Volatile Organic Compounds in Indoor Environments

Godwin A Ayoko and Hao Wang

Abstract This chapter provides an overview of the types, sources and current techniques for characterising volatile organic compounds (VOC) in nonindustrial indoor environments. It reviews current knowledge on the levels of volatile organic compounds in indoor environments, discusses concepts for regulating indoor levels of volatile organic compounds and appraises current efforts to understand the links between VOCs and building-related health/sensory effects. It also provides an up-to-date outline of new trends in and perspectives for indoor air VOC research.

Keywords Characterisation, Purification, Regulation, Sampling, Volatile organic compounds (VOCs)

Contents

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Abbreviations

AFoDAS/AVODAS	Automated formaldehyde data acquisition system/automated VOC data acquisition system
AM	Arithmetic mean
BRI	Building-related illness
BTEX	Benzene toluene, ethylbenzene and xylene
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
ECA	European Collaborative Action
ECD	Electron capture detector
ETS	Environmental tobacco smoke
EXPOLIS	Air pollution exposure distributions of adult urban populations in Europe
FID	Flame ionisation detector
GC	Gas chromatography
HPLC	High-performance liquid chromatography
I/O	Indoor/outdoor
IAQ	Indoor air quality
MCS	Multiple chemical sensitivity
MS	Mass spectrometry
OCIA	Organic compounds in indoor air
PAS	Photoacoustic spectroscopy
PDMS	Polydimethylsiloxane
SBS	Sick building syndrome
SER	Area specific emission rate
SSVs	Safe sampling volumes
SVOC	Semi-volatile organic compounds
TVOC	Total volatile organic compounds
US EPA	United States Environmental Protection Agency
VOC	Volatile organic compounds
VVOC	Very volatile organic compounds

1 Introduction

There is a long history of interest in volatile organic compounds (VOCs) in indoor environments. This is evidenced by the large number of national and regional studies/campaigns that have been undertaken to model, identify or quantify indoor VOCs or relate indoor levels of VOCs to indoor materials, indoor activities and some perceived health/sensory effects. The main interest in such studies lies in the fact that most people spend up to 80% of the day in one indoor environment or another, where pollution levels can be higher, pollutant sources are more varied and exposures are more important than those found in outdoor microenvironments. Many novel insights have emerged from the studies, and some of the main features of these insights are outlined in this chapter. In particular, the types of VOCs commonly found in indoor air, sources/source characteristics of indoor VOCs, measurement techniques for profiling indoor VOCs, typical results from indoor air VOC studies, health effects of VOCs, concepts for reducing indoor VOCs and new trends in indoor VOC studies, particularly in the last decade, are discussed in the following sections.

To put the concepts discussed in the chapter in the right context, distinction must first be made among the terms very volatile organic compounds (VVOCs), VOCs, semi-volatile organic compounds (SVOCs) and particulate organic matters (POMs), which are commonly used to describe organic compounds in indoor air. According to WHO [1], VVOCs, VOCs, SVOCs and POMs are compounds with boiling ranges between 0°C and 50–100°C, 50–100°C and 240–260°C, 240–260°C and 360–400°C and higher than 380°C, respectively.

2 Types of Indoor VOCs

Hundreds of VOCs are found in a typical nonindustrial indoor environment. Many of these compounds are aromatic hydrocarbons, alkenes, alcohols, aliphatic hydrocarbons, aldehydes, ketones, esters, glycols, glycolethers, halocarbons, cycloalkanes and terpenes [2] but amines like nicotine, pyridine, 2- picoline, 3-ethenylpyridine and myosmine are also widespread, especially in smoking microenvironments [3]. Moreover, low molecular weight carboxylic acids, siloxanes, alkenes, cycloalkenes and Freon 11 are also frequently encountered in typical nonindustrial indoor air [1].

3 Sources of Indoor VOCs

VOCs are ubiquitous in indoor environments. They are widespread in household and consumer products, furnishing and building materials, office equipment, air fresheners[4], paints [5, 6], paint strippers, household solvents and in microorganisms found in indoor environments. In addition, humans and their indoor activities such as cooking, cleaning, building renovation and tobacco smoking generate high levels and wide varieties of VOCs. Apart from these indoor sources, intrusions of VOCs from attached garages [7–9], outdoor traffic as well as biogenic and industrial emissions contribute significantly to indoor VOC levels. Furthermore, indoor air reactions are now recognised as sources of indoor VOCs [10], as exemplified by the reaction of ozone with primary VOC emissions from building products to generate appreciable amounts of aldehydes [11].

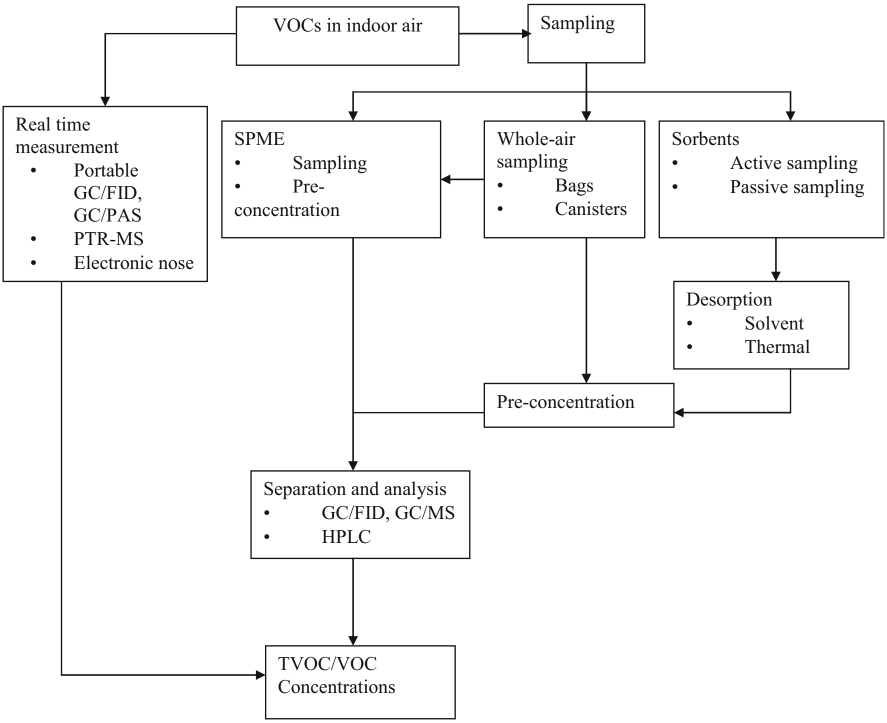
While some common indoor VOCs originate exclusively from indoor sources, others have multiple indoor and outdoor sources. Consequently, the indoor level of a particular VOC is the summation of the contributions of its various indoor and outdoor sources. In recent years various authors have undertaken comprehensive reviews of indoor VOC sources [4, 10, 12–16], and it is apparent from these reviews that the main sources of the typical indoor VOCs together with the major chemical classes associated with the sources are as summarised in the following:

- *Outdoor sources*: traffic, industry, agriculture, green plants and waste storage and treatment (aliphatic and aromatic hydrocarbons, aldehydes, ketones, esters)
- *Building materials*: insulation, paint, plywood and adhesives (aliphatic and aromatic hydrocarbons, alcohols, ketones, esters)
- *Furnishing materials*: furniture and floor/wall coverings (aliphatic and aromatic hydrocarbons, alcohols, halocarbons, aldehydes, ketones, ethers, esters)
- *Consumer products*: cleaning agents, polishes, incenses, air freshener, personal care products and newspaper (aliphatic and aromatic hydrocarbons, alcohols, halocarbons, aldehydes, ketones, terpenes, ethers, esters)
- *Equipment*: laser printers, photocopiers, computers, other office equipment and vehicles parked inside (aromatic hydrocarbons, aldehydes, ketones, esters)
- *Indoor activities*: cooking, tobacco smoking and use of candle and solvents (amines, aliphatic and aromatic hydrocarbons, aldehydes, halocarbons)
- *Ventilation systems*: filters of HVAC systems (aliphatic and aromatic hydrocarbons, alcohols, halocarbons, aldehydes, ketones, terpenes, ethers, esters)
- *Biological sources*: humans, moulds, bacteria and indoor plants (terpenes, glycoesters, alcohols, esters, aldehydes)

4 Sampling and Characterisation of Indoor VOCs

Interest in indoor air monitoring is driven by a wide variety of reasons [17]; the most prominent ones include the desire to:

- Undertake baseline measurements in order to set limits.
- Identify the presence of specific pollutants (e.g. formaldehyde).
- Apportion indoor VOC sources.
- Evaluate levels of compliance with legislations.
- Assess contaminated buildings.



Scheme 1 Summary of the steps involved in the characterisation of indoor VOCs

- Apply and validate sampling/analysis methods.
- Validate models.
- Evaluate ventilation systems.
- Evaluate the strength of a specific source.
- Relate sick building syndrome (SBS)/health effects to VOC levels.
- Understand the mechanisms of VOC transport from source to receptor sites.

While specific details may differ, the general analytical procedures described below and summarised in Scheme 1 apply to most monitoring exercises. Firstly, the purpose of the monitoring exercise must be clearly set out, then an appropriate method of sampling must be chosen, followed (where applicable) by the choice of suitable methods for sample storage, sample preparation or preconcentration and sample separation. Lastly, identification and/or quantification of the components are performed [18].

