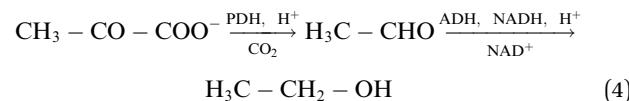
Ethanol combustion also takes place indoors, mostly with open flames. Typical sources are ethanol stoves and fondue burners.^{35,36}

3.2.2 Wood combustion and thermal degradation. One of the main concerns related to residential wood firing is their high level of emissions from incomplete combustion.³⁷ These emissions are very variable and depend on factors such as combustion conditions and wood properties. The incomplete oxidation produces organics and carbonyl compounds are among the main components. The mechanism of formation is primarily based on the pyrolysis of cellulose, hemicellulose, and lignin. The process starts at 300–500 °C *via* the depolymerization of cellulose, producing levoglucosan as the main component.³⁸ Above 500 °C, the ring opening of levoglucosan takes place, and dehydration and decarboxylation processes then lead to the formation of formaldehyde, furfural, acetaldehyde, and other degradation products.³⁹ Substances such as formic acid, acetaldehyde, and acetic acid can already be formed under mild thermal stress on wood and wood products. The hemicelluloses of wood, especially the xylans of hardwoods, contain carboxyl and acetyl groups that can split off even at low temperatures.⁴⁰

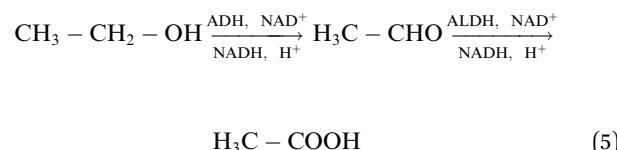
3.2.3 Smoking and vaping. With the conventional consumption of tobacco products through smoking, the formation processes of acetaldehyde are similar to those of wood combustion. The natural polysaccharides, including cellulose, are the primary precursors to acetaldehyde in mainstream and sidestream smoke.⁴¹ Additives such as sugar, sorbitol, and glycerol are added to tobacco products, which can also form pyrolytic acetaldehyde. The formation of formaldehyde, acetaldehyde, and acrolein from glycerol has been particularly well investigated both theoretically and experimentally.⁴² In addition to the health effects, the role of acetaldehyde in relation to tobacco smoke addiction is discussed in the literature.⁴³ In electronic cigarettes, it is essentially glycerol, propylene glycol, and triacetin that are the precursor compounds from which acetaldehyde is formed by pyrolysis.^{44,45} Depending on their chemical composition, the flavorings can also play a role.⁴⁶

3.2.4 Thermal degradation of fatty acids. Certain foods and their preparation processes are significant sources of acetaldehyde release.^{47,48} The reaction mechanisms have been well studied and are explained in the following example. A product of the thermal autoxidation of linoleic acid (*cis,cis*-9,12-octadecadienoic acid) is 2,4-decadienal. In a deep frying process, this is split into 2-octenal and acetaldehyde after the addition of water. In the analogous subsequent step, degradation to acetaldehyde and *n*-hexanal takes place.⁴⁹ It should be mentioned that acetaldehyde is found in a variety of foods. It is either formed by the Strecker degradation of amino acids, for example, as part of the Maillard reaction, or it is actively added to the product as a flavoring.⁵⁰

3.2.5 Alcoholic fermentation. The decomposition of glucose under anaerobic conditions in the presence of yeast and other microorganisms leads to ethanol. In the first phase, glycolysis, glucose is converted in several enzymatically catalyzed steps to pyruvate, the anion of pyruvic acid. The pyruvate is then decarboxylated, catalyzed by the enzyme pyruvate decarboxylase (PDH). This produces acetaldehyde, which is reduced to ethanol by alcohol dehydrogenase (ADH) involving nicotinamide adenine dinucleotide (NAD⁺/NADH) as shown in eqn (4).⁵¹



3.2.6 Ethanol metabolism. In the human body, ethanol is metabolized to acetaldehyde with the participation of NAD⁺/NADH and catalyzed by ADH. As shown in eqn (5), this is then metabolized to acetic acid *via* the enzyme aldehyde dehydrogenase (ALDH) and NAD⁺/NADH.⁵¹ The process leads to a significantly increased concentration of acetaldehyde in human breath after alcohol consumption.⁵²



3.2.7 Biosynthesis in plants. Koppmann⁵³ summarized available publications on the biogenic formation of acetaldehyde. Alcohol dehydrogenase also occurs in the leaves of plants. The production of acetaldehyde is particularly strong in plant stress situations such as anaerobic conditions in the roots, drought, extreme cold, and high concentrations of ozone and sulfur dioxide. A clear increase in acetaldehyde emissions was observed during abrupt light-dark transitions. Seinfeld und Pandis estimate the annual release of acetaldehyde into the atmosphere at 213 Tg per year.⁵⁴

3.2.8 Indoor chemistry. As already mentioned, acetaldehyde is an important intermediate in atmospheric chemistry. It is formed by both ozonolysis and photolysis of VOCs. Sommariva *et al.*⁵⁵ provided a comprehensive listing of atmospheric precursors. Calogirou *et al.*⁵⁶ as well as Lee *et al.*⁵⁷ described the formation of acetaldehyde from terpene/ozone reactions. These reactions can occur in the gas phase or on surfaces. Lee *et al.*⁵⁷ also found that the yield of acetaldehyde from the ozonolysis of non-cyclic terpenes such as myrcene and linalool is higher than that of cyclic terpenes. Because many products used indoors contain precursors, acetaldehyde also plays a role in indoor chemistry.⁵⁸ Well-documented sources include the reaction of wall paint with ozone,⁵⁹ reaction of carpet with ozone,^{60,61} reaction of terpene-based air fresheners with ozone,⁶² reaction of carpet deodorizers with ozone,⁶³ photocatalytic wall paint,^{64,65} and use of mobile UV air-cleaning devices.⁶⁶

3.2.9 Degradation of polymers. Some polymers contain carboxyl groups as esters of acetic acid. These include polyvinyl acetate (PVAC), ethylene vinyl acetate copolymer (EVA), and



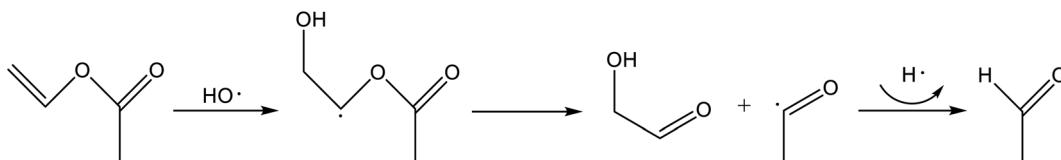


Fig. 2 Photocatalytic formation of acetaldehyde from vinyl acetate as proposed by Gandolfo *et al.*⁶⁹

cellulose acetate (CA). PVAC is often found indoors because it is used as a binder in paints and varnishes, in glue, wallpaper paste, and adhesive. Polymeric esters can release acetaldehyde through thermal⁶⁷ or photochemical decomposition,⁶⁸ but these processes hardly take place under normal living conditions. However, the photocatalytic degradation of PVAC *via* OH radicals as proposed by Gandolfo *et al.*⁶⁹ and shown in Fig. 2 seems to be of particular relevance indoors.

4 Sampling and analysis of acetaldehyde

The concentration of short-chain aldehydes in the gas phase can be precisely measured using a variety of methods. A good overview is provided by Vairavamurthy *et al.*⁷⁰ For the specific determination of individual components, however, colorimetric methods using UV detection are not recommended, since the sum values of different carbonyls are essentially determined. This applies both to derivatization with the Hantzsch reagent 3,5-diacyl-1,4-dihydrolutidine (DDL) and to 3-methyl-2-benzothiazolonehydrazone (MBTH).⁷¹ The DNPH method and online mass spectrometry are of major practical importance today. These methods are discussed in detail below.

