



Review Article

Indoor Air Pollution, Sorbent Selection, and Analytical Techniques for Volatile Organic Compounds

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ABSTRACT Indoor air quality has received wide spread attention due to the recognition of the presence of diverse toxic volatile organic compounds (VOCs) and their harmful impacts on human health. This review discusses the chemicals in indoor air and their sources and associated chemical (primary/secondary) reactions. The merits and demerits of commercially available adsorbents and synthetically prepared carbon/non-carbon-based adsorbents for indoor air sampling are discussed. Also, important parameters (like breakthrough volume, specific adsorption capacity, reaction mechanism, and desorption efficiency) are evaluated. The recent advancements in analytical techniques and insight into the complexity involved in air sampling are emphasized. The application of commercially available adsorbents and synthetically prepared carbon/non-carbon-based adsorbents for indoor air sample collection are discussed.

KEY WORDS Indoor air chemistry, Sorbent, Air sampling, Adsorbent, Volatile organic compounds, Analytical techniques

1. INTRODUCTION AND SCOPE OF THE REVIEW

The increasing emissions of diverse forms of VOCs are attributable to the rapid increase in urbanized population and excessive use of synthetically prepared chemical-based consumer products (U.S. EPA, 2011, 1999). Among the various VOCs observed in indoor air samples, the compounds like 1,4-dichlorobenzene, isopropyl-benzene, 1,2-dichloroethane, naphthalene, benzene, chloroform, ethylbenzene, styrene, tetrachloroethene, trichloroethylene etc., are identified as carcinogens (Chin *et al.*, 2014; U.S. EPA, 2011). The most commonly observed priority indoor air VOCs are acrolein, benzene, acetaldehyde, 1,4-dichlorobenzene, 1,3-butadiene, naphthalene and formaldehyde (Chin *et al.*, 2014). The World Health Organization (WHO) recognized benzene, styrene, toluene, trichloroethylene and tetrachloroethene as the priority pollutants in indoor atmosphere. Similarly, benzene, naphthalene and formaldehyde are commonly identified in indoor air samples and considered as the priority pollutants in most of the European countries. The presence of most commonly identified VOCs and their maximum concentration in indoor air samples are given in Fig. 1.

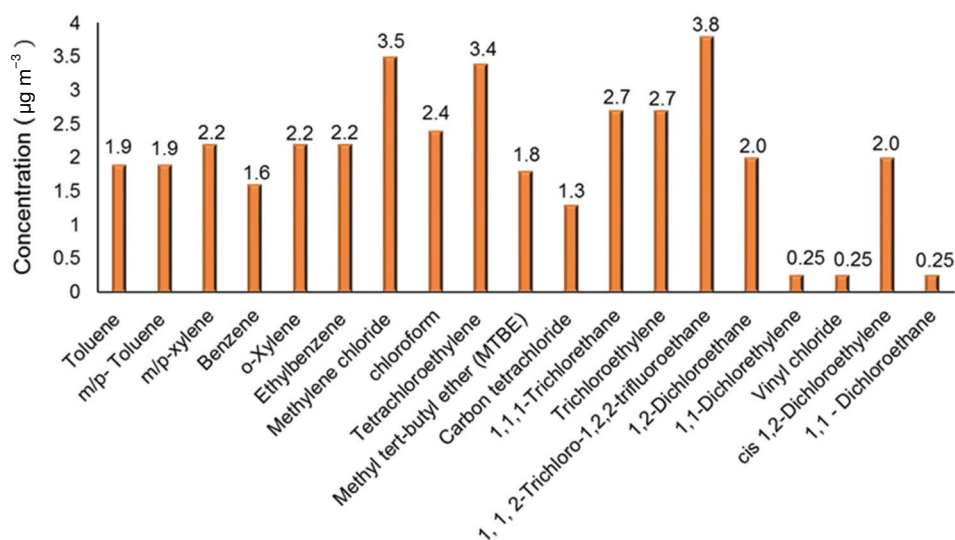


Fig. 1. The concentration ($\mu\text{g m}^{-3}$) of most commonly identified VOCs present in indoor air (Adopted and modified from U.S. EPA, (2011) report no 530-R-10-001).

The importance of air quality in indoor environment particularly in industrial buildings, residences, schools, hospitals, market place, restaurants, etc., and their impact on human health and environment have been increasingly understood (Kataoka *et al.*, 2012). Among various pollutants in indoor, VOCs are well-known for toxic and harmful effects as carcinogen or mutagen (Wolkoff, 2018). There are various sources of VOCs with different types and nature (e.g., adhesives, carpet, paints, printers, cleaning products, deodorizers, linoleum, textiles, wall covering, furniture, window shades, flooring adhesives, house hold cleaning products, personal care products, and dry-cleaned clothing) that have been studied extensively (Lucattini *et al.*, 2018; Bulian and Fragassa, 2016; Can *et al.*, 2015; Dinh *et al.*, 2015; Barrese *et al.*, 2014; Kim and Kim, 2014; Lim *et al.*, 2014; Liu *et al.*, 2013; Kabir and Kim, 2011; Kim *et al.*, 2011; Bernstein *et al.*, 2008; Kwon and Jo, 2007; Mendell *et al.*, 2007; Lee *et al.*, 2006; Yu and Crump, 2003; Igielska *et al.*, 2002; Räisänen *et al.*, 2001). The types and nature of VOCs emitted from different indoor sources are given in Table 1.

The concentration of VOCs present in indoor is much higher than those present in outdoor (Mirzaei *et al.*, 2016; Tiwary and Colls, 2009). The outdoor reaction is predominantly controlled by intense solar radiation where the concentration of VOCs present is much lower than that of indoor condition (Morrison *et al.*, 2015; Panagiotaras *et al.*, 2014). Indoor concentration

of VOCs is controlled by many factors such as the nature of source, outdoor air quality, degree of ventilation, air exchange rate, and pollutant depletion mechanisms (Panagiotaras *et al.*, 2014). A major shortcoming of the existing standards for qualitative and quantitative estimation of VOCs in indoor air samples are: (i) diversities of VOCs released from various sources and associated technical difficulties in their quantitation, (ii) difficulties in the development of standard methods for sorptive capture for all VOCs without recovery issues (e.g., due to large differences in chemical and physical properties of the VOCs), (iii) selection of commercial sorbent for VOCs sampling without doing initial assessment, (iv) oxidation reaction of VOCs with O_3 which is coming through ventilation system, (v) formation of intermediate products and secondary aerosol formation, and (vi) influence of other factor such as artifact levels due to the improper sorbent conditioning, moisture content, temperature and wind velocity. As such, all these issues remain a challenging task and require in-depth research. In this review, merits/demerits of thermal-desorption techniques are discussed in association with adsorbent materials along with the current status of VOCs emission in indoor environment. The challenges involved in the identification of secondary organic aerosol (SOA), stable intermediates produced during the formation of radical reaction, sampling strategies and recent progress in analytical advancement in VOCs analysis are also dis-

Table 1. List of VOCs identified in indoor environment and their possible sources.

S. No	Source	Volatile organic compounds	Ref.
1	Adhesives	Toluene, xylenes, styrene, ethylbenzene, formaldehyde, butyl ether, vinyl cyclohexane, 2-propenoic acid and propylene glycol	Bernstein <i>et al.</i> , 2008; Mendell <i>et al.</i> , 2007
2	Carpet	Formaldehyde, 4-phenylcyclohexene, vinyl acetate styrene, dodecanol and acetaldehyde	Mendell <i>et al.</i> , 2007
3	Paints	Toluene, benzene, m, p-xylenes, o-xylene, Styrene, ethylbenzene, 2-methylhexane, cyclohexane, 2,4 dimethyl pentane, methyl cyclopentane, n-heptane, methyl cyclohexane and n-octane.	Can <i>et al.</i> , 2015; Mendell <i>et al.</i> , 2007
4	Printers/copiers	Formaldehyde, styrene, ethylbenzene, xylenes, benzene, 2-ethyl-1-hexanol and toluene etc.	Barrese <i>et al.</i> , 2014; Lee <i>et al.</i> , 2006
5	Cleaning products	Limonene, isopropanol, butoxyethanol, 1,4 dichlorobenzene, ethanol, limonene, toluene, decane, phenol, 1-propanol, o-xylene and chlorobenzene	Kwon and Jo, 2007
6	House hold spray products	Propane, acetaldehyde, butyraldehyde, methyl ethyl ketone, ethyl alcohol, iso-valeraldehyde, benzene, valeraldehyde, methyl isobutyl ketone, toluene, isobutyl alcohol, p-xylene, m-xylene, ethylene acetal and o-xylene, styrene.	Rahman and Kim, 2014
7	Textiles	Formaldehyde, acrylonitrile, acetaldehyde, toluene, o-xylene, 1,2,4-trimethylbenzene, ethylbenzene and m,p-xylene	Igielska <i>et al.</i> , 2002
8	Wall covering	Naphthalene, methyl pyrrolidinone, styrene, phenol, formaldehyde, acetaldehyde, tetradecane, toluene, o-xylene, 1,2,4-trimethylbenzene, ethylbenzene and m,p-xylene	Lim <i>et al.</i> , 2014
9	Barbecue charcoal	Benzene, toluene, ethyl benzene, meta para xylene, styrene, formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde and valeraldehyde.	Kabir <i>et al.</i> , 2010
10	Furniture	Formaldehyde, acetaldehyde, benzene, benzaldehyde, toluene, tetrachloroethylene, xylene, trimethyl benzene, dichloro benzene, ethyl benzene, butoxy ethanol, styrene, butylacetate, hexanal and cyclohexanone.	Bulian and Fragassa, 2016; Liu <i>et al.</i> , 2013; Ho <i>et al.</i> , 2011
11	Window shades	Ethylhexanoic acid, decanol, dodecene, ethyl hexanol and naphthalene	Bernstein <i>et al.</i> , 2008; Mendell <i>et al.</i> , 2007
12	Flooring adhesives	Vinyl acetate, 1,2-propanediol, 2-ethylhexanol, 2-(2-butoxyethoxy) ethanol, 4-phenylcyclohexene, 2-(2-butoxyethoxy)ethyl acetate, β -caryophyllene, α -humulene, longifolene, formaldehyde and acetaldehyde	Yu and Crump, 2003
13	Cleaning products	Polyfluorinated compounds, ethanol, methanol, toluene, styrene and limonene	Lucattini <i>et al.</i> , 2018, Dinh <i>et al.</i> , 2015
14	Cooking activities	Acetaldehyde, propionaldehyde, butyraldehyde, iso-valeraldehyde, toluene, styrene, para-xylene, methyl ethyl ketone, methyl isobutyl ketone, butyl acetate, isobutyl alcohol, propionic acid, butyric acid, isovaleric acid and valeric acid	Kabir and Kim, 2011, Kim <i>et al.</i> , 2011; Kim and Kim, 2014.
15	Personal care products	Air freshener and body wash: alcohol, aldehyde, terpene, organic acid, hexane, benzene, toluene, ethylbenzene, m,p-xylene, styrene, α -pinene, camphene, β -pinene, β -myrcene and n-decane and 3-carene	Dinh <i>et al.</i> , 2015; Weschler and Carslaw, 2018

cussed.