Assessment of VOC levels in an indoor microenvironment may be accomplished by direct measurements or by collection of a sample of air followed by subsequent laboratory analysis of the sample. Both of the approaches can be devised to answer the basic questions: what is present and how much is present?

4.1 Online Measurements

In general, direct measurement is achieved through the use of proton transfer reaction mass spectrometry (PTR-MS), portable gas chromatography (GC), photoacoustic spectroscopy (PAS), photoionisation detectors (PIDs) and infrared spectroscopy and by the so-called electronic noses [13, 19, 20] . Zhang and Mo [21] recently reviewed direct reading instruments used in monitoring indoor organic compounds and provided comprehensive knowledge on their detection or measurement principle, sensitivity and accuracy as well as application illustrations. Such real-time measurement instruments facilitate rapid data acquisition and are especially useful for rapid assessment of contaminated sites and for screening purposes. However, because logistics demand that the equipment involved is portable, some of them are relatively expensive and do not always afford detection limits that are as low as those obtained by conventional laboratory instruments [22]. In addition, it is often necessary to 'calibrate' or 'train' the equipment with the analytes of interest. For example, 'electronic noses' are specially 'trained' through extensive chemometrics procedures [23], while PIDs are calibrated with a particular VOC (e.g. toluene), and the other components of the air sample are determined as equivalents of that VOC. Measurements obtained in this way give little or no qualitative information about the constituent of the air sample. For example, Li et al. [24] measured the total volatile organic compounds (TVOCs) in indoor microenvironment continuously with photoacoustic Multi-Gas monitor, but apart from formaldehyde, the other constituents of the samples were unknown.

PTR-MS has also been recently [19, 25–31] developed to allow real-time online measurement of VOCs in indoor and outdoor environments. In the past 10 years, it has been successfully applied in a number of studies to continuously measure the VOC concentration in various indoor environments, such as animal buildings [31, 32], aircraft cabins [29, 30] and workplace [33]. It has also been used in laboratory experiments. For example, Mo et al. investigated by-products resulting from photocatalytic oxidation of toluene by PTR-MS [27]. Zhang et al. used the PTR-MS technique to characterise VOC emission signatures of individual building materials, resulting in the establishment of a database which can be utilised for indoor emission source identification [19, 26]. Recently, Jordan et al. further improved the resolution and sensitivity of PTR-MS by using a time-of-flight mass spectrometer, which is capable of measuring VOCs at ultra-low concentrations (as low as a few pptv) under high mass resolution with a mass range beyond 100,000 amu [28].

Various types of portable gas chromatographs are now available for the direct measurements of VOCs. These include gas chromatographs with high-speed temperature and pressure programming and a GC-ion mobility spectrometer [22]. In addition, portable GC time-of-flight (TOF) mass spectrometers [34] are available. But GC–MS is not routinely used for indoor air field measurements because of size, vacuum and energy requirements [22]. According to Santos and Galceran [22], portable GCs provide near real-time measurements, interactive sampling and quick solution to the problem faced at the time of the investigation. Nevertheless, they are usually expensive and are only able to achieve detection limits of the order of micrograms per cubic metres. However, a commercial portable GC–MS is now available to provide fast analysis (with less than 10 min turnaround time) and low detection limits (usually less than 1 μg/m^3) for indoor VOCs [35, 36].

4.2 *Offline Measurement*

Sampling can be done by passive or active techniques. Irrespective of the sampling technique adopted, subsequent laboratory analysis can be time-consuming and labour-intensive. Some of the common techniques used to collect and analyse indoor air samples are outlined below.

4.2.1 Active Air Sampling

This technique entails moving a predetermined volume of air at a controlled flow rate into a container or onto a sorbent. In its various forms, it is the most common technique used for the sampling of indoor VOCs.

Whole-Air Sampling

In whole-air sampling, a sufficient quantity of air is pumped into a container such as a polymer bag (Tedlar, Teflon or Mylar) [37] or a passivated stainless canister (e.g. SUMMA® or Silocan® canisters) [38–40]. The attraction in using whole-air sampling is that sample collection is relatively simple and rapid, especially when time-weighted sampling is not required. In addition, the analyst has the opportunity to monitor the presence of a wide variety of polar and nonpolar VOCs from one sample and to carry out replicated analysis on the sample. Furthermore, there is no sample breakthrough (i.e. some of the analytes do not pass through the sampler without being held). However, loss of VOCs due to chemical reactions within the container, physical adsorption by the walls of the container and dissolution in the water condensed in the container is not uncommon [41]. To minimise these, Tedlar bags should be protected from light by covering them with black bags and the internal surfaces of canisters should be electroplated or covered with siloxane [41]. Other shortcomings associated with the use of this sampling method include the high cost involved in purchasing and the inconveniences in transporting canisters. Despite these drawbacks, it is the method of choice for sampling and storing very volatile hydrocarbons (e.g. C_2–C_4 compounds) and reactive compounds such as terpenes and aldehydes [42]. Hsieh et al. [41] showed that the half-lives of 56 VOCs, including several highly reactive alkenes in SUMMA® canisters, Silocan® canisters and Tedlar, were generally in excess of 30 days.

Sampling onto Sorbent Tubes

Excellent reviews on the use of sorbents for sampling air in general [43, 44] and indoor VOCs in particular have appeared in the literature [45]. The most popular sorbents for sampling indoor VOCs can be classified into three broad categories: porous polymer-based sorbents (e.g. Tenax, Chromosorb), carbon-based sorbents (activated charcoal, graphitised carbon blacks, Carbotraps, Anasorb, Carboxens and Carbosieve) and silica gels. Of these, porous polymers and carbon-based sorbents are the most widely used for indoor VOC sampling.

The choice of the sorbent material employed for a specific sampling depends on the absorption and desorption efficiencies of the sorbent for the target VOCs as well as the stability of the VOCs on the sorbent. Additionally, the amount of VOCs retained on a sorbent is determined to a large extent by the sorbent bed length and sorbent mass. Thus, a typical sorbent tube has a length of 90 mm and an outer diameter of 6 mm and contains 0.1–1 g of the sorbent(s) [46, 47]. Some parameters that should be considered when choosing the most appropriate sorbent method for a particular study include the 'hydrophobicity', the 'thermostability' and the 'loadability' of the sorbent [48]. The less water is retained by the sorbent, the less interference is experienced during analysis; the more stable the sorbent is, the more robust it is during thermal desorption of the analyte. Lastly, the more the air that can be sampled onto a sorbent without sample breakthrough, the lower the detection limit that can be achieved.

Tenax TA, poly (2,6-diphenyl-*p*-phenylene oxide), is highly thermally stable and does not retain water. In addition, it affords high desorption efficiency for a wide range of VOCs. Consequently, it is the most widely used sorbent for sampling multicomponent indoor VOCs in the carbon size range C_5–C_6 to C_{18}. The literature on indoor air is filled with examples of measurement studies conducted with this sorbent as the VOC trapping medium [47, 49–54]. However, care must be exercised when using Tenax TA as a sorbent since it reacts with ozone and NO_x to form compounds which may facilitate the degradation of the sorbent [55]. To avoid this, ozone scrubbers must be used in conjunction with the sorbent, particularly when sampling is carried out in environments with high ozone concentrations [56].

When a single sorbent is not sufficiently efficient in capturing a wide suite of VOCs, combinations of sorbents are employed to increase the range of compounds that can be confidently sampled. Consequently, multi-bed sorbents made up of Anasorb®GCB1, Carbotrap® and CarbopackB® have been employed in some validated methods [56]. Similarly, multi-bed sorbents consisting of Carbotrap, Carbopack X and Carboxen 569 [57] and CarbopackB® and Carbosieve SIII® [17] have been used to trap a wide diversity of indoor VOCs.

Baltussen et al. [58] described the versatility of liquid polydimethylsiloxane (PDMS) as a sorbent material for volatile organic compounds. Unlike other common solid sorbent materials, retention on PDMS occurs as a result of dissolution rather than adsorption. In addition, it also has several advantages over the other forms of sorbents that are commonly used for indoor air sampling. For example, Baltussen et al. [58] showed that (1) it is more inert than other common sorbents and, therefore, it undergoes less reactions with the analytes and forms less artefacts, (2) it is more efficient in trapping polar compounds like organic acids, and (3) it requires lower thermal desorption temperatures than other sorbents. Also, Stefan et al. [59] showed that it does not absorb or introduce water into the analytes. Despite these advantages, PDMS is not as widely used in sorbent tubes for indoor VOC monitoring as Tenax. However, it is becoming more frequently employed in headspace sampling of VOCs and as a fibre coating material in solid-phase microextraction (SPME) [60–62].

Active sampling onto sorbents entails storing known amounts of sorbent material(s) in glass or stainless steel tubes and drawing the sample through the tube by means of small battery-powered pumps. Since sorbents do not possess unlimited capacities to hold samples, caution must be exercised not to sample too much air onto the sorbent; otherwise, 'sample breakthrough' will occur. Representative samples are only obtained when the appropriate volume of air and size of sorbent that minimises breakthrough are employed. To minimise errors due to sample breakthrough, the total volume of sample collected must be scrupulously monitored and a second bed of sorbent arranged in series with the first must be analysed. When the percent of a particular VOC in the second bed is greater than 5% of the amount in the first, sample breakthrough is implied [56]. While the safe sampling volumes (SSVs) suggested by US EPA Method TO-17 for various VOCs are a useful sampling guide, care should be taken in applying the SSVs since breakthrough volumes (BTV) are influenced by environmental factors like humidity, temperature and other factors. In keeping with this, US EPA Method TO-17 [56] suggested that sampling volume should not be greater than approximately 66% of the breakthrough volume [56].