4.1 DNPH method

As shown in Fig. 3, carbonyl compounds can react with 2,4-dinitrophenylhydrazine (DNPH) to form the hydrazone by elimination of water. The derivatives are analyzed utilizing high-performance liquid chromatography (HPLC) with UV detection or diode array detection. This method, as described in ISO 16000-3,⁷² is used most frequently worldwide to determine acetaldehyde in indoor air. Cartridges packed with silica gel are used to sample aldehydes and ketones. The silica gel is coated with dinitrophenylhydrazine as the derivatization reagent. Approximately 50–100 L of air is drawn through the cartridge with a volume flow of 0.5–1.5 L min⁻¹. The derivatization, therefore, takes place directly on the cartridge. The hydrazones formed are then eluted with acetonitrile. This eluate is used for the HPLC determination.

The chromatographic separation is carried out using a reverse phase C18 column and a water/acetonitrile or water/methanol solvent combination as the mobile phase. The absorption maxima for the different hydrazones are in the range of 345–425 nm.⁷⁰ For the acetaldehyde DNPH derivative the absorption maximum is 363 nm. The precise analytical parameters for the DNPH method can also be found in ISO 16000-3.⁷² Fig. 4 shows the chromatogram of a multistandard. Modern HPLC devices allow complete spectra to be recorded, which significantly improves the sensitivity of the method. Interference of ozone⁷³ can be avoided by the use of an ozone scrubber placed in front of the cartridge. Nitrogen dioxide (NO₂) also interferes by forming 2,4-dinitrophenyl azide.⁷⁴ An automated sampling and analysis system based on DNPH was introduced by Aiello and McLaren.⁷⁵

For standardized analysis, the usual detection limits are in the range of 0.5–1.0 $\mu\text{g m}^{-3}$. Note that the DNPH method is primarily suitable for short-chain aldehydes C1–C4. From C5 (pentanal), sampling on Tenax TA followed by thermal desorption gas chromatography/mass spectrometry (GC/MS) is preferable.⁷⁶ Acrolein cannot be reliably analyzed by the DNPH method.⁷⁷ DNPH is also suitable for passive sampling. The collection rates for acetaldehyde and other carbonyl compounds were determined by Birmili *et al.*⁷⁸

4.2 PTR-MS and SIFT-MS

If a high time resolution is required, proton transfer reaction mass spectrometry (PTR-MS) can be used to measure acetaldehyde. In this method, the corresponding compound of molecular weight MW is protonated by H₃O⁺ according to eqn (6), so the target ion is *m/z* [MW + 1].



Reaction (6) takes place because the proton affinity of acetaldehyde, at 768.5 kJ mol⁻¹,²³ is significantly higher than that of water, at 691 kJ mol⁻¹.⁷⁹ The essential components of a PTR-MS instrument are the ion source, the drift tube and the analysis system (quadrupole mass analyzer or time-of-flight (TOF) mass spectrometer). Commercially available PTR-MS devices have

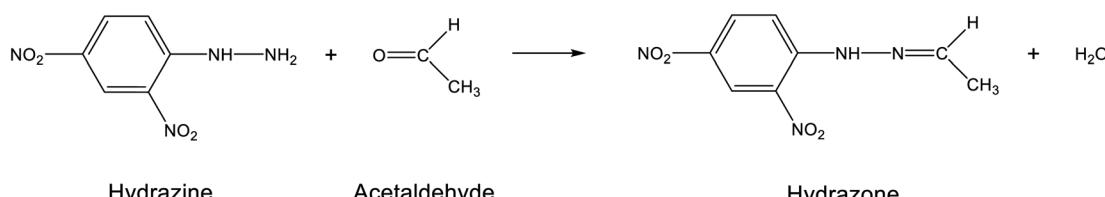


Fig. 3 Formation of 2,4-dinitrophenylhydrazone from DNPH and acetaldehyde. See ISO 16000-3 (ref. 72) for the analytical parameters.



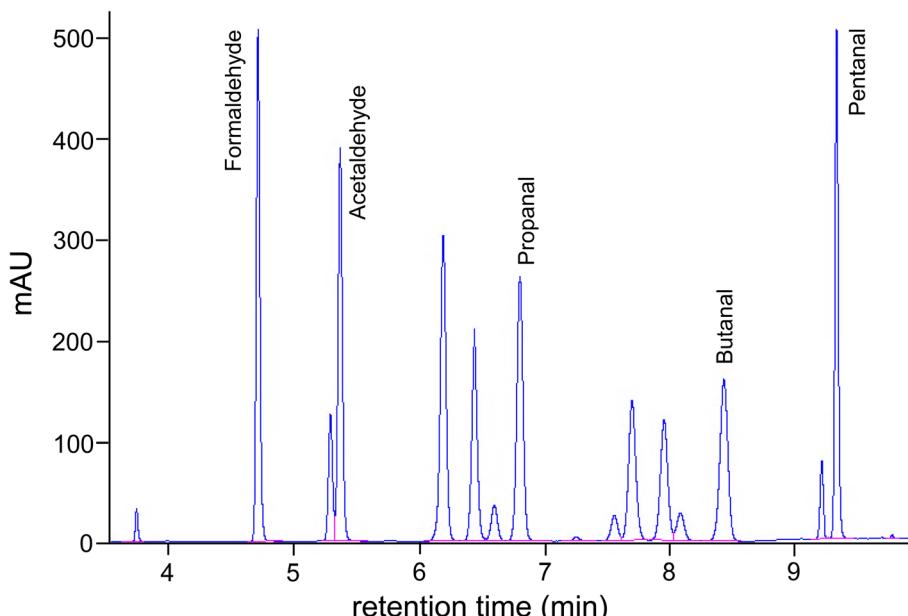


Fig. 4 Chromatogram (HPLC) of a DNPH multistandard.

a response time of about 100 ms, which enables a high temporal resolution, and reach a detection limit in the lower ppt range. The theoretical and technical details of the technique are described in detail in the book by Ellis and Mayhew.⁸⁰

With a molecular weight of 44.05 g mol⁻¹, the nominal mass of the target ion when detected with a low-resolution quadrupole mass filter is *m/z* 45. It is advantageous that only comparatively few substances such as carbon dioxide, propane, and ethylene oxide can interfere with this *m/z* value. At 541 kJ mol⁻¹, carbon dioxide has a lower proton affinity than water and is therefore hardly protonated, but the CO₂H⁺ ion can still cause interference due to the high concentration of carbon dioxide in the air. The proton affinity of propane is 626 kJ mol⁻¹. However, the concentration in the outside and inside air can vary greatly,⁸¹ since propane is a component of liquid gas and is also released through combustion processes. Ethylene oxide is not common in indoor air. Price *et al.*⁸² discussed correction factors for acetaldehyde when using a quadrupole PTR-MS to account for possible interference from the ethylene glycol fragment HO-CH₂-CH₂. An exact assignment can be made with high-resolution TOF mass spectrometry, which also allows the analysis of isotopes and complex mixtures of substances, which usually occur in the indoor environment.⁸³ The monoisotopic mass of acetaldehyde (sum of the most abundant stable isotope masses of each atom in the molecule) is 44.026 Da. A comparison of the quadrupole and the TOF technique for indoor applications is provided by Schripp *et al.*⁸⁴

A much-discussed question concerns the calibration of the PTR-MS. The use of standard compounds is possible, but usually the calibration is done *via* the proton transfer reaction rate constant *k*_{pt} according to eqn (7).

$$[R] = \frac{1}{k_{pt} \times t_r} \frac{[\text{RH}^+]}{[\text{H}_3\text{O}^+]} \quad (7)$$

[R] is the concentration of the target compound and *t*_r is the average drift time of the ions in the reaction region. The reaction constant *k*_{pt} can be calculated from ion-molecule collision theory⁸⁵ using the dipole moment and the polarizability of the target molecule. Cappellin *et al.*⁸⁶ have published acetaldehyde *k*_{pt} values between 2.83 × 10⁻⁹ cm³ s⁻¹ and 3.40 × 10⁻⁹ cm³ s⁻¹ for various *E/N* ratios, where *E* is the electric field in the drift tube, and *N* is the gas number density. Zhao and Zhang¹⁶ provide a value of 3.36 × 10⁻⁹ cm³ s⁻¹.

