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Research paper

Volatile Organic Compound Analysis by Sorbent Tube-Thermal Desorption-Gas Chromatography: A Review

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Abstract

Volatile organic compounds (VOCs) play an important role in the generation of ground level ozone and secondary organic aerosol. Most tropical countries such as Malaysia, Singapore, Indonesia, Brunei experience high ozone pollution. Beside ozone, oxides of nitrogen (NOx) from vehicular emissions also play an important role in photochemical pollution. NOx, particularly nitric oxide (NO), helps to ‘clean up’ ozone concentrations close to traffic in the ambient air of urban areas. Thus, knowledge of the chemistry of ozone-VOCs-NOx and finding the sources of VOCs are crucial to proceed with an appropriate mitigation strategy. Thus, the detection of ozone precursors and related VOCs is thoroughly discussed. This review finds that the inertness, hydrophobicity, and the effect of the artefact materials are very significant factors to be explored in the selection of the sorbent materials. In the SEA region, relative humidity is relatively high and exceeds 90% during the northeast monsoon. Thus, the hydrophobic properties of the sampling material need careful consideration. Further to the effect of relative humidity (RH), the artefact effect of the material itself is a challenge to be optimized and multi-sorbent material in a single tube could be a viable choice to minimize the effect of the unwanted signal in the spectrum.

Keywords*: Detection; Ozone precursors; Method optimization; Biomass burning; Biogenic VOCs.*

1. Introduction

Volatile organic compounds (VOCs) are compounds normally present in the vapour phase at room temperature. VOCs are defined as organic compounds whose boiling points are in the range of 50–100 °C to 240–260 °C [1]. Very volatile organic compounds (VVOCs) can be defined as organic compounds whose boiling points range from < 0 to 50–100 °C and semi-volatile organic compounds (SVOCs) have boiling points of > 280 °C. VOCs are ubiquitous atmospheric constituents of both anthropogenic and natural origin. VOCs have significant impacts on the environment and human health even at ppb levels. The environmental effects of VOCs include the accumulation and persistence of pollutants, the depletion of stratospheric ozone and the formation of tropospheric photochemical ozone [2-4]. VOCs are important precursors of tropospheric ozone (O_3), and can impact air quality and global climate. Primary VOCs and their oxidized products make up a major fraction of secondary pollutants in urbanized regions. Due to fast reaction rates, mainly with the hydroxyl radical (OH), VOCs control the oxidizing capacity of the troposphere. Measurements of VOCs are important in the study of photochemical transformations, both qualitatively and quantitatively. In [5] observed that the ozone formation potential (OFP) was three and four times higher in Dhaka than the OFP value was observed at the street sites in Hanoi and Manila, respectively. Many aspects of VOCs in the atmosphere remain poorly understood – these include the detection and quantification of by-products of VOCs, their oxidation reactions and their role in oxidant and secondary aerosol formation. In the photochemistry of the tropical troposphere, VOCs play a key role due to high abundance of water vapour (H_2O) and intense solar radiation flux [6]. VOCs in the Earth’s

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atmosphere are emitted from a wide variety of natural and man-made sources [7-9]. VOCs from natural source such as microbial volatile organic compounds (MVOCs) are emitted via bio-aerosol of microbial, plant and animal origin. MVOCs are secondary metabolites produced by fermentation and are volatile due to their physicochemical properties (low molecular weight, low boiling point and high vapour pressure) [10]. A critical review and the most suitable technique for analysis were recently reported by [11]. Globally, the largest natural sources of VOCs are tropical and extra-tropical forests which emit large quantities of VOCs such as isoprene, α- and β-pinene and methanol [12-13]. Biomass burning is a large source of VOCs worldwide [14], which leads to emission of numerous VOCs, including many oxygenated species (organic acids, carbonyls and multifunctional species), nitriles (HCN, CH_3CN) and aromatics (benzene, toluene) [15-17]. It is worth noted that biomass burning can occur either naturally (for example in forest fires) or can be caused by human activities (for example the burning of forests to clear agricultural land or the burning of agricultural waste). The production, storage, and use of fossil fuels are large anthropogenic sources of VOCs such as alkanes, alkenes, and aromatics. Although these are much smaller sources on a global scale, these can easily dominate on regional scales. Finally, the production and use of solvents, paints, and many other (household) chemicals leads to the release of several VOCs [16]. Transformation of VOCs via photochemical process is a potential contribution to the fine particulate pollution [18].

