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Analytical chemistry of carbonyl compounds in indoor air

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Carbonyl compounds are ubiquitous in outdoor and indoor air. Due to the high electronegativity of the oxygen atom, they are polar in nature and the C═O group opens possibilities for many types of chemical reactions. Their physical and chemical properties are additionally influenced by substituents and conjugated double bonds. The concentration ranges are also highly variable. Formaldehyde can reach 100 ppb or more in indoor air, but reaction products such as 4-oxopentanal (4-OPA) are in the lower ppb range or even below 1 ppb. Another point concerns the dynamics of carbonyls. When examining the emission of formaldehyde in test chambers, an equilibrium concentration is usually established, so that changes over time can be neglected during the measurement. On the other hand, many substances and scenarios are subject to strong fluctuations in concentration over short time periods. The analysis is also made more difficult by the fact that different methods are often required for saturated carbonyls, unsaturated carbonyls and dicarbonyls. This work focuses on aprotic carbonyl compounds such as aldehydes, ketones, lactams and pyrones with relevance for the indoor environment that do not contain any other reactive groups. The range of interesting compounds has grown significantly in recent years, notably through the derivation of health-based guide values, as well as through investigations into new products, human activities and human emissions from the skin and respiratory gas. Classical and modern analysis methods are discussed, which can be considered for the respective research question. Many small molecules require derivatization as a first step, followed by separation *via* gas chromatography or HPLC. Substance-specific detection without chromatographic separation is routinely used for formaldehyde. With some limitations, the identification of carbonyls in multicomponent mixtures is possible using online mass spectrometry. In particular, proton-transfer-reaction mass spectrometry (PTR-MS) has established as a method with high sensitivity and high time resolution.

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1 Introduction

To date, thousands of organic compounds have been analytically detected in indoor air. A systematic compilation is just as impossible as it is useless, since the spectrum of substances changes over time for a variety of reasons such as substance substitution, legislation and lifestyle. In addition, many substances are not directly introduced into the room air, but are formed by biotic and abiotic chemical processes.

In order to still get an overview, classical environmental chemistry distinguishes between the concepts media-related, sector-related, substance-related[1] and effect-related.[2] A media-related concept is used when specific matrices such as air or dust are to be examined. This is the case with surveys. Sectors relate to defined product groups (*e.g.* building materials, furniture) and processes (*e.g.* cooking, combustion, ozone reactions), while effect-related concepts focus on exposure and health aspects. Substance-related concepts can relate to individual chemicals such as formaldehyde and radon, but also to substance groups such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons and phthalates.

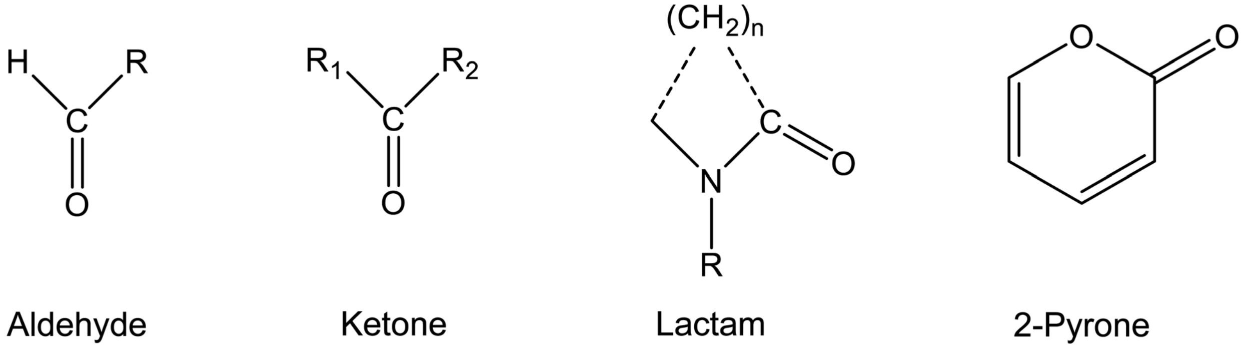

Fig. 1 Chemical structures of carbonyl compounds.

This review is substance-related and deals with carbonyl compounds that are of importance for the indoor environment. Only aprotic substances that do not have a functional group from which hydrogen atoms can be split off as protons are discussed. Esters are also not taken into account, but only aldehydes, ketones, lactams and pyrones with the chemical structures shown in Fig. 1.

The question of whether such work is necessary arises from history and the current situation. In the early years, formaldehyde was almost exclusively discussed.[3] A summary of historical methods for determining formaldehyde in different phases can be found in Walker.[4] With the beginning of systematic room air measurements, attention was drawn to solvents such as 2-butanone (MEK) and other volatile organic compounds (VOCs).[5–7] The saturated and unsaturated aldehydes came into focus with investigations into oxidation reactions of unsaturated hydrocarbons and fatty acids through thermal influences, atmospheric oxygen and ozone.[8] Over time, more relevant carbonyl compounds were identified, in particular through studies on wood and wood-based materials,[9,10] textile floor coverings,[11,12] fragrances,[13] 3D printers,[14,15] cooking and frying,[16] but also through reactions on the human skin surface.[17]

From an analytical point of view, the problem is that carbonyl compounds are chemically very different. Formaldehyde, the simplest aldehyde, is a typical VVOC (very volatile organic compound) with a boiling point of −20 °C; benzophenone is an SVOC (semi-volatile organic compound) with a boiling point of +305 °C. The concentrations can also cover several orders of magnitude. Some substances like 4-oxopentanal (4-OPA) and 6-methyl-5-hepten-2-one (6-MHO) are common products in the reaction of unsaturated hydrocarbons with ozone. Usually, they do not occur in high concentrations, but they are subject to fast dynamics. On the other hand, formaldehyde can cover a wide concentration range from sub-ppb to sub-ppm (note that ppb and ppm refer to volume mixing ratios) and the concentration changes over time take place within seconds as well as within days.

The spectroscopic properties of the C═O group limit the possibilities for direct analysis of carbonyl compounds using UV/VIS and infrared (IR). Therefore, mass spectrometric and chromatographic methods are common. In the past, polarography and ion chromatography have also been considered for the analysis of airborne aldehydes.[18] It is advantageous that targeted derivatization reactions are possible *via* the C═O group. Nevertheless, analytical methods are often used today that are hardly suitable for the respective target compounds, and at the same time the results of analytical measurements are sometimes misunderstood or misinterpreted. This article offers an up-to-date overview of the analytical determination of organic carbonyl compounds in indoor air and discusses which methods can be applied for the respective task and which cannot.

2 Carbonyls relevant for the indoor environment

The available literature was evaluated in order to obtain an overview of the organic carbonyl compounds mainly found indoors. In particular, original papers, reviews and the results of environmental surveys were considered. Table 1 represents the result of this search with a total of 54 compounds. The selection is purely analytical and must not be interpreted in terms of health. This means that the substances listed in Table 1 are often detected in the indoor environment, but this is not automatically associated with a health risk. Of course, there are many other carbonyl compounds that can or have been identified in the indoor environment, usually in traces. This is especially true for the oxidation products of terpenes.[19]

In detail, the selection is based on the following references: formaldehyde;[20,21] acetaldehyde;[22,23] other saturated aldehydes (C3–C11);[24] acrolein;[25] methacrolein;[16] other unsaturated aldehydes (C4–C11);[8] pinonaldehyde;[26] furfural;[9,27] glyoxal, methylglyoxal;[28] diacetyl;[29] acetone, MEK, MIBK, 2-pentanone, 3-octanone;[30] MVK;[31] benzaldehyde, cyclohexanone, acetophenone, benzophenone;[32] 2,5-dimethyl benzaldehyde;[33] geranial, neral, lilial, *trans*-cinnamaldehyde, amyl cinnamal;[13] geranylacetone, 4-OPA, 6-MHO;[17] caprolactam;[15] 1-methyl-2-pyrrolidone, 1 ethyl-2-pyrrolidone.[34]

Table 1 CAS numbers, molecular properties and preferred analytical method of the selected carbonyl compounds (T = Tenax TA, BC = black carbon). Only experimentally determined boiling points at standard atmospheric pressure are given. The respective literature sources are not listed