A closely related technique is selected-ion-flow-tube-mass-spectrometry (SIFT-MS). The main difference is that a quadrupole mass filter selects the ions produced in the source based on their mass-to-charge ratio. As a result, only certain ions get into the reaction chamber. The ions are generated by plasma discharge from cleaned, humidified air using a microwave resonator. This means that other ions such as NO⁺, O₂⁺, etc. are available for selection in addition to H₃O⁺. Fundamentals and applications are detailed in the review by Smith and Španěl.⁸⁷

4.3 Other methods

Many other methods for measuring acetaldehyde in the atmosphere have been published, but these are practically irrelevant for indoor use and will not be discussed further here. A compilation of methods based on colorimetry, fluorescence, and gas chromatography, specific and non-specific for acetaldehyde, is offered by Vairavamurthy *et al.*⁷⁰ Various reagents for the derivatization of aldehydes are described by Vogel *et al.*⁸⁸

5 Indoor emission rates and sources

The basic mechanisms of acetaldehyde formation have already been described in Section 3. This part now deals with the categorization of the specific indoor sources as compiled in Table 2. The influence of the outside air is discussed in a later section.



Table 2 Acetaldehyde sources in the indoor environment

Source	Comment	Ref.
Candles (scented, unscented)	24 candles; 8 m ³ chamber; range \leq 16–82 μg per candle per h	89
Candles (scented)	5 candles, chamber; max. emission rate: 1.12 $\mu\text{g g}^{-1}$	90
Mosquito coils and candles	5 mosquito coils; 18 m ³ chamber emission rate: 1000–2000 $\mu\text{g g}^{-1}$	91
Ethanol fireplaces	Different fuels; 42 m ³ chamber concentration: 150–570 $\mu\text{g m}^{-3}$	35
Wood-burning fireplace ovens	7 private homes; range 12–89 $\mu\text{g m}^{-3}$	92
Wood combustion	Different wood types and ovens emission rate: 1.3–1704 mg kg ⁻¹	37, 38, 93 and 94
Environmental tobacco smoke	Conventional cigarettes emission rate: 2360 μg per cig.; 2480 μg per cig.	95
e-cigarettes	Formation from propylene glycol: 50–1650 $\mu\text{g m}^{-3}$ in puffs	96 and 97
e-cigarettes	Formation from triacetin	45
e-cigarettes	Release per puff maximum emission rate: 135 468 ng per puff	98
Heated tobacco products	3 heatsticks, 200 L chamber emission rates: 18–181 μg per heatstick	99
Cooking	Laboratory kitchen, different food types emission rates: 19–110 $\mu\text{g (g}_{\text{oil}}\text{ h})^{-1}$	48
Cooking	Laboratory kitchen, different food types concentrations in fume: 7–274 $\mu\text{g m}^{-3}$	47
Building materials	23 products; 23 L chamber emission rates: \leq 1.3–500 $\mu\text{g (m}^2\text{ h})^{-1}$	100
Plaster with vegetable oil	Different oils, 20 L chamber emission rate: 8.0–523 $\mu\text{g (m}^2\text{ h})^{-1}$	101
Wood-based materials	20 L chamber emission rates in dependency of time	102
Wood, wood-based materials	34 samples; 1 m ³ chamber concentration: \leq 3–245 $\mu\text{g m}^{-3}$	103
Particleboard	4 samples; 1 m ³ chamber emission in dependency of surface coating	104
Leather	Emissions at 80 °C	105
Photocatalytic wall paint	3 products; 1 m ³ chamber maximum concentration: 106 $\mu\text{g m}^{-3}$	64
Photocatalytic wall paint	6 products; 27 L chamber concentration (2 h): 15–898 $\mu\text{g m}^{-3}$	65
Photocatalytic wall paint	3 products, flow tube photoreactor emission rate: 257 $\mu\text{g (m}^2\text{ h})^{-1}$	69
Photocatalytic air cleaners	4 devices; 24 m ³ and 48 m ³ chamber maximum concentration: 8–67 $\mu\text{g m}^{-3}$	66
Photocatalytic air cleaner	1 device, model room: 9.2–189 $\mu\text{mol h}^{-1}$	106
Exhaled human breath	10 probands range: 29–82 ppb	52
Exhaled human breath	30 probands: 50-P = 22 ppb; 95-P = 52 ppb	107

Combustion processes are certainly the strongest and most important indoor sources. With regard to the starting materials, these can be roughly divided into candles, ethanol, and wood. Tobacco products are more complex in their application. In addition to the classic cigarette, there are electronic cigarettes, heat-not-burn techniques, and water pipes. However, individual product groups can also show significant differences in their emission behavior, as will be demonstrated using the example of candles. In order of an optimized burning performance, fuel, additives, wick, and candle geometry must be matched to each other. Common fuels are paraffin, stearin, wax, and palm. With scented candles, different types of additives are added. Salthammer *et al.*⁸⁹ have detailed the constituents of various fragrances. It was found that the release of acetaldehyde from burning candles depended largely on their chemical composition. This is shown in Fig. 5, where the use of the “Fresh” and “Fruit” fragrances leads to significantly increased acetaldehyde emission rates of up to 82 μg per candle per h. These two fragrances already contain different aldehydes, esters, and oils in their formulation.⁸⁹ If the candle does not contain any fragrances, only low acetaldehyde emissions result. All investigations were carried out in an 8 m³ chamber under identical conditions. In their test chamber investigations, Derudi *et al.*⁹⁰ arrived at emission rates of between approximately 0.5 $\mu\text{g g}^{-1}$ and 1.12 $\mu\text{g g}^{-1}$ for five scented candles. The authors state that their results are in the range of similar studies. Lee and Wang⁹¹ examined the emissions from mosquito coils and measured high emission rates for acetaldehyde of around 1000–2000 $\mu\text{g g}^{-1}$. The result could be expected since mosquito coils usually

smolder more than they burn, which leads to the formation of byproducts. Habarta *et al.*³⁵ measured acetaldehyde concentrations between 150 $\mu\text{g m}^{-3}$ and 570 $\mu\text{g m}^{-3}$ in 42 m³ chamber experiments on ethanol fireplaces. Wegscheider *et al.*¹⁰⁸ studied the emissions of sauna essences on hot stones at 500 °C and found release rates for acetaldehyde up to 61 mg ml⁻¹ essence.