Gas Chromatography (GC) is the process which is largely used to measure VOCs in the atmosphere. In this analysis the air samples are collected either in canisters on adsorbents or in cryostats [19]. Such measurements are very sensitive. However, there are several disadvantages to such method. Using adsorbents and cryostats, a sampling time of several minutes is required to get enough sample material. As a consequence, in rapidly changing atmospheric conditions, GC measurements will not be able to follow those changes with a suitable response time [16]. In spite of having disadvantages gas chromatography (GC) and proton-transfer reaction - mass spectrometry (PTR-MS) have attain tremendous technological progress in VOC detection and quantification so that is why measurements of VOCs from local to regional scales can be accomplished. The observations of VOCs along with other species like NO_x will be important to understand the photochemistry leading to formation of O_3 and secondary organic aerosol at urban, rural and remote (both marine and terrestrial) locations [6].

There are several techniques for the analysis of VOCs. Some of them are GC coupled with flame ionization detector (FID) and MS. Due to technical limitations, many VOCs that play an important role in atmospheric pollution chemistry cannot be detected using GC-based techniques. The PTR-MS technique has been used recently for the detection of a wider spectrum of VOCs in air [6]. However, these near-real-time instruments have limitations of cost, stability, field calibration and power supply which may detract from their use. For collecting whole -air samples evacuated canisters or polymer bags are often used, but collection of only the VOC portion is possible by trapping on a sorbent medium [20]. A method develop by [21] to determine the VOCs particularly 2-propanol, acetone, cyclohexane and ethanol using Fe (III) based metalloporphyrins Langmuir-Blodgett thin films. A bulk acoustic sensor system was fabricated to detect few VOCs such as ethanol, acetone, cyclohexane, toluene, o-xylene and 2-propanol by [22]. A room temperature fluorescence gas sensor was developed based on TiO2 nanoparticles coated with porphyrin dye thin films. The porphyrin dye was used for this sensor development were mainly Iron (III) meso-tetraphenylporphine chloride (IMTPPCl) and Manganase (III) 5,10,15,20 tetra (4-pyridyl)-21H, 23H porphine chloride tetrakis (metachloride). This sensor was capable to determine the VOCs such as ethanol, acetone and 2-propanol [23].

To determine the trace level of organic gases, the selection of the appropriate adsorbing material is an important step. This review will cover the use of different types of sorbents in a thermal desorption-gas-chromatography (TD-GC) system and will summarize the program used in determining the various gas phase samples. The biggest advantage of the use of a sorbent tube is that it can eliminate the complicated pre-treatment process of the samples. Photo chemically-produced ozone (O_3) in the troposphere is a great concern in many parts of the world. At surface level, O_3 is formed from the two major classes of precursor, i.e. VOCs and NO_x. In particular, in urban and regional atmospheres, O_3 formation is driven by the VOCs released from anthropogenic and biogenic sources [24]. Broadly, the terms used to represent VOCs are substituted by organic compounds (e.g. oxygenated, chlorinated, and sulfur-containing organic compounds), hydrocarbons (HCs), reactive organic gases, and non-methane volatile organic compounds (NMVOCs) [25]. The sources of major VOCs are vehicle exhaust, gasoline vapour, paint, asphalt, industrial and residential coal burning, biomass burning and petrochemical industry [26]. Further, the elevated atmospheric concentration of NMVOCs coincided with the ambient level of ozone concentration as NMVOCs react rapidly to the other O_3 precursors [27] (Table 1).

In urban areas and work places, VOCs have become of great health concern. A study by [28] found that the concentration of VOCs indoor is much higher than outdoor which impacted the lifetime cancer risk for the human population. VOCs were found to have a detrimental effect by increasing rates of chronic respiratory symptoms [29]. Formaldehyde, benzene and naphthalene were of the most health concern [30] and benzene was used as an indicator of VOC in the lifetime cancer risk (LCR) [31] (Table 2).

In this manuscript, an evaluation and overview of the sample preparation techniques in relation to the analysis of VOCs using a sorbent tube in air are given. Thus, the purposes of this review are to: (i) give a comparison of the performance of commercially available sorbent material; (ii) evaluate the methodologies in relation to calibration of the TD coupled with sorbent tube; and (iii) discuss the interference of humidity and moisture in the proposed TD-sorbent tube method.

2. Measurement of Vocs Using Different Methods

The pre-concentration of VOCs in adsorbent tube and subsequent measurement by thermal desorption-gas chromatography-mass spectrophotometry (TD-GC-MS) is a widely-used method. TD is fast sample preparation technique in the determination of VOCs and SVOCs in air. Furthermore, TD, which is compatible with GC, can easily release the adsorbed or trapped compounds on the sorbent tube [32]. The selection of the type of sorbent in the tube is dependent on the target VOCs, for example for VVOCs we used a strong sorbent (Carboxen®) and for VOCs a medium to weak sorbent (Tenax®).

