

MONITORING INDOOR AIR FOR VOLATILE ORGANIC COMPOUNDS



Clean air contains very few volatile organic compounds (VOCs). Methane is only present at 2000 ppb (parts per billion), ethane at 1 ppb and formaldehyde at 0.5 ppb. Higher concentrations of VOCs arise from human activity, burning vegetation, or occasionally volcanic activity.

Total emissions of particulates and volatile organic compounds other than methane (NMVOCs) in the UK have decreased by more than 50% since 1990. This is good news, and largely thanks to a dramatic decrease in vehicle emissions, a trend seen in many other countries. Simultaneously, research has revealed in more detail the exposure of people to particulates and VOCs, and their effect on health. Definitive thresholds have been compiled for VOC concentrations indoors such as those provided by Public Health England in 2019, presented in the table below.

Compared to the 8 hr time weighted average (TWA) safety thresholds presented in the table, the short term guideline exposure limits are orders of magnitude lower. There are several reasons for this. The guideline limits are advisory and refer to persistent exposure, whereas safety thresholds are mandatory and relate to workplace exposure. The guidelines arise from long-term exposure studies. The tabled data is reflective of very contemporary long-term studies. Recommended exposure limits have tended to decrease in line with better management of volatiles, more detailed research and societal expectations.

Some public locations present special and exceptional levels of specific VOCs. For example, indoor environments located close to transportation, such as petrol stations, bus stations, garages, or airport departure gate entrances, may on occasion be subject to high fugitive fuel emissions. Dry-cleaning shops are exposed to dry-cleaning fluids such as trichloroethylene. Refectory and restaurant kitchens are liable to generate acetaldehyde or acetamide. In any space where air internally circulated, any solvents in use will accumulate. Organic acid and sulphur containing VOCs are also common 'nuisance odours' affecting indoor air quality, though usually the 'nuisance' is at concentrations that are not readily discernible with commercial detectors.

Monitoring VOCs indoors

Given the range of VOC's in air and their variable harmfulness, it might seem preferable to monitor the more ubiquitous and harmful of them individually. Despite the technological revolution of recent decades, analysis of individual VOCs continues to rely

VOC	Guideline exposure limits		EH40 TWA limit ppb	Main sources								
	short term ppb	long term ppb		building materials, furnishings, A	varnishes, paints, lacquers B	domestic cleaning products C	cooking D	secondary pollutant E	external - combustion F	external - fuel vapour G	external - other H	tobacco smoke I
formaldehyde	80	8	2,000	x	x	x	x	x	x			x
acetaldehyde	770	150	20,000	x			x	x	x			x
benzene	0	0	1,000	x	x					x		x
trichloroethylene	0	0	100,000		x						x	
toluene	3,900	590	50,000		x					x	x	x
tetrachloro-ethylene		6	20,000		x	x						x
xylenes		22	50,000		x						x	
styrene		190	100,000	x							x	x
α-pinene	7,800	780				x						
D-limonene	15,700	1570				x						
naphthalene		1								x		x
TVOC		~100										

Table. IAQ guideline data from the UK in 2019. The exposure limits have been converted to ppb at 1 bar and 25 °C. Short term limits are for exposures averages over 0 to 60 min, long term for a day or a year. 'EH40 TWA limits' are provided for comparison, also from the UK. 'TVOC' refers to 'Total Volatile Organic Carbon'. The ppb value is derived from 0.3 mg/m³ assuming a mean molecular weight of 80 g/mol, sourced from European guidelines for building regulations.

upon gas chromatographic separation of volatiles, followed by their detection. The cost and service burden of such VOC analysers remains high – much too high for wide deployment. But some specific VOC detectors and sensors are commercially available.

Formaldehyde is a major air contaminant indoors, especially in newly furnished rooms, typically outgassing from fibreboard and plastics or a few months after installation. Fairly inexpensive monitors engaging metal oxide semiconductor based sensors provide robust responsivity. A potential drawback is their significant cross sensitivity and slow clear down on exposure to other gases. Sensors which provide selective formaldehyde detection at low levels appear to be commercially elusive.

Benzene arises primarily from external sources but is also found in paints. Selective monitors are available which engage miniaturised GC-PID (gas chromatography-photoionisation detection).