2. RECENT ADVANCEMENT IN INDOOR CHEMISTRY

2.1 Chemicals that are Identified and Possible Reaction in Indoor Air and Sources

Chemical reaction in indoor environment is a complex one and many factors (such as climate and ventilation, cleaning conditions, properties of buildings, nature of house-holds products, and habits) are involved in controlling the VOCs emissions. Chemical reaction of

VOCs in indoor environment is mainly initiated in the presence of O_3 and $\cdot OH$ or other radicals (Waring and Wells, 2015). In indoors, laser printers, photocopiers, electrostatic air cleaners, and fresh air coming from ventilation system are the main source of O_3 (Britigan *et al.*, 2006). Similarly, the reaction between O_3 and alkene emitted from the indoor are the main source of $\cdot OH$ radical generation (Fig. 2). Air coming through ventilation system may also contain alkenes such as isoprene, terpene etc. emitted from several plant species of different genera. Further, alkenes and their derivatives emitted from indoor sources such as cleaners, air fresheners, wood and personal care products are also sub-

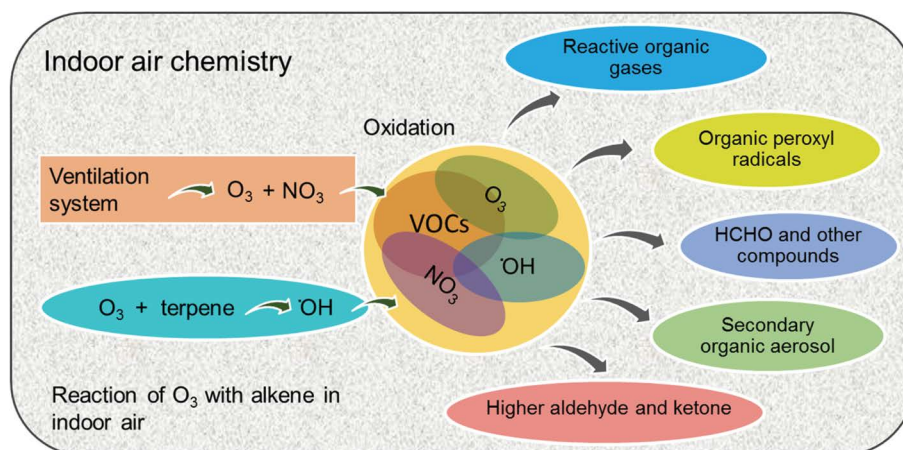


Fig. 2. Reaction of O_3 , NO_3 and OH radicals with alkenes and other VOCs, and formation of SOA, stable intermediates and other possible reaction.

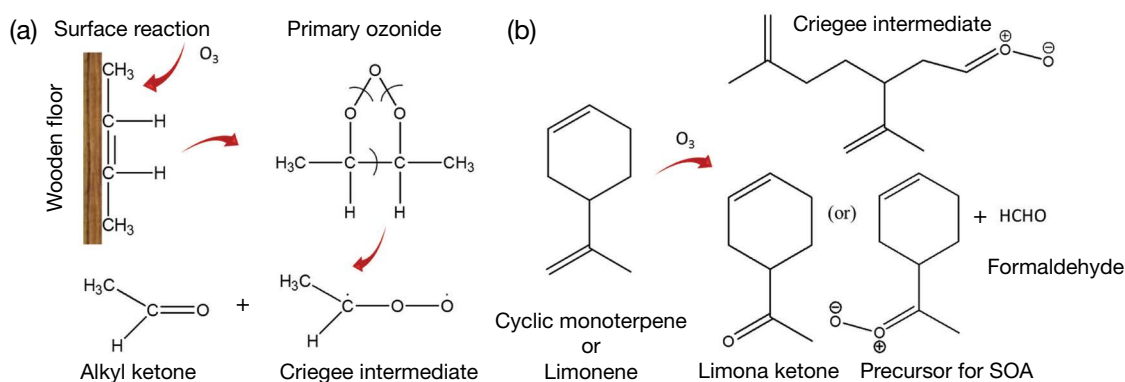


Fig. 3. Surface reaction of O_3 with unsaturated alkene (a) formation of alkyl ketone and Criegee intermediate, (b) Proposed pathway of limonene or cyclic monoterpene reaction with O_3 and formation of ketone, formaldehyde and SOA (adopted and modified from Weschler *et al.*, 2000 and Donahue *et al.*, 2007).

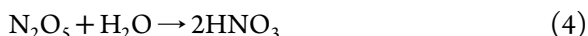
jected to readily undergo oxidation reaction (reaction rate $10^{-4} - 10^{-2} \text{ ppb}^{-1} \text{ h}^{-1}$) with O_3 (Waring and Wells, 2015; Nazaroff and Weschler, 2004; Hodgson *et al.*, 2002).

The important reactions that are taking place in indoor environment are (i) reaction of O_3 with unsaturated hydrocarbons, (ii) generation of OH radicals by the reaction with O_3 and NO_x , (iii) decomposition of PAN (peroxyacetyl-nitrate), (iv) free radical reaction with VOCs, and (v) other heterogeneous reactions (Weschler and Carslaw, 2018; Araki *et al.*, 2009; Weschler, 2004; Weschler, 2001; Roumelis and Glavas, 1992). Note that the reactions described above for the indoor environment are thermodynamically favorable. Hence, due to the absence of sun light, their reaction rate

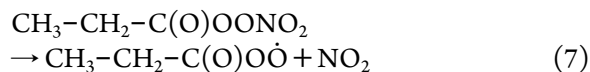
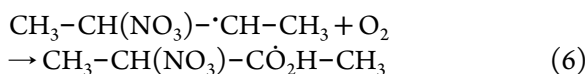
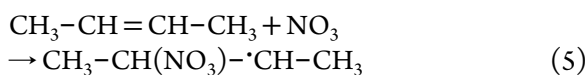
is much lower than that in outdoor condition (Ingrosso, 2002; Weschler, 2000). OH and NO_x are nonselective in nature and readily react with a wide range of VOCs, O_3 has high affinity towards alkenes such as d-limonene, α -/ β -pinene, terpinolene, γ -terpinene, α -terpineol, linalool, dihydromyrcenol, etc. (Mellouki *et al.*, 2015; Waring and Wells, 2015; Atkinson and Arey, 2003; Arey *et al.*, 1990). In indoors, terpenes can react with O_3 to form a precursor for the secondary aerosol and other intermediate products (Wolkoff *et al.*, 2006; Sarwar *et al.*, 2004). The emission of secondary or intermediate products can be much more toxic to the human health than the primary VOCs (Kruza *et al.*, 2017). O_3 readily reacts with unsaturated hydrocarbon or other compounds present on solid surface (such as furniture, carpet, wooden floor, and

painted wall) to liberate a range of higher aldehyde, ketone, and secondary aerosol (Morrison, 2015; Waring and Siegel, 2013; Hodgson *et al.*, 2002). The possible surface reaction of O₃ with alkene present in the solid surface is given in Fig. 3a and b.

The secondary emission or intermediates formed during the reaction of alkene (or VOCs) by O₃ or HO· radicals in indoor condition is poorly identified (Katakoka *et al.*, 2012). Weschler *et al.* (1992) reported the considerable enhancement of formaldehyde, acetaldehyde, and other aldehydes (C₅ to C₁₀) concentration during the reaction of O₃ with carpet emission such as 4-phenylcyclohexene (PCH), 4-vinylcyclohexene (VCH), and styrene in a confined condition. In contrast, in the absence of O₃ there was no significant change in the concentration of formaldehyde, acetaldehyde, and other aldehydes (Weschler *et al.*, 1992). The above observations clearly indicate the oxidation of alkenes with O₃ and formation of formaldehyde, acetaldehyde, and other aldehydes in indoor air condition (Salthammer *et al.*, 2010; Wolkoff *et al.*, 1997). Like O₃, nitric oxide (NO) also comes through air ventilation system while it can also be generated by indoor combustion process (Skalska *et al.*, 2010; Ingrosso *et al.*, 2002). In indoor condition, O₃ readily undergo series of reaction with NO and forms of NO₂, NO₃, N₂O₅, and HNO₃ as given in the equations (1) to (4) (Skalska *et al.*, 2010).



Further, NO₃ can react with alkene and generate alkyl peroxy radical as given in equations (5) and (6) (Ingrosso *et al.*, 2002). These reactions are most favorable for unbranched alkenes. Similarly, peroxyacyl nitrate present in the indoor air are thermally unstable and readily undergo decomposition reaction to yield peroxyacyl radicals and NO₂ (eq. 7) (Zhang *et al.*, 2015; Ingrosso *et al.*, 2002).



As seen in Fig. 2, the indoor reactions are complicated while highly dependent on the combined effects of both chemical (O₃, NO_x, alkenes, and other VOCs) and physical parameters (e.g., humidity, temperature, ventilation rate, and light intensity). Further, most of the above conditions are completely different from one location to another (Morrison, 2015).

3. SYNTHETICALLY PREPARED CARBON/NONCARBON BASED ADSORBENT FOR INDOOR AIR SAMPLING

The use of carbon and noncarbon based materials as sorbent for the removal of VOCs from ambient air and indoor environment have been extensively studied by various research groups (Vellingiri *et al.*, 2017). The carbon and noncarbon-based materials used for the removal of VOCs are discussed in the following section.