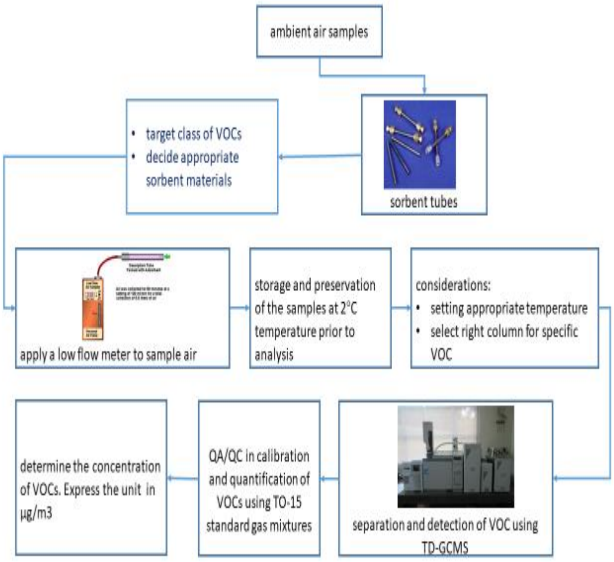

Fig. 1: The significant steps to determine the VOCs

This method has been used in the measurement of landfill, ozone precursor and soil gases [33] (Table 3). The interference of water during sampling in chromatographic analysis is a key issue. However, the advantage of tube monitoring methods is that the most of the available sorbent tubes do not retain moisture during the sampling process [34]. Several approaches are usually applied to resolve moisture problems in sorbent tubes, e.g. i) selection of a weak sorbent type i.e. Tenax®, ii) application of multiple sorbent types; iii) longer purging time in TD. However, there are several issues that need to be resolved in the injection of the liquid working standard (L-WS). The most commonly used practices for loading the L-WS (calibration) into sorbent tube are direct injection and vaporization of L-WS. A study by [35] reported that the reliability of the direct liquid injection for the quantification of unknown gas samples is highly compound- and sorbent-specific. Thus, a critical review of the sorbent types for a particular group of gas compounds is necessary in the selection of a right trapping material in a proposed study.

Different types of adsorbents were tested for their ability to efficiently trap SVOC pesticides: Tenax® TA; Carbopack Y; Carbopack B; Carbotrap; Carboxen®; Chromosorb® 106; and XAD-4. Results of the experiment showed that Tenax® gave better results for all the pesticides used but the best result in the test of the TD method, especially for pesticides with low volatility and/or poor thermal stability [36]. Carbotrap 349 was found to have the best performance in the determination of VOCs emitted from cut tobacco via TD-GC-MS. It provided the best adsorption efficiency compared to other sorbents such as Carbotrap 300 and Carbotrap 317 [37]. MVOCs were determined using Tenax®TA and Carboxen®1000 by [38] and the different of groups of VOCs detectable by TD-GCMS included aromatics, hydrocarbons, aldehydes, alcohols, halogenated compounds, terpenes, and reduced sulphur compounds. There are ranges of factors to consider when selecting suitable sorbents or sorbent combinations. The factors are as following.

2.1. Sorbent Strength of the Sorbent Material

This is an active sampling for trapping the VOCs on the sorbent material. The sorbent or the selected sorbents must have high efficiency for the pre-concentration of the target species and weak enough to release the analytes during desorption phase. Sorbent strength is usually measured in terms of retention or breakthrough volumes. Breakthrough volumes are susceptible to temperature. Retention volumes are typically quoted at 20 °C. As a general rule, the retention volume halves for every 10 °C rise in temperature. Strong sorbents, such as carbonized molecular sieves, are adversely affected by high relative humidity (RH). Possibility to use multi-sorbent beds can allow the pre-concentration of a wide range of volatilities as suggested by [39]. Adsorptive enrichment of volatile organic compounds has become an important technique in ambient air analysis and interference of the humidity and ozone can be avoided using carbon based adsorbent [40].

2.2. Inertness

The sorbent material should not chemically react with the analytes. Some sorbents contain materials which are chemically active. These sorbents are unsuitable for sulfur compounds, terpenes and amines [41].