Most classes of VOCs found in the indoor environment are sampled onto sorbents by adsorption, but highly reactive VOCs like carbonyl compounds are sampled by chemical reactions with the sorbent. Thus, aldehydes and ketones are sampled by their reactions with sorbent gels coated with 2,4-dinitrophenylhydrazine (2,4-DNPH) to form stable hydrazones [49, 63]. Similarly, formaldehyde has been sampled by its reaction with *N*-benzylethanolamine to give 3-benzyloxazolidine [64] or with hydroxymethyl piperidine to form oxazolidine derivative [65, 66].

Despite its widespread use in indoor VOC sampling, sorbent trapping provides no information about (1) all of the VOCs present in the sampled air since some VOCs are either not trapped by the sorbent(s) or are too reactive to remain on the sorbent surface and (2) the temporal variations in the concentrations of the VOCs that are being monitored.

4.2.2 Passive Air Sampling

Solid-Phase Microextraction

Ouyang and Pawliszyn [67] reviewed the application of this combined sampling and sample preconcentration procedure to indoor air VOC measurement. Typically, an SPME sampler consists of a fused silica fibre that is coated by a suitable polymer (e.g. polydimethylsiloxane (PDMS), PDMS/divinylbenzene, carboxene/PDMS) and housed inside a needle [67]. The fibre is exposed to indoor air, and after sampling is complete, it is retracted into the needle until the sample is analysed. Compared to other sampling methods, it is simple to use and reasonably sensitive. However, samples collected by the procedure are markedly affected by environmental factors such as temperature. Therefore, they cannot be stored for extended periods of time without refrigeration [68].

Koziel and Novak's review of SPME [69] is replete with examples of its use for (1) indoor VOC sampling followed by off-site laboratory analysis, (2) on-site sampling and analysis of indoor VOCs, (3) preconcentration of samples collected into canisters as well as (4) headspace sampling of the solvents extracted from samples collected by sorbent tubes. In addition to its ability to sample chlorinated VOCs [70], *n*-alkanes, aromatic hydrocarbons [61] and oxygenated hydrocarbons [61, 62, 70], the fibres of SPME can be doped with derivatising agents to make them amenable to sampling reactive VOCs such as formaldehyde [71]. Despite its virtues, relatively few examples of the application of this technique for indoor air sampling have been described in the literature.

Passive Sampling onto Sorbents

The sorbents used for passive sampling are identical to those described for active sampling. The only difference is that while samples are pumped through the sorbents in the latter, they diffuse into the sorbents in the former. Woolfenden [44] has shown that the diffusive uptake rates of VOCs commonly found in indoor air on different sorbents vary from about 0.8–15 (ng/ppm/min). Consequently, passive sampling is generally relatively slower than active sampling and may occur over several hours or days. Nevertheless, it is a popular sampling method, particularly for the evaluation of personal exposure. Raw et al. [72] used diffusive tubes packed with Tenax TA to monitor VOCs in 876 English homes; Missia et al. [73] employed Radiello passive samplers with charcoal/carbograph to monitor indoor and outdoor VOC levels in five European cities, while Schieweck et al. [74] used it to measure VOC levels in museum showcases in Germany. As in active sampling, chemical coated sorbents are also employed for the passive sampling of carbonyl compounds [73].

4.2.3 Sample Desorption/Preconcentration

Whole-Air Samples

Preconcentration of samples collected into canisters and polymeric bags is accomplished by passing known quantities of the samples through narrow capillary tubes held at very low temperatures by means of liquid cryogens [42, 75]. The tubes are then rapidly heated to release the analytes into a cryofocussing unit and eventually to the GC. The procedure affords excellent recoveries for many VOCs, but recoveries from samples stored in Tedlar bags are generally lower than those stored in canisters [41]. The main drawbacks of this procedure include the high cost of the cryogen and the susceptibility of the transfer tube to blockage.

SPME Samples

Extraction occurs when the needle of the syringe is exposed to fast moving, hot streams of gas within the injection port of the GC [76].

Samples Collected onto Sorbents

Depending on the sorbents used, solvent desorption or thermal desorption may be applied to the sampled analytes. For silica gel and carbon-based sorbents, solvent desorption [56, 77] and microwave desorption [48] are the preconcentration methods of choice.

Solvent Desorption

Acetonitrile is frequently used for the desorption of 2,4-dinitrophenylhydrazones of carbonyl compounds collected on silica gel [78, 79], while CS_2 is used for samples collected onto charcoal and dichloromethane for samples collected onto Anasorb 747 [79]. Carbon disulphide is particularly suitable for the desorption of nonpolar compounds but gives less satisfactory outcomes for polar compounds. To overcome this shortcoming, polar co-solvents such as DMF, DMSO and EtOH are added to CS_2 to increase the recovery of polar analytes [68]. In addition, the use of CS_2 suffers from a number of other drawbacks, including the facts that (1) it reacts with amines and volatile chlorocarbons, (2) it is unsuitable when electron detectors (e.g. electron capture detectors) are used, (3) it is toxic and (4) it has an unpleasant odour [68].

Compared to thermal desorption, solvent desorption is plagued by a number of shortcomings. For example, very volatile organic compounds are lost when the liquid sample is reconcentrated prior to its analysis. Moreover, solvent peaks may overlap with the peaks of very volatile organic compounds. According to Wolkoff [48], solvent desorption leads to loss of analytical sensitivity. Similarly, a comparison of the efficiencies of thermal and solvent desorption techniques showed that with few exceptions, solvent desorption consistently underestimates various classes of VOCs found in typical indoor air [79].

Thermal Desorption

This is a very popular method of transferring indoor VOC samples trapped by polymeric and carbon-based sorbents into analytical instruments. It usually entails running a stream of hot carrier gas (usually helium or argon), through the tubes in a direction opposite to that used for the sample collection. Typically, thermal desorption is carried at ca. 250°C [80]. After desorption, the compounds are reconcentrated by cryotrapping and then transferred directly by heat into the GC column. Although it affords greater sample desorption efficiency than solvent desorption, the desorbed sample can only be analysed once. Therefore, the only way to test the reproducibility of the method is to analyse multiple samples [68].

4.2.4 Characterisation of Indoor VOCs

Laboratory-based analyses of indoor VOCs are usually performed with gas chromatography, which are coupled with flame ionisation detectors (FIDs), electron capture detector (ECDs) or mass spectrometry (MS). Alternatively high-performance liquid chromatography (HPLC) is used. Of these techniques, GC–MS provides the most conclusive qualitative and quantitative information, although a combination of FID and ECD has also been reported to permit the identification of compounds with widely different properties [18, 81]. Nonetheless, GC–MS remains the most widely used technique for the characterisation of indoor VOCs [7, 47, 49, 82, 83]. Total ion chromatogram (TIC) is usually conducted to obtain global information on the ranges of compounds present, and selected ion monitoring (SIM) is performed to identify and monitor particular analytes. To facilitate the acquisition of quantitative information, the response factors of individual VOCs are often calculated against that of toluene, which is present in many indoor air samples and also acts as an internal standard. Typically, splitless injection technique is employed [22, 84] to ensure the detection of compounds that are present at low levels. Various validated US EPA Methods recommend the use of dimethyl polysiloxane capillary column for the speciation and quantification of a suite of VOCs [56, 85]. Similarly, the ECA Report No 19 recommended a column with a polarity not exceeding that of 8% diphenyl polysiloxane [2]. Such nonpolar columns are widely used in indoor air studies [74, 86–88].

In order to increase the number of compounds that can be separated in a single analysis, it is not unusual to use a combination of GC columns with different polarities [81]. Temperature programming is also often required to achieve acceptable separation of analytes. A typical temperature programme, which has been used to separate different classes of indoor VOCs, is summarised below: (1) hold at 40°C for 1 min, (2) raise at 15°C/min to 105°C, (3) hold at 105°C for 5 min, (4) raise at 20°C/min to 245°C and (5) hold at 245°C for 5 min [17]. Column diameters ranging from 0.25 to 0.53 mm and lengths from 25 to 100 m have been employed for indoor VOC measurements [83, 86, 89]. The choice of column dimensions depends on the properties of the compounds to be separated.

In their review of the application of GC in environmental analysis, Santos and Galceran [22] suggested that future perspectives of GC analysis include increasing the use of:

- GC–MS with positive and negative ion capabilities and sensitivities as low as ppq (parts per quadrillion)
- HSGC (high-speed GC) – with reduced sizes and capabilities for providing near real-time monitoring
- GC x GC (multidimensional GC) – which remarkably increase the separation capabilities of the two columns used
- GC–TOF–MS – with scanning capabilities of the order of 500 scan/s

Such developments are beginning to affect indoor VOCs measurement markedly.

HPLC is only used for the analysis of the derivatives of low molecular weight carbonyl compounds such as formaldehyde [49, 56, 90]. However, formaldehyde is also quantified by a variety of other procedures, including spectrometric acetylacetone method [91] and chromotropic acid procedure [92].