3.1 Carbon-Based Adsorbent for Indoor Air Sampling

Carbon is one of the important and most effective sorbents for the collection of various forms of VOCs. The important allotropes of carbons (e.g., amorphous, diamond, graphite carbon, fullerenes, nanotubes, and graphene) have been extensively studied for a wide range of applications (Yoshimura and Senthilnathan, 2017). The property of each allotrope is different from the other. For example, activated carbon is amorphous in nature and extensively used for adsorption process. Whereas, diamond is a crystalline carbon (sp³ carbon), nonconductive and highly inert in almost all the conditions (Senthilnathan *et al.*, 2014). The other allotropes (such as graphite carbon, fullerenes, nanotubes, and graphene) are crystalline and highly conductive in nature with very high surface area (Agnihotri *et al.*, 2005). Among the various carbons, activated carbon, granular activated carbon (GAC), single and multiwalled carbon nanotubes (SWCNTs and MWCNTs) have been studied extensively for the removal of diverse nature of organic compounds (Li *et al.*, 2011; Oh *et al.*, 2010; Delage *et al.*, 2000). Among these, activated carbon is the extensively studied adsorbent due to its large surface

Table 2. Comparison of breakthrough volume, recoveries and adsorption capacities of different MWCNT for the sorption of VOCs.

S. No	Name of the VOCs (70% humidity)	Recoveries (%) (MWCNTs)	Adsorption capacities (mg g ⁻¹) MWCNTs	Breakthrough volume (L g ⁻¹) or (%)		Ref.
				Carbopack B	MWCNTs (98 m ² g ⁻¹)	
1	Benzene	107 ± 2	–	3.72 × 10 ²	7.96 × 10 ⁴	Li <i>et al.</i> , 2004
2	Toluene	104 ± 6	–	1.34 × 10 ⁴	5.24 × 10 ⁶	
3	Ethylbenzene	88 ± 5	–	2.10 × 10 ⁴	7.73 × 10 ⁷	
4	p-Xylene	88 ± 6	–	3.23 × 10 ⁵	4.75 × 10 ⁸	
5	Cyclohexane	108 ± 2	–	6.10 × 10 ¹	6.13 × 10 ³	
6	Dichloromethane	105 ± 2	–	3.60 × 10 ⁻¹	1.74 × 10 ¹	
7	Trichloromethane	104 ± 4	–	6.70 × 10 ⁰	3.70 × 10 ²	
HC-MWCNT at 50°C; Surface area 25 m ² g ⁻¹				HC-MWCNT		
1	Benzene	104.16	–	–	–	Sone <i>et al.</i> , 2008
2	Toluene	105.04	–	–	–	
3	m,p-Xylene	104.11	–	–	–	
4	Chloroform	104.47	–	–	–	
5	Carbon tetrachloride	107.99	–	–	–	
MWCNT Surface are 111.3 m ² g ⁻¹				MWCNT	Tenax TA	
1	1, 2-Dichloroethane	103 ± 2	0.220	22 ± 3	–	Liu <i>et al.</i> , 2008
2	Benzene	90 ± 2	0.210	21 ± 4	–	
3	Toluene	90 ± 3	0.370	37 ± 3	–	
4	n-Heptane	98 ± 2	0.230	23 ± 3	–	
5	Ethylbenzene	101 ± 2	0.510	51 ± 4	–	
6	p-Xylene	99 ± 2	0.160	16 ± 3	–	
7	Styrene	77 ± 3	0.690	69 ± 4	–	
TerphApm@MWCNTs				MWCNT	TerphApm@MWCNTs	
1	Benzene	98	492	144 ± 34	182 ± 36	Abadi <i>et al.</i> , 2018

area, porous structure, chemical stability, cost effectiveness, eco-friendly, great accessibility and simple procedures involved in the synthesis process. The main mechanism involved in the adsorption of VOCs on GAC are physical or chemical adsorption of the target compounds on the pore wall, pore diffusion and others like convection, axial dispersion, liquefaction, condensation etc. (Dobre *et al.*, 2014). VOCs, which have a high boiling points and high molecular weights readily undergo capillary condensation and considerably increase the specific adsorption capacity (Li *et al.*, 2012). The adsorption of nonpolar VOCs like benzene, toluene, xylene etc., on GAC mainly follow van der Waals force of attraction or physical adsorptions. A highly polar compound like acetone which has a molecular diameter (0.308 nm) less than the pore diameter of adsorbent, follow pore diffusion mechanism (Li *et al.*, 2004). The adsorption property of GAC depends on various factors that includes size and shape of the adsorbent, particle density, surface area, pores size, porosity, void fraction etc. (Dobre *et al.*, 2014; Bhargavi *et al.*, 2011). The

nature of the VOCs and their chemical/physical properties (such as boiling point, vapor pressure, size, and concentration) are also important controlling factors for the adsorption process (Dobre *et al.*, 2014; Kawasaki *et al.*, 2004; Chuang *et al.*, 2003).

Nanocarbons such as SWCNTs and MWCNTs have been used as the adsorbent for the removal of aliphatic VOCs such as methane, methyl ethyl ketone, hexane, butane and n-nonane and aromatic hydrocarbon like toluene, cyclohexane and benzene from ambient air sample (Agnihotri *et al.*, 2007; Crespo and Yang, 2006; Hilding *et al.*, 2004; Talapatra and Migone, 2002; Iijima, 1991). The adsorption of various VOCs using MWCNTs and SWCNTs from ambient and indoor environment and their percentage of recoveries, maximum adsorption capacity, and breakthrough volume are given in Table 2. Both SWCNTs and MWCNTs follow heterogeneous adsorption mechanism due to the presence of high energy defective sites, oxygen functional groups, and interstitial and groove regions between CNT bundles (Pan and Xing, 2008; Fagan *et al.*, 2004; Hirsch, 2002;

Zhao *et al.*, 2002). Further, SWCNTs and MWCNTs facilitate a surface and/or capillary condensation of gas when VOCs contact with the surface leading to a multilayer adsorption or surface condensation (Pan and Xing, 2008; Gotovac *et al.*, 2007; Gotovac *et al.*, 2006). SWCNTs and MWCNTs adsorbents highly favor the adsorption of high molecular non-polar aromatic organic compounds due to the presence of hydrophobic sites (Cho *et al.*, 2008; Pan and Xing, 2008; Piao *et al.*, 2008). The hexagonal arrays of sp^2 carbon present in the graphene tubular sheets or CNTs highly favor the adsorption of aromatic VOCs due to the transfer of the π -electrons from the HOMO of the CNTs to the LUMO of the aromatic VOCs (Sone *et al.*, 2008). Further, the aromatic VOCs, which have lower HOMO to LUMO gap will have a higher attraction to the CNTs. The specific adsorption capacity and HOMO to LUMO gaps of VOCs (e.g., p-dichlorobenzene, xylene, toluene, and benzene) were found to be $1048.3 \mu\text{g g}^{-1}$ (9.03 eV), $740.3 \mu\text{g g}^{-1}$ (9.63 eV), $274.1 \mu\text{g g}^{-1}$ (9.63 eV), and $178.6 \mu\text{g g}^{-1}$ (9.74 eV), respectively (Sone *et al.*, 2008). The presence of functional groups like a hydroxy, carboxy and carbonyl groups alter the wettability of the surface, attract the partially polar and polar VOCs and reduces the affinity of non-polar compounds due to the increase in diffusional resistance (Cho *et al.*, 2008; Piao *et al.*, 2008; Onyestyak *et al.*, 2004). Li *et al.*, studied the adsorption of different aromatic VOCs like benzene, toluene, ethylbenzene and p-xylene with MWCNT and compared with Carbo-pack B commercial adsorbent (Li *et al.*, 2004). The MWCNT displayed higher breakthrough volume (BTV) when compared to Carbo-pack B due to the presence of high pore volume which favors a pore diffusion mechanism. Similar trend was observed in alkanes (n-pentane, cyclohexane, n-hexane and n-heptane), halogenated hydrocarbon (dichloromethane, trichloromethane, tetrachloromethane and 1,2-dichloroethane) and other VOCs like acetone, ether, ethyl acetate and n-propanol (Li *et al.*, 2004). The recovery study and break through volume (BTV) was performed with purge gas containing relative humidity of 70%. VOCs like dichloromethane, n-pentane, acetone, cyclohexane, ether, n-propanol, trichloromethane, n-hexane, benzene, n-heptane, ethyl acetate, n-butanol, ethyl benzene, toluene, p-xylene, and o-xylene showed more than 90% recovery (Li *et al.*, 2004; Mastrogiacomo *et al.*, 1998). Similarly, its BTV of the target VOCs

showed much higher than those on Carbo-pack B, especially for polar compounds like dichloromethane, acetone, and n-propanol (Li *et al.*, 2004). The high specific adsorption property and BTV is due to the open-ended, larger internal surface area and stronger binding energy of MWCNTs (Fujiwara *et al.*, 2001; Mastrogiacomo *et al.*, 1998). Liu *et al.*, studied the BTV of VOCs (1,2-dichloroethane, benzene, toluene, n-heptane, ethylbenzene, p-xylene, m-xylene, styrene and o-xylene) with MWCNTs adsorbent connected in a series along with Tenax TA and Corboxen 564 (Standard mixture: $10 \mu\text{g L}^{-1}$; flow-rate 0.1 L min^{-1}) (Liu *et al.*, 2008). The BTV and the safe sampling volume of MWCNTs sampling tube was found to be in the range of $10\text{--}70 \text{ L g}^{-1}$. Similarly, the breakthrough and safe sampling capacity were found to be $100\text{--}700 \mu\text{g g}^{-1}$, which clearly shows that the MWCNTs can be used for the air sampling application with suitable modification (Liu *et al.*, 2008).