2.3. Hydrophobicity

Most common weak-and medium-strength sorbents are very hydrophobic; thus their sorbent strength is not compromised at a high sampling rate. However, most strong sorbents comprise some form of carbonized molecular sieve and in this case sorbent strength is reduced by as much as a factor of 10% at 90% RH [41]. Excess water on the capillary column can change the adsorption properties of the stationary phase and cause unpredictable changes in the retention times. In some instances, it does irreparable damage to the column [42]. Tropical countries are relatively humid in ambient conditions. RH goes above 90% during the northeast monsoon in Southeast Asia (SEA). Thus, the effect of RH should be considered carefully during the measurement stage. In [43] evaluated the humidity problem. The results showed that humidity problems were demonstrated with carbon-based tubes, while Tenax-based tubes did not display any influence. Silica gel, a molecular sieve and $CaCl_2$ were tried out as materials for drying tube to remove air humidity, placed prior to the sampling tube to prevent water from entering. The pre-tubes filled with 0.5 g of $CaCl_2$ showed the best results with respect to their blanks, the analytes recoveries and their ability to remove ambient humidity. To avoid the possible agglomeration of $CaCl_2$ during the sampling process in high relative humidity atmospheres, 0.1 g of diatomaceous earth were mixed with the desiccant agent. The applicability of the $CaCl_2$ pre-tube as drying agent prior to Carbotrap B/Carbopack X/Carboxen 569 tubes was tested in urban and industrial locations with samplings of air at high relative humidity. In [44] suggested that the tube temperature should be regulated at 5–10 °C above the air temperature to minimize condensation under RHs > 30%.

2.4. Safe Sampling Volume

Safe sampling volume is usually calculated by halving the retention volume (indirect method) or taking two-thirds of the breakthrough volume (direct method). A stronger sorbent is one which offers greater safe sampling volumes for most/all VOC analytes relative to another, weaker sorbent. Generally, sorbent strength is related to surface area [34].

2.5. Artefacts

Depending on the artefact levels sorbents vary significantly. The Chromosorb® Century series, PoraPak^{TM} and HaveSep^{TM} series among porous polymers have relatively high artefacts with several peaks at 5 - 10 ng levels. For well-conditioned materials Tenax® TA is better with minimum levels between 0.1 and 1 ng [41]. An ideal sorbent for pre concentrating VOCs from an air matrix needs to have four main properties namely: infinite breakthrough volume; complete desorption of the target compounds at moderate temperatures; no generation of artefacts and no retention of water vapour [45].

2.6. Consideration of Single Sorbent or Multi-Sorbent Materials

Only one single available sorbent material cannot meet all of these criteria for a wide range of VOCs thus there is a tendency to use multiple adsorbents [42]. From the sampling side the sorbents in the tube are arranged in the order of increasing strength. The key factors to consider during multi-sorbent tubes are:

- The volatility range, quantitative retention and efficient desorption of each sorbent
- The temperature range for conditioning thermally-stable sorbents must not exceed the temperature limit of the sorbents used
- During storage in a multi-sorbent tube, loosely bound analytes may transfer from weak to strong sorbents. This might lead to irreversible adsorption and incomplete recovery. The migration can be reduced by inserting a medium-strength sorbent in between the weak and strong sorbent [46].

Table 1: Detailed of material types, methods and sensitivity to determine the selective class of volatile organic compounds (VOCs) in ambient air

Samples	Type of sorbent	Brand	Sampling method	Program used in TD	Program used in GCMS	GC column type	Analytical performances	References
Ambient	Carboxen 1000 VOCARB 3000 (Combination of Carbopack B, Carboxen 1000 and Carboxen 1001, and Carbopack B 60–80 mesh, 100 m^2/g) Glass column (50cm x 3mm ID) packed with 0.3g PMWCNTs and Carbopack B. Carbotrap, Carbopack X, Carboxen 569 (20/40 mesh) Carbograph 4 (35/50 mesh) with Radiello Tenax + Carbopack X (89 mm x 6.4 mm OD)	Supelco Markes International	Active Active Active Passive Active		Carboxen 1000 VOCARB 3000 Splitless, DB-624 Carbotrap Carbograph 4 Tenax + Carbopack X	column (25 m x 0.32 mm x 5 μm) column (70 m x 0.53 mm, ID =3 μm DB-624, 60 m x 0.25 mm x 1.4 μm film) DB-624, 60 m x 0.25 mm x 1.4 μm film 60m x 250 μm x 1.4 μm DB-VRX 1219.45766	Carbotrap: LOD = 1 x 10^{-5} to 2 x 10^{-3} μg m^{-3} Carbograph 4: LOD = 1 x 10^{-5} to 3 x 10^{-3} μg m^{-3} LOD = 0.01 – 1.31	[48-50, 52]
	Tenax + Carbopack X (89 mm x 6.4 mm OD)	Markes International	Active (Portable pump MTS32 autosampler)	280 ^{0}C for 10 min. Tenax trap. Cold trap -10 ^{0}C. Then, flashed heated to 300 ^{0}C for 7 min.	Oven Temp. 30 ^{0}C for 12 min, increased to 60 ^{0}C by 30 ^{0}C/min., followed by an increase to 124 ^{0}C a rate of 40 ^{0}C/min. Hold at 200 ^{0}C for another 2 min.	Agilent J & W 122-1564 260 ^{0}C (60 m x 250 μm x 1.4 μm DB-VRX 1219.45766)	LOD = 0.01 – 1.31 LOQ = 0.02 – 2.24 Accuracy = 55 – 113. MDL = 0.002 – 0.26 μg m^{-3} MQL = 0.004 – 0.45 μg m^{-3}	[52]
	VOCARB 3000 (Combination of Carbopack B, Carboxen 1000 and Carboxen 1001, and Carbopack B 60 – 80 mesh, 100 m^2 g^{-1}) Glass column (50 cm x 3 mm ID) packed with 0.3g PMWCNTs and Carbopack B.	Supelco	Trap injection (RH gas = 70%) ENCON purge and trap system (EST Co.)	-	Injection port and detector at 250 ^{0}C. N_2 Flow rate: 48 ml/min. Oven temperature: 40 – 320 ^{0}C.	CP3800 GC (Varian Co.) equipped with FID. Splitless injection model with DB-624 column (70 m x 0.53 mm, ID =3 μm, J&W Scientific). Column temp. at 45 ^{0}C for 4.5 min, increased to 110 ^{0}C in 10 ^{0}C/min and to 160 ^{0}C at 25 ^{0}C/min and maintain for 1.5 min.	Carbopack B > 90% for most compounds. VOCARB ~ 100% Recoveries of Ethyl benzene and p-Xylene, o-Xylene in all types of absorbent were ~82 – 99 %	[50]
	Carbotrap, Carbopack X, Carboxen 569 (20/40 mesh) PE glass tubes (Pyrex, 6 mm OD, 90 mm long)	Supelco	Active (Air collector pump sampler, LCMA-UPC)	Desorption 300 ^{0}C Cold trap at -30 ^{0}C 2nd Desorp at 300 ^{0}C for 10 min.	Oven temp. at 40 ^{0}C for 1 min, to 230 ^{0}C at a rate of 6 ^{0}C/min, then maintain at 230 ^{0}C for 5 min.	DB-624, 60 m x 0.25 mm x 1.4 μm film)	LOD = 1 x 10^{-5} to 2 x 10^{-3} μg m^{-3}	[49]