Various works have been published on the formation of acetaldehyde during wood combustion. A summary is provided by Reda *et al.*³⁸ on the basis of their own data with reference to the publications by Schauer *et al.*,⁹³ Hedberg *et al.*⁹⁴ and Cerqueira *et al.*³⁷ The results differed widely with emission rates between 1.3 mg kg⁻¹ (pellet boiler) and 1704 mg kg⁻¹ (fireplace). The most important influencing factors were the type of wood, the wood moisture content, and the combustion process. All measurements were carried out in the exhaust gas section of the chimney. The direct impact of wood burning on indoor air quality was studied by Salthammer *et al.*⁹² When measurements were taken in a total of seven living rooms, the acetaldehyde concentration was between 12 $\mu\text{g m}^{-3}$ and 80 $\mu\text{g m}^{-3}$. Gustafson *et al.*¹⁰⁹ also found that domestic wood burning increases the acetaldehyde concentration in living spaces.

A frequently discussed topic is emissions from smoking and vaping. The classic cigarettes are studied in detail, and the amounts of pollutants, including acetaldehyde, in mainstream, sidestream, and environmental tobacco smoke (ETS), are well known. Singer *et al.*⁹⁵ measured acetaldehyde emission rates of 2360 μg per cigarette and 2480 μg per cigarette in ETS of a 50 m³ room. The formation of acetaldehyde in e-cigarettes is also well studied. Sleiman *et al.*⁹⁷ as well as Azimi *et al.*⁹⁶ assume that the



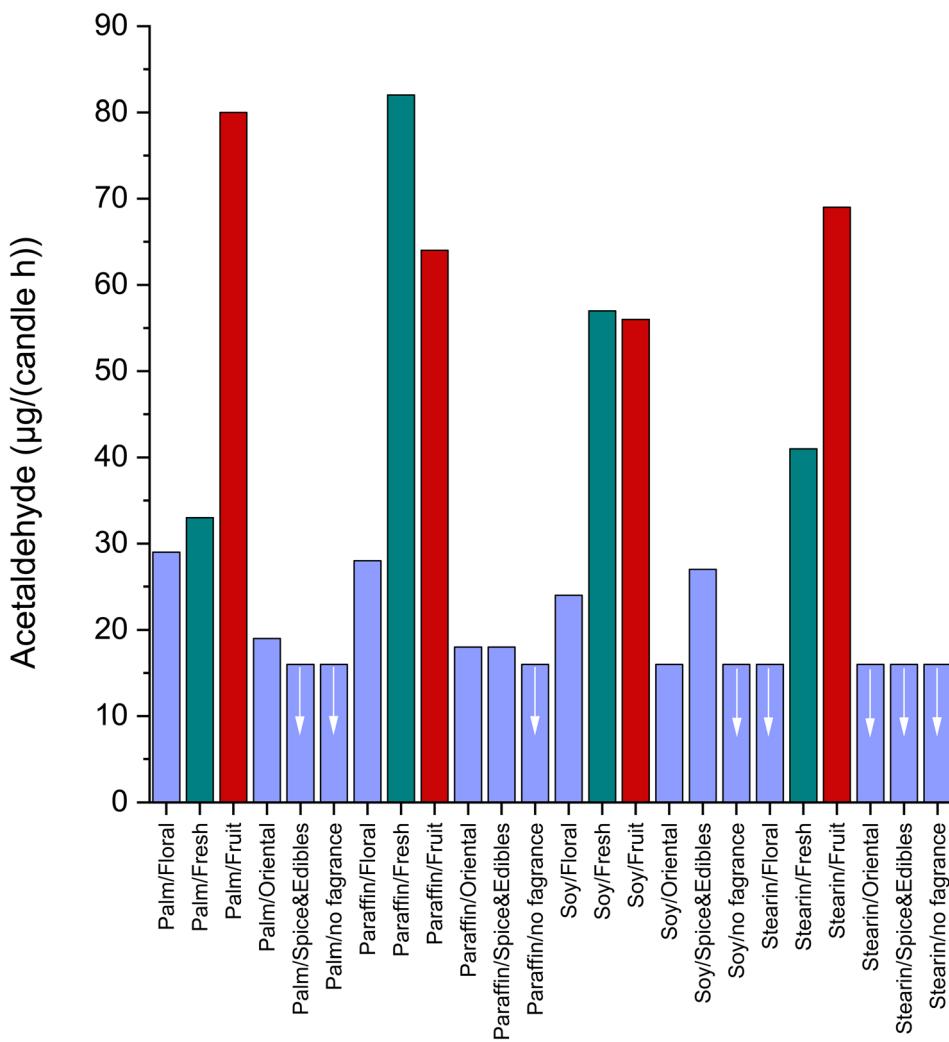


Fig. 5 Acetaldehyde emission rates from burning candles in dependence of fuel and fragrance. Green bars represent "Fresh", red bars represent "Fruit" and blue bars represent all other fuel/fragrance combinations. The arrows indicate an emission rate $\leq 16 \mu\text{g}$ (candle per h). See Salthammer *et al.*⁸⁹ for details on candles and experimental conditions.

first step is a dehydrogenation of propylene glycol. The methylglyoxal thus formed then thermally decomposes to formaldehyde and acetaldehyde. The acetaldehyde concentrations in the e-cigarette puffs varied between $50 \mu\text{g m}^{-3}$ and $1650 \mu\text{g m}^{-3}$. Vreeke *et al.*⁴⁵ found that triacetin enhances the levels of acetaldehyde and other substances in the aerosol of e-cigarettes. The publication by Beauval *et al.*⁹⁸ contains a compilation of literature data on the release of acetaldehyde from e-cigarettes with emission rates up to $135\text{--}468 \text{ ng per puff}$. Geiss *et al.*¹¹⁰ found a significant increase in the release of acetaldehyde from e-cigarettes when the electrical power of the heating coil was increased.

With some technologies, tobacco is just heated. Such so-called heat-not-burn products were investigated by Cancelada *et al.*⁹⁹ Acetaldehyde emission rates of $151\text{--}181 \mu\text{g}$ per heatstick were measured in the mainstream and emission rates of $19\text{--}24 \mu\text{g}$ per heatstick in the sidestream. The authors conclude that exposure to acetaldehyde is significantly higher for heat-not-burn products than for e-cigarettes. Other studies also

compared the release of pollutants when using indoor combustion sources, e-cigarettes, and tobacco heating systems under realistic conditions. Mitova *et al.*¹¹¹ found an increase in acetaldehyde concentration when using a tobacco heating system, but the highest values were achieved with conventional cigarettes. Ruprecht *et al.*¹¹² came to analogous results.

It has long been known that food preparation can also be a strong indoor source for acetaldehyde. A comprehensive study was published by Zhang *et al.*⁴⁸ The emissions of carbonyl compounds from heating 5 edible oils, 3 seasonings, and 2 dishes were examined in a laboratory kitchen. The sampling took place in the air duct above the ventilation range hood. The emission rates for acetaldehyde ranged from $19 \mu\text{g (g}_{\text{oil}} \text{ h)}^{-1}$ (heating soybean oil and chili powder) to $110 \mu\text{g (g}_{\text{oil}} \text{ h)}^{-1}$ (heating rapeseed oil). A study with a similar design was previously performed by Peng *et al.*⁴⁷ The aldehyde emissions in cooking oil fumes were examined. The results are essentially the same as those of Zhang *et al.*,⁴⁸ but only the concentrations are given. For acetaldehyde, these range from $7 \mu\text{g m}^{-3}$ (stir frying

of soybean oil) to $274 \mu\text{g m}^{-3}$ (deep frying of rapeseed oil). Acetaldehyde is also a flavor component in bread¹¹³ and orange juice.¹¹⁴