3.2 Noncarbon-Based Adsorbents for Indoor/Ambient Air Sampling

Metal-Organic Framework (MOF) have emerged as novel crystalline materials which have ultrahigh porosity and surface areas (Langmuir surface area of $10,000 \text{ m}^2 \text{ g}^{-1}$) (Kumar *et al.*, 2016; Zhu *et al.*, 2014). MOF has wide range of applications that includes sorbent, sensing, catalytic, gas storage, separation, proton conduction, drug delivery etc. (Zhu *et al.*, 2014; Meek *et al.*, 2011; Umeyama *et al.*, 2011; Horcajada *et al.*, 2010; Chen *et al.*, 2007). MOFs based porous adsorbents have been extensively studied for the removal of VOCs from indoor and ambient air by various research groups due to its large pore volume, high surface area ($> 3000 \text{ m}^2 \text{ g}^{-1}$), availability of unsaturated metal sites etc. (Meek *et al.*, 2011; Yang *et al.*, 2011). In MOFs, metal cation and organic ligand are linked through coordination or strong metal-ligand bonds (Meek *et al.*, 2011; Nicolau *et al.*, 2009). Among different MOFs such as MOF-5, MOF-74, MOF-177, MOF-199, MIL-47, MIL-96, Zn (BDC)-(Dabco)_{0.5}, IRMOF-3 and IRMOF-62, the MIL-101 ($\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{OE}(\text{O}_2\text{C})-\text{C}_6\text{H}_4-(\text{CO}_2)_3 \cdot n\text{H}_2\text{O}$; n is ~ 25) is one of the most studied MOFs for the adsorption of various VOCs (Yang *et al.*, 2011). Further, MIL-101 frameworks have large cell volume, large surface area, highly mesoporous (12 and 16 Å in diameter) and unsaturated metal sites (Hong *et al.*, 2009). The highly porous nature of MIL-101 is extensively used for the

Table 3. Adsorption capacities of metallo organic framework and other adsorbents for selected VOCs (adopted and modified from K. Yang *et al.* Journal of Hazardous Materials 195 (2011) 124–131).

S. No	Adsorbate	Adsorbent	Tem. (°C)	Surface area (m ² g ⁻¹)	Maximum adsorption of VOCs (mg g ⁻¹)	Capacity (mL g ⁻¹)	Absolute pressure (p/p ₀)	Ref.
1	Benzene	MOF-5	25	2205	2	0.002	–	Britt <i>et al.</i> , 2008
		IRMOF-3	25	1568	56	0.064	–	
		MOF-74	25	632	96	0.109	–	
		MOF-177	25	3875	1	0.001	–	
		MOF-199	25	1264	176	0.200	–	
		IRMOF-62	25	1814	109	0.124	–	Jhung <i>et al.</i> , 2007
		SAB-15	30	805	3.0 mmol g ⁻¹	0.269	0.5	
		MIL-101	30	3900	16.7 mmol g ⁻¹	1.495	0.5	
		MIL-101	15	3054	15.5 mmol g ⁻¹	1.388	55 mbar	
		MIL-101	25	3980	1291	1.477	0.55	
Eu-MOF	25	281	1.00	–	0.95	Vellingiri <i>et al.</i> , 2016		
MOF-199	25	1591	> 1.1	–	0.46			
2	Styrene	Eu-MOF	25	281	0.85	–	0.95	Vellingiri <i>et al.</i> , 2016
		MOF-199	25	1591	> 4.9	–	0.46	
3	Acetone	MIL-101	25	3980	1291	1.645	0.55	Yang <i>et al.</i> , 2011
4	Toluene	MIL-101	25	3980	1096	1.270	0.55	
5	Ethylbenzene	Zn(BDC)-(Dabco) _{0.5}	120	1450	347	0.527	0.1 bar	Nicolau <i>et al.</i> , 2009
		MOF-5	150	773	99	0.146	2.8 kPa	Gu <i>et al.</i> , 2010
		MOF-monoclinic	150	225	5	0.007	1.3 kPa	
		MIL-47	130	930	35 wt%	0.526	0.035 bar	
MIL-101	25	3980	1105	1.228	0.55	Yang <i>et al.</i> , 2011		
6	o-Xylene	Zn(BDC)-(Dabco) _{0.5}	120	1450	338	0.505	0.1 bar	Nicolau <i>et al.</i> , 2009
		MOF-5	150	773	125	0.181	3.4 kPa	Gu <i>et al.</i> , 2010
		MOF-monoclinic	150	225	4	0.006	1.3 kPa	
		MIL-47	130	930	36 wt%	0.532	0.028 bar	Finsy <i>et al.</i> , 2008
		MIL-101	25	3980	758	0.866	0.55	Yang <i>et al.</i> , 2011
7	m-Xylene	Zn(BDC)-(Dabco) _{0.5}	120	1450	345	0.511	0.1 bar	Nicolau <i>et al.</i> , 2009
		MOF-5	150	773	151	0.217	3.0 kPa	Gu <i>et al.</i> , 2010
		MOF-monoclinic	150	225	4	0.006	1.3 kPa	
		MIL-47	130	930	37 wt%	0.542	0.03 bar	Finsy <i>et al.</i> , 2008
		MIL-96	30	532	0.81	0.814	0.87	Lee <i>et al.</i> , 2010
		MIL-101	25	3980	727	0.846	0.55	Yang <i>et al.</i> , 2011
8	p-Xylene	Zn(BDC)-(Dabco) _{0.5}	120	1450	342 mg g ⁻¹	0.506	0.1 bar	Nicolau <i>et al.</i> , 2009
		MOF-5	150	773	138 mg g ⁻¹	0.198	2.5 kPa	Gu <i>et al.</i> , 2010
		MOF-monoclinic	150	225	13 mg g ⁻¹	0.019	1.2 kPa	Finsy <i>et al.</i> , 2008
		MIL-47	130	930	40 wt%	0.586	0.035 bar	Lee <i>et al.</i> , 2010
		MIL-96	30	532	–	0.105	0.78	
		MIL-101	25	3980	1067	1.246	0.55	Yang <i>et al.</i> , 2011
9	Phenol	Eu-MOF	25	281	1.5	–	0.95	Vellingiri <i>et al.</i> , 2016
		MOF-199	25	1591	13	–	0.46	
10	Indole	Eu-MOF	25	281	1.5	–	0.95	Vellingiri <i>et al.</i> , 2016
		MOF-199	25	1591	4.5	–	0.46	
11	Formaldehyde	UiO-66-NH ₂	25	1250	58.5% (20 ppm)	–	1.101 bar	Vellingiri <i>et al.</i> , 2017
12	Propionaldehyde	UiO-66-NH ₂	25	1250	34.1% (20 ppm)	–	1.101 bar	
13	Butyraldehyde	UiO-66-NH ₂	25	1250	36.1% (20 ppm)	–	1.101 bar	
14	Valeraldehyde	UiO-66-NH ₂	25	1250	34.5% (20 ppm)	–	1.101 bar	

adsorption of different VOCs like acetone, benzene, toluene, methane, alkane, butane, xylene, hydrocarbon etc., due to its high pore volume ($\approx 2.0 \text{ cm}^3 \text{ g}^{-1}$) and surface area ($5900 \pm 300 \text{ m}^2 \text{ g}^{-1}$) (Huang *et al.*, 2011; Yang *et al.*, 2011; Gu *et al.*, 2010; Klein *et al.*, 2010; Trung *et al.*, 2010; Llewellyn *et al.*, 2008; Jhung *et al.*, 2007; Ferey *et al.*, 2005). Various forms of MOFs and their physical and adsorption properties such as breakthrough volume, surface area and adsorption capacity of different forms of VOCs are given in Table 3. The adsorption of VOCs on the MOFs surface follows predominantly pore-filling, π -complexation and van der Waals force mechanism (Yang *et al.*, 2011). Vellingiri *et al.* (2016) studied adsorption properties of four different aromatic VOCs (benzene, toluene, p-xylene and styrene) and 10 semi-volatile organic compounds (volatile fatty acids, phenol, indole etc.) with MOF-5, Eu-MOF, and MOF-199 adsorbents. The outcome of the results was compared with commercially available adsorbents like Tenax TA, Carboxen-1000 and Carboxen-1000 at ambient condition. The MOF-199 and Eu-MOF showed mean equilibrium adsorption capacities for benzene, toluene, p-xylene and styrene to be > 13.8 and 3.56 mg g^{-1} , respectively (15 L of a ~ 100 ppb (~ 0.01 Pa) gaseous standard loaded at $\sim 25^\circ\text{C}$). Whereas, the mean equilibrium adsorption capacities of VFAs (MOF-199: 18.6 and Eu-MOF: 15.3 mg g^{-1}), phenol (MOF-199: 28 and Eu-MOF: 4.8 mg g^{-1}) and indole (MOF-199: > 71.7 and Eu-MOF: 27.9 mg g^{-1}) showed much higher adsorption properties when compared with aromatic VOCs. Furthermore, MOF-199 displayed much higher adsorption properties due to the presence of strong π - π interactions and polarity of the guest molecule (Vellingiri *et al.*, 2016). Yang *et al.* (2011) reported that MIL-101 possess superior property for the removal of different VOCs such as acetone, toluene, benzene, ethylbenzene, o-xylenes, p-xylene and m-xylene. In this study, the adsorption mechanism of different VOCs is discussed with pore diffusion mechanism and shape and structure of the target VOCs. The experiments were conducted in two different relative pressure ($P/P_0 < 0.1$ and at P/P_0 from 0.1 to 0.2) for VOCs such as acetone, toluene, benzene, ethylbenzene and xylene on MIL-101. The VOCs like acetone, benzene and toluene showed higher adsorption efficiency even at low relative pressure of $P/P_0 < 0.1$. Whereas, ethylbenzene and xylenes did not show any amount of adsorption on MIL-101 at low relative pres-

sure (Yang *et al.*, 2011; Tolmachev *et al.*, 2009; Guo *et al.*, 2000). When the relative pressure is increased more than 0.1, considerable amount of ethylbenzene and xylene are adsorbed on the MIL-101 (Yang *et al.*, 2013, 2011; Hartmann *et al.*, 2008). This clearly shows that at low relative pressure, large cross-sectional molecule like ethylbenzene and xylene are difficult to accommodate in the pores of the MIL-101 (Yang *et al.*, 2013, 2011; Alaerts *et al.*, 2007). The above observation shows that the pore filling mechanism is highly favoring the adsorption of smaller cross-sectional compound like benzene (0.34 nm^2) (Vellingiri *et al.*, 2016). Apart from pore filling mechanism, other factors like compound polarity and electron density also play a role in the adsorption of VOCs on MOF. For example, acetone has smaller cross-sectional area (0.269 nm^2) showing a much lower absorption capacity on MOF-177. This might be due to the strong polar nature of acetone inhibited by the strong π - π coupling or electron cloud (Vellingiri *et al.*, 2016; Yang *et al.*, 2013, 2011). Huang *et al.* (2011) reported that the heterogeneous nature of MIL-101 surface shows strong adsorption properties of heteroatoms containing molecules like n-butylamine or dichloromethane rather than n-hexane and toluene. Further, toluene displayed higher adsorption than n-hexane due to the π - π interaction between MIL-101 and toluene (Huang *et al.*, 2011). Similarly, adsorption of benzene on MIL-101 showed 1,304 mg g^{-1} specific adsorption value when compared to activated carbon and zeolites (Jhung *et al.*, 2007). The different types and properties of MOFs have been extensively studied by various research groups and their possible crystallographic structure are given in Fig. 4. The main advantage of use of MOFs as adsorbent for the removal VOCs are their non-toxicity, high chemical/thermal stability, high internal surface area, porosity, pore volume, selectivity, tunable porosity and chemical functionality (Vellingiri *et al.*, 2016). Further, materials of this kind can be good replacement for the materials like zeolites, activated carbon and some of the commercially available adsorbents. The major shortcoming of MOFs is that their adsorption kinetics are much lower when compared to the commercial adsorbents. In addition, most of the procedures, chemicals or ligands used as the precursor for the formation of MOFs are very expensive. Further, the long-term stability and reusability has to be studied in detail. Hence, a low cost and environment friendly approach should be