A widely-used combination of sorbent packed into a single tube for pumped monitoring of uncharacterized atmospheres is Tenax® TA backed up by medium-strength graphitized carbon black (e.g. Carbopack™ B or Carbograph™1TD) backed up by a carbonized molecular sieve (UniCarb™ or Carboxen®1003). This combination gives a quantitative retention and release of hydrocarbon compounds in the volatility range from C_3 to n-C_{26} [47].

Another useful combination of sorbents is a short (∼5mm) bed of clean quartz wool, backed up by Tenax®TA, backed up again by Carbopack ™ X or Carbograph ™ 5 TD with the bed lengths of Tenax®:carbon being roughly in the proportion of 3.5:2 [41]. A study by [42] reported that the TD method using multi-sorbent tubes including Carbopack™ B, Carbopack™ C and Carbosieve® SIII has been successfully applied to the analysis of VOCs in workplace air [46].

For odorous and/or reactive compounds of interest the starting point for monitoring uncharacterized atmospheres is to sample using several replicates of two slightly different sampling trains in parallel. The first would use a totally inert combination of sorbents for example; the front tube packed with Tenax® TA, the middle one packed with a stronger porous polymer such as Chromosorb® 106 and the third tube packed with UniCarb™ or Carboxen® 1003. The second sampling train would be similar but with an alternative black carbon medium-strength sorbent used in the middle tube. Subsequent analysis of each of the separate sorbent tubes used in both types of sampling train would highlight any analyte losses caused by the use of carbon rather than a porous polymer medium-strength sorbent and would also help identify the optimum combination of sorbents for subsequent monitoring of the same area using single tubes packed with multiple sorbents [38, 41, 48-53].

Carbon nano tubes (CNTs) have attracted great attention in this field because of their unique properties. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, with either single walled or multi-walled structures. Currently, the large-scale preparation of CNTs has been realized. Having high potential in analyzing VOCs it has become more urgent to discover applications of CNTs. Due to the porous graphite structure of CNTs, it is possible to use CNTs as adsorbent in pre concentrating VOCs from environmental samples [50, 54].