4.2.5 Quality Assurance/Quality Control

Caution must be exercised to minimise errors at every stage of the characterisation. Therefore, quality assurance/quality control principles must be applied to: sampling, sample storage, sample reconcentration and sample analysis [56]. For testing and calibration laboratories, the standard ISO/IEC 17025 has been published. Accreditation bodies have been established worldwide on national levels and which follow up the implementation of this standard. In many countries certification or notification procedures and strict quality control measures are required for laboratories working in the field of indoor air quality.

Sampling

Short-term samplings are subject to temporal variations because of changes in source strength and ventilation conditions, while long-term measurements may show diurnal and seasonal variations [48]. These facts should be considered when planning sampling. Prior to sampling, sorbent tubes should be conditioned using a stream of carrier gas and temperatures that are higher than those that will be used for the analysis [47, 50]. Similarly, canisters need to be cleaned by repeated cycles of evacuation, flushing with humidified zero air and analysis for any trace levels of undesired gases [39, 41, 93]. As part of the quality control, sample breakthrough must be checked when sorbent tubes are used. Breakthrough may be a serious problem resulting in underestimation of concentrations in indoor air. Uhde has discussed this in more detail [45]. In addition, field and method blanks as well as field duplicates must be collected and analysed.

Sample Storage

As a general rule, samples should be analysed as soon as possible after sampling and when immediate analysis is not feasible, they must be stored and transported under conditions that minimise artefact formation. Thus samples trapped onto sorbent tubes are commonly covered with Swagelok type of screw caps fitted with ferrules and stored in clean containers filled with nitrogen gas or activated charcoal [44, 80]. Tedlar bags must be protected from direct exposure to UV radiation, while canisters must be sealed airtight and transported to the laboratory in cool containers [17, 41].

Sample Desorption

Regardless of the desorption method used (solvent or thermal) it is essential to ascertain the recovery efficiency of the VOCs of interest by spiking sorbent tubes and canisters.

Calibrations

Pumps should be calibrated with a rotameter prior to and after sampling. Analytical instruments must also be calibrated before measurements. For example, GC–MS must be calibrated for mass and retention times using reference standard materials [89] and comparison made with the fragmentation patterns of known standards, usually a deuterated compound like toluene-d8. Similarly, the method detection limit must be determined by finding the standard deviation of seven replicate analyses and multiplying it by the *t*-test value for 99% confidence of seven values [56, 93]. It is also usual for internal standards to be added to the samples and to evaluate the correlation coefficients of each standard used when multilevel calibration is employed. For automatic thermal desorption tubes, external and internal standardisations are achieved by injecting solutions of standards into the tubes [57]; for canisters, solutions of standards are injected into the canisters followed by zero air.

In addition, the identity of each species must be obtained by comparing its retention time with that of an authentic standard sample or to inter laboratory set of established retention times and by comparing its mass spectrum with that contained in a National Bureau of Standards (NBS) or National Institute of Standards and Technology (NIST) library installed on most modern instruments. It is usual to assign positive identification to a compound if its retention time is within 1% that of the corresponding standard and the ratio of its quantifying ion to the target ion is not more than 10 times the standard deviation of the analogous ratio for an associated standard [94].

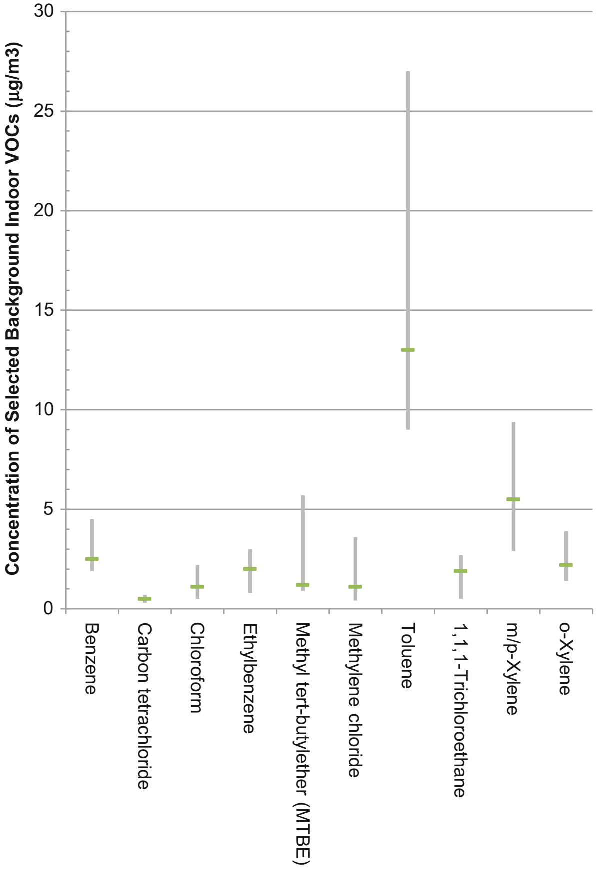
5 Current Knowledge on the Levels of VOCs in Indoor Microenvironments

Several studies have been undertaken to measure the level of indoor VOCs, in dwellings and offices in the past two decades, and some results from such studies have been reviewed [12, 95, 96]. For example, Dawson and McAlary (2009) reviewed VOCs from post-1990 indoor air concentration studies in North American residences unaffected by subsurface vapour intrusion [95]. They found that eleven compounds were detected in more than 50% of samples collected and for several compounds (benzene, carbon tetrachloride, chloroform, ethylbenzene and tetrachloroethene), the lower and upper quartiles of the indoor air concentrations are within the range of typical risk-based target levels (Fig. 1).

A survey of two reference databases, CAPLUS and MEDLINE on the web version of SciFinder Scholar (American Chemical Society, 2013), confirmed that interest in the characterisation of VOCs in various environments has not abated. Although the survey did not capture all of the research done on indoor VOC, it gave a good indication of what has been done and where. Three thousand one hundred and thirty-four hits (3,134) were recorded when ‘VOC, indoor air’ was searched on SciFinder. Further searches conducted to find out where these studies were done revealed that most have been conducted in the USA and European countries, although some significant results have also emanated from China, Japan, Canada, Hong Kong, Australia and Brazil in the past 10 years. Representative examples of some of the studies are presented in Table 1, while the concentration levels of BTEX (benzene, toluene, ethylbenzene and xylenes) in selected nonindustrial indoor air are presented in Table 2. The salient features of the studies reviewed reiterate some facts that have previously been known while others emphasise current trends.

1. GC–MS and GC–FID were used in most of the studies and are clearly the most popular detection methods used for VOCs quantification. Nevertheless, for reactive carbonyl compounds such as aldehydes and ketones, HPLC analysis of their derivatised products is still the method of choice.
2. Compared to whole-air sampling into Tedlar bags and canisters, active sampling onto sorbent materials is used more widely in these IAQ studies. Only a few studies made use of OVM passive samplers. Of the sorbent materials used, Tenax is the most frequently employed, possibly because of its virtues, which are mentioned in Sect. 4.2.1. It has been used for the characterisation of aromatics, alkenes, cycloalkanes, aldehydes, ketones, esters, alcohols, terpenes, glycol derivatives and even amines [79, 94].
3. For samples collected onto sorbents materials, thermal desorption is used, except for a few instances where CS2 desorption [97] and isooctane desorption [64] were preferred.
4. Generally, more studies have been conducted in residential indoor microenvironments than in offices. Although most of the studies were conducted in established rather than new buildings, many VOCs found in the former were

Fig. 1 The 25th, 75th and mean background concentrations for selected indoor VOCs measured in North American Residences between 1990 and 2005. Data from Dawson and McAlary [95]



also present in the latter but at higher concentrations. This is consistent with the thinking that VOC emission rates from building materials decrease with the age of the building [92]. Based on measurements in 243 homes, Herbarth and Matysik showed that a waiting period in the range of 60 days after renovation of a building should be observed to allow a decrease of VOC concentrations to a reference level [98].

5. Only a few of the studies estimated the TVOC of the microenvironment reported [64, 99] or focussed on complaint buildings [100] [101]. Because different definitions and methods of TVOC have been employed to estimate the quoted values, it is difficult to make direct inter-study comparisons; nevertheless, it appears that TVOC can range from 10 µg/m^3 to several thousand µg/m^3 in indoor environments.
6. Direct comparison of the concentration levels found in each study is difficult since the sampling was conducted over different times, with different sampling techniques and different sample treatments, and methods of analysis were used.