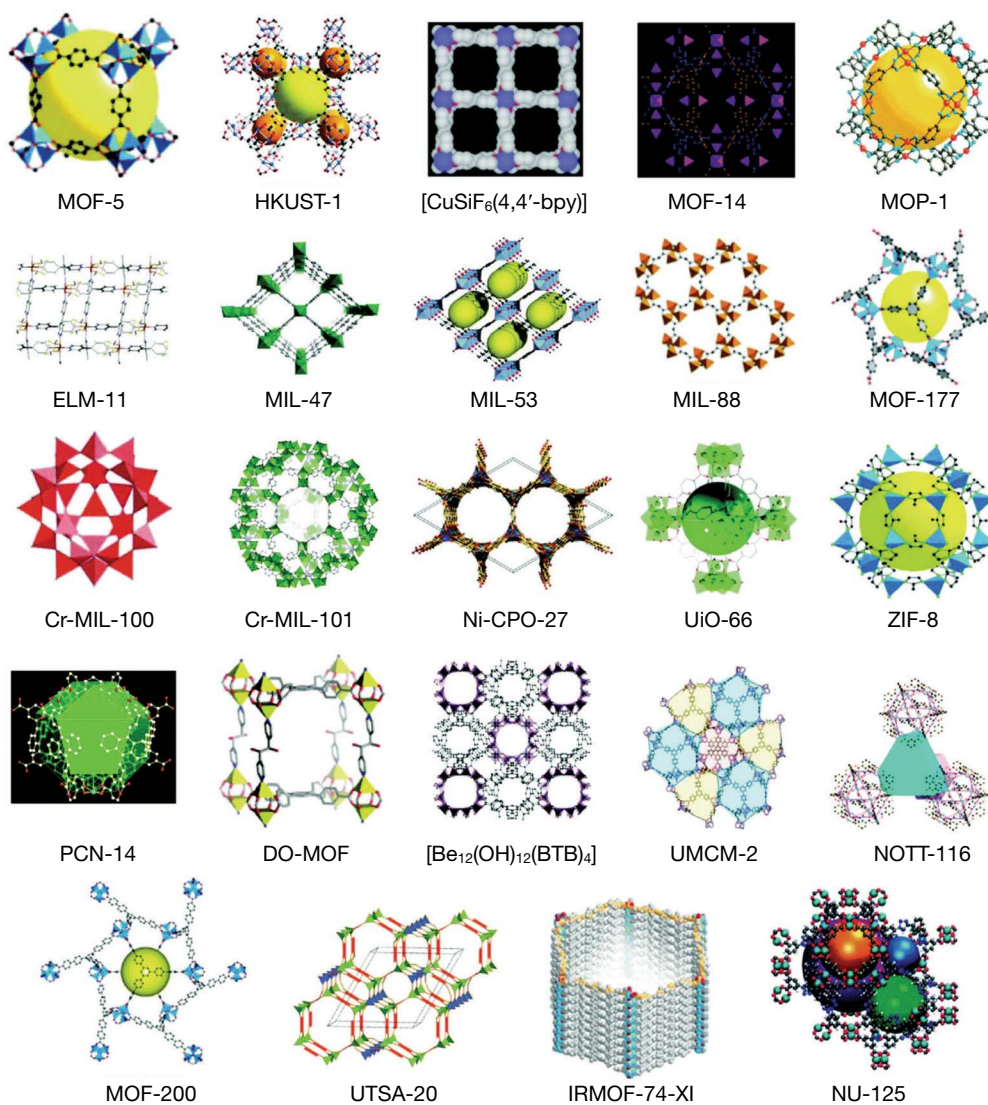


Fig. 4. Porous MOFs prepared by several research groups aiming the accommodation/retention of chemical species in their pores/channels (reproduced with permission from Ref. (Silva *et al.* (2015) *Chemical Society Reviews* 44, 6774–6803), © Elsevier 2015). Note: MOF 5: $Zn_4O(BDC)_3$, BDC = 1,4-benzodicarboxylate; HKUST 1: $[Cu_3(BTC)_2(H_2O)_3]$ (BTC: Benzene-1,3,5-tricarboxylate); BPY = bipyridine; MOF 14: $(Cu_3(BTB))_2$, BTB = 4,4',4''-benzenetribenzoate); ELM-11: $[Cu(BF_4)_2(4,4'-bipyridine)_2]$.

adopted for the larger scale synthesis.

4. IMPORTANT ELEMENTS OF A SAMPLING STRATEGY AND SORBENT SELECTION IN INDOOR AIR

The accurate measurement of VOCs present in the indoor environment requires highly advanced instrumental systems which demand the proficiency of operator and minimal intervention of unwanted steps to

reduce the analytical errors (Schripp *et al.*, 2014). The important factors involved in the indoor sampling process are the VOCs coming from outdoor air, temperature, wind direction, air exchange rate, humidity, barometric pressure, sampling time, duration, quality assurance etc. (Panagiotaras *et al.*, 2014). Qualitative and quantitative analysis of VOCs present in indoor air sample is accomplished by active or passive sampling techniques. In active sampling, VOCs are concentrated in a suitable sorbent connected with a pump which will regulate flow rate of the sampling (U.S. EPA, 1995).

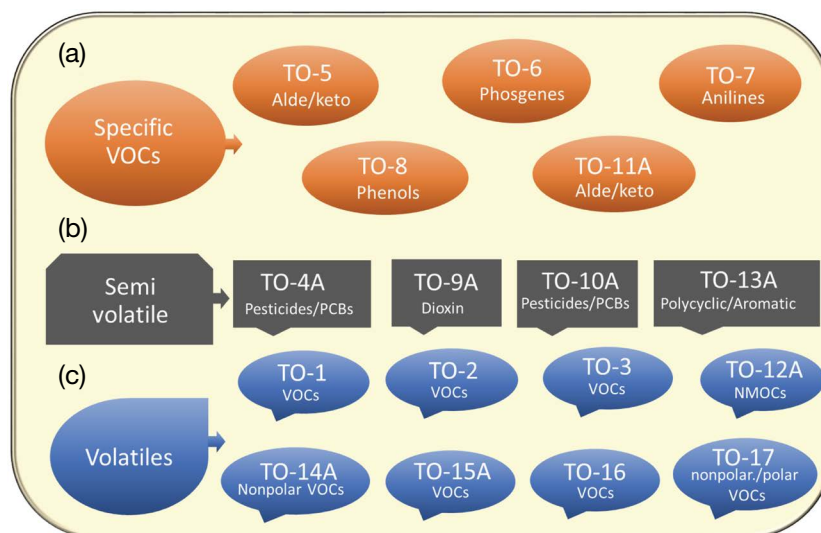


Fig. 5. U.S. EPA Compendium methods TO-1 (Tenax®-GC adsorption and GC/MS or GC/FID analysis), TO-2 (molecular sieve adsorption and GC/MS or GC/FID analysis), TO-3 (Cryogenic preconcentration and GC (FID/ECD) detection), TO-4A (Pesticides and PCBs using polyurethane foam sampling with GC (GC/MD), TO-5 (Aldehydes and ketones in ambient air using HPLC, TO-6 (Phosgene in ambient air using HPLC, TO-7 (N-NDMA in ambient air using GC), TO-8 (Phenol and Cresols in HPLC), TO-9 (Dioxin/Furan/PCBs in ambient air), TO-10 (PUF adsorbent and GC/ECD/PID/FID analysis), TO-11A (Aldehydes and ketones using DNPH-cartridge HPLC/UV detection), TO-12 (NMOC in ambient air using cryogenic preconcentration and PDFID), TO-13A (PUF/XAD-2 adsorbent cartridge GC/MS), TO-14 (Non-polar VOCs GC/FID/ECD OR GC/MS detection), TO-15 (Polar/non-polar VOCs by GC/MS), TO-16 (Polar/non-polar VOCs by FTIR open path spectroscopy and TO-17 (Multi-bed adsorbent tube by GC/MS (adopted and modified from U.S. EPA, 1999a, b).