The release of acetaldehyde from building products varies greatly. Plaisance *et al.*¹⁰⁰ examined the emission of 23 building products using chamber studies. Two finishing plasters were responsible for the by far highest emission rates of $291 \mu\text{g (m}^2\text{ h})^{-1}$ and $500 \mu\text{g (m}^2\text{ h})^{-1}$. In contrast, two other finishing plasters were unremarkable with regard to the release of acetaldehyde. Odaka *et al.*¹⁰¹ investigated the release of acetaldehyde from the plaster in dependence of their vegetable oil content. The highest emission rates were found when using linseed oil and perilla oil with the suspected precursor substance linolenic acid. For pine wood and plywood, Plaisance *et al.*¹⁰⁰ measured $57 \mu\text{g (m}^2\text{ h})^{-1}$ and $32 \mu\text{g (m}^2\text{ h})^{-1}$, respectively. For all other products, the emission rate was $\leq 15 \mu\text{g (m}^2\text{ h})^{-1}$. Suzuki *et al.*¹⁰² have studied the acetaldehyde emission rates of wood-based materials as a function of time, temperature, and humidity. With initial values between about $10 \mu\text{g (m}^2\text{ h})^{-1}$ and $35 \mu\text{g (m}^2\text{ h})^{-1}$, a clear decay behavior was observed within 14 days. In their chamber studies on preventing VOC diffusion through surface-coated particleboard, Pibiri *et al.*¹⁰⁴ also found a rapid decay in the acetaldehyde concentration that was independent of the layer. Schieweck¹⁰³ tested wood and wood-based materials in a 1 m^3 chamber under standard conditions ($T = 23^\circ\text{C}$, $\text{RH} = 50\%$, $\text{AER} = 0.4 \text{ h}^{-1}$) and realistic loading rates. The chamber concentrations within 72 h were between $\leq 3 \mu\text{g m}^{-3}$ and $245 \mu\text{g m}^{-3}$.

Ammenn *et al.*¹⁰⁵ reported that acetaldehyde, although not actively used, is a relevant substance in the manufacture of leather. The authors postulate that acetaldehyde is bound in the form of an imine through lysine residues in collagen and is released when the leather surface is thermally stressed. This can lead to high concentrations, especially in the automotive sector.

One phenomenon was the release of acetaldehyde and other pollutants from photocatalytic wall paints, which are supposed to clean the indoor air of such substances. It was quickly shown that the pollutants origin from the paint itself.^{64,65} Typical recipes contain the photocatalyst titanium dioxide and blends from organic binders. The OH radicals and O_2^- ions formed by TiO_2 upon irradiation oxidize the organic components of the binder. Salthammer and Fuhrmann,⁶⁴ as well as Auvinen and Wirtanen,⁶⁵ measured considerable concentrations of acetaldehyde in their chamber investigations. Based on the results of Ye *et al.*,¹¹⁵ Geiss *et al.*¹¹⁶ postulate that higher aldehydes and acids are first formed from hydrocarbon groups, which then decompose to lower aldehydes. Polyvinyl acetate is a common component of organic binders in paints, so that the reaction scheme presented by Gandolfo *et al.*⁶⁹ (see Fig. 2) is also plausible here. Fiorentino *et al.*¹¹⁷ carried out measurements in an office room and found a significant increase in the acetaldehyde concentration in the presence of paints containing titanium dioxide and under the influence of UV light.

Another point is air-cleaning devices that work on a photocatalytic basis. Destaillats *et al.*¹¹⁸ showed that the effectiveness of many devices for acetaldehyde is insufficient, and the degradation rate is less than 50%. Hodgson *et al.*¹⁰⁶ found a net

production of acetaldehyde from the ultraviolet photocatalytic oxidation of typical indoor VOCs. Gunschera *et al.*⁶⁶ conducted test chamber experiments with air purifiers and various test substances. Acetaldehyde was formed and released in relevant amounts. Some air cleaning devices work with ozone. It should therefore be noted at this point that components of the air and the ingredients of many building products such as paints⁵⁹ and carpets⁶¹ form aldehydes in the presence of ozone.

The last source to be discussed here concerns human respiratory gas. Acetaldehyde is a natural component, but its concentration is highly dependent on an individual's metabolism. In experiments lasting 35 minutes each, Riess *et al.*⁵² measured typical concentrations of 30 ppb to 50 ppb acetaldehyde in the respiratory gas of 10 healthy volunteers during light physical exertion. For a person who had previously consumed alcohol, the concentration was 82 ppb. Turner *et al.*¹⁰⁷ came to analogous results earlier in respiratory gas studies on 30 subjects. This can be relevant to the indoor environment. At 37°C and 1013 mbar, 50 ppb acetaldehyde corresponds to approx. $87 \mu\text{g m}^{-3}$. With an assumed respiratory minute volume of 8 l at rest, the emission rate is $42 \mu\text{g h}^{-1}$ per person.

There are only a few studies that deal with the reverse case, *i.e.* with the removal of acetaldehyde from room air. Yamashita *et al.*¹¹⁹ describe the chemisorption through L-cysteine. Reactions between carbonyl compounds and amino groups are common and lead to the formation of a Schiff base. Krou *et al.*¹²⁰ investigated the reactivity between acetaldehyde and cement-based hydrates. An overview of passive removal materials for indoor air pollutants is provided by Shayegan *et al.*¹²¹

6 Indoor guide values

Guide and reference values are valuable tools for assessing indoor air quality and exposure for evaluating potential health hazards and from a statistical point of view. However, it must be clear which criteria are used to derive guide and reference values and under which conditions they can be applied.¹²² For acetaldehyde, country and organization-specific guide values are available. Most are listed in the Toyinbo *et al.* database.¹²³ Others, such as the reference exposure limits (REL), can be found on the OEHHA (Office of Environmental Health Hazard Assessment) website. Table 3 provides a compilation of published guide values for acetaldehyde.

Health Canada¹²⁴ uses a Reference Concentration (RfC) extracted from key toxicological, controlled human exposure, and indoor epidemiological studies as a starting point. For the short-term guideline, this is the 95-P lower confidence limit of 142 mg m^{-3} from a study on asthmatic subjects. With uncertainty factors of 10 to account for a use of the lowest observed adverse effects level (LOAEL) and 10 to account for additional sensitivity in the human population, a short-term RfC of $1420 \mu\text{g m}^{-3}$ is obtained, which is also interpreted as a short-term guide value. A concentration of 120 mg m^{-3} is used as starting point for the long-term value, which is based on a study of the olfactory epithelium in rats. This value is adjusted for continuous exposure, to account for toxicodynamic differences between animals and humans, for additional sensitivity in the



Table 3 International indoor guide and reference values for acetaldehyde^{a,b,c}

Value	Comment	Country	Ref.
48 $\mu\text{g m}^{-3}$ (0.03 ppm)	Chronic effects	Japan	123
0.10 mg m^{-3}	GV I (precautionary value)	Germany	129
1.0 mg m^{-3}	GV II (effect related)	Germany	129
1420 $\mu\text{g m}^{-3}$ (795 ppb)	Acute effects (1 hour)	Canada	124
280 $\mu\text{g m}^{-3}$ (157 ppb)	Chronic effects (24 hours)	Canada	124
1420 $\mu\text{g m}^{-3}$	Acute effects (1 hour)	UK	130
280 $\mu\text{g m}^{-3}$	Chronic effects (24 hours)	UK	130
140 $\mu\text{g m}^{-3}$	ISHRAE standard 10 001: 2019	India	123
470 $\mu\text{g m}^{-3}$	Acute REL	United States	OEHHA
300 $\mu\text{g m}^{-3}$	Inhalation REL (8 hours)	United States	OEHHA
140 $\mu\text{g m}^{-3}$	Chronic inhalation REL	United States	OEHHA