Table 1 Selected indoor air VOC studies conducted in the last two decades

Type of indoor	Compounds	Country	Collection medium	Sample treatment	Analytical instrument	References
Office	11	Singapore	CarbopackB and Carbosieve SIII	Thermal desorption	GC–MS	[17]
Homes	10	Korea	OVM 3500 passive sampler badges	Carbon disulphide (chemical desorption)	GC–MS	[77]
Office	60	Europe	Tenax tubes	Thermal desorption	GC–FID, GC–MS, PAS	[145]
Homes	6 Chlorinated VOCs	Japan and Sweden	Diffusion sampler packed with activated charcoal	Toluene (chemical desorption)	GC–ECD	[223]
Homes	30	Germany	OVM 3500 passive sampler badges	Carbon disulphide (chemical desorption)	GC–FID, ECD	[224]
Homes	25	Belgium	Tenax tubes	Thermal desorption	GC–MS	[50]
Furniture: showcase	45	Germany	Tenax tubes	Thermal desorption	GC–MS	[74]
Shopping mall	14	China	Tenax tubes	Thermal desorption	GC–MS	[54]
Homes	8	China	3L stainless steel evacuated canisters	Cryogenic preconcentrator	GC–MS	[75]
Public sites and homes	4 Aldehydes	France	2,4-DNPH cartridges	Acetonitrile (chemical desorption)	HPLC–UV	[225, 226]
Flemish homes	25	Belgium	Diffusion sampler packed with Tenax tubes	Thermal desorption	GC–MS	[50]
Public building/schools/kindergartens	23	European	Diffusion sampler packed with charcoal for hydrogens and DNPH for carbonyls	ISO/FDIS 16200-2 method	GC–FID, LC–DAD	[87]
Ships	5	South Korea	Tenax tubes	Thermal desorption	GC–MS	[227]
Homes	23	USA	Perkin Elmer tubes packed with Supelco Carbopack B	Thermal desorption	GC–MS	[127]
Museum	46	Germany	Tenax tubes	Thermal desorption	GC–MS	[228]
Apartment	240	Finland	Tenax tubes	Thermal desorption	GC–MS/FID	[229]
Homes	8 Chlorinated VOCs	USA	‘Tri-bed’ sorbent trap	Thermal Desorption	Portable GC–MS	[35]

Table 2 Arithmetic mean of the concentrations (μg/m^3) of BTEX in selected countries

Compound	Australia [92]	Finland [84]	Hong Kong [40]	USA [17]	Seoul, Korea [77]
Benzene	7.0	1.66	15.0	4.1	43.71
Toluene	14	5.62	206.3	15.3	170.67
m, p-Xylene	6.9	3.12	25.1	34.9	27.49[b]
Ethylbenzene	1.8	0.99	50.4	9.71	1.33
o-Xylene	8.9[a]	1.26	17.3	11.2	33.45

[a] *o*-Xylene/nonane
[b] *p*-Xylene only

However, the frequency with which the 64 VOCs that are of interest to the ECA are encountered in the different microenvironments can be classified as shown in Table 3.

The web-based Japanese automated formaldehyde data acquisition system/ automated VOC data acquisition system (AFoDAS/AVODAS) [102] showed that toluene was detected in 78% of the 1,422 homes monitored and that *p*-xylene, styrene, limonene and *α*-pinene were present in more than 50% of the homes. The data corroborates the classification in Table 3. However, most of the VOCs are not frequently quantified. Therefore, comparison between different studies is complicated.

5.1 The Total Volatile Organic Compounds (TVOCs) Concept

Hundreds of VOCs are present in some typical indoor environments. It is therefore not practically possible to identify and quantify every compound, even with the most sensitive and selective techniques [48]. Consequently, different techniques have been used to express the total volatile organic compounds (TVOCs) (for reviews of the methods, see [2, 18, 48, 103]).

To redress problems caused by the different approaches to TVOC estimation, a uniform procedure was proposed [2, 18]. The procedure, which is based on sampling of VOCs on Tenax tubes followed by thermal desorption and GC–MS analysis (with nonpolar columns), proposed that TVOC be defined as:

$$\mathrm{TVOC} = S_{\mathrm{id}} + S_{\mathrm{un}}$$

where S_{id} is the sum of identified VOCs expressed in milligram per cubic metre and S_{un} is the sum of unidentified VOCs relative to the response factor of toluene.

The procedure further recommends that as many VOCs as possible should be quantified in the analytical window bounded by the retention times of hexane and hexadecane and that these VOCs should as far as possible include the 64 VOCs that are of special interest to the European Community [2]. A major shortcoming of

Table 3 Frequency with which the 64 ECA VOCs were monitored in selected studies

Always[a]	Frequently[b]	Normally[c]	Occasionally[d]
Toluene, benzene	Ethylbenzene, styrene, *o*-xylene, limonene, tetrachloroethylene, *α*-pinene, *n*-hexane, trichloroethene, *n*-decane, hexanal, 1,4-dichlorobenzene benzaldehyde	1-Butanol, *n*-undecane, 1,1,1-trichloroethane, 1,2,4-trimethylbenzene, *n*-nonane, *n*-heptane, *n*-dodecane, naphthalene, 1,3,5-trimethylbenzene, nonanal, *n*-octane, cyclohexane, 2-ethyl-1-hexanol, 2-propanol, pentanal, methylisobutylketone (MIBK), *n*-tridecane, *β*-pinene, butanal, *n*-propylbenzene, *n*-pentadecane, 3-carene, 2-butoxyethanol, *n*-hexadecane, methylcyclohexane, hexanoic acid, acetophenone, 2-ethyltoluene, cyclohexanone, *m*/*p*-xylene, butylacetate, methylcyclopentane, 2-methylpentane, ethylacetate, 2-pentylfuran, 1-octene, texanolisobutyrates (TXIB), *n*-tetradecan, 2-ethoxyethanol 4-phenylcyclohexene, 3-methylpentane, tetrahydrofuran (THF), 2-butoxyethoxyethanol	1-Decene, 1-methoxy-2-propanol, isopropylacetate, methylethylketone, 2-methoxyethanol, 2-ethoxyethylacetate

Note: Three thousand one hundred and thirty-four references searched through SciFinder with key words of ‘Indoor’ and ‘VOC’ on 9 May 2013 were used as a database for this analysis

[a] Monitored in >40% of the studies

[b] Monitored in 10–39% of the studies

[c] Monitored in 1–9% of the studies

[d] Monitored in <1% of the studies

the recommendation is that not all VOCs present in indoor air are included in the approach. For example, important indoor VOCs like 2-propanol, 2-methylpentane, 3-methylpentane and butanal elute before hexane, while texanolisobutyrate (TXIB) elutes after hexadecane [104]. It was also expected that the definition would enhance interlaboratory of TVOC values, classification and screening of indoor materials and the identification of problems with ventilation design, indoor activities or materials [18]. However, De Bortoli et al. [105] observed large variances in interlaboratory studies performed with the approach. Nevertheless, it has been adopted in many indoor air studies [17, 104, 106].

5.2 Trends in Indoor VOC Concentrations

A couple of excellent papers have reviewed the trend of indoor VOC levels in the past several decades. Indoor VOC concentrations measured in North American offices and homes since 1990 were reviewed by Hodgson and Levin [107]. They concluded that there was a significant decrease in the average concentrations of some toxic VOCs, including benzene, 111-trichloroethane and tetrachloroethylene by comparing the dataset from 1990 to 2003 with two published reviews of data obtained in the 1980s [107].

Weschler [12] also examined the changes in indoor VOCs since the 1950s. He found that while average indoor concentrations of most VOCs decreased, some aldehydes and terpenoids increased due to increased indoor chemistry and use of solvents and scents, respectively. In addition, it was observed that the use of dimethyl and diethyl phthalates in personal care products and cosmetics, as well as the use of cyclopentasiloxane in antiperspirants, has increased during the past several decades [12].

6 Concepts for Regulating Indoor VOCs

Wolkoff [108] reviewed initiatives taken in Europe to reduce indoor air pollution by VOCs. Initiatives mentioned in the review include:

- Source control
- Control of emission from building materials
- Establishment of a Europe-wise database of outdoor and indoor VOC levels through EXPOLIS programme
- Indoor air quality audit projects
- Labelling scheme
- Establishment of guidelines for TVOC/VOCs
- Avoiding nonessential VOC

In addition to the above initiatives, various schemes aimed at reducing formaldehyde emission from building products, sensitising people to the effects of the presence of unsaturated fragrances in indoor air, use of labelled or low VOC, low isocyanate and acid anhydride emitting products have been introduced [108]. Because of their vast contribution to indoor VOCs, particularly in newly constructed buildings, a lot of the efforts highlighted above have focussed on the reduction of emissions from building products.

Bluyssen [109] reviewed more recent initiatives to improve and/or regulate IAQ, including:

- Development of WHO guidelines for indoor air quality which covers VOCs such as formaldehyde and benzene [110]
- European Parliament and the Council of Europe's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) and ECHA (European Chemical Agency) initiatives [111]
- Implementation of mandate 366 for CPD (Construction Products Directive) [112]
- EnVIE [113]
- BUMA [114]
- Harmonisation of labelling schemes for construction and furnishing products [115]
- Establishment of the European Commission's Scientific Committee on Health and Environmental Risk [116]
- Healthy Air Initiative [117]

She also identified nine facts and problems associated with IAQ. In the light of those facts and problems, she proposed an integrative approach to improving indoor air quality that incorporated the occupant(s), the air and the sources of pollution [109]. Kephalopoulus et al. critically reviewed the existing indoor materials labelling systems in the European Union [118], while Yu and Time [119] discussed the requirements for investigation of sick buildings with a particular focus on emissions of VOCs and formaldehyde in indoor environments, as well as some guidelines for assessment of exposure risks.