Compound	CAS	MW (g mol^{-1})	BP (°C)	Preferred method
Formaldehyde	50-00-0	30.03	−20	DNPH,[35] Hantzsch[36]
Acetaldehyde	75-07-0	44.05	21	DNPH[35]
Propanal	123-38-6	58.08	48	DNPH[35]
Butanal	123-72-8	72.11	75	DNPH[35]
2-Methyl propanal	78-84-2	72.11	64	TD(T)-GC/MS[37]
Pentanal	110-62-3	86.13	103	DNPH,[35] TD(T)-GC/MS[37]
3-Methyl butanal	590-86-3	86.13	93	DNPH[35]
Hexanal	66-25-1	100.16	130	DNPH,[35] TD(T)-GC/MS[37]
Heptanal	111-71-7	114.19	153	TD(T)-GC/MS[37]
Octanal	124-13-0	128.21	171	TD(T)-GC/MS[37]
Nonanal	124-19-6	142.24	195	TD(T)-GC/MS[37]
Decanal	112-31-2	156.26	212	TD(T)-GC/MS[37]
Undecanal	112-44-7	170.29	225	TD(T)-GC/MS[37]
Acrolein	107-02-8	56.06	52	TD(BC)-GC/MS[25]
Methacrolein	78-85-3	70.09	73	TD(BC)-GC/MS[38]
cis-2-Butenal	15798-64-8	70.09	104	TD(T)-GC/MS[37]
trans-2-Butenal	123-73-9	70.09	102	TD(T)-GC/MS[37]
3-Methyl-2-butenal	107-86-8	84.12	134	TD(T)-GC/MS[37]
trans-2-Pentenal	1576-87-0	84.12	124	TD(T)-GC/MS[37]
3-Methyl-2-pentenal	3592-19-6	98.14		TD(T)-GC/MS[37]
trans-2-Hexenal	6728-26-3	98.14	147	TD(T)-GC/MS[37]
trans-2-Heptenal	18829-55-5	112.17	166	TD(T)-GC/MS[37]
trans-2-Octenal	2548-87-0	126.20		TD(T)-GC/MS[37]
trans-2-Nonenal	18829-56-6	140.22	189	TD(T)-GC/MS[37]
trans-2-Decenal	3913-81-3	154.25	229	TD(T)-GC/MS[37]
trans-2-Undecenal	53448-07-0	168.28	245	TD(T)-GC/MS[37]
Furfural	98-01-1	96.08	162	TD(T)-GC/MS[37]
Benzaldehyde	100-52-7	106.12	179	DNPH,[35] TD(T)-GC/MS[37]
2,5-Dimethyl benzaldehyde	5779-94-2	134.17	245	DNPH,[35] TD(T)-GC/MS[37]
Glyoxal	107-22-2	58.04	50	PFBHA[39–41]
Methylglyoxal	78-98-8	72.06	72	PFBHA[39–41]
Diacetyl	431-03-8	86.02	88	TD(T)-GC/MS[37]
4-Oxopentanal (4-OPA)	626-96-0	100.12		PFBHA,[41] PTR-MS[17]
Pinonaldehyde	2704-78-1	168.23		TD(T)-GC/MS[37]
trans-Cinnamaldehyde	14371-10-9	132.16	253	TD(T)-GC/MS[37]
Geranial	141-27-5	152.24	229	TD(T)-GC/MS[37]
Neral	106-26-3	152.24	228	TD(T)-GC/MS[37]
Amyl cinnamal	122-40-7	202.29	284	TD(T)-GC/MS[37]
Lilial	80-54-6	204.31	275	TD(T)-GC/MS[37]
Acetone	67-64-1	58.08	56	DNPH[35]
2-Butanone (MEK)	78-93-3	72.11	80	TD(T)-GC/MS[37]
3-Buten-2-one (MVK)	78-94-4	70.09	81	TD(BC)-GC/MS[38]
2-Pentanone	107-87-9	86.13	102	TD(T)-GC/MS[37]
4-Methyl-2-pentanone (MIBK)	108-10-1	100.16	116	TD(T)-GC/MS[37]
3-Octanone	106-68-3	128.21	168	TD(T)-GC/MS[37]
6-Methyl-5-hepten-2-one (6-MHO)	110-93-0	126.20	173	PTR-MS[17]
Geranylacetone	3796-70-1	194.31	256	TD(T)-GC/MS[37]
Cyclohexanone	108-94-1	98.15	156	TD(T)-GC/MS[37]
Acetophenone	98-86-2	120.15	202	TD(T)-GC/MS[37]
Benzophenone	119-61-9	182.22	305	TD(T)-GC/MS[37]
1-Methyl-2-pyrrolidone	872-50-4	99.13	203	TD(T)-GC/MS[37]
1-Ethyl-2-pyrrolidone	2687-91-4	113.16	213	TD(T)-GC/MS[37]
Caprolactam	105-60-2	113.16	270	TD(T)-GC/MS[37]
Coumarin	91-64-5	146.14	302	TD(T)-GC/MS[37]

3 The carbonyl (C═O) group

3.1 Electronic structure and spectroscopy

In carbonyl groups, the carbon atom is approximately sp^2 hybridized and forms a σ-bond to the oxygen atom. The remaining p orbital of carbon overlaps with a p orbital of the oxygen atom to form a π-bond. In addition, two non-bonding (n) orbitals remain at the oxygen atom (see Fig. 2).[42]

The absorption of electromagnetic radiation in the visible (VIS) and ultraviolet (UV) range causes electronic excitation. Organic molecules with an isolated C═O group have an absorption band in the UV range between 250 nm and 350 nm. This corresponds to an $n \rightarrow \pi^*$ transition, *i.e.* the promotion of an electron from a nonbonding orbital on oxygen to the antibonding π^* molecular orbital. In this process, charge is shifted from the electronegative oxygen atom to the delocalized π^* orbital, which is associated with a change in the

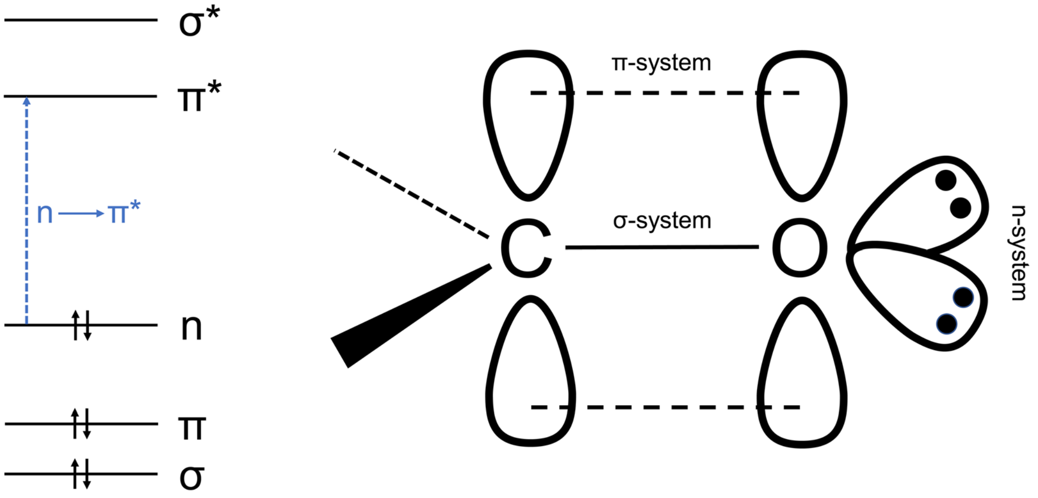

Fig. 2 Electronic structure of the carbonyl group and qualitative view of the energy level scheme.

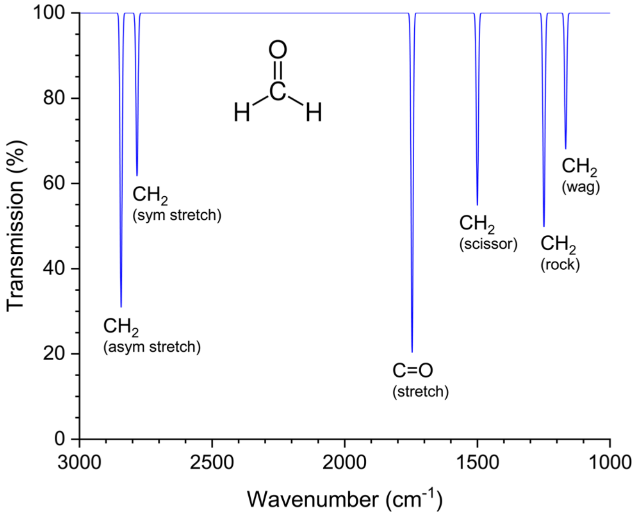

Fig. 3 Simulated IR spectrum of formaldehyde in the gas phase. The wavenumbers of the six normal modes were taken from the publication by Nakanaga *et al.*[50] The terms in brackets refer to different types of molecular vibrations (*sym* stretch: symmetrical stretching; *asym* stretch: antisymmetrical stretching; stretch: linear stretching; scissor: scissoring oder bending, rock: rocking; wag: wagging).

dipole moment. In the case of formaldehyde, the dipole moment of the first excited singlet and triplet state is smaller than that in the ground state.[43] Transitions with n → π* character are forbidden for reasons of symmetry, so the transition intensities are usually small.[44] For formaldehyde, the maximum of the UV absorption is at 294 nm, the peak cross section is 8.4×10^{-20} cm^2 per molecule at 296 K.[45] For the higher aldehydes and ketones with an isolated C═O group, the cross sections of the n → π* transition are in a similar range, but the maxima are shifted towards shorter wavelengths, which is due to the electron-donating alkyl groups.[46] The absorption spectra of various aldehydes are discussed by Calvert and Pitts.[47] Due to the simplicity of structure, the rotational and vibrational bands of formaldehyde can be resolved, allowing this molecule to be selectively excited.

Infrared spectroscopy offers an excellent opportunity for the analysis of carbonyl compounds, which is used in atmospheric chemistry for monitoring formaldehyde.[48] The excitation of the C═O stretching vibration is associated with a large change in the dipole moment.[49] As a result, the IR band of the isolated C═O group, which is in the wave number range from 1700 cm^{-1} to 1800 cm^{-1}, has a particularly high intensity. Fig. 3 shows the theoretical IR spectrum of formaldehyde in the gas phase with the six possible normal modes according to the selection rules. The C═O band is at 1746 cm^{-1}.[50] In general, electron-donating neighboring groups result in a shift to lower wave numbers and electron-withdrawing neighboring groups result in a shift to higher wave numbers. However, the IR spectroscopic differences are usually too small to be able to distinguish between carbonyl compounds in the room air.