The time and flow rate needed for their sampling should be adjustable depending upon nature of VOCs and sorbent used. At the end of the sampling, VOCs will be desorbed from the collection tube using either solvents or thermal desorption technique for the final quantitation by gas chromatography (GC) and GC mass spectroscopy (GC-MS) methods (Mirzaei *et al.*, 2016; U.S. EPA, 1995). Diffusive or passive sampling of VOCs does not require a pump as the sampling is completed by the natural flow (or diffusion) of air through the sorption media. Similarly, direct collection of air sample using Tedlar bags is one of the simplest processes. The accuracy of the VOCs measurements in indoor air by the use of above techniques depends upon different factors such as sorption capacity of the VOCs, sampling location, desorption capacity of sorbent, and sensitivity of the analytical instruments (Des-taillats *et al.*, 2008). Preconcentration of indoor and/or ambient air is one of the important steps in sampling process. The main advantages of active sampling preconcentration step into solid adsorbent are (i) the use of multi-sorbent beds which can capture wide range of VOCs, (ii) high preconcentration efficiency, (iii) provi-

sion of addition moisture trap which completely eliminate the interference of water molecule in the preconcentration of VOCs (Ras *et al.*, 2009; EPA, TO-17). Whereas, passive sampling is a simple process and no pump or flow meter device is required. The main disadvantages of passive sampling process are (i) non-appropriate, if the fluctuation is there in VOCs concentration in the ambient air, (ii) preconcentration efficiency is less effective when compared to active sampling, and (iii) preconcentration is affected by temperature variation and air movement (Ras *et al.*, 2009; Des-taillats *et al.*, 2008). The Environmental Protection Agency (U.S. EPA, 1999a, b) methods such as TO 1, 2, 14, 15 and 17 are used to analyze VOCs samples collected on a single and multi-bed sorbent tubes in both indoor and ambient air samples (U.S. EPA, 1999a, b, 1990, 1984). The U.S. EPA - method TO 1 recommends the use of Tenax GC cartridge for the sampling of volatile and nonpolar aromatic and chlorinated hydrocarbons which have a boiling point between 80 to 200°C by the use of GC-MS or GC-FID (Fig. 5). Similarly, the method TO 2 recommends the use of carbon molecular sieve cartridge for the sampling of

highly volatile and aliphatic/aromatic nonpolar organic compounds like benzene, toluene, xylene, vinyl chlorine etc., which have a boiling point between -15 to 120°C by the use of GC-MS or GC-FID (Fig. 5). The US EPA - method TO 14 and 15 describes the use of specially prepared canister for the sampling of volatile and non-polar organics (e.g., toluene, benzene, chlorobenzene) and volatile and polar/non-polar organics (e.g., methanol, benzene, toluene, xylene, nitrobenzene etc.) (Panagiotaras *et al.*, 2014; U.S. EPA, 1999a, b, 1990, 1984). In contrast, the method TO 17 recommends the use of multi bed adsorbent tube to cover both polar and non-polar organic compounds (e.g., alcohols, ketones, benzene, toluene, o-xylene, and chlorobenzene) (Panagiotaras *et al.*, 2014; U.S. EPA, 1999a, b). There are different types and nature of sorbents commercially available for the sampling of a range of VOCs present in the ambient and indoor air. The important criteria for the sorbents are: (i) the sorbent should have a high surface area and/or pore volume to display a complete sorption of the target compounds, (ii) high BTV of the compound, (iii) good desorption property, (iv) nonreactive with reactive species like O_2 , water and other gases (e.g., NO_x , SO_x , CO_2 , and O_3), (v) reusability, and (vi) thermal stability (Dettmer and Engewald, 2002). In light of the significance on the selection of suitable sorbent for the sampling VOCs, there are a few important parameters that have to be considered before sampling. If the boiling point of the target compound is high (e.g., $>100^{\circ}\text{C}$), a weak strength sorbent such as Tenax TA, Tenax GR, and Carb 2TD can be used (Panagiotaras *et al.*, 2014). Similarly, if the boiling point is ranging between 30 – 100°C , sorbents of medium strength like

Carbotrap B, Carbotrap C and Carbograph 1TD) can be used. If the boiling point of the compounds is fairly low (e.g., -30 – -50°C), high strength sorbents like Carbotrap X, Carboxen 1000, Carbosieve SIII or equivalent sorbent can be used. The thermal stability of the sorbent is also one of the important factors for sorbent selection (e.g., graphitized carbon blacks and carbonized molecular sieves $>400^{\circ}\text{C}$). Further, inertness (porous polymers and carbonized molecular sieves) and hydrophobicity are also important factors to be considered (U.S. EPA, 1999a, b). As such, commercially available sorbent tubes are compatible with a wider range of VOCs which have wider volatility and polarity (Watson *et al.*, 2011). There are four important categories of commercially available sorbents are Carbon Molecular Sieves (CMC), Graphitized Carbon Block (GCB), Porous Organic Polymers and other sorbents (Glass beads, Silica gel 15, Petroleum charcoal, Coconut charcoal etc.) (Dettmer and Engewald, 2002). The adsorption and desorption properties purely depend on chemical nature, shape and size of the molecule. The Carbosieve (SI, SII and SIII) and Carboxene (Carboxen - 563, 564, 569, 1000, 1001, 1002, 1003, 1016 and 1018) are the two main classes of the CMC sorbent. The Carbosieve S-II is very effective against the VOCs such as ethane, ethylene, acetylene and methane (C_1 – C_2). Among CMC family, Carbosieve S-III is one of the strongest adsorbent, which has the surface area of $\sim 820 \text{ m}^2 \text{ g}^{-1}$ and pore size of 15 – 40 \AA . Similarly, Carboxene group of adsorbents (Carboxen - 563, 564, 569, 1000, 1001, 1002, 1003, 1016 and 1018) are hydrophobic in nature, which have a surface area in the range of 400 to $1200 \text{ m}^2 \text{ g}^{-1}$ and the maximum desorption temperature

Table 4. Important commercially available sorbents for the adsorptive enrichment and thermal desorption in ambient/indoor air analysis.

S. No	Commercial sorbent	Type	Size (mesh)	Sampling range	^b Density (g mL^{-1})	^b Specific surface area ($\text{m}^2 \text{ g}^{-1}$)	^b TMax. ($^{\circ}\text{C}$)	^b Pore volume (mgL g^{-1})	
								Micro pore	Total
1	Tenax TA	^a PDP	60/80	C_7 – C_{26}	0.25	35	>350	0.002	0.05
2	Tenax GR	30% Graphite; 70% Tenax	35/60	–	0.55	24.1	>350	0.002	0.05
3	Carbosieve SIII	CMS	60/80	C_2 – C_5	0.61	820	>400	0.38	0.39
4	Carboxen 1000	CMS	60/80	C_2 – C_5	0.44	1200	>400	0.42	0.85
5	Carboxen 569	CMS	20/45	C_2 – C_5	0.58	485	>400	0.07	0.39
6	Carbotrap B	GCB	60/80	C_5 – C_{12}	0.37	100	>400	–	–
7	Carbotrap C	GCB	20/40	C_{12} – C_{20}	0.72	10	>400	–	0.02
8	Carbotrap	GCB	20/40	C_5 – C_{12}	0.36	100	>400	–	0.58
9	Carbograph 5TD	GCB	20/40	C_3 – C_5	0.58	560	>400	–	–
10	Carbopack X	GCB	20/40	C_3 – C_5	0.43	240	>400	0.0	0.63

^aPDP: poly-(2,6-diphenyl)-p-phenylenoxide; ^cCMS: carbon molecular sieves; ^dGCB: graphitized carbon blacks; ^bManufacturer's data (Adopted and modified from Dettmer and Engewald, Analytical & Bioanalytical Chemistry (2002) 373: 490–500).

is $>400^{\circ}\text{C}$ (U.S. EPA, 1999a, b). GCB adsorbent provides a weaker adsorptive strength compared to CMC adsorbents. There are different types of GCB adsorbents such as Carbo-pack - F, Carbo-pack - C, Carbo-pack - Y, Carbo-pack - B and Carbo-pack - X available in market. GCB are hydrophobic in nature and their surface area are in the range of 5 to $240\text{ m}^2\text{ g}^{-1}$. Porous organic polymers such as Tenax TA (2,6-diphenyl-p-phenylene-oxide), Tenax GR (30% graphite and 2,6-diphenyl-p-phenyleneoxide), Porapak N (Divinylbenzene/copolymer ethylene glycol dimethylacrylate), Chromosorb 106 (cross linked poly styrene) and HayeSep D (divinyl benzene) are granular sorbents with a surface area in the range of 24 to $795\text{ m}^2\text{ g}^{-1}$. Porous organic polymer sorbents are effective against adsorption and desorption of mid to large molecular weight compounds and their desorption temperature is in the range of $220^{\circ}\text{--}350^{\circ}\text{C}$ (WHO, 1989). Among different porous organic polymers, Tenax TA is one of the widely used adsorbents for the pre-concentration of VOCs and it is very effective against high boiling VOCs which have a boiling point of more than 100°C (Gallego *et al.*, 2010; Ras *et al.*, 2009). The most commonly used commercially available sorbents and their properties are given in Table 4.

5. RECENT PROGRESS IN ANALYTICAL TECHNIQUES AND THE COMPLEXITY INVOLVED IN ANALYSIS OF VOCs

Gas Chromatography (GC) and GC - Mass Spectroscopy (GC-MS) techniques have been extensively studied for the qualitative and quantitative analysis of diverse nature VOCs present in the ambient and indoor environment. Further, it can provide a separation and retention time data of VOCs which is not possible in most advanced technique like PTR MS (Kaser *et al.*, 2013; Biasioli, 2011a). However, GC-MS is highly time-consuming process and not suitable for the real time online monitoring of VOCs. Recently different types of instruments are available for the real time online monitoring of VOCs such as proton transfer reaction time of flight mass spectrometer (PTR-TOF-MS), proton transfer reaction quadrupole mass spectrometer (PTR-MS), fast-online gas-chromatograph coupled to a mass spectrometer (GC/MS; TOGA), thermal dissociation chemical ionization mass spectrometer (PAN-CIMS) etc. (Kaser *et al.*, 2013). Among various types and com-

ination, PTR MS is the commonly used technique for real-time monitoring of VOCs, which do not require any pre-concentration steps and is able to detect part per billion (ppb) level concentration (Panagiotaras *et al.*, 2014). PTR-MS system is the most advanced and highly sensitive instrument for real-time continuous monitoring of various VOCs, such as isoprene, monoterpene, acetone, acetaldehyde, methanol, benzene, xylene, ethanol, some inorganic compounds etc., which have a range of boiling points and molecular weights (Schripp *et al.*, 2014; Han *et al.*, 2010). PTR-MS has several advantages over GC-MS like pre-extraction or separation or sampling is not required. It shows very high sensitivity ($<1\text{ pptv}$) for the detection of ultralow concentration of VOCs and very efficient when compared to GC or GC-MS (Han *et al.*, 2010; Destailats *et al.*, 2008). Further, PTR-MS can be used to measure a set of preselected mass with high sensitivity and high sampling frequency, which can help to quantify a very reactive, less volatile and low concentration of VOCs in an indoor air. VOCs generated from the indoor air are measured using PTR-MS, which can be adjusted to withdraw a sample for every $\sim 5\text{ min}$ (suction time ~ 5 to 20 s). Background correction is performed at regular time intervals with zero air and calibration is performed with an air mixture containing 10 to 15 different concentrations (ppb level) of VOCs, which are commonly observed in VOCs emission as specified and recommended by the manufacturer for accurate and robust operation (Schripp *et al.*, 2014). Quadrupole-based PTR-QMS can be used to monitor the emission characteristics of the source when the source VOCs emission concentration decreases with respect to time. To understand the real-time indoor chemistry, Teflon coated or suitable chamber connected with target VOCs, NO_x cylinders and O_3 generator can be used to the study the formation of SOA and other VOCs by PTR-MS technique. The aerosol formed is trapped in bubbler sampler by providing Teflon membrane filters and collected with ethyl acetate or suitable solvent and can be used for further analysis (Ziemann, 2003).