^a Ref. Toyinbo *et al.*¹²³ was accessed on 28.10.2022. ^b ISHRAE: India Society of Heating, Refrigerating and Air Conditioning Engineers. ^c REL = OEHHA Reference Exposure Limit; see <https://oehha.ca.gov/air/chemicals/acetaldehyde>, assessed on 28.10.2022.

human population, and for uncertainty in the shape of the lower region of the concentration-response curve. The resulting long-term RfC is 280 $\mu\text{g m}^{-3}$, which is interpreted as a long-term guide value. For acetaldehyde, the United Kingdom (UK) has adopted the guide values derived from Health Canada.¹²⁵

The procedure for deriving the German guide values is similar but not identical.²⁷ It is interesting that both the German and Canadian approach is based on the same study. However, the German *ad hoc* working group assumes the lowest observed adverse effect concentration (LOAEC) of 48 $\mu\text{g m}^{-3}$ (subchronic, rat) by extrapolating the intermittent value of Dorman *et al.*²⁸ to continuous exposure. Taking into account factors for subchronic/chronic, interspecies differences, interindividual variability, and the physiology of children, an effect-related guide value GV II of 1.0 mg m^{-3} (rounded) results. A safety factor of 10 was considered appropriate for the derivation of the precautionary guide value. This results in GV I = 0.10 mg m^{-3} (rounded). The basic scheme for deriving guideline values in Germany is published in the *Bundesgesundheitsblatt*.¹²⁶

In Japan, an indoor guideline value of 48 $\mu\text{g m}^{-3}$ was published, but without a consistent derivation. Effects on the nasal olfactory epithelium in rats are mentioned as the toxicological endpoint. The Indian value of 140 $\mu\text{g m}^{-3}$ is consistent with the OEHHA chronic inhalation reference exposure limit (REL). Each REL (acute, 8 hours, chronic) is derived toxicologically, where essentially the studies by Appelman *et al.*^{127,128} were used.

According to Table 3, the indoor guide values can be roughly divided into two ranges: 50–250 $\mu\text{g m}^{-3}$ for chronic effects and 500–1500 $\mu\text{g m}^{-3}$ for acute effects. It is noteworthy that the guideline values have not yet been withdrawn, despite the classification of acetaldehyde as a substance that is carcinogenic to humans.

7 Acetaldehyde concentrations in indoor and outdoor air

After formation mechanisms, indoor sources, and guide values have been explained, the indoor concentrations can now be discussed and evaluated. Note that the concentration unit used in the original work (ppb or $\mu\text{g m}^{-3}$) is given in each case. This is

due to the fact that temperature and air pressure are needed to convert from ppb to $\mu\text{g m}^{-3}$ and *vice versa*. Before 1990, the interest in acetaldehyde in indoor air was low. Grosjean *et al.*¹³¹ measured indoor air concentrations in Brazil, but the reason for this was the noticeably high values in urban ambient air. The first systematic measurements of acetaldehyde concentrations in indoor air were carried out by Reiss *et al.*¹³² and Zhang *et al.*¹³³ Since then acetaldehyde was measured frequently in the room air. The studies discussed in this section provide a representative overview of exposure to acetaldehyde under various conditions. In Table 4, only studies are considered that were not cause-related, comprised at least 10 data points, and were based on percentiles or the geometric mean (GM) for the statistical analysis. Under the premise of a logarithmic normal distribution,¹³⁴ it is assumed that 50-P and GM are largely identical. Studies whose discussion is based on the arithmetic mean are not included but are cited.^{135–137} Outside air concentrations are only given in Table 4 if they were measured at the same time as the room air concentration.

The outdoor air concentrations of acetaldehyde vary greatly. Finlayson-Pitts and Pitts² give typical values for different areas of ≤ 0.22 ppb (remote), 0.1–4 ppb (rural-suburban), and 1–18 ppb (urban). This is also reflected by the outdoor values in Table 4. Very high values usually have specific causes. Corrêa *et al.*³³ measured peak concentrations of 46 ppb in Rio de Janeiro in 2001, which were due to direct emissions from vehicles and photochemically initiated oxidation of organic compounds. Duan *et al.*¹⁵⁸ recorded maximum values of 53 $\mu\text{g m}^{-3}$ during haze days in Beijing, and Delikhoon *et al.*¹⁵⁹ reported maximum concentrations of 34 $\mu\text{g m}^{-3}$ in Shiraz, Iran. Loh *et al.*¹⁶⁰ state that indoor acetaldehyde mainly comes from outdoor sources. However, with the data presented in this work, it is clear that outdoor air is an important source, but there are also many relevant indoor sources that can lead to high concentrations of acetaldehyde. This is especially true in the winter months as shown by Wang *et al.*¹⁶¹ in an indoor/outdoor study in China.

As already explained, the results of the studies listed in Table 4 are not case-related. Some come from surveys, others from specific research projects. The acetaldehyde results of the



Table 4 Acetaldehyde concentrations in indoor and outdoor air

Location and no. of samples	$\mu\text{g m}^{-3}$		
	50-P/GM	95-P	Max.
Indoor, US homes ($N = 353$)	18.6	50.2	138
Indoor, California childhood education ($N = 40$)	7.5		139
Indoor, US residences ($N = 15$)			55.4
Indoor, California kitchen ($N = 340$)	8.0	23	141
Indoor, California bedrooms ($N = 340$)	7.9	23	141
Indoor, California commercial buildings ($N = 40$)	8.9		142
Indoor, Canadian residences ($N = 59$)	18.9		143
Indoor, Italian homes ($N = 59$)	8.4		144
Indoor European private houses ($N = 96$)	11.2	24.8	145
Indoor European public buildings/schools ($N = 186$)	7.2	18.8	145
Indoor European office buildings in summer ($N = 143$)	6.1	10	146
Indoor European office buildings in winter ($N = 140$)	4.5	8.3	146
Indoor, German homes (GerES IV, $N = 586$)	15.5	50.3	863
Indoor, German homes (GerES V, $N = 639$)	5.5	16.8	49.9
Indoor, French dwellings ($N = 554$)	11.5		95
Indoor, French homes ($N = 162$)	9.3	19.1	149
Indoor, French schools ($N = 10$)	5.2		150
Indoor, Portuguese classrooms ($N = 73$)	7.7		64.6
Indoor, Spanish living rooms ($N = 25$)	14.3		151
Indoor, Spanish bedrooms ($N = 25$)	15.8		152
Indoor, Japanese households, 1.5 years ($N = 4843$)	12	37	153
Indoor, Japanese households, 3 years ($N = 4843$)	12	35	153
Indoor, Japanese households, winter ($N = 602$)	15		230
Indoor, Japanese households, summer ($N = 602$)	13		210
Indoor, Chinese residences ($N = 27$)	18.7		99.7
Indoor, Malaysian private residences ($N = 39$)	5.2		67.6
Indoor, Australian dwellings ($N = 76$)	7.1		156
Outdoor, US ($N = 353$)	5.4	14.9	157
Outdoor, California ($N = 19$)	1.8		138
Outdoor, California ($N = 178$)	1.4	4.6	139
Outdoor, Italy ($N = 27$)	3.2		141
Outdoor Europe ($N = 105$)	1.8	4.2	144
Outdoor, France ($N = 10$)	1.4		145
Outdoor, Spain ($N = 25$)	2.2		150
Outdoor, Japan ($N = 4843$)	0.9	1.8	152
Outdoor, Japan ($N = 4843$)	1.1	1.9	153
Outdoor, Japan winter ($N = 602$)	2.2		153
Outdoor, Japan summer ($N = 602$)	3.1		154
Outdoor, Australia ($N = 69$)	0.7		154

environmental survey (GerES V)⁷⁸ shown in Fig. 6 are representative for Germany. The concentrations measured with passive samplers are 7-day mean values. The 50-P is $5.5 \mu\text{g m}^{-3}$ and the 95-P is $16.8 \mu\text{g m}^{-3}$.