Specific air quality monitors are unknown for tri and



tetrachloroethylene, which are extensively used as solvents in cleaning, and are prone to high retention times within soil. In industry, as with other VOCs, chlorocarbons are most commonly monitored over a workday's exposure by personnel wearing a badge or patch on which VOCs are trapped. VOCs are subsequently thermally released and analysed. Such technology is not really appropriate in the home or public space.

Why monitor VOCs generically

Despite the variable thresholds recommended for indoor VOCs, there is strong justification for non-selective VOC monitoring. Clean air is extremely free of VOC's. So, as long as it doesn't sense methane, a generic air quality monitor, can prospectively detect very low levels of any VOC without alarming excessively. This approach is supported by the fact that VOCs often co-occur: they appear together from a particular source. In these instances, a more abundant and less toxic VOC can often present itself as a 'tag' for one that is more toxic. For example, benzene is considered so carcinogenic that in the air quality guidelines tabled above 'no safe level' is recommended. But because benzene usually co-occurs with other less toxic VOCs at much higher concentrations, such as fugitive fuel vapours or volatilising paint solvents, it is reasonable to monitor and respond to such compounds at a higher and more practically measurable level. This principle is embraced in various guidelines, by providing a total indoor VOC concentration threshold, such as $0.3 \mu\text{g}/\text{m}^3$ (~100 ppb) for building ventilation. A single threshold such as this enables a standard to be applied diversely, as well as providing a single performance criterion against which monitoring technologies can be assessed and calibrated.

Routine VOC monitoring is usually considered after every effort has been made to reduce or eliminate VOC sources. In a domestic environment, VOC removal is typically just a matter of opening a window to a 'stuffy' room. For large buildings, where VOCs arise from internal sources, (see Table, columns A to E) the primary means of their removal is by forced extraction. VOC monitoring then provides a means to regulate ventilation, safeguarding health whilst minimising the costs of air conditioning.

At some locations, external air may be prone to contain VOCs (see Table, columns E to I). In such cases, it may be filter replacement costs that are minimised by VOC monitoring.



Whatever the case, VOC monitors form part of a procedural system, in which reliable measurement is required both above and below target exposure limits: false alarms and failure to alarm are equally compromising.

Additionally, monitors are normally expected to require minimal service and maintenance, and cost is also critical, particularly in monitors that might be deployed in generic VOC monitoring.

Generic indoor air monitors

As is always the case with technology, there is a trade off between price and performance. But within performance, servicing must also be considered. As a high cost option, Flame Ionisation Detection (FID) provides the sensitivity, linearity and rapidity of response required for air quality monitoring. It delivers a fair measurement of total VOC in mg/m^3 . However, the requirement for a hydrogen flame has prevented the technology from being available without a continuous service burden. It also responds to 2000 ppb methane in air, which is liable to compromise the discernment of non-methane VOCs at lower concentrations.

Amongst low cost sensing options, all of which provide an adequately fast and reliable response, IR sensors are fairly non-VOC discriminating, but lack sensitivity to sub-ppm (<1000 ppb) levels.

Metal oxide sensors are more sensitive, but non-linear and over-selective to specific VOCs. Additionally, they are subject to drift.

The generic VOC monitor of choice is photo-ionisation detection (PID) engaging a krypton lamp ('PID-Kr'). It responds to few inorganic compounds such as ammonia and sour gas. It detects any VOC which ionises at less than 10.6 eV. This includes all VOCs containing two carbons or more except for most fluorocarbons, saturated chlorocarbons, ethane, ethyne and propane. PID is now available as compact sensors which resolve all the compounds except formaldehyde in the table at levels of a few ppb (1 ppb = 0.001 ppm) or less.

Summary

Clean air is largely defined by the absence of VOCs apart from methane, and particulates. The VOCs of concern are chemically diverse, vary in their toxicity, and arise from several sources, both from indoors and out of doors. None the less, the concept of 'total volatile organic compounds' is well recognised, being stipulated for example, in building ventilation guidelines. A few technologies are capable of detecting VOCs non-selectively. Of these, PID is the best suited and most widely deployed.

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