Table 2: Detailed of material types, methods and sensitivity to determine the selective class of volatile organic compounds (VOCs) in indoor environment

Type of sorbent	Brand	Sampling method	Program used in TD	Program used in GCMS	GC column type	Analytical performances	References
Carbotrap (20/40mesh), Carbopack X (40/60mesh), Carboxen 569 (20/45mesh). Tenax TA (60/80) 200 mg.	Supelco	Active	Perkin Elmer ATD 400			LOD = 0.001 – 10 ng. Repeatability < 25%	[46]
CarbopackTM B (Supelco) 60/80 mesh (Hydrophobic)	Supelco	Active		CarbopackTM B: DB-5 ms (60 m x 0.25 mm ID x 1 µm film)		Reproducibility = 6.6% VC	[55]
Tenax TA (35 – 60 mesh) Quartz wool + Tenax TA + Carbograph 5TD (40 – 60 mesh) total mass of sorbent ~ 300 mg	Buchem BV	Active		Tenax TA: DB5 column (60 m x 0.25 mm ID x 0.5 µm film)			[1]
PE Glass tube (6mm OD, 90 mm long). Unsilanised wool, Carbotrap (20/40mesh), Carbopack X (40/60mesh), Carboxen 569 (20/45mesh). Tenax TA (60/80) 200 mg.	Supelco	Active (air sampler, LCMA-UPC)	Perkin Elmer ATD 400	-	-	LOD = 0.001 - 10 ng. Repeatability < 25%	[46]
PE SS tubes packed with CarbopackTM B (Supelco) 60/80 mesh (Hydrophobic)	Supelco	Active (sampling for 20 min with sampling flow 25 mL/min) Pumping device = Laboport	Desorption = 300 ^{0}C (2nd desorption) Cryo trap = -30 ^{0}C (1st desorption) with outlet split of 5 mL/min	Agilent 6890 N Network GC system interface with a 5973 Network MSD Full scan/SIM mode, 200 ^{0}C	Agilent DB-5 ms (60 m x 0.25 mm ID x 1 µm film)	Reproducibility = 6.6% VC	[55]
SS (89mm length x 6mm OD) Tenax TA (35 – 60 mesh)	Buchem BV	Active (TSI SidePak SP130 air sampling pumps)	Cold trap at -10 ^{0}C materials = quartz wool + Tenax TA + Carbograph 5TD Desorption at 300 ^{0}C for 3 min.	Oven Temp. at 35 ^{0}C for 1 min, 2 ^{0}C/min to 75 ^{0}C, 5 min to 140 ^{0}C, 10 ^{0}C/min to 300 and held for 12 min.	DB5 column (60 m x 0.25 mm ID x 0.5 µm film)	-	[1]
Quartz wool + Tenax TA + Carbograph 5TD (40 – 60 mesh) total mass of sorbent ~ 300 mg	Buchem BV	Active (Casella Tuff Plus personal sampling pump)	Cold trap at -10 ^{0}C materials = quartz wool + Tenax TA + Carbograph 5TD Desorption at 300 ^{0}C for 3 min.	Oven Temp. at 35 ^{0}C for 1 min, 5 ^{0}C/min to 100 ^{0}C, and held for 2 min.	DB5 column (60 m x 0.25 mm ID x 0.5 µm film)	-	[1]

Table 3: Detailed of material types, methods and sensitivity to determine the selective class of volatile organic compounds (VOCs) in several other sources

Samples	Type of sorbent	Brand	Sampling method	Program used in TD	Program used in GCMS	GC column type	Analytical performances	References
VOCs (landfill)	Tenax TA, 100 mg Carboxen 1000	Supelco	Active		Varian Factor Four		LOD of all compounds	[38]