The data presented in Table 4 are largely identical to the literature review by Shrubsole *et al.*¹²⁵ Logue *et al.*¹⁶² assumed a population-average indoor acetaldehyde concentration of $22 \mu\text{g m}^{-3}$. The 50-P values or geometric means (GM) from Table 4 determined under normal living conditions are between approximately $5 \mu\text{g m}^{-3}$ and $19 \mu\text{g m}^{-3}$. The highest 95-P value is $50 \mu\text{g m}^{-3}$. The maximum value assumed was $230 \mu\text{g m}^{-3}$. The conspicuous maximum of $863 \mu\text{g m}^{-3}$ from the German 2003–2006 study GerES IV was not taken into account. This value seems to be extreme or questionable, the 98-P of GerES IV is $60 \mu\text{g m}^{-3}$. The large differences between the GerES IV and GerES V studies are also unusual. The data from Table 4 can be

used to roughly classify the concentrations, which is shown in Fig. 7. The upper limit of the “low range” was assumed to be $10 \mu\text{g m}^{-3}$, about half of the highest 50-P. The highest value of the 95-P was chosen as the upper limit of the “medium range”. The classification of the outdoor air values is based on Finlayson-Pitts and Pitts,² but takes into account the extreme values measured by Duan *et al.*¹⁵⁸ and Corrêa *et al.*³³ The assumed ranges of the guide values have already been discussed.

From the statistical data of the cited studies, it is difficult to evaluate how the room air concentrations relate to the guide values. The highest 95-P values are in the range of the smallest acute value of $48 \mu\text{g m}^{-3}$ (see Tables 3 and 4). Even taking into account the maximum values, exceeding $50 \mu\text{g m}^{-3}$ appears to be unlikely under normal living conditions. On the basis of a conservative estimate, also taking into account published percentiles that are not listed in Table 4, the proportion of



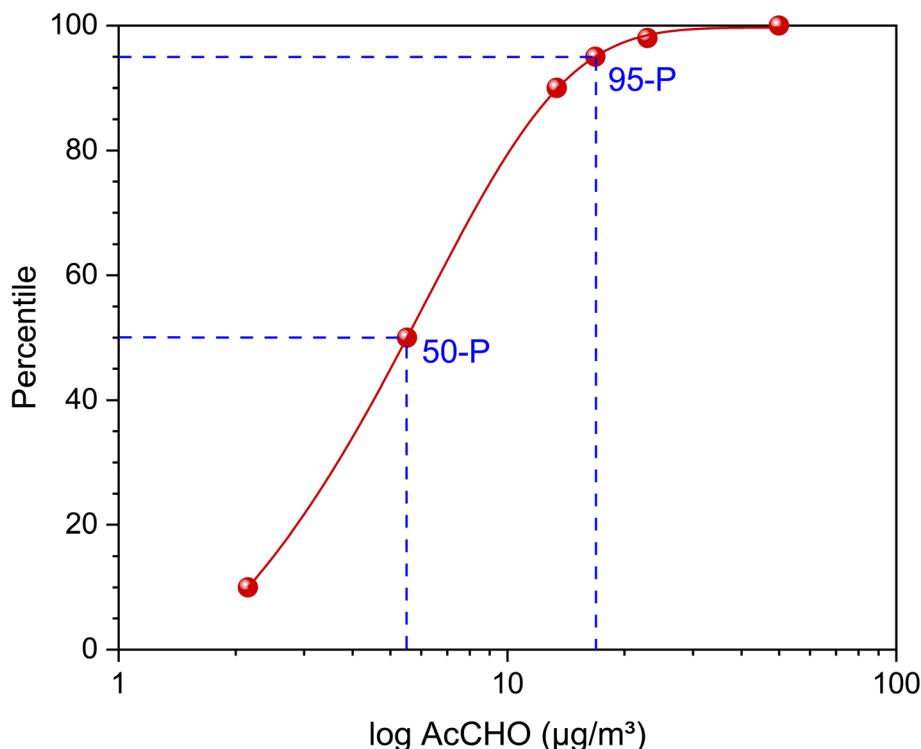


Fig. 6 Plot of log acetaldehyde concentrations versus percentile (639 households) for the results from the German Environmental Survey 2014–2017 (GerES V).⁷⁸ The data were fitted with a sigmoidal curve. The 50-P value is $5.5 \mu\text{g m}^{-3}$ and the 95-P is $16.8 \mu\text{g m}^{-3}$.

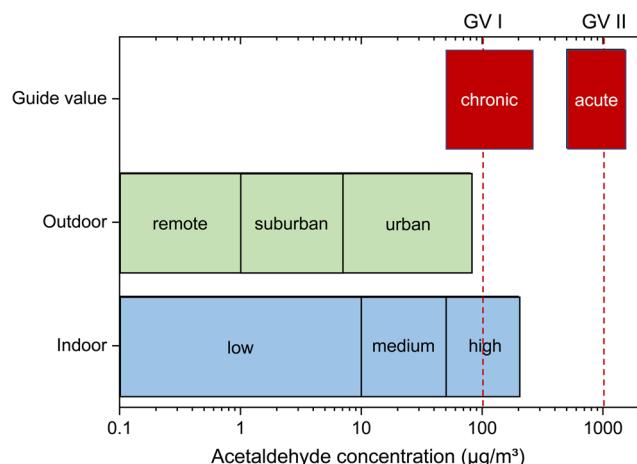


Fig. 7 Classification of indoor air and outdoor air concentrations of acetaldehyde. The ranges of guideline values based on acute and chronic effects (see Table 3) are also given. The German guide values GV I and GV II are specially marked because they were justified most carefully. The classification was based on the evaluation of the cited studies.

concentrations of $\geq 50 \mu\text{g m}^{-3}$ is below 1%. Liu *et al.*¹⁶³ evaluated studies on indoor measurements in China published between 2001 and 2021. With a 50-P of $12.9 \mu\text{g m}^{-3}$ for acetaldehyde in residences, small differences with a slightly increasing trend were found between different periods. However, the number of sample sizes was small and therefore

hardly assessable. On average, indoor concentrations between $10 \mu\text{g m}^{-3}$ and $20 \mu\text{g m}^{-3}$ can be assumed to be plausible globally.

Nevertheless, the question still arises which level the acetaldehyde concentrations in the indoor environment can achieve under extreme conditions. Naddafi *et al.*¹⁶⁴ measured acetaldehyde concentrations in 40 cafés serving water pipes in Ardabil, Iran. For fruit-flavored tobacco the concentrations were between $64 \mu\text{g m}^{-3}$ and $563 \mu\text{g m}^{-3}$, for regular tobacco between $31 \mu\text{g m}^{-3}$ and $183 \mu\text{g m}^{-3}$. Sousa *et al.*¹⁶⁵ measured acetaldehyde concentrations between $12 \mu\text{g m}^{-3}$ and $55 \mu\text{g m}^{-3}$ in two Brazilian hospitals. In other Brazilian hospitals, the values were significantly higher with $17 \mu\text{g m}^{-3}$ to $263 \mu\text{g m}^{-3}$. In a Chinese hospital, on the other hand, the concentrations were unremarkable. The high acetaldehyde concentrations between $53 \mu\text{g m}^{-3}$ and $110 \mu\text{g m}^{-3}$ resulting from the burning of incense sticks in Hong Kong temples are not surprising.¹⁶⁶ A much-discussed topic is the pollution of the indoor air in new buildings shortly after construction. Shinohara *et al.*¹⁶⁷ conducted measurements in 19 temporary houses built after the Fukushima earthquake before residents moved in. The results were very different. In some cases, concentrations around $100 \mu\text{g m}^{-3}$ or higher were measured, while other houses showed significantly lower values. Derbez *et al.*¹⁶⁸ found that acetaldehyde concentrations in newly built, energy-efficient houses in France were slightly higher than average values, but the differences were small. Schieweck¹⁰³ examined the acetaldehyde concentrations in German prefabricated houses during different phases (P1: after completion of the shell, P2: after completion of

interior work, P3: during the occupation). High concentrations of up to $350 \mu\text{g m}^{-3}$ were measured during P1 and P2. At P3, normal concentrations were reached by manual ventilation or when the ventilation system was switched on.