6. PERFORMANCE EVALUATION AND MERITS AND DEMERITS OF COMMERCIALY AVAILABLE SORBENTS

The different types of synthetically prepared adsor-

bents like MOFs, MWCNTs, polymers, electrospun nanofibers, biochar, and activated carbon from various natural products are extensively studied and reported in the literature (Zhang *et al.*, 2017). Most of the adsorbents are highly selective in nature and their adsorption and desorption properties for wider range of VOCs has to be explored in detail and not suitable for commercial application. The commercially available adsorbents are highly suitable for VOCs sampling application. The type and physical properties of commercially available solid sorbents and their possible applications for capturing ambient and indoor air samples are listed in Table 4. The main objective of the sampling process is to enrich the VOCs present in trace quantities in indoor or ambient air condition. Each adsorbent has particular retention time for adsorbing VOC and their specific adsorption efficiency for a single and mixed conditions are different from each other (Ho *et al.*, 2018; Ribes *et al.*, 2007). The major shortcomings of single adsorbents are (i) it is very effective for the adsorption of low concentration of VOCs and within the safe range of breakthrough volume, (ii) the adsorption/desorption properties of the sorbent against mixture or different combination of VOCs should be defined, (iii) competitive adsorption such as the presence of high and low affinity VOCs towards sorbent in the air sample is not discussed in detail, (iv) humidity and temperature can influence adsorption efficiency, and (v) stability and storage condition for the adsorbed VOCs cartridge, (vi) some of the adsorbent material (e.g., Tenax TR) are sensitive towards oxidant like O₃, SO_x and NO_x. Further, some compounds present in VOCs exhibit dissenting properties such as strong sorption, high thermal stability, and poor desorption properties (Hafkenscheid, 1997). Tenax TA is one commonly used adsorbent for capturing of VOCs and it has a high thermal stability and low bleeding material. However, Tenax TA is very vulnerable to the oxidizing agents such as O₃, NO_x and SO_x and also thermally decomposes to form compounds like acetophenone, benzaldehyde, phenol and some fragmented products (Ho *et al.*, 2018). Tenax TA is a highly suitable sorbent for heptane to decane, which have a high boiling point of more than 100°C. Also, it effectively captures the aromatic compounds like benzene, xylene, toluene, trimethylbenzene and compounds like esters, ketones, chlorinated hydrocarbons, alcohols and ethers etc., (Pollmann *et al.*, 2006; U.S. EPA, 1999a, b). BTV are

low for highly volatile substances which have a boiling point less than 100°C. Tenax TA is a weaker adsorbent when compared to Anasorb GCB1, Anasorb GCB2, and Carbosieve III for the adsorption of highly volatile compounds (e.g., C₂-C₄). Carbosieve SIII is an efficient and the strongest adsorbent for capturing low molecular and low boiling VOCs (Badol *et al.*, 2004; Sturges *et al.*, 1993). Pollmann *et al.* (2006) studied the comparison of nine commercially available solid adsorbent such as Carboxen 1000, Carbosieve S III, Molecular Sieve 5A, Molecular Sieve 4A, Silica Gel, Carboxen 563, Activated Alumina, Carbotrap and Carboxen 1016 for the adsorption of 23 non-methane hydrocarbon (C₂-C₆) and methylene chloride at -10 and -30°C. The outcome of the results shows that the adsorbents like a molecular sieve 5A, Carbotrap and Silica Gel were proven to be unfit for trapping for non-methane hydrocarbon (C₂-C₆) and methylene chloride under given condition (Pollmann *et al.*, 2006). Among these, Carbosieve SIII was found to be the strongest adsorbent exhibiting high adsorption properties that include ethane and ethene (Pollmann *et al.*, 2006). Similarly, the adsorption of ethane was studied with the comparison of ten different adsorbents that includes Carbosieve S III, Carbosieve S II, Carboxen 563, Carbosieve 564 and Carbosieve 569. This showed that Carbosieve S III displayed highest efficiency when compared to rest of the adsorbents (Betz and Supina, 1989). Further, Carbosieve III showed very high adsorption efficiency for hydrohalocarbon and halocarbon when compared to Carboxen 1000 and Carboxen1001 adsorbents (Sturges and Elkins, 1993). Like Carboxen SIII, Carboxen 1000 is also a very strong adsorbent and its property is very similar to Carboxen SIII, Carboxen 1001 and Carboxen 1002. Carboxen-1000 adsorbent is stable up to 300°C and one of the disadvantages of Carboxen-1000 is adsorption of CO₂ which will interfere with other compounds (U.S. EPA. 1999a, b; Sturges and Elkins, 1993). Similarly, Carbopack B (Anasorb GCB1) can effectively capture the VOCs in the range of C₅-C₁₂ and their efficiency is much higher compared to Tenax TA except for n-heptane and n-octane (Tolnai *et al.*, 1999). It clearly indicates that Tenax TA is the ideal adsorbent for the VOCs which have a higher molecular VOCs and Carbopack B is very effective for the adsorption of low boiling or low molecular VOCs (Tolnai *et al.*, 1999). Similarly, Carbopack C (Anasorb GCB2) can effectively capture VOCs which are in the

Table 5. Performance matrix of commonly observed aromatic VOCs (Benzene, Toluene, p-Xylene and Styrene) collected by commercially available sorbent.

S. No	Sorbents	Mixture of VOCs, con. & volume	Adsorption capacity (mg g ⁻¹)				Breakthrough volume (L g ⁻¹) or (%)				Ref.
			B	T	p-X	Sty	B	T	p-X	Sty	
1	Tenax TA		0.25	0.24	0.27	0.2	-	-	-	-	
2	Carbopack-X	14 comps and 15 L (100 ppb)	0.42	0.62	1.5	1.2	-	-	-	-	Vellingiri <i>et al.</i> , 2016
3	Carboxen-1000		4.8	5.4	>6	>6	-	-	-	-	
4	Tenax TA	13 comps and 1-3 L (50 ppb)	-	-	-	-	~15	> 15	> 15	> 15	Kim <i>et al.</i> , 2014
5	^a Multi-bed sorbent	29 comps. 90 L (0.28 µg m ⁻³)	-	-	-	-	0.15%	0.04%	0.02%	0.4%	Gallego <i>et al.</i> , 2010
6	Tenax TA		-	-	-	-	49%	56%	27%	54%	
7	Tenax GC	20 comps and 0.5-5 L 150 mL min ⁻¹	2.3	5.0	5.5	12	5.1	16	45	53	Comes <i>et al.</i> , 1998

B: Benzene; T: Toluene; p-X: Para-xylene; Sty: Styrene; ^aMulti-bed sorbent combination: Carbotrap, Carbopack X and Carboxen 569.

range of C₁₂-C₂₀. Performance metric of commonly observed aromatic VOCs (Benzene, Toluene, p-Xylene and Styrene) collected by commercially available single and multi-bed sorbents are given in Table 5.

Indoor and ambient air contains wide range of VOCs which have different physical and chemical properties and sampling with single adsorbent is not adequate. A combination of different adsorbents or multi-sorbent bed technique needs to be adopted (U.S. EPA, 1999a, b). The commercially available multi bed adsorbent connected with a high-end analytical instrument considerably enhances the precision and accuracy of the VOCs measurements (Chang *et al.*, 2016). The commonly used adsorbent for multi-bed adsorbents combination are Tenax TA, Tenax GR, Anasorb GCB1 (Anasorb GCB1 is equivalent to Carbopack B), Anasorb GCB2 (Anasorb GCB2 is equivalent to Carbopack C), Carbosieve III, Chromosorb 106 (U.S. EPA, 1999a, b). Generally, these adsorbents can be used in combinations of two or three or multi-bed form depending upon nature of the VOCs present in the source. If the source air sample contains VOCs in the range of C₆ to C₂₀, Tenax GR and Carbopack B separated by quartz wool is the suitable one with air volumes of 2-5 L at any humidity (Woolfenden, 1996). The multi-bed adsorbent with the combination of Carbopack B, Carbosieve SIII separated by quartz wool is highly suitable for compounds ranging from C₃ to C₁₂ with the suitable air volumes of 2 to 5 L at relative humidity less than 65% (U.S. EPA, 1999a, b; Woolfenden, 1996). Similarly, the combination of Carbopack C, Carbopack B and Carbosieve SIII with each bed separated by

quartz wool is suitable for the compounds ranging from C₃ to C₁₆ for air volumes of 2 L at relative humidity less than 65% (Woolfenden, 1996). Comparison of BTV of highly VOCs (C₁-C₆, boiling point < 100°C) collected by Carbopack X, Carbotrap, Tenax TA and Carbograph 5TD sorbents are given in Table 6. Wu *et al.* (2003) studied the sampling efficiency of multi-bed adsorbents (Carbopack B, Carbopack C, and Carbosieve SIII) with mixture of VOCs and observed high percentage of recovery for acetone, iso-propyl alcohol, benzene, trichloroethylene, toluene, butyl acetate, cyclopentanone, m,p-xylene, 2-heptanone, and o-xylene which were 97, 95, 101, 98, 97, 99, 94, 97, 100 and 96%, respectively. Pollmann *et al.* (2006) studied the adsorption of non-methane hydrocarbon ranging from C₂-C₆ using multi-bed adsorption tube packed with Carboxen 1016, Carboxen 563, and Carbosieve SIII at -10 and -30°C trapping temperature. Recovery rates for all the VOCs showed almost 95 and 100% efficiency and these findings demonstrate advantage of using multi-bed adsorbent compared to single adsorbent (Pollmann *et al.*, 2006; Wu *et al.*, 2003; Woolfenden, 1996). The main advantage for the use of multi-bed adsorbents are (i) use of multi bed sorbent considerably reduces the competitive adsorption in second and third sorbent interface, (ii) it can capture wider range of VOCs, (iii) highly polar and non-polar VOCs can be adsorbed and desorbed, (iv) hydrophobic sorbents can be used to eliminate the water interference, (v) size and cost advantages in sampling equipment (U.S. EPA, 1999). The disadvantages of multi-bed adsorbent are (i) regeneration of sorbent tube is a difficult process and

Table 6. Comparison of breakthrough volume of VVOCs (C₁-C₆ boiling point less than ~100°C) collected by Carboxpack X, Carbotrap, Tenax TA and Carbograph 5TD sorbents (modified from Schieweck *et al.* (2018) Analytical & Bioanalytical Chemistry 410(13), 3171-3183).