					VF-624 (40 m x 0.15 mm x 0.84 µm film)		= 1.1 – 4213 pg	
Polar & non Polar VOCs (Work place)	0.2g Carbopack B, 0.2g Carbopack C, 0.2g Carbosieve S-III (Glass tube 16 cm x 4 mm ID, wall thickness 2mm)	Supelco	Active (Sequential Tube Sampler) PE STS 25.	Desorption at 220^{0}C for 6 min. Trap at -160 ^{0}C for 6 min by Teflon tube. Reheated to 200 ^{0}C at 50 ^{0}C/s for 5 min. Transfer line at 180 ^{0}C	Oven Temperature: start at 35^{0}C; ramp at 3 ^{0}C/min to 100 ^{0}C for 5 min; finally ramp from 5 to 160 ^{0}C/min for 5 min. Transfer line GCMS at 280 ^{0}C.	CP-Wax fuse silica (60 m x 0.32 mm, 0.5 µm film)	Recoveries = 96.2 – 98.2% Method DL: 0.38 – 0.78 ppb Repeatability CV% = 1.1 – 3.4 (Toluene)	[42]
Chemical Warfare Agents (CWA)	Tenax TA packed GC liner (borosilicate, one ring restriction, 88mm length, and 3 mm ID) ~70 mg Tenax TA, 60.80 mesh used as TD tube	Obtained from Joint Analytical System Benelux, Eindhoven	Active (Sampling train)	Splitless mode.	Agilent 6850 GC/5973 or 5975 Inert MSD, Full scan mode. Purge flow = 50ml/min at 2.0 min (GasSaver 20 ml/min at 4.0 min)	RXI – 5MS (30 m x 0.25mm ID, 0.25µm film). Initial temp. at 40 ^{0}C (held 2 min.), increased to 20 ^{0}C/min to 160 ^{0}C, then to 280 ^{0}C at 30 ^{0}C/min, final temperature held for 5.00 min.	LOD = 0.8 – 2.9 ng	[56]
PFAs (Indoor) include FTOHs, FOSAs, FOSEs	SS 150mg Tenax TA (35/60 mesh) + 200mg Carbograph 1TD (40/60 mesh), 89 mm length, 6.4 mm OD)	Markes International	Active (Portable pump – AirChek XR 5000) / LVS	TD-100TM (Markes international) Desorption at 320 ^{0}C for 10min. Gas flow 40 mL/min. Splitless. Cold trap at 335 ^{0}C for 5 min. Split by 5 mL/min.	Oven temp. = 50 ^{0}C for 2 min, 2 ^{0}C/min to 80 ^{0}C, hold for 0 min, then 10 ^{0}C until 230 ^{0}C followed by 5 min holds. SIM mode. Transfer line = 220 ^{0}C.	HP-INNOWAX (60 m x 0.25mm x 250 µm film) J&W Scientific.	Recoveries = 88 – 119% for FTOHs, 86 – 138% for FOSAs and 139 – 210% for FOSEs. Repeatability for all compounds < 10%.	[53]
VOC (Urban/Industrial air)	SS Carbograph1/Carboxen 1000 (89mm x 6.4mm OD) and SS Tenax/Carbograph 1TD (89 mm x 6.4 mm OD)	Markes International	Active (air sampling pump, SKC, Eighty Four)	UNITY TD. Desorption at 275 ^{0}C for 10 min. Cold trap at -10 ^{0}C. Splitless.	Oven temp: 40 ^{0}C for 5 min to 140 ^{0}C at 6 ^{0}C/min, then to 220 ^{0}C at 15 ^{0}C/min and held for 3 min.	TRACSIL Meta.X5 (60 m x 0.32 mm x 1.0 µm film)	Recoveries > 98.9% except for methylene dichloride (74.9%) MDL = 0.01 and 1.25 µg m^{-3}. Repeatability = RSD < 4%.	[37]
Odorous VOCs (Landfill)	PE SS tubes (6.9 mm OD x 4.9 mm ID x 88.9 mm length) 150 mg Tenax TA, 100 mg Carboxen 1000.	Supelco	Active (Gilian LFS-1130 pump)	Desorption at 225 ^{0}C for 5 min, cryo trap at -30^{0}C. 2nd desorption at 280 ^{0}C for 1 min (flashed heating).	35 ^{0}C hold for 3 min, 35 – 100 ^{0}C at 12 ^{0}C/min, hold for 8 min. 100 ^{0}C – 120 ^{0}C by 45 ^{0}C/min, hold 7 min. 120 – 140 ^{0}C by 23 ^{0}C/min, hold 5 min. 140 – 180 ^{0}C by 10 ^{0}C/min, hold 0 min.	Varian Factor Four VF-624 (40 m x 0.15 mm x 0.84 µm film).	LOD of all compounds = 1.1 – 4213 pg	[38]
Trihalomethanes (in	SS (6mm OD x 90 mm X 5mm	Supelco	Active (SKC Sidekick	UNITY TD Desorption	Oven temp = 40 ^{0}C for	HP-5MS capillary column (60	MDL = 0.03 ng	[57]