The US EPA [120] suggests, among other steps, that using household products as directed by the manufacturers and increasing ventilation when using household products could reduce indoor VOCs. In Japan, a database system for indoor formaldehyde and VOC (AFoDAS/AVODAS) has been established [102]. This should facilitate direct access to vital information needed by building designers, engineers and occupants to implement control measures [102]. In the USA, Hodgson et al. [78] have suggested the use of low VOC latex paints and carpet systems and decreased infiltration of unconditioned air. Mesaros [121] described the construction of 'a low VOC house' in Australia, in which materials with low VOC emission factors like ceramics are used in preference to those with high VOC emission factors such as carpets. The house provides a good illustration of the use of source control in eliminating indoor VOCs. Another low VOC emission house, which employed low VOC emission materials and high ventilation rates, was independently reported by Guo et al. [122]. The marked difference in the TVOC levels in the house and those in normal houses provide support for the fact that indoor air quality can be improved through a combination of source control and building designs that minimise the negative impact of uncontrollable sources. Consequently in Scandinavian and other

European countries recent standards for residential houses have combined strict energetic and ventilation requirements [123].

6.1 Source Identification

Unlike ambient VOCs, which originate predominantly from natural, vehicular and industrial emissions, indoor VOCs have numerous and diverse origins. Therefore, source identification is an important factor in source control and the prime driving force for many IAQ studies. It can be accomplished by many methods, including:

6.1.1 Comparison of Indoor-to-Outdoor Concentration Ratios

This method assumes that indoor/outdoor pollutant ratio depends on indoor and outdoor pollutant sources as well as the ventilation rates of the source and the sink, as shown in the following equation [124]:

$$C_{\mathrm{I}}/C_0 = 1 + 1/C_0[(S_{\mathrm{source}} - S_{\mathrm{sink}})/(q_{\mathrm{source}} - q_{\mathrm{sink}})]$$

where q is the rate of ventilation, S_{sink} is the indoor pollutant sinks, S_{source} is the indoor pollutant sources and C is the pollution concentration level.

When the indoor-to-outdoor pollutant ratio is approximately 1 for a VOC, it has comparable indoor and outdoor sources, and when the ratio is greater than 1, it has dominantly indoor sources [54, 77, 87, 125–127]. Typical indoor-to-outdoor pollutant ratio values for some VOCs are presented in Table 4, and these suggest that some VOCs have predominantly indoor sources while others have mainly outdoor sources. The method is often used in combination with statistical methods like Kruskal–Wallis, Wilcoxon *W* and Kolmogorov–Smirnov *Z* tests [84, 126].

6.1.2 Multivariate Data Analysis

These techniques reduce a large number of indoor VOCs to a few factors that can account for most of the cumulative variance in the VOCs data [126, 128, 129]. A factor loading matrix, which shows the correlation between the factors and the variables, is often obtained. Edwards et al. [129] have used this method to reduce 23 indoor VOCs in ETS-free microenvironments to 6 factors and to identify the most likely sources of the VOCs. A summary of the VOC classes that loaded on each factor and their probable sources are presented in Table 5. It is, however, noteworthy that UNMIX and positive matrix factorisation, both of which are based on factor analysis and have been applied frequently to ambient air quality data [130], have not featured prominently in indoor VOC source identification reports.

Table 4 Comparison of the ratios of the arithmetic mean of indoor concentration/arithmetic mean of outdoor concentration for selected VOCs in six homes

Compound	Living room	Kitchen
Benzene	2.35	2.05
Toluene	1.30	1.45
m,p-Xylene	0.62	0.84
o-Xylene	1.00	0.97
Ethylbenzene	0.54	0.75
1,3,5-Trimethylbenzene	0.82	0.77
Trichloroethane	1.06	1.24
Tetrachloroethene	0.52	0.48
1,4-Dichlorobenezene	0.90	1.03
Chloroform	2.00	2.38
Methylene chloride	0.92	0.84

Data was extracted from Lee et al. [125]

Table 5 The use of factor analysis for source apportionment of VOCs identified in residential indoor air

% variance accounted for	Component	Associated VOC classes	Assigned source
18	1	Alcohols and alkanals	Cleaning products, fragrances, consumer products, particle board
18	2	*n*-Alkenes, substituted aromatics, hydrocarbons	Traffic emissions
17	3	Aromatics	Long-range transport
9	4	Alcohols and alkanals	Carpets, rubber, adhesives
6	6	Mainly 2-butoxy ethanol	Cleaning products

Deduced from the data of Edwards et al. [129]

In addition, a number of studies have used principal component analysis (PCA) to recognise the sources of indoor VOCs [128, 131–136]. For example, Santarsiero and Fuselli investigated indoor and outdoor carbonyl compounds sources in Rome residential area as well as their mutual interrelations by means of PCA [135]. They identified six different sources of which four have a seasonal variation and observed a strong indoor/outdoor carbonyl compounds exchange.

6.1.3 Chemical Mass Balance Modelling

Watson et al. [137] undertook a review of the application of chemical mass balance modelling as a source identification technique for volatile organic compounds. The model assumes that the concentration of a chemical pollutant in a given sampling site is the summation of the contributions of all of the sources of the pollutant at the site. Thus, the concentration of the pollutant at the site can be predicted using the following equation [138]:

$$X_i = \sum_{j}^{P} a_{ij} S_j \; i = 1, \ldots, m$$

where X_i is the predicted concentrations of pollutants at the site, a_{ij} is the source signature for the pollutant i from source j, S_j is the contribution of source j, m is the number of pollutants (VOCs in this case) and p is the number of sources.

Although the model is frequently used to identify contributions of ambient VOCs from different sources [137], it has not been widely used for source identification of indoor VOCs. Won et al. [138] used the model to show that wall adhesive, caulking, I-beam joist and particle board were the dominant sources of 24 indoor VOCs that were measured from a newly constructed building. However, similarities in the signatures of the various sources were observed. Such high correlations (collinearity) among measured chemical species could lead to large uncertainties in the estimated source contributions [137].

6.1.4 Recognition of Source Emission Signature

With the development of online measurement technology for indoor VOCs, some researchers have started to build up a database of emission signature of individual materials using PTR-MS. This database can be used for source identification of indoor VOC by comparing the emission profile of mixed VOC samples using the method of multiple regression least squares (MRLS) and a normalisation technique [26].

6.1.5 Instruments Used for Source Identification

Field and laboratory emission cell (FLEC) affords a portable, nondestructive method of testing the surfaces of potential VOC sources. In addition to its utility as a climatic chamber, it provides valuable information on source strength, which can be used for source identification and to formulate strategies for emission control. Wolkoff et al. [139] used it to identify emission processes in a number of building materials, while Jarnström and Saarela [140] utilised it to show that the dominant source of TXIB (2,2,4-trimethyl-1,3-pentadiol-butyrate) in the indoor air of some problem apartments was the floor surface.

Apart from FLEC, other instruments that have been used for source identification and apportionment include:

- Direct measurements by portable instruments [141]
- Passive samplers [142]
- Headspace samplers [143]
- Multisorbent tubes [144]

6.2 Understanding Emissions from Indoor Sources

Indoor VOC levels are influenced by a large number of factors [17, 48, 145]. The most prominent ones include: (1) air exchange rate; (2) source characteristics; (3) ventilation systems; (4) meteorology (temperature and relative humidity); (5) age of a building; (6) building design; (7) type of indoor activities (e.g. cooking, smoking and photocopying); (8) sorption, desorption and deposition rates; (9) mixing and distribution of pollutants and (10) removal rate.

Of these factors, source characteristics, particularly characteristics of building materials, have been the most explored in the literature. Thus, various studies have attempted to link emission rates and sink effects of building and furnishing materials with indoor VOC levels [5, 138, 146, 147]. Many studies indicate that emission levels in new buildings are much higher than those in established buildings [78, 92]. This is possibly because emissions from building materials generally exhibit a decaying profile that is illustrated by the following equation [101]:

$$\mathrm{EF} = M_0 k_1 \exp(k_1 t)$$

where EF is the emission factor for source material (usually expressed in µg/m^2/h), M_0 is the quantity of pollutant on the surface of the material (usually expressed as µg/m^2) and k_1 is the decay constant (h).

Alternatively, when there are multiple decay processes, the equation shown below is useful:

$$\mathrm{EF} = \mathrm{EF}_{01} \exp(-k_1 t) + \mathrm{EF}_{02} \exp(-k_2 t)$$

where EF_{01} and EF_{02} are the initial decay constants for two simultaneous decay processes. Thus, decay is initially fast and VOC level is higher in new buildings [92] as illustrated by Fig. 2.

Another approach that is commonly used to evaluate the emission rates of VOCs in indoor microenvironments is to estimate an area specific emission rate (SER). This approach assumes that the VOCs are homogeneously mixed in the environment and that SER can be calculated with the following equation [17]:

$$\mathrm{SER} = NV(C_1 - C_0)/A,$$

where the SER is in micrograms per square metre per hour, V is the volume of the space (cubic metres), N is the air exchange or infiltration rate (per hour), A is the floor area space (square metres), C_1 is the indoor concentration (micrograms per cubic metre) and C_2 is the outdoor concentration (micrograms per cubic metre).