3.2 Chemistry

The C═O double bond is highly polar due to the different electronegativity of C and O and the easy polarizability of the π bond. Thus, because of its strong partial positive charge, the carbonyl carbon is a prominent electrophilic center in the aldehydes and ketones and is easily attacked by nucleophiles. Conversely, the oxygen is a nucleophilic center that is attacked by acid cations, for example H^+. In the presence of an α-hydrogen atom, they undergo keto–enol tautomerism. So the chemistry of carbonyl compounds is diverse.[42]

Fig. 4 shows five reactions that are important from an analytical point of view. Hemiacetals or hemiketals are formed with alcohols, which then react further with the elimination of water to form acetals and ketals. The reaction can be catalysed by acids and bases. However, even in the absence, a noticeable reaction is observed if the alcohol is used as the solvent. This is important when preparing analytical standards in methanol. The Hantzsch reaction originally served to synthesize 1,4-dihy-

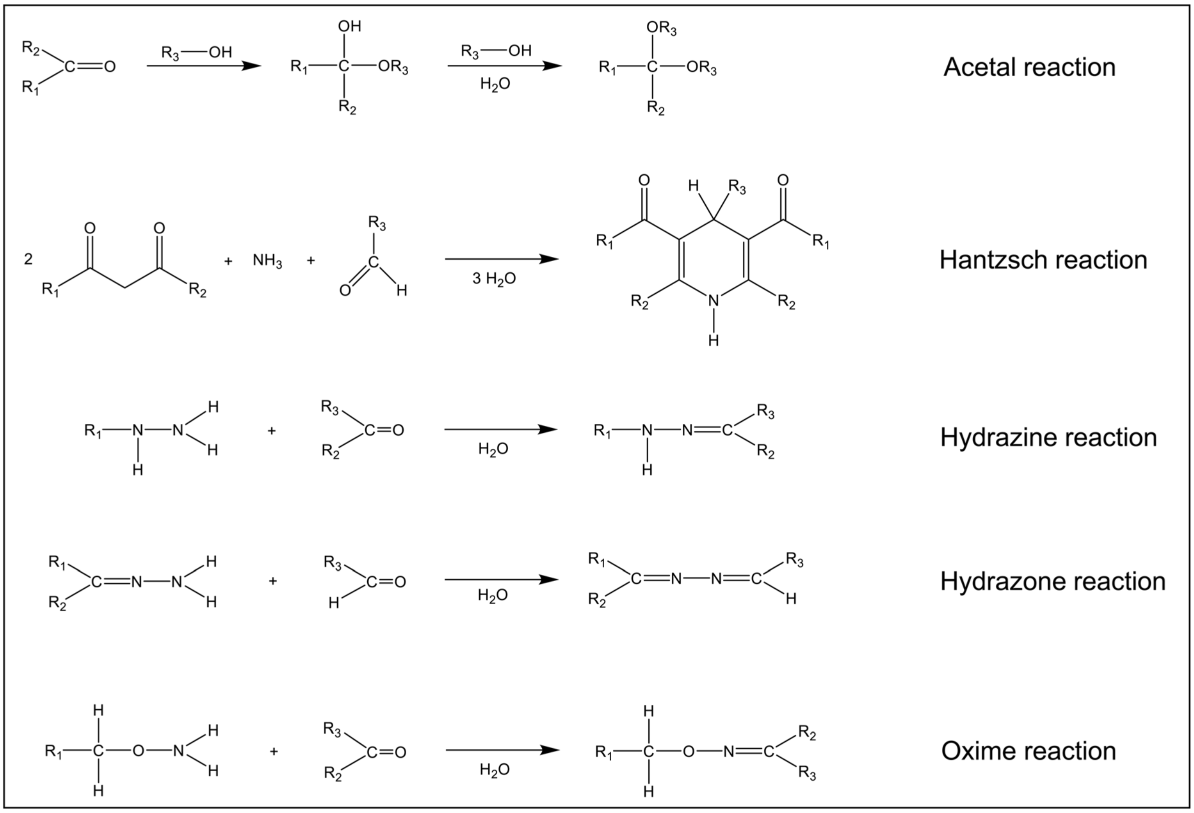

Fig. 4 Chemical reactions of carbonyl compounds relevant to the analytical chemistry of these compounds.

dropyridines and pyridines.[42] However, it has been shown that the dihydrolutidines synthesized with aldehydes and ketones are chromophores with broad absorption bands in the visible range and some of them also fluoresce. This makes these compounds interesting for analytical applications. The reaction of aldehydes and ketones with hydrazines to form hydrazones and the reaction of aldehydes with certain hydrazones also find wide attention in analytical chemistry. The resulting compounds have broad absorption bands in the UV and/or VIS. Oximes are formed when aldehydes and ketones react with hydroxylamine or its derivatives. It should be noted that only the formal reaction equations are shown in Fig. 4. The exact mechanisms can be found in organic chemistry textbooks.[42,51] Other derivatization reactions for the analysis of aldehydes and ketones have been published,[18,52] but these have largely lost their importance and will not be discussed here.

4 Colorimetry

4.1 UV/VIS spectrometry and fluorescence

The simple colorimetric methods have the general disadvantage that no substance separation takes place. In the case of substance mixtures, one must therefore ensure that the wavelength selected for detection, whether in absorption or emission, is specific to the target compound, which is essentially formaldehyde. The application of the Hantzsch reaction to formaldehyde analysis with 2,4-pentanedione (acetyl acetone) and ammonium acetate using UV spectrometry of the formed 3,5-diacetyl-1,4-dihydrolutidine (DDL) (see Fig. 5) was first published by Nash.[53] Belman[54] suggested using the fluorescence of DDL for formaldehyde analysis because of higher selectivity and sensitivity. The full photophysical properties of DDL (absorption coefficient, fluorescence quantum yield, thermal and photochemical degradation) were later described in detail.[55] DDL shows a broad absorption band at 412 nm and a fluorescence band at 510 nm. The derivatives of other carbonyl compounds with 2,4-pentanedione and ammonium acetate do not fluoresce, so the detection is specific for formaldehyde.[56] However, the fluorescence quantum yield is strongly temperature dependent,[57] so that attention must be paid to temperature constancy during the analysis. Salthammer[55] showed that the fluorescence quantum yield of DDL decreases by 11% when the temperature is increased from 20 °C to 30 °C.

Sampling is carried out by passing formaldehyde laden air through an absorber bottle where formaldehyde is quantitatively trapped in distilled water. The typical collected air volume is 60–80 l with an air flow rate of 2 l min^{-1}. Then the reagents are added and at 40 °C the reaction is complete in a few minutes. This so-called acetyl acetone method is available as a European standard.[58] The analytical details and comparisons with other methods are published in several papers,[20,52,59–61]

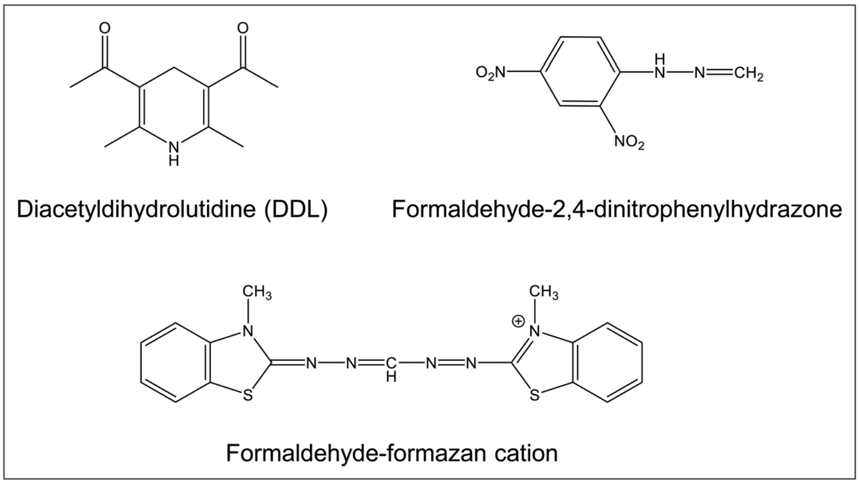

Fig. 5 Chromophores resulting from the reaction of formaldehyde with acetyl actone (2,4-pentanedione), DNPH and MBTH.

the full procedure can be found in EN 717-1.[58] In Europe, EN 717-1 is recommended for determining the release of formaldehyde from wood-based materials in test chambers.

At this point, two publications must be addressed separately. Roffael's book[62] deals with the role of formaldehyde in relation to wood and wood-based materials. Not only the historical and current methods for determining formaldehyde are discussed, but also the numerous international standards. Dugheri *et al.*[63] provide an excellent overview of sampling and analysis methods for formaldehyde. Active and passive sampling devices are listed in detail, as well as the various analysis techniques.

The fast course of the Hantzsch reaction and the simple fluorimetric detection also make the acetyl acetone method interesting for automated online analysis with high time resolution. Corresponding devices are commercially available and their suitability for the sensitive formaldehyde analysis indoors and outdoors has been proven.[20,64–66] When used in the field, however, the disadvantage is that the relatively large bottles with reagents also have to be carried along. With the conventional acetylacetone method, quantification limits (LOQ) of around 1 ppb ($1.2\ \mu g\ m^{-3}$) can be reached. The online method is even more sensitive at 0.3–0.5 ppb.