S. No	Name of the VVOCs	Chemical formula	B.P °C	Breakthrough volume (L g ⁻¹) or (%)				Ref.
13 comps and 1-3 L (50 ppb)				Tenax TA				
1	Acetaldehyde	C ₂ H ₄ O	20.2	~0.00	-	-	-	Kim <i>et al.</i> , 2014
2	Propionaldehyde	C ₃ H ₆ O	48.8	<5	-	-	-	
3	Butyraldehyde	C ₄ H ₈ O	74.8	>15	-	-	-	
4	Methyl ethyl ketone	C ₄ H ₈ O	79.64	~15	-	-	-	
21 compounds, flow rate 125 mL min ⁻¹				Tenax TA	Carbograph 5 TD	Carboxpack X	Carbotrap	
1	Ethanol	C ₂ H ₅ OH	78.3	48.88 ± 6.69	35.43 ± 8.49	32.58 ± 7.8	15.26 ± 0.62	Schieweck <i>et al.</i> , 2018
2	Acetaldehyde	CH ₃ CHO	20.8	19.28 ± 3.60	9.48 ± 0.04	8.61 ± 1.16	9.21 ± 2.56	
3	1-Propanol	CH ₃ (CH ₂) ₂ OH	97.2	37.30 ± 8.31	0.00 ± 0.00	0.01 ± 0.01	79.88 ± 0.69	
4	2-Propanol	CH ₃ CH(OH)CH ₃	82.3	65.18 ± 2.37	0.10 ± 0.02	0.17 ± 0.01	74.84 ± 15.38	
5	Propanal	C ₃ H ₆ O	48.0	58.72 ± 4.20	0.49 ± 0.26	0.45 ± 0.10	15.47 ± 4.31	
6	2-Propanone	CO(CH ₃) ₂	56.1	34.56 ± 2.70	1.12 ± 0.07	1.46 ± 0.31	6.29 ± 1.99	
7	Methyl acetate	CH ₃ COOCH ₃	56.8	35.12 ± 8.73	0.40 ± 0.13	0.63 ± 0.07	92.38 ± 2.78	
8	2-Chloropropane	CH ₃ CHClCH ₃	35.0	52.09 ± 3.02	0.02 ± 0.02	0.11 ± 0.01	89.38 ± 6.54	
9	Trimethylsilanol	C ₃ H ₁₀ OSi	99	2.88 ± 0.95	0.25 ± 0.05	0.25 ± 0.01	0.36 ± 0.22	
10	n-Butanal	C ₄ H ₈ O	74.8	1.50 ± 1.02	0.03 ± 0.05	0.01 ± 0.00	0.72 ± 0.67	
11	2-Methylpropanal	CH ₃ CH(CH ₃)CHO	63.5	18.20 ± 8.03	n.d	0.33 ± 0.47	6.33 ± 4.37	
12	2-Methyl-2-propanol	CH ₃ C(CH ₃)(OH)CH ₃	82.9	6.50 ± 2.96	0.06 ± 0.01	0.11 ± 0.00	4.92 ± 4.20	
13	Methacroleine	CH ₂ C(CH ₃)CHO	72.9	8.69 ± 3.76	0.04 ± 0.05	0.08 ± 0.00	1.87 ± 0.76	
14	Methyl vinyl ketone	CH ₃ C(O)CHCH ₂	81.4	2.99 ± 1.87	0.05 ± 0.07	0.14 ± 0.09	0.07 ± 0.08	
15	Vinyl acetate	CH ₃ C(O)OCHCH ₂	71.6	2.49 ± 1.39	0.01 ± 0.01	0.05 ± 0.02	0.04 ± 0.06	
16	n-Pentane	C ₅ H ₁₂	36.1	61.61 ± 4.98	0.10 ± 0.03	0.20 ± 0.00	0.12 ± 0.05	
17	Isoprene	CH ₂ C(CH ₃)CHCH ₂	34.0	49.66 ± 4.18	0.10 ± 0.01	0.13 ± 0.01	0.10 ± 0.06	
18	3-Methylpentane	C ₂ H ₅ CH(CH ₃)C ₂ H ₅	63.3	8.44 ± 0.63	0.01 ± 0.02	0.08 ± 0.01	0.08 ± 0.01	
29 comps. 90 L (0.28 µg m ⁻³)				Tenax TA	^a Multi-Sorbent			
19	Acetone	C ₃ H ₆ O	56	27 ± 1	12 ± 5	-	-	Gallego <i>et al.</i> , 2010
20	Carbon disulphide	CS ₂	46.3	43 ± 2	14 ± 16	-	-	
21	Dichloromethane	CH ₂ Cl ₂	39.6	44 ± 8	32 ± 18	-	-	
22	n-Hexane	C ₆ H ₁₄	68	60 ± 1	0.4 ± 0.1	-	-	
23	Chloroform	CHCl ₃	61.2	50 ± 3	1.4 ± 0.3	-	-	
24	Carbon tetrachloride	CCl ₄	76.72	57 ± 3	0.00	-	-	
25	n-Heptane	C ₇ H ₁₆	98.42	69 ± 2	0.00	-	-	
26	Trichloroethylene	C ₂ HCl ₃	87.2	71 ± 5	0.00	-	-	
Bag exp. 7.5 L; 3.5 L for another comp.				Tenax TA	^b Multi-Sorbent			
27	Acetaldehyde*	CH ₃ CHO	20.8	<0.2	<0.2	-	-	Brown and Crump, 2013
28	Isoprene*	CH ₂ C(CH ₃)CHCH ₂	34.0	0.4	≥10	-	-	
29	n-Pentane*	C ₅ H ₁₂	36.1	<0.46	≥0.46	-	-	
30	Methyl cyclo butane	C ₅ H ₁₀	36	<0.46	≥0.46	-	-	
31	Acetone*	C ₃ H ₆ O	56	0.2	4.0	-	-	
32	Chloroform*	CHCl ₃	61.2	1.0	≥10	-	-	
33	Tetrahydrofuran*	C ₄ H ₈ O	66	2.0	≥10	-	-	
34	Vinyl acetate*	C ₄ H ₆ O ₂	72	2.0	≥10	-	-	
35	Ethyl acetate*	C ₄ H ₈ O ₂	77.1	3.5	≥10	-	-	
36	Ethanol*	C ₂ H ₅ OH	78	<0.2	0.5	-	-	
37	Dimethyl ether	C ₂ H ₆ O	-24	<0.2	<0.2	-	-	
38	Isopentane	C ₅ H ₁₂	27.8	<0.4	≥2.6	-	-	
39	Isobutane	C ₄ H ₁₀	-10	<0.2	3.0	-	-	
40	n-Butane	C ₄ H ₁₀	-0.5	<0.2	5.0	-	-	

^aMulti-Sorbent: Carbotrap, Carboxpack X, Carboxen 569; ^bMulti-Sorbent: quartz wool/Tenax TA/Carbograph 5TD; *VOCs studied in breakthrough experiments using Nalophan bags.

rigorous clean-up is needed, (ii) desorption of some VOCs are very difficult, (iii) additional thermal desorption unit has to be purchased, (vi) contamination of adsorbent can be a problem (U.S. EPA, 1999a, b).

7. SUMMARY AND OUTLOOK

Adsorption/desorption of VOCs with commercially available adsorbent using single/multi-bed adsorption tubes by both active and passive sampling provides better sensitivity, desorption efficiency, and reasonable reproducibility compared to conventional solvent extraction and other techniques. In adsorption of VOCs, sampling duration must be explored further to prevent the breakthrough of any particular VOC of interest. Further, maintaining of optimum flow rate for ambient/indoor air sample which contain mixture of VOCs has to be arrived after several trial studies. For the adsorbents such as Anasorb GCB1, Carbopack X, Tenax TA, and Chromosorb 106, the fixed sampling time recommended for most of the VOCs are 8–24 h. Whereas, optimum flow rate of n-hexane, n-heptane, acrylonitrile, benzene, toluene, trichloroethylene, and ethanol are 13.9, 14.3, 20.4, 16, 14.5, 13.1, 11.9, and 20.3 mL min⁻¹, respectively (Kajos *et al.*, 2015). The disparity between the optimum flow rate of each VOCs and their influence on the sampling efficiency has to be studied in detail. The preconcentration of VOCs is highly suitable for the ambient/indoor air sample which does not have much fluctuation in the source concentration. Preconcentration air sampling with lower time duration leads to wrong perception and the outcome will be completely different from the actual concentration. Also, preconcentration process is affected by different external factors and most important are relative humidity, temperature variation and wind movement. Presence of isomers are one of the most common interference and also some of low concentration of organic species are difficult to remove from the adsorbent (U.S. EPA, 1999a, b). The well-conditioned CMSGCB shows minimal artefact (< 0.1 ng/component) when compared to Tenax TA/GR. Similarly, such sorbents like well-conditioned Tenax TA/GR show still fairly low artefact levels (< 1.0 ng/component), although it can increase if the sampling air contains oxidizing agents like O₃, NO_x, or SO_x. Ongoing rapid urbanization, industrialization and population

growth brings new types of toxic pollutants and challenges to the air sampling and analytical procedures. Hence, it is highly essential for the periodic review and upgradation of the standards and methodology for the ambient/indoor air sampling and analytical procedures.

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