Van Winkle and Scheff [148] used a variant of this equation to show that indoor VOCs have predominantly indoor sources, while Hodgson et al. [78] reported the SER values for a wide range of VOCs in manufactured and site-built homes in the

Fig. 2 Dependence of TVOC (in μg/m^3) on the age of a newly constructed home. Data from [92]

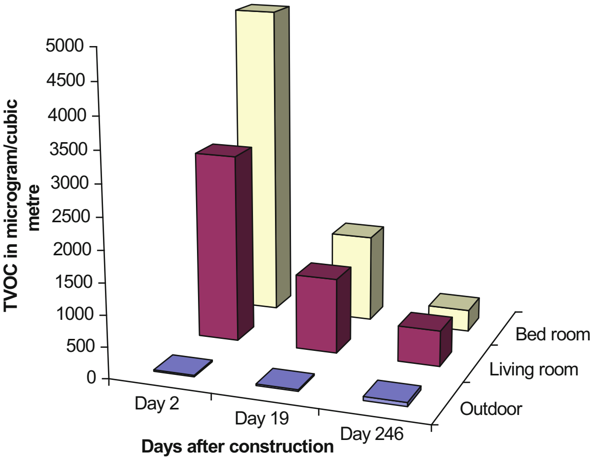
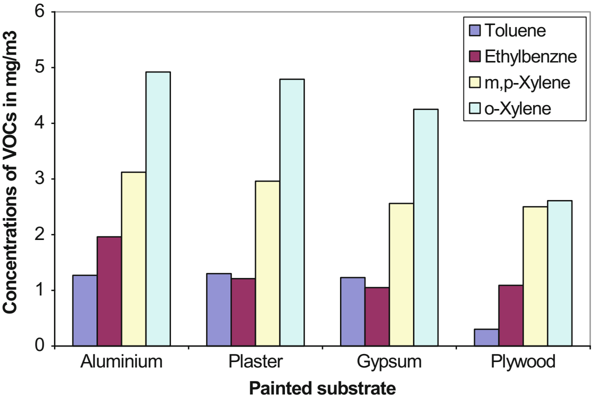


Fig. 3 Effect of substrate on VOC emissions from indoor building materials. Constructed from the data of Kwok et al. [152]



USA. As expected, many of the VOCs monitored by Hodgson et al. [107] showed decreased emission rates with the age of the building.

It is noteworthy that the VOC emission rates of building materials vary widely [92, 149, 150]. Thus Mølhave [151] reported over a few decades ago that the emission rates of wall/flooring glue, water-based PVA glue and gypsum board are of the order 2.7×10^5, 2.1×10^3 and 30 μg/m^2/h, respectively. Kwok et al. [152] reported VOC emission rates for varnish-painted aluminium, plaster, gypsum and plywood for toluene, *o*-xylene, *m*/*p*-xylene and ethylbenzene are also significantly different, with that of aluminium being approximately 65% higher than that of plywood as illustrated by Fig. 3.

It is also worth mentioning that emission rates vary with different indoor activities. Van Winkle and Scheff [153] associated 1,1,1-trichloroethane emission factors of 353, 522, 988, 1,419 and 2,790 μg/h with the presence of washer/drier in a utility room, storage of hair products, storage of chemicals, periodic dry cleaning and storage of moth balls, respectively. Occupants of air-conditioned offices and

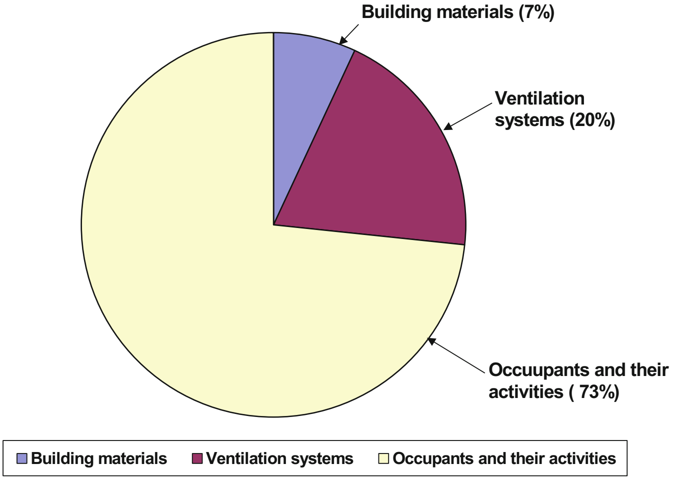


Fig. 4 Source apportionment of indoor aromatics. Data from Zuraimi et al. [144]

their activities have also been shown to contribute more to VOC levels in commercial offices in Singapore than ventilation systems and building materials [17], as illustrated by Fig. 4. This result corroborates the findings of Hodgson et al. [78], which suggested that occupants of new office buildings contributed more VOCs to the indoor air than other sources.

6.3 Understanding the Interaction of VOCs with Indoor Materials

In the past two decades, over 250 peer-reviewed publications addressing chemical reactions among indoor pollutants have appeared [10]. Diffusive interactions of VOCs with the surfaces of building walls, floors and household materials have been the subject of several experimental investigations, modelling and simulation [11, 29, 154–156]. Such interactions regulate peak levels of indoor VOCs, while subsequent desorption of the adsorbed VOCs delays their disappearance from the indoor environment. In order to predict and model the VOC emission rates of indoor materials, it is essential to know the diffusion and partition coefficients of individual VOCs. These coefficients can be simultaneously estimated through inverse analysis [157]. In addition, a couple of extraction methods have been developed to determine the initial concentration emitted and the partition coefficient of VOC in dry building materials [158, 159].

Secondly, VOCs react with indoor ozone to produce submicron particles [160–163]. Thus, terpenes, which is commonly found in many household consumer products, interacts with ozone, which is also widespread in indoor air through outdoor infiltration and use of office equipment like laser printers and photocopiers, to form particles [164–166]. Such reactions can markedly increase the number and mass concentrations of sub-micrometre particles. In addition, styrene and skin lipids react with ozone to generate appreciable amounts of aldehydes [33, 167].

6.4 Indoor VOC Guidelines

According to Mølhave [168], *"A guideline is a set of criteria (*i.e. *standards for making judgements) specifically assembled to indicate threshold levels of a harmful or noxious agent consistent with the good health."* The first notable attempt to provide some guidelines for indoor VOCs was made by Seifert [169] in which he classified indoor VOCs into alkenes, aromatic hydrocarbons, terpenes, halocarbons, esters, aldehydes and ketones (excluding formaldehyde) and proposed that:

- TVOC should not exceed 300 μg/m^3.
- No individual compound should have a concentration greater than 10% of TVOC or 10% of the concentration apportioned to that class of VOC.

Pluschke [170] reviewed Seifert's paper [171] and showed that only a few countries have guidelines for indoor TVOC. The USA has a value of 200 μg/m^3 [172], Germany 300 μg/m^3 [171] and Australia 500 μg/m^3 [173]. Pluschke [170] also stated that Seifert modified his original concept to include a target value defined as 200–300 μg/m^3 and a recommendation for official intervention if the TVOC concentration exceeds 1,000–3,000 μg/m^3. In Germany the federal and state authorities have developed a joint concept for the evaluation of indoor air contaminants by means of reference and guideline values and some guiding principles for the assessment of TVOC concentrations [174, 175].

Guidelines for individual VOCs are also available in some countries. In Poland, the maximum allowable concentrations for some VOCs have been set at 10 μg/m^3 for benzene, 200 μg/m^3 for toluene, 100 μg/m^3 for butyl acetate, 100 μg/m^3 for ethylbenzene, 100 μg/m^3 for *m*-xylene, 20 μg/m^3 for styrene and 30 μg/m^3 for *p*-dichlorobenzene [176]. In the context of the 64 VOCs of interest to the European Commission [177], only toluene, 2-ethoxyethanol, 2-butoxyethoxylethanol and 1-methoxy-2-propanol have readily available guideline values [178]. The odour threshold, sensory irritation exposure limit and health-based indoor exposure limits of these VOCs are presented in Table 6.

Despite the ubiquitous nature and importance of VOC in the indoor environment, it is surprising that no international indoor VOC guideline has emerged. Nielson et al. [178] have linked the difficulty experienced in evaluating sensory and health effects of indoor VOCs with the absence of indoor VOC standards and guidelines. Although the European Commission Report No 19 [2] recommended that indoor VOCs should be kept as low as reasonably achievable, more concerted efforts should be made to formulate a universally acceptable set of guidelines for as many indoor VOCs as possible.

Table 6 Guideline levels for some VOCs

Compound	Odour threshold (mg/m$^{3)}$	Sensory irritation exposure limit estimate (mg/m^3)	Health-based indoor air exposure limit estimate (mg/m^3)
Toluene	1	8	8
2-Ethoxyethanol	4.6	10	0.4
2-Butoxyethoxylethanol	0.0092	–	9
1-Methoxy-2-propanol	0.7	10	10

According to Pluschke [170] and Nielsen et al. [178]

7 Health Effects of Indoor VOCs

Mølhave [168] suggested that the health effects of VOCs could be grouped into:

- Immune effects and other hypersensitivity effects (e.g. asthma and allergy)
- Cellular effects (e.g. cancer)
- Cardiovascular effects
- Neurogenic and sensory effects (e.g. odour and irritation)
- Respiratory effects other than immunological

The US EPA website [120], assessed in May 2012, provides more details, suggesting that the health effects of indoor VOCs include: eye, nose and throat irritations; headaches; loss of coordination; nausea; damage to liver, kidneys and central nervous system; and cancer. Similarly, the health effects of environmental tobacco smoke (ETS), which contains several VOCs as well as nicotine, 3-ethenylpyridine, carbon monoxide and particulate matter, include: eye, nose and throat irritation, carcinogenic effects, activation of the immune system and exacerbation of asthma and respiratory tract illnesses [179].