A completely different picture emerges with the MBTH method. Here, aldehydes react with 3-methyl-2-benzothiazolinone hydrazone (MBTH) to form a colored formazon cation (see Fig. 5).[67,68] Sampling is carried out directly in an aqueous solution of MBTH. Ammonia iron(III) sulfate and acetic acid are then added to complete the reaction. Similar to acetyl acetone, MBTH is suitable for automated analysis. Goebel *et al.*,[69] as well as Toda *et al.*[70] present devices for the near real time measurement of gaseous formaldehyde. However, the detection technique is UV/VIS spectrometry at 628–629 nm, which makes the method non-specific. With the MBTH method, a sum value is always determined for different aldehydes, only the calibration is done with formaldehyde. This aspect is often ignored or misinterpreted. Therefore it can be assumed that formaldehyde concentrations measured with the MBTH method tend to be too high. This can cause problems when comparing formaldehyde data measured with different methods.[71] Chan *et al.*[72] argue that concentrations of aliphatic aldehydes are generally lower than formaldehyde, but this is not necessarily the case. Fig. 6 shows the results of a study by Giesen *et al.*[73] It is a comparison of aldehyde measurements with 13 different materials (samples) in the air of environmental test chambers. The MBTH method suggests a formaldehyde concentration, which in fact results from the sum of several aldehyde components. Similar problems also arise for other colorimetric methods, which are not discussed here.[20,52]

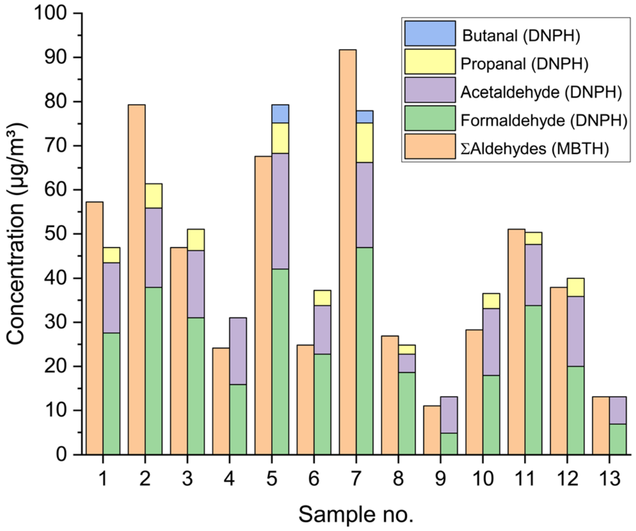

Fig. 6 Results of aldehyde measurements with DNPH and MBTH in test chambers on 13 different materials. Experimental details and data are published by Giesen *et al.*[73]

4.2 Enzymatic detection of formaldehyde

For an initial estimation of the formaldehyde concentration in the indoor environment, quick tests are sometimes used, which are available in pharmacies and drugstores and can also be handeled by non-experts. The principle is often based on an enzymatic reaction with a color change, the assessment is made optically against reference colors that are assigned to the corresponding concentration ranges. Such quick tests are quite suitable for an initial screening. However, one must always be aware that this is a very rough method that neither allows an exact concentration determination nor a health-related assessment.

Feldbrügge *et al.*[74] describe the formaldehyde dehydrogenase catalyzed reaction of formaldehyde with NAD^+ to formic acid and NADH. A diaphorase enzyme then transfers NADH and a colorless tetrazolium salt into NAD^+ and a colored formazan derivative. A further development of this method was published by Monkawa *et al.*,[75] who used the water soluble tetrazolium salt WST-8. In principle, it is also possible to determine the formaldehyde concentration by means of absorption measurements, although optical comparison has prevailed in the quick tests for reasons of simplicity.

5 Chromatography

5.1 HPLC-UV

The most important method for the analytical determination of low-molecular-weight carbonyl compounds in ambient air worldwide is DNPH. The exact procedures for sampling, separation of signals by HPLC and analysis are specified in ISO 16000-3[35] and can be read there. It is common practice that derivatization with 2,4-dinitrophenylhydrazine (see Fig. 4) is performed directly during sampling on DNPH impregnated silica cartridges. This can lead to the release of acetonitrile into the room air, so that VOC sampling using Tenax TA must not be carried out at the same time. The hydrazone formed with formaldehyde is shown in Fig. 5. The analysis is carried out by means of HPLC-UV (360 nm) after the formed hydrazones have been eluted from the cartridge with acetonitrile. The different hydrazones absorb light between 340 nm and 427 nm.[52] Typical sampling times are 5–60 min at an air flow rate of 0.5–1.5 $\mathrm{l\ min^{-1}}$. To achieve a limit of quantification (LOQ) of 1–2 $\mu\mathrm{g\ m^{-3}}$, an air collection volume of at least 60 l is required. The European standard EN 16516[76] "Construction products: Assessment of release of dangerous substances – determination of emissions into indoor air" stipulates the use of ISO 16000-3 for formaldehyde, acetaldehyde, propanal and butanal. Based on the DNPH reaction, Aiello and McLaren[77] have developed an automated sampling analysis system that enables the sensitive determination of formaldehyde, acetaldehyde, propanal, acetone and benzaldehyde over 2 h cycles. The DNPH method is sensitive to nitrogen oxides[78] and ozone,[79] so these compounds must be removed before the sampled air reaches the cartridge. Williams *et al.*[80] showed that carbon monoxide reacts with DNPH and interferes with the determination of acetone. DNPH-coated precolumns can also be used to remove interfering aldehydes and ketones from sampled air. This principle is applied in the gas chromatographic reactive sorption concentration (RSC) method.[81]

However, the DNPH method specified according to the 2022 version of ISO 16000-3[35] is far from being suitable for all carbonyl compounds. The standard applies to the saturated linear C1–C6 aldehydes, 3-methylbutanal, acetone, benzaldehyde, the methyl benzaldehydes and 2,5-dimethyl benzaldehyde. Acrolein and 2-butenal (crotonaldehyde) cannot be determined according to ISO 16000-3.[35] Ho *et al.*[82] examined the hydrazone derivatives of the unsaturated carbonyls acrolein, methacrolein, 2-butenal and 3-buten-2-one (MVK) and found that the DNPH is not suitable for these compounds. This is due in particular to the formation of dimers and trimers. However, Ho *et al.*[83] also applied the DNPH method to the analysis of dicarbonyls and C7–C10 aldehydes. Salthammer and Mentese[61] compared analytical methods for the determination of carbonyl compounds and found a very good agreement between the acetyl acetone and the DNPH method for formaldehyde. In contrast, when sampling on impregnated cartridges, the DNPH method gave lower results for pentanal and hexanal in comparison with thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) using Tenax TA as the adsorbent. The reason for this lies in the increasing hydrophobicity of the aldehyde with the chain length. The formation of water from the condensation reaction increasingly wets the silica surfaces of the cartridge as the reaction progresses. DNPH is also only slightly soluble in water.

The DNPH method is very well suited for passive sampling, whereby furfural and the higher aldehydes up to C11 (undecanal) can also be analytically recorded. Birmili *et al.*[24] determined the collection rates of a badge type passive sampler in a test chamber *versus* active methods according to ISO 16000-3 and TD-GC/MS for a total of 14 aldehydes. Villanueva *et al.*[84] applied a cylinder type passive sampler with integrated ozone scubber for the analysis of formaldehyde and acetaldehyde in air. These and other types of passive samplers are discussed by Dugheri *et al.*[63] Note that sampling rates only apply to a specific type of passive sampler and must therefore be determined individually.

Many variants of the DNPH method are known in the literature. Chi *et al.*[85] present a method for 32 carbonyl compounds by HPLC and electrospray ionization (ESI) tandem mass spectrometry (MS/MS) after derivatization with DNPH. A gradient capillary electrochromatography method was developed by Feng and Zhu[86] to measure 12 carbonyls in indoor air. Zhang *et al.*[87] optimized a DNPH-HPLC-MS method for the simultaneous determination of 30 atmospheric carbonyls. These and other methods have their place in special tasks, for example in the analysis of exhaust gas, but are rarely used to examine indoor air quality.