8 Final discussion and conclusion

The frequent detection of acetaldehyde in the environment is not primarily due to its use as an industrial chemical. The production quantities are comparatively small and the importance as a starting material in chemical synthesis is declining. However, acetaldehyde is a product of metabolic processes in animalia, plantae and fungi, combustion chemistry, thermal degradation, and photochemistry. In the outside air, the acetaldehyde concentration essentially depends on road traffic, photosmog, and fire incidents. This also leads to concentrations that fluctuate diurnally. Duan *et al.*¹⁵⁸ were able to show that on haze days the acetaldehyde outdoor concentration in Beijing correlates with the ozone concentration. It was also found that the concentrations of formaldehyde, acetaldehyde, and acetone correlate. From their findings, Duan *et al.*¹⁵⁸ concluded that the three abundant compounds were formed in photochemical reactions. In this respect, the concentrations given in Table 4 for the outside air only represent background concentrations for urban areas, but these levels cannot generally be expected and will vary greatly from region to region.

Outdoor air is certainly an important source of indoor acetaldehyde, but a relationship is not necessarily given. This was investigated by Santarsiero and Fuselli¹⁶⁹ using principal component analysis. Indoor concentrations measured in different rooms of Italian apartments were strongly correlated but independent of the outdoor concentration. In any case, high acetaldehyde concentrations in the indoor environment can only be explained by the outdoor air concentration in exceptional cases, but usually indoor-specific sources are active. Looking at the individual sources in detail, a problem becomes obvious. As a rule, acetaldehyde is not emitted directly but is created by chemical and thermal processes. In some cases, such as wood burning and cooking, acetaldehyde emissions can be removed *via* exhaust gas ducts. In contrast, candles, ethanol burners, and incense sticks are designed for indoor use. So when these products are used, exposure to acetaldehyde and other emitted pollutants is accepted at the same time. Thus, many sources of acetaldehyde are linked to human activities, and indeed Cheng *et al.*¹⁵⁷ found that acetaldehyde was elevated in dwellings with higher occupant densities. Pagonis *et al.*¹⁷⁰ speculated that elevated acetaldehyde concentrations in a museum might be due to the alcohol consumption of attendees.

The use of conventional cigarettes and e-cigarettes is no longer an issue in public buildings and the population is well informed about the disadvantages of passive smoking and passive vaping. Visiting a smoker's pub or a shisha bar is voluntary, but the question still arises if visitors can be expected to deal with high concentrations of pollutants or whether the owner must ensure adequate ventilation. However, it must also

be made clear that acetaldehyde plays only a minor role in the emissions from these products.

The release of acetaldehyde from photocatalytic reactions is still a problem as the substance is one of the main components here. As long as organic polymers, such as PVAC, are used as binders, the formation of acetaldehyde cannot be prevented. In the case of photocatalytic air cleaners, the reaction rarely leads to the complete mineralization of the pollutants, and the formation of byproducts is more the rule than the exception. Whether acetaldehyde and other substances are formed depends on the technical design of the respective device.

An ambivalent situation concerns the construction and consumer products. The xylans contained in hardwood are rich in acetyl groups ($\text{H}_3\text{C}-\text{C}(\text{O})\cdots$).⁴⁰ Therefore, such woods can release acetaldehyde. Other substances derived from xylan structure of hardwood are formic acid and acetic acid.¹⁰⁴ On the other hand, hardwood contains few terpenes. Softwood xylans are comparatively low in acetyl groups, but mono- and sesquiterpenes dominate, the release of which into the room air is also only desired to a limited extent. When adding vegetable oil to plaster, the release of acetaldehyde can be limited by selecting certain oils, but this leads to an increased emission of higher aldehydes such as hexanal.¹⁰¹ These examples show that substitution can be quite difficult since by regulating one substance one accepts the higher emission of another substance. Leather is potentially a strong source of acetaldehyde, but relevant emissions occur at temperatures above 50 °C, affecting particular automotive applications. Here, too, there is the problem that the precursor substances are already present in the leather matrix.

The essential question to be addressed is whether indoor exposure to acetaldehyde poses a health risk to occupants. The main result of practically all surveys is that acetaldehyde only rarely dominates the spectrum of indoor air pollutants. Nevertheless, health-based guide values were derived for the substance, with the help of which an assessment can be made. None of the studies listed in Table 4 significantly exceeded the Japanese guide value of $48 \mu\text{g m}^{-3}$ for chronic effects in the 95-P; in most cases, the measured value is significantly lower. The toxicologically based German guideline value GV I = 0.10 mg m^{-3} for chronic exposure is well above the 95-P. The maximum values listed in Table 4 are still below the chronic inhalation REL of the OEHHA and the chronic 24-hour value of Health Canada. With the exception of one concentration in the GEREs IV study, the guide values for acute exposure are never reached. Consequently, the risk of acute and chronic health impairments from indoor acetaldehyde can be considered to be low under normal living conditions. Koistinen *et al.*⁴ also concluded that people in Europe do not experience increased health hazards associated with acetaldehyde levels in their homes. Acetaldehyde concentrations under extreme conditions have already been discussed in Section 7. The increased values in pre-fabricated houses measured by Schieweck¹⁰³ during the construction phase can be regarded as typical when using new wood-based materials. However, the release of acetaldehyde from wood decreases rapidly¹⁰⁴ and with adequate ventilation after the residents moved in, the concentrations are in the usual



range. The high values in a shisha bar,¹⁶⁴ which are in the region of the OEEHA acute REL, must be viewed as significantly more critical. The acetaldehyde concentration in vehicle cabins should also be considered, as measurements by Wang *et al.*¹⁷¹ on leather-containing fabrics at 25 °C and 65 °C have shown.

In summary, it can be said that acetaldehyde is inevitable in indoor air, which is essentially due to the natural formation of the substance. However, the concentration can be kept in the non-critical range through responsible handling of products and living behavior. A sufficiently high air exchange from a hygienic point of view is also advantageous in reducing high concentrations of pollutants, but this must not be understood as a request to combat high emission rates with high air exchange rates. Moreover, it is up to the people themselves if they are a potential acetaldehyde source, since the concentration in the respiratory gas correlates closely with the consumption of ethanol. Statistically based studies and surveys with randomized selection of the measuring sites have shown that acetaldehyde hardly poses acute and chronic health problems under normal living conditions. Nevertheless, the compound definitely belongs to the list of priority pollutants due to its ubiquity and carcinogenic potential and should always be included in indoor measurement programs.

Conflicts of interest

The author has no conflicts of interest to declare.

Acknowledgements

The 3D structure image in the Graphical Abstract was taken from PubChem® (CID 177) <https://pubchem.ncbi.nlm.nih.gov/>.

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