While individual VOCs like benzene and toluene have been linked with acute myeloid leukaemia and neurotoxicity, respectively [180, 181], epidemiological studies of the health effects of indoor VOCs have related TVOC rather than individual VOC levels to exposure. The outcomes of such studies have been mixed [182]. In some cases, positive associations between sick building syndrome (SBS), building-related illness (BRI) or multiple chemical sensitivity (MCS) syndromes and TVOC levels were observed [183, 184], while negative associations were reported by Sundell et al. [185]. Yet, no association was found in a few studies [186].

Several reasons may be adduced for the inconsistent association between SBS complaints and TVOC levels [18, 48]. Some these are outlined below:

- Indoor air chemistry leads to the formation of VOCs and other species that are different from those monitored. For example, ozone reacts with VOCs to give secondary products that could be responsible for the observed SBS [187].
- Only compounds in a narrow chromatographic window are normally monitored; low molecular weight aldehydes, which may play a significant role in SBS, are not routinely monitored as part of TVOC [188].

- Ventilation systems are significantly associated with SBS complaints [189, 190].
- Particles present in indoor environment might contribute significantly to SBS systems [48].
- Environmental tobacco smoke is associated with many SBS-type symptoms [191].
- Measurements are usually carried out as mean time-integrated concentrations at the centre of the room rather than in the breathing zones of the subject [191].
- Self-reporting questionnaires are subjective means of assessing SBS [183].
- The influences of psychosocial factors are being ignored [184].
- TVOC is not biologically important [188].
- Biologically important VOCs have not been found and are not being monitored [188].

Thus, the role of VOCs in SBS complaints is far from being fully understood. More research is particularly required in the:

- Development of validated methods for TVOC and dose–response relationship
- Risk indicators for multiple exposures [182]
- Evaluation of TVOC and SBS/health effects from carefully designed epidemiological studies
- Development of universal guidelines for evaluating exposures [192]

Since TVOC does not permit consistent exposure–dose relationship, Mølhave [168] suggested that it should be treated as an indicator of the presence of VOCs and used only for source identification, indoor air quality assessment and as a screening tool for exposure assessment rather than a guideline or an official recommendation.

However, despite the statistically insignificant difference between the TVOC values in buildings with and without SBS problems, the underlining difference among such buildings was manifested in Coomans plot and partial least squares discriminant analysis plots [193]. Similarly, principal component analysis has been used to separate buildings with low and high prevalence of SBS [194]. It therefore appears that multivariate projection methods could play significant roles in the identification of causality in indoor VOC exposure studies.

8 Purification of Indoor VOCs

Although technologies for particle removal are rather well established, there are no satisfactory methods for VOC control because removing indoor VOC sources or increasing ventilation rates is often not feasible or economical [195]. Nevertheless, new technologies for the removal of indoor VOCs are emerging and some of them are outlined below.

8.1 Biological Treatment

Guieysse et al. reviewed the potential and challenges of biological treatment approaches in the removal of indoor VOC pollutants [195]. Although biological methods have shown some potential for indoor VOC removal, specific characteristics of indoor air and the indoor air environment pose numerous challenges, which may include the (1) maintenance of suitable and diverse catabolic ability under conditions that do not sustain microbial growth and (2) purification of large amounts of air in confined environments with minimal nuisances and release of microorganisms [195]. Liu et al. screened 73 ornamental plant species for their ability to remove 150 ppb benzene from indoor air [196]. The results showed that over 10 species, including Crassula portulacea and Hydrangea macrophylla, have the greatest capacity to remove benzene from indoor air. Wang and Zhang developed and evaluated a dynamic botanic air filtration system (DBAF), a fan-assisted with controlled airflow activated carbon/hydroculture-based potted plant unit [197]. They concluded that the DBAF effectively removed both formaldehyde and toluene under 5–32% volumetric water content of the root bed.

The removal efficiencies of formaldehyde by common indoor plant species were evaluated under various growing media, including three porous materials (growstone, expanded clay and activated carbon) [198]. It was found that the formaldehyde removal by the root zone was more rapid than the removal by the aerial plant parts. Lu et al. studied four bacterial strains isolated from the biotrickling filter for indoor VOC removal [199], demonstrating high removal efficiencies for formaldehyde, benzene, toluene and xylenes.

8.2 General Air Cleaning Technology

A multidisciplinary panel of experts has recently undertaken a thorough and critical review [200] of the existing fan-driven air cleaning technologies. They concluded that (1) none of the reviewed technologies was able to effectively remove all indoor pollutants and many were found to generate undesirable by-products during operation; (2) particle filtration and sorption of gaseous pollutants were among the most effective air cleaning technologies, but there is insufficient information regarding long-term performance and proper maintenance; (3) the existing data make it difficult to extract information such as Clean Air Delivery Rate (CADR), which represents a common benchmark for comparing the performance of different air cleaning technologies; (4) to compare and select suitable indoor air cleaning devices, a labelling system accounting for characteristics such as CADR, energy consumption, volume, harmful by-products and life span is necessary. For that purpose, a standard test room and condition should be built and studied; (5) although there is evidence that some air cleaning technologies improve indoor air quality, further research is needed before any of them can be confidently recommended for use in indoor environments.

Air cleaners can remove indoor organic compounds, but also generate ozone, another indoor air pollutant [201]. Yu et al. [202] evaluated the effective ozone emission rates and the VOC removal efficiencies of six selected air cleaners by combinations of chamber experiments and modelling studies. They found that the removal of toluene and formaldehyde might have resulted from the adsorption on the filters and the decomposition by the high-voltage electric discharge or the ionisation that generated ozone.

8.3 Bake-Out

The effect of bake-out using a radiant floor heating system on reducing VOC emissions and indoor concentrations in a residential housing unit has been investigated recently [203]. It was shown that there were differences in the time for each material to reach the desired surface temperature, which resulted in different reduction ratio of VOC emissions and concentrations.

8.4 Optimised Ventilation

Indoor air quality is significantly affected by ventilation parameters, such as building recirculation rates (BRR) [204] and airflow profile [205]. A Singapore study recently investigated the impact of BRR on formation of SOAs [204]. They found that number and mass concentrations of SOA decreased significantly at higher recirculation rates primarily due to the lower precursor concentrations, which is confirmed by the study conducted by Fadeyi et al. [206].

8.5 Adsorption

A number of materials have been selected to absorb indoor VOCs, including porous clay heterostructures (PCH) [207], carbon nanotubes [208], metal-organic frameworks [209], activated carbon fibre [210] as well as packed-bed absorber using triethylene glycol [211] and other porous materials [198].

8.6 Photocatalytic Oxidation

In the past decade, a number of studies have been conducted to assess indoor VOC removal by photocatalytic oxidation techniques [27, 212–220]. An excellent review was undertaken by Mo et al. on photocatalytic purification of indoor VOCs [218]. In the paper, the preparation and coating of various photocatalytic catalysts, different kinetic experiments and models, novel measurement methods and reaction mechanisms are reviewed and discussed in detail. However, the by-products resulting from photocatalytic oxidation of indoor VOCs may bring new health risks to exposed people. Mo et al. investigated the by-products of toluene (at ppb level) during photocatalytic oxidation by using PTR-MS. The identified main by-products included benzaldehyde, methanol, acetaldehyde, acetone/propionaldehyde, formic acid/ethanol and acetic acid. They calculated the health-related index and concluded that these by-products may not have negative effects to human health due to their low concentrations.

9 Trends/Perspectives

It is evident from the above sections that:

- The TVOC concept has limited use and must be used with caution [188].
- A compound-to-compound approach of evaluating the health effects of OCIA as suggested by Wolkoff [108] should be explored in place of the TVOC approach.
- More research is required on the role of reactive chemistry in the causation of SBS.
- The roles of ionic species, hydroxyl and peroxide radicals as well as substances absorbed onto particles in the causation of SBS should be researched [221].
- Attempts have been made to estimate OH radicals through modelling and indirect measurements [221], but limited direct measurements have been made to date. Future work is required in this area.
- More research is required in order to understand the health effects of secondary products like ketones, PAN (peroxyacetyl nitrate) and organic acids, which are generated from the reactions of VOCs in indoor air [221].
- More indoor air audits are required in developing nations.
- Need for collaborative approach from environmental scientists and health agencies.
- Need for practical applications of the knowledge gained in the various areas of IAQ.
- Need for development of appropriate indicators for IAQ, such as indoor fungi [222].
- Need for further work on emerging technologies designed to remove indoor VOCs.

10 Concluding Remarks

The past decades have witnessed tremendous growth in indoor air audits, development of a quasi-uniform definition of VOC levels in indoor microenvironments and improvement of concepts for screening indoor air quality and assessing exposure. Significant advancements have been made in emission modelling, source identification, source control, source characteristics and interaction of indoor VOCs with indoor materials, particularly the formation of indoor secondary organic aerosols. Some progress, albeit slow, have occurred in the development of universally acceptable exposure guidelines. The entrance of smaller, faster and smarter instrumentation into the market could enhance fieldwork markedly. However, the link between health/sensory effects and indoor VOC levels is still largely unclear. Further work is urgently required in this area and in the search for insights on the role of reactive chemistry in the generation, degradation and transformation of indoor VOCs.

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