5.2 TD-GC/MS

Similar to the HPLC method discussed in the previous section, sampling on adsorbents with subsequent thermal desorption

(TD) and GC/MS analysis is also standardized with ISO 16000-6.[37] VOCs are defined as compounds that elute between *n*-hexane and *n*-hexadecane on a 5% phenyl 95% methyl polysiloxane phase capillary column. Tenax TA is the preferred adsorbent for this retention range. Organic compounds eluting before *n*-hexane are defined as VVOCs and organic compounds eluting after *n*-hexadecane are defined as SVOCs. For compounds with higher vapor pressures than that of *n*-hexane (approx. 16 kPa at 20 °C), other sorbents such as graphitized carbon, carbon molecular sieve and multiple sorbents are preferred. An air collection tube is normally filled with 200 mg Tenax TA, typical collection rates are 4–6 l at an air flow rate of 100–150 ml min^{-1}. The desorption of the collected molecules takes place at 300 °C in an inert gas stream. A quadrupole mass filter is standard for detection and quantification after gas chromatographic separation.[88] Identification is based on a retention index *versus* internal and external standards and using the electron ionization mass spectrum (70 eV). If a six-membered transition state is possible after excitation, carbonyl compounds undergo rearrangement and fragmentation reactions. However, identification with the help of spectral libraries usually succeeds without problems.[89] ISO 16000-6[37] generally requires a limit of quantification (LOQ) of at least 1 μg m^{-3} or less. This can be achieved with the usual sampling volumes of 4–6 l. An important issue concerns the accuracy and repeatability of ISO 16000-6 measurements. Wilke *et al.*[90] evaluated the results of six round robin tests carried out in test chambers with a typical VOC spectrum and found a relative standard deviation of 28%. It must also be stated at this point that there are alternative definitions for VVOCs, VOCs and SVOCs, for example from the World Health Organization (WHO) and the U.S. EPA.[31,91]

The thermal desorption process is also ideal for the passive detection of indoor air pollutants. In the axial collection type, single sorbent filled stainless steel tubes are fitted with a cap containing a fine mesh gauze that defines the sample surface. The other end of the tube is capped and kept sealed. Radial collectors are cylindrical and comprise a sorbent sampling cartridge housed in a porous polymer that allows sampling along and around the whole surface.[92] When sampling in the field, it must be remembered that Tenax TA (2,6-diphenyl oxide polymer) decomposes in the presence of ozone, nitrogen oxides and other reactive gases to form carbonyl compounds.[93,94]

From Table 1 it can be seen that the carbonyl compounds relevant for indoor environments cover a wide boiling point range between approximately −20 °C and +305 °C, but only a small proportion can be analyzed using the DNPH method. In Fig. 7 the retention indices of some carbonyl compounds are plotted in comparison to *n*-hexane and *n*-hexadecane. The horizontal red lines mark the boundary between VVOC/VOC and VOC/SVOC. The indices were calculated based on an alkane series for non-isothermal conditions.[88] Strictly speaking, MEK is a VVOC and benzophenone is an SVOC, but these substances can be determined analytically after sampling on Tenax TA using TD-GC/MS according to ISO 16000-6.[37] Even 2-methylpropanal (not displayed in Fig. 7), which is a VVOC with a retention index of around 500, can be analyzed using TD-GC/MS. Pentanal, although a C5 compound, already belongs to the group of VOCs. A comparison with the DNPH method has shown that aldehydes from C5 can be determined more precisely using TD-GC-MS with sampling on Tenax TA.[61] Benzaldehyde and its methyl derivatives are qualified for analysis according to ISO 16000-3, but can be determined more easily and precisely according to ISO 16000-6. Acetone is clearly a VVOC and can be reliably determined using the DNPH method. The general problem with VVOCs is that not all substances are covered by one sampling technique.[31] Schieweck *et al.*[38] have developed a thermal desorption method for C3–C6 compounds with sampling on graphitized carbon, which also works for various carbonyl compounds (see Table 1). A medium-polarity capillary column proved to be suitable for the gas chromatographic separation. Richter *et al.*[95] recommend combinations of graphitized carbon black, carbon molecular sieve and Tenax GR for the sampling of C1–C6 VVOCs with gas chromatographic separation on a polar capillary column. Even *et al.*[96] have compared several gas chromatographic methods for VVOC analysis and conclude that water removal is the greatest practical challenge.

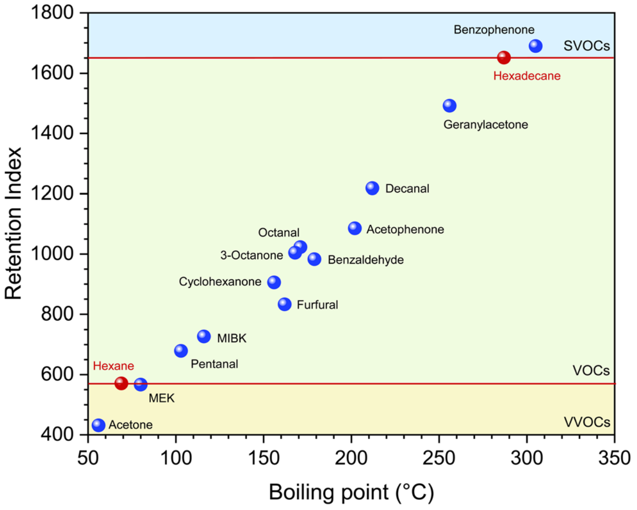

Fig. 7 Gas chromatographic retention indices of several carbonyl compounds *versus* boiling point in comparison to *n*-hexane and *n*-hexadecane. The indices were determined against a series of alkanes using a laboratory-specific method for non-isothermal conditions.[88]

Particular analytical problems are caused by the unsaturated compounds and dicarbonyls.[82,97] Various methods have been published for acrolein, the simplest unsaturated aldehyde, which are summarized by Schieweck *et al.*[25] The authors conclude that TD-GC/MS after sampling on graphitized carbon black is the most practical method for acrolein, because it is robust, easy-to-handle and very suitable for routine analyzes and surveys. With an air collection volume of 4 l a LOQ of 0.3 μg m^{-3} can be achieved. Sampling on graphitized black carbon with subsequent TD-GC/MS analysis also allows the determination of methylacrolein and MVK.[38] The higher unsaturated aldehydes starting from butenal can be determined using TD-GC/MS and with Tenax TA as a sorbent. Fig. 8 shows a multistandard. The substances were dissolved in methanol, spiked onto Tenax TA and the solvent was evaporated in an inert gas flow. The compounds shown in red color and in italics are used only to identify their retention time on the capillary gas chromatographic column. The analytical details are provided in the figure caption.

An alternative sampling technique is to collect air in stainless steel canisters. The contained VOCs are then pre-concentrated and injected into a GC/MS for separation, identification and quantification. Method TO-15A[98] of the U.S. EPA for ambient air provides a list of organic compounds that can be determined in this way, including acrolein, acetone, MEK, MIBK and 2-hexanone. With appropriate validation, other carbonyl compounds can also be determined according to TO-15A.

The preparation of liquid standards for identification and quantification in GC/MS measurements can lead to a well-known artifact in carbonyl analysis. Methanol is often used as a solvent because it can be easily removed after spiking onto the respective sorbent. However, as shown in Fig. 4, carbonyl compounds react with alcohols first to form hemiacetals and then further to form acetals. Uhde and Salthammer[99] observed the formation of 1,1-dimethoxy-cyclohexane from cyclohexanone in methanolic standard solutions. However, the reaction proceeds slowly under these conditions and can be prevented by storing the standard solution at −80 °C.

5.3 Other chromatographic methods

Most of the methods discussed in the following were developed for applications in outdoor air. Anderson *et al.*[41] studied dicarbonyl compounds (glyoxal, methylglyoxal, glutaraldehyde, diacetyl, and 4-OPA) in a simulated indoor air environment. The target compounds were collected in methanol and then derivatized to oximes (see Fig. 4) with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) according to a method published by Yu *et al.*[39] The mass spectrometric detection after gas chromatographic separation was carried out using an ion trap.[100] PFBHA was used by Seaman *et al.*[40] to determine the unsaturated aldehydes acrolein, methacrolein, MVK, 2-butenal and the dicarbonyls glyoxal and methylglyoxal. In this case, however, before the derivatization step, a formation of carbonyl-bisulfite adducts takes place. Wells and Ham used oxime formation with *O-tert*-butylhydroxylamine hydrochloride (TBOX) for the GC/MS detection of dicarbonyls resulting from the reaction of limonene with ozone.[101]

As an alternative to DNPH, dansylhydrazine (DNSH) can be used as a derivatization reagent with separation and detection *via* HPLC-UV for the analysis of carbonyl compounds. However, in the case of the unsaturated aldehydes, the identification of the derivatives is complex. For example, acrolein forms two mono-derivative isomers and one dimeric derivative with DNSH.[102]

Ho and Yu[82,103] developed a technique based on derivatization with pentafluorophenyl hydrazine (PFPH) and TD-GC/MS. The carbonyl compounds are collected on Tenax TA coated with PFPH. The authors describe their method as suitable for a wide range of aliphatic aldehydes (up to C8), acrolein, furfural and dicarbonyls. Li *et al.*[104] used collection onto solid sorbent coated with PFPH, followed by solvent extraction and GC/MS for the analysis of 20 airborne carbonyl compounds in

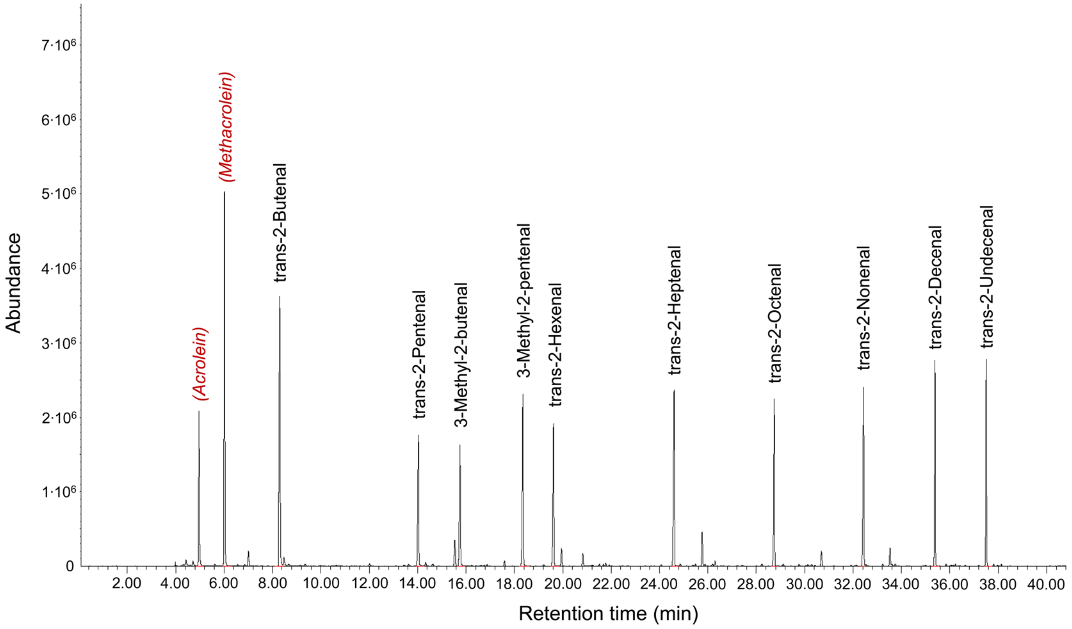

Fig. 8 Chromatogram of a multistandard of unsaturated aliphatic aldehydes for analysis according to ISO 16000-6.[37] Acrolein and methacrolein (in red) only serve to identify them on the capillary column *via* the retention time. Analytical parameters: GC: Agilent 7890; MS: 5977A; TD: Markes Unity TD100; Trap: −30 °C/300 °C; column: 5 MS Ultra inert 60 m × 250 µm × 0.25 µm; carier gas: He; oven: 32 °C → 300 °C; Mode: scan.

the C1–C10 range. Pang *et al.*[105] collected carbonyls on PFPH-coated Tenax TA, followed by solvent desorption and GC/MS analysis. The authors state that their method is reliable for 21 investigated carbonyl compounds in the C1–C9 range. When sampling takes place in a liquid medium, the relative derivatization performance between carbonyl compound and PFPH depends on the solvent.[106] Bourdin and Desauziers[107] used solid-phase microextraction (SPME) for the on-fiber derivatization of carbonyl compounds. The combination of a polydimethylsiloxane-divinylbenzene fiber with PFBHA proved to be suitable. For the investigated compounds formaldehyde, acetaldehyde and hexanal, acceptable to good limits of quantification were achieved using GC/MS analysis in the single ion mode (SIM) and in the extracted ion chromatogram (EIC). In general, SPME and other micromethods are well suited for screening purposes due to their easy handling.[108] However, this is often offset by disadvantages in terms of sensitivity and calibration effort compared to conventional sampling techniques.

6 Molecular spectroscopy

Finlayson-Pitts and Pitts[48] summarize the state-of-the-art analysis of carbonyl compounds in ambient air up to the year 2000. Many online methods have been developed for sensitive formaldehyde analysis in the ppt range. These include tunable diode laser spectroscopy (TDLS), cavity ring-down spectroscopy (CRDS), Fourier transform infrared (FTIR) and differential absorption optical spectroscopy (DOAS). Various comparison measurements with classical methods have been published: DOAS and CRDS with Hantzsch;[109] DOAS and PTR-MS (see next section) with Hantzsch and DNPH.[110] DOAS and FTIR with Hantzsch and DNPH.[64] A work by Hanoune *et al.*[111] comparing infrared diode laser spectroscopy with DNPH was performed indoors.

Another technique that has now become established for measuring formaldehyde in environmental test chambers and indoor air is photoacoustic spectroscopy (PAS). This involves irradiation of a sample with intermittent infrared light and detecting the periodic temperature changes in the sample as pressure fluctuations.[112] The type of excitation is decisive for the selectivity and sensitivity. Conventional PAS devices work with a broadband IR source, the desired wavelength is selected with a narrow-band filter. In the case of carbonyl compounds, the less specific C–H vibrations between 2500 cm^{-1} and 3000 cm^{-1} (see Fig. 3) are usually observed. The poor resolution makes conventional PA spectroscopy unsuitable for the indoor air analysis of carbonyls. More advanced devices use laser excitation, whereby the analysis is usually limited to the well-resolved vibrational bands of formaldehyde. Hirschmann *et al.*[113] measured the spectrum of formaldehyde from 1772 cm^{-1} to 1777 cm^{-1} by tuning a quantum cascade laser with a spectral resolution of 0.018 cm^{-1}. The band at 1773.959 cm^{-1} was finally selected for analysis. The cross section of the formaldehyde $C{=}O$ IR absorption band in this range is in the order of 10^{-18} cm^2 per molecule,[114] depending on the spectral integration width. This enables the specific monitoring of formaldehyde with detection limits in the sub-ppb range. Photoacoustics with quantum cascade lasers as a light source has now been further developed for routine analysis and, like the online Hantzsch method, enables specific, sensitive and precise formaldehyde analysis in indoor test chamber environments with high time resolution.

This is shown in Fig. 9 using the example of a chamber experiment with a burning candle according to EN 16738.[115] The blue curve represents the time course of the formaldehyde chamber concentration, which was measured with a photoacoustic device (Gasera Ltd) and laser excitation of the $C{=}O$ vibrational band at a time resolution of 10 s. The DNPH measurements (red dots) carried out for comparison correctly reflect the respective mean value over the sampling period of 60 minutes (red bars), but cannot depict the dynamics of the concentration profile.

When using suitable IR laser light sources and multi-pass optical cells, classic IR spectroscopy can also be used under certain conditions for the specific determination of formaldehyde. The gas analysis to determine the formaldehyde release from wood-based materials is standardized according to ISO 12460-3,[117] with the formaldehyde determination being carried out using the acetylacetone method. It is currently under discussion whether IR laser spectroscopy should also be permitted, provided the method shows equivalent test results to acetylacetone analysis.

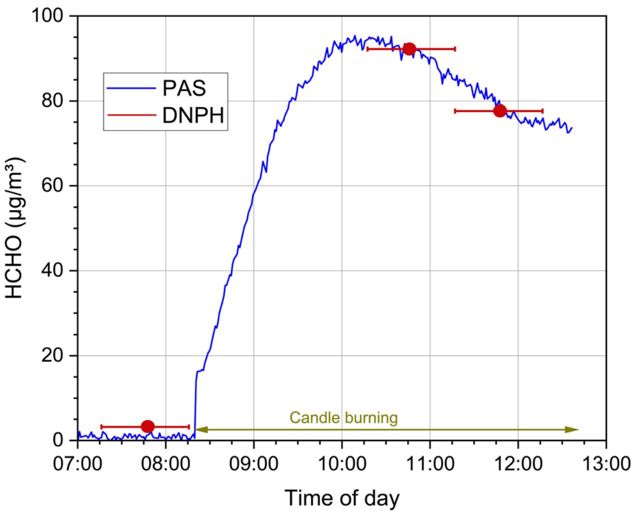

Fig. 9 Time course of the formaldehyde concentration when burning a candle in a 1 m^3 test chamber according to EN 16738[115] (T = 23 °C, relative humidity = 50%, air exchange rate = 2 h^{-1}, see also Salthammer *et al.*[116] for the detailed experimental conditions). The blue curve represents the online measurement with a photoacoustic device (Gasera One), the red dots are the concentrations determined from a 60 min sampling using the DNPH method, the red lines indicate the duration of the sampling.

7 Online mass spectrometry

In recent years, proton-transfer-reaction mass spectrometry (PTR-MS)[118,119] has experienced increased application to indoor air issues. The reason for this is a wide range of studies on trace substances,[120] chemical reactions[121] and the personal chemical cloud of humans.[122,123] A PTR-MS device consists of an ion source, a reaction and drift tube for transferring the proton to the target molecule (R) and a mass selective detector. In most cases, H_3O^+ ions are used, so the reaction proceeds according to eqn (1). A related technique is Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), which is particularly applied for breath gas analysis.[124] SIFT-MS employs eight reagent ions (H_3O^+, NO^+, O_2^+, OH^-, O^-, O_2^-, NO_2^- and NO_3^-), which greatly facilitates the identification of isomeric organic compounds.

$$R + H_3O^+ \rightleftharpoons RH^+ + H_2O \tag{1}$$

The $[M + 1]^+$ ions generated in the PTR-MS drift tube can be analyzed using either a low-resolution quadrupole filter (QMS) or a high-resolution time-of-flight (ToF) detector. Quadrupoles have only limited applications and are not usually used to identify components in mixtures of substances.[125] However, reaction (1) only occurs if the proton affinity of the target molecule is higher than that of water (691 kJ mol^{-1}).[126] This means that PTR-MS is hardly suitable for the analysis of formaldehyde, which has a proton affinity of 712 kJ mol^{-1}.[126] In this case increasing humidity strongly supports the back reaction.[127,128] Another analytical problem is the fragmentation of molecules with longer chain lengths, which has been investigated for aldehydes and ketones by Španěl *et al.*[129] There is no fragmentation observable up to propanal (C3). Starting with butanal (C4), the $[M + 1]^+$ ions increasingly split off water, which is shown in eqn (2) for the hexanal example. The ratio of *m*/*z* 101.096 to *m*/*z* 83.086 is approximately 1 : 1.[129,130] On the other hand, the fragmentation of aldehydes is advantageous insofar that it can be used to distinguish from ketones of the same molecular mass, which, according to the results of Španěl *et al.*,[129] do not fragment. A comprehensive library with fragmentation reactions of organic compounds after protonation was published by Pagonis *et al.*[131]

$$C_5H_{11}CHO \xrightarrow{H_3O^+} C_5H_{11}CHOH^+ \xrightarrow[H_2O]{} C_6H_{11}{}^+ \tag{2}$$

The concentration of the target molecule [R] can be obtained from eqn (3) if the drift time t_r in the reaction tube and the proton-transfer rate constant k_{PT} are known. $[RH^+]$ and $[H_3O^+]$ are the concentrations of the product and the primary ion, respectively. This shows the difference between PTR-MS and other analytical procedures, because there is no calibration in the classic sense using conventional statistical methods.[132] The drift time t_r has to be calculated from the respective instrument settings.[133]

$$[R] = \frac{1}{k_{PT} \cdot t_r} \frac{[RH^+]}{[H_3O^+]} \tag{3}$$

The reaction rate constant k_{PT} can only be determined experimentally to a very limited extent, since the corresponding test gas is required for this. It is much easier to calculate k_{PT} from the ion-dipole collision theory. With the so-called "capture theory", Su[134] has developed parameterizations based on trajectory analyses. Eqn (4) shows the principle. According to Langevin, the reaction constant consists of a non-polar part k_L, which only takes into account the polarizability α, and a polar part k_{μ_D}. In practice, k_{PT} is obtained by multiplying k_L with the capture parameter K_{cap}, which depends on the dipole moment μ_D of the molecule and the temperature T in the reaction chamber. The parametrization procedure for calculating K_{cap} was originally published by Su[134] and has been summarized by Cappellin *et al.*[133] and Salthammer *et al.*[135] for PTR-MS applications.

$$k_{PT} = k_L + k_{\mu_D} = k_L(\alpha) \times K_{cap}(\mu_D, T) \tag{4}$$

The calculation according to the capture theory also raises some problems. Firstly, the polarizabilities and dipole moments for many organic compounds in the gas phase are not known or only known imprecisely. Secondly, k_{PT} also depends on the reaction conditions in the drift tube, in particular on the ratio of the electric field strength (E) to the molecular density (N). Fig. 10 shows the k_{PT} values for three polar molecules as a function of E/N. Note that the k_{PT} of non polar compounds is not affected by the E/N value. E/N ratios of 100–120 Td are typical for PTR-MS measurements. Lower values result in more water clusters, higher values result in more complicated fragmentation patterns.

Table 2 lists carbonyl compounds for which k_{PT} values calculated according to the capture theory (E/N = 120 Townsend) are available. The dipole moments and polarizabilities for the

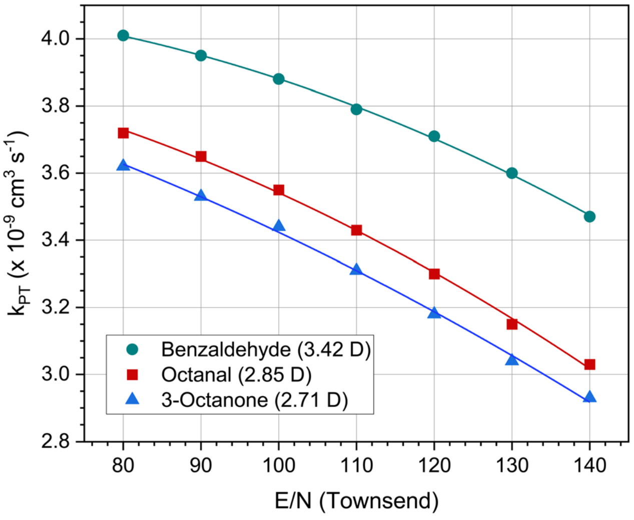

Fig. 10 Dependence of the proton-transfer reaction constant k_{PT} on the *E*/*N* ratio (electric field to molecular density) set in the PTR-MS device at 353 K for benzaldehyde, octanal and 3-octanone. The values in brackets indicate the respective dipole moment in Debye. The data were taken from Salthammer *et al.*[135]

Table 2 CAS numbers, proton affinities (PA),[126] dipole moments (μ_D), polarizabilities (α) and proton-transfer rate coefficients k_{PT} at 353 K[135] or 363 K[133] (120 Td) of carbonyl compounds

Compound	CAS	PA (kJ mol^{-1})	μ_D (Debye)	α (10^{-24} cm^3)	k_{PT} (10^{-9} cm^3 s^{-1})
Acetaldehyde[135]	75-07-0	768.5	2.94	4.45	3.13
Propanal[135]	123-38-6	786.0	2.85	6.14	3.12
Butanal[135]	123-72-8	792.7	2.83	7.90	3.16
2-Methyl propanal[135]	78-84-2	797.3	2.91	7.88	3.21
Pentanal[135]	110-62-3	796.6	2.85	9.68	3.22
Hexanal[135]	66-25-1		2.83	11.45	3.24
Heptanal[135]	111-71-7		2.86	13.25	3.29
Octanal[135]	124-13-0		2.85	15.04	3.30
Nonanal[135]	124-19-6		2.85	16.84	3.32
Decanal[135]	112-31-2		2.85	18.66	3.35
Acrolein (*trans*)[135]	107-02-8	797.0	3.43	6.34	3.54
Acrolein (*cis*)[135]	107-02-8	797.0	2.81	6.14	3.11
Methacrolein[133]	78-85-3	808.7	2.80	8.41	3.20
trans-2-Butenal[135]	123-73-9		4.20	8.40	4.11
trans-2-Hexenal[135]	6728-26-3		4.37	12.02	4.33
Furfural (*trans*)[135]	98-01-1		3.60	9.82	3.70
Furfural (*cis*)[135]	98-01-1		4.31	9.88	4.15
Benzaldehyde[135]	100-52-7	834.0	3.42	12.53	3.71
Glyoxal (*cis*)[135]	107-22-2		3.68	4.64	3.51
4-OPA[135]	626-96-0		2.95	9.73	3.24
Pinonaldehyde[133]	2704-78-1		2.26	18.56	2.96
Acetone[135]	67-64-1	812.0	3.11	6.15	3.29
MEK[135]	78-93-3	827.3	2.97	7.86	3.25
2-Pentanone[133]	107-87-9	832.7	2.84	10.07	3.24
MIBK[135]	108-10-1		2.87	11.36	3.27
3-Octanone[135]	106-68-3		2.71	14.90	3.18
6-MHO[135]	110-93-0		2.88	15.12	3.34
Geranylacetone[135]	3796-70-1		2.78	23.77	3.44
Cyclohexanone[135]	108-94-1	841.0	3.45	10.57	3.65
Acetophenone[135]	98-86-2	861.1	3.16	14.20	3.55
Benzophenone[135]	119-61-9	882.3	3.11	22.62	3.63
1-Methyl-2-pyrrolidone[135]	872-50-4	923.5	4.12	10.28	4.05

gas phase were calculated using quantum chemical methods. The values of Salthammer *et al.*[135] refer to 353 K, those of Cappellin *et al.*[133] to 363 K.

The PTR-MS method is now firmly established in the determination of airborne carbonyl compounds and is always in demand when small concentrations with high dynamics have to be monitored. However, one must not overlook the disadvantages related to calibration, which will be discussed in a later section.

8 Ion mobility spectrometry

Another analysis method that works with a drift tube is ion mobility spectrometry (IMS). The technique is widely used for routine detection of explosives and drugs. With regard to carbonyls, IMS is suitable for monitoring the production process of beer with the off-flavor target compounds diacetyl and 2,3-pentanedione.[136] The molecule is ionized in the tube and moves in an electric field depending on its mass and other molecular properties with a specific drift velocity to the detector, which is often an electrometer. The drift time of the ions is usually in the millisecond range and also depends on the length of the drift tube. Sensitivity and selectivity of the IMS can be significantly increased by combination with gas chromatography and mass spectrometry.[137–139]

So far there have only been a few applications of the IMS in the chemical analysis of indoor air. The reason for this is that other methods such as TD-GC/MS have clear advantages in non-target analysis. IMS can always be considered when dealing with a small and defined spectrum of organic molecules. Tiebe *et al.*[140] used IMS to detect 14 microbial volatile organic compounds (MVOCs), including various ketones, that can serve to screen for mold infestation in rooms. However, the detection limits for these carbonyls were disproportionately high at 8–14 μg m^{-3}. A combination of gas chromatography and IMS was used by Ruzsanyi *et al.*[141] to detect saturated and unsaturated carbonyl compounds released from the skin surface. By using a short multi-capillary column, a time resolution of about 5 min could be achieved.

There are a few other publications that deal with the application of IMS for analytical questions of indoor air.[142] In conclusion it can be stated that the method certainly has some interesting features, but no significant advantages over those already discussed.

9 Discussion

Szulejko and Kim[143] provide a summary of derivatization techniques for the determination of carbonyls in air, which also addresses sampling techniques such as solid phase micro extraction (SPME), which is not addressed in detail in this work. The authors conclude that despite many problems, carbonyl analysis techniques still rely heavily on the combined application of DNPH derivatization, HPLC separation and UV or MS detection. Table 1 lists analytical methods recommended for each compound. However, this does not mean that the determination must always be carried out using this method. The release of formaldehyde from wood-based materials is a slow process[144] that can be easily tracked using EN 717-1.[36] In contrast, 4-OPA and 6-MHO are formed and released within seconds when the skin surface is exposed to ozone, which necessitates high-resolution online detection.[17] Table 3 summarizes the methods discussed in this work. The table is not complete, but derivatization methods that are rarely used today, such as chromotropic acid and pararosaniline, are not considered and can be looked up in Vairavamurthy *et al.*[52] and Szulejko and Kim.[143] Moreover, some of the methods listed in Table 3 aim at detecting outdoor air species, which often requires very low detection limits. In the indoor environment, however, compliance with guide values is often important,[145] which requires good precision and reproducibility, but usually does not pose an analytical challenge with regard to the detection limit. An exception is acrolein.[25]

One has to realize that several methods are usually required to detect a wide range of carbonyl compounds in the room air. By default, this is the DNPH method according to ISO 16000-3[35] in combination with the TD-GC/MS method according to ISO 16000-6.[37] Some substances can be determined using both methods. As a rule of thumb, the TD-GC/MS method delivers better results from a chain length of C5.[61] Other methods can be used alternatively or additionally. Today it is undisputed that unsaturated carbonyls cannot be determined quantitatively with the DNPH method. With regard to the dicarbonyls, the statements are contradictory.

Most absorption and IR spectroscopic online methods are only suitable for formaldehyde. In absorption spectroscopy, this is due to the comparatively well-resolved and red-shifted spectral structure. However, the weak $n \rightarrow \pi^*$ transition requires long light paths, so techniques such as DOAS cannot necessarily be recommended for indoor use. A different picture emerges for photoacoustics. Quantum cascade lasers enable the targeted excitation of the C═O stretching vibration band of formaldehyde and the necessary detection limits can also be achieved.[113] The technical designs of the available devices correspond to practical requirements.

The PTR-MS method requires a detailed evaluation and critical discussion. The method undoubtedly has a number of advantages when it comes to sensitivity and temporal resolution. However, even when using a time-of-flight mass detector (ToF), it is not possible to distinguish the $[M + 1]^+$ ions from molecules of identical monoisotopic masses. This is only possible using typical fragmentation patterns. Moreover, the fragmentation reactions depend on the E/N ratio in the drift tube and increase with increasing E/N.[118] This may also be the reason why different ratios of fragmentation ions are reported in the literature.[131] The interpretation of fragmentation patterns becomes more difficult with increasing number of chlorine, bromine and sulfur atoms due to their natural isotopic distribution. In addition, substances such as 1-octen-3-ol and octanal show almost indistinguishable fragmentation patterns.[148]

The more important point concerns the calibration of PTR-MS measurements. Standard methods such as ISO 16000-3[35] and 16000-6[37] have the advantage that their calibration is traceable and they can therefore be accredited. This is not the

Table 3 Analytical methods for the quantitative determination of carbonyl compounds in indoor and outdoor air

Method	Comments
Hantzsch[53,54]	Selective for formaldehyde with fluorescence detection,[55] standardized by EN 717-1[36]
Hantzsch online[110]	Selective for formaldehyde with fluorescence detection
DNPH (HPLC-UV)	Recommended for selected aldehydes and ketones, standardized by ISO 16000-3[35] and ASTM 5197-21[146]
DNPH (HPLC-MS)[87]	30 carbonyls
DNPH (HPLC-MS/MS)[85]	32 carbonyl compounds
DNSH (HPLC-UV)[102]	15 saturated and unsatured aldehydes
PFPH (TD-GC/MS)[103]	14 carbonyls and dicarbonyls
PFPH (GC/MS)[105]	21 carbonyls
PFBHA (GC-MS)[41]	Dicarbonyls
PFBHA (GC/MS)[40]	Dicarbonyls and unsaturated aldehydes
TBOX (GC/MS)[101]	Dicarbonyls from limonene/ozone reaction
TD-GC/MS (Tenax TA)	Carbonyls ≥C4, standardized by ISO 16000-6[37]
TD-GC/MS (carbon black)[25,38]	Saturated and unsaturated aldehydes ≤C4
Canister sampling (GC/MS)[98]	Acrolein, acetone, MEK, MIBK, 2-hexanone, standardized by U.S. EPA TO-15A
MBTH[73]	Not specific, sum value for aldehydes
TDLS[111]	Selective for formaldehyde
DOAS[109,110]	Selective for formaldehyde
CRDS[109]	Selective for formaldehyde
FTIR[64]	Selective for formaldehyde
PAS (laser excitation)[113]	Selective for formaldehyde
PTR-MS[118,147]	Broad range of carbonyls and dicarbonyls
SIFT-MS[124]	Broad range of carbonyls and dicarbonyls
IMS[138,139]	Suitable for preselected carbonyls and dicarbonyls
Other methods	Vairavamurthy *et al.*,[52] Szulejko and Kim[143]

case with the PTR-MS. The k_{PT} values at 353 K of the three carbonyls shown in Fig. 10 are calculated and differ by 15–25% in the range from 80 Td to 140 Td. Another critical parameter in eqn (3) is the drift time t_r, which is made up of measured variables such as the length of the drift tube and the drift voltage, but also of calculated variables such as the reduced ion mobility. Therefore, the PTR-MS can only be calibrated for a specific device setting. Pham *et al.*[149] investigated the VOC release rates from 3D printed samples by coupling a microchamber/thermal extractor system with a PTR-MS. Where available, the authors use compound specific reaction rate coefficients for calibration. Otherwise a default value of $k_{PT} = 2.0 \times 10^{-9} \text{cm}^3 \text{ s}^{-1}$ was applied. Pagonis *et al.*[150] used a 10 component test gas for six point calibration. For other compounds, calibration factors were determined by averaging the factors of all calibrants. Lunderberg *et al.*[120] also performed the calibration of their PTR-MS with authentic external standards. If these were not available, the default values of the device were used; the authors estimate the error at −40% to +60%. It is clear that the use of such default values disqualifies analytical methods when it comes to health assessments of building product emissions or indoor air quality. The three cited publications[120,149,150] correctly emphasize that PTR-MS is the method of choice to characterize the dynamic nature of VVOCs and VOCs and is especially suited to measuring highly volatile compounds. However, there is still a long way to go before the method can be used for tasks that require accredited measurements. This applies in particular to the polar carbonyl compounds, whose reaction constants are strongly influenced by the system settings.

10 Conclusion

For various reasons, it is important and necessary to determine the quality and quantity of carbonyl compounds in the room air. Substances such as formaldehyde[20] and acetaldehyde[23] are classified as carcinogenic and are subject to strict regulations, guide values have been published for various aldehydes, ketones and lactams,[145] substances such as decanal,[151] 4-OPA, 6-MHO, geranylacetone,[17] glyoxal and acroleine[152] are markers for chemical reactions. Individual compounds can be specifically analyzed and with the necessary accuracy. However, the task becomes more difficult when many carbonyl compounds have to be determined in parallel and the appropriate methods have to be selected in a targeted manner. This contribution should help to choose the right analytical method and to keep the effort as low as possible but as large as necessary.

Abbreviations

BP	Boiling point
CRDS	Cavity ring down spectroscopy
DDL	3,5-Diacetyl-1,4-dihydrolutidine
DNPH	2,4-Dinitrophenylhydrazine
DNSH	Dansylhydrazine
DOAS	Differential optical absorption spectroscopy
EIC	Extracted ion chromatogram
EN	European norm
E/N	Ratio of electric field strength and molecular density in the PTR-MS drift tube
ESI	Electrospray ionization
FTIR	Fourier-transform infrared
GC/MS	Gas chromatography/mass spectrometry
HPLC	High performance liquid chromatography
IMS	Ion mobility spectrometry
IR	Infrared
ISO	International organization for standardization
K_{cap}	Capture parameter in ion-dipole collisional theory
k_L	Proton-transfer rate constant according to Langevin
k_{PT}	Proton-transfer rate constant
k_{μ_D}	Dipole related proton-transfer rate constant
LOQ	Limit of quantitation
MBTH	3-Methyl-2-benzothiazolinone hydrazone
MS/MS	Tandem mass spectrometry
MVOC	Microbial volatile organic compound
MW	Molecular weight
NAD^+	Oxidized nicotinamide adenine dinucleotide
NADH	Reduced nicotinamide adenine dinucleotide
PAS	Photo acoustic spectroscopy
PFBHA	*O*-(2,3,4,5,6-Pentafluorobenzyl) hydroxylamine
PFPH	Pentafluorophenyl hydrazine
ppb	Parts per billion (refers to the volume mixing ratio)
ppm	Parts per million (refers to the volume mixing ratio)
PTR-MS	Proton-transfer-reaction mass spectrometry
SIFT-MS	Selected ion flow tube mass spectrometry
SIM	Single ion mode
SPME	Solid phase micro extraction
SVOC	Semi volatile organic compound
TBOX	*O-tert*-Butylhydroxylamine hydrochloride
TD	Thermal desorption
TDLS	Tunable diode laser spectroscopy
Tenax GR	Graphitized Tenax
UV	Ultraviolet
VIS	Visible
VOC	Volatile organic compound
VVOC	Very volatile organic compound
WST-8	Sodium-2-(2-methoxy-4-nitrophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2*H*-tetrazolium

Conflicts of interest

The author has no conflicts of interest to declare.

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