humid air)	ID)Chromosorb 102/Tenax TA, Carbopack B		pump)	@ 200^{0}C for Chromosorb 102, 250 ^{0}C for Tenax TA and 300 ^{0}C for Carbopack B in 10 min. Flow rate = 30 ml/min Cold trap at -10^{0}C	4 min, then 125 ^{0}C at 10 ^{0}C/min and to 200 ^{0}C at 25 ^{0}C/min for 2 min. In SIM mode.	m x 0.25 mm ID x 0.25 µm film) J&W Scientific.	Recoveries = 92 – 97% for all compounds. LOD = 0.02 to 0.03 ng.	
Trihalomethanes (in breath gas)	SS (6mm OD x 90 mm X 5mm ID)Chromosorb 102/Tenax TA, Carbopack B	Supelco	Active (Bio-VOC sampler)	UNITY TD Desorption at 200^{0}C for Chromosorb 102, 250 ^{0}C for Tenax TA and 300 ^{0}C for Carbopack B in 10 min. Flow rate = 30ml/min Cold trap at -10 ^{0}C	Oven temp = 40 ^{0}C for 4 min, then 125 ^{0}C at 10 ^{0}C/min and to 200 ^{0}C at 25 ^{0}C/min for 2 min. In SIM mode.	HP-5MS capillary column (60 m x 0.25 mm ID x 0.25µm film) J&W Scientific.	MDL = 0.03 ng Recoveries = 92 – 97% for all compounds.	[57]
VOCs (Industrial area)	SS tubes (89 mm x 6.4mm OD) Tenax/Carbograph 1 TD	Markes International	Active (FLEC Air Pump 1001, Markes)	UNITY TD. Primary desorption at 275 ^{0}C. Cold trap at -5 ^{0}C. 2nd desorption at 300 ^{0}C for 3 min.	Oven temp. 40 ^{0}C for 5 min, raised to 140 ^{0}C a rate of 6 ^{0}C/min, raised again to 220 ^{0}C with 15 ^{0}C/min and held for 8 min.	TRACSIL Meta.X5 (60 m x 0.32 mm x 1.0 µm) by TEKNOKROMA	MDL = 4 x 10^{-4} µg m^{-3} to 0.4 µg m^{-3}, depends on the compounds analyzed.	[58]
Odorous VOCs, BTEX etc. Biogas (Landfill)	SS tubes (89mm x 6.4mm OD) 400 mg of Tenax TA and Unicarb	Markes International	Active (Tedlar bags and sorption tubes) Sampling pump (FLEC Air Pump 1001)	Cold trap at -10 ^{0}C using Tenax Ta and Unicarb. Then flash heated to 300 ^{0}C for 8 min. Split flow applied.	For C_3 – C_7, Oven temp. at 40 ^{0}C for 2 min, raised to 220 ^{0}C at 50 ^{0}C/min and held for 12 min. For C_8 – C_{20}, oven temp. at 36 ^{0}C, for 5 min, raised to 120 ^{0}C, 10^{0}C/min, and then to 220 ^{0}C, 20 ^{0}C/min, held for 25 min.	For C_3 – C_7, GS-GASPRO (30 m x 0.32 mm x 1.0 µm film) (Agilent Technologies) For C_8 – C_{20}, ZB-5 (60 m, 0.32 mm x 1.0 µm film) (Teknokroma). SIM mode.	~ 1 x 10^{-4} mg m^{-3} for most of the compounds.	[59]
Odorous VOCs, BTEX etc. Biogas (Landfill)	SS tubes (89mm x 6.4mm OD) 400 mg of Tenax TA and Unicarb	Markes International	Active (Tedlar bags and sorption tubes) Sampling pump (FLEC Air Pump 1001)	Desorption at 200 ^{0}C for 5 min. Cold trap with same materials to -10 ^{0}C. Splitless. 2nd desorb at 300 ^{0}C for 8 min. Split flow applied here.	For C_3 – C_7, Oven temp. 40 ^{0}C for 2 min., raised to 220 ^{0}C, 50 ^{0}C/min and held for 12 min. For C_8 – C_{20}, oven temp. 36 ^{0}C, for 5 min, raised to 120 ^{0}C, 10 ^{0}C/min, and then to	For C_3 – C_7, GS-GASPRO (30m x 0.32 mm x 1.0 µm film) (Agilent Technologies) For C_8 – C_{20}, ZB-5 (60 m, 0.32 mm x 1.0 µm film) (Teknokroma). SIM mode.	~ 1 x 10^{-4} mg m^{-3} for most of the compounds.	[59]

					220 ^{0}C, 20 ^{0}C/min, held for 25 min.			
Pesticides	PE SS tubes (4 mm ID x 89 mm length). Tenax TA, Carbopack Y, Carbopack B, Carbopack B, Carbotrap, Carboxen, Chromosorb 106 and XAD-4.	Supelco	Active (AMETEK 205 pump)	Desorption at 300 ^{0}C for 15 min. Cold trap at -30 ^{0}C. Then flashed heated to 390 ^{0}C for 15 min. Split mode.	Oven temp. 60 ^{0}C held for 1 min, raised by 15 ^{0}C/min to 200 ^{0}C and increased by 15 ^{0}C/min to 200 ^{0}C, finally, increased at 5 ^{0}C/min to 260 ^{0}C, held for 5 min.	J&W, DB-1 (30m x 0.249mm ID x 0.25µm film)	-	[60]
VOCs (Hexane, Ethyl acetate, Toluene, Limonene)	200 mg Tenax TA (3.5 in x 0.25 in x 4mm) (35/60 mesh)	Markes International	Passive (Homemade exposure chamber)	Desorption at 50 ^{0}C for 1 min, then raised to 260 ^{0}C for 7 min. Cold trap at -10 ^{0}C in 22 mg of Tenax TA and 34 mg Carbograph 1TD sorbent (v/v 50:50). Flashed heat at 270 ^{0}C during 3 min.	Oven temp. First, ramped from 35 ^{0}C to 60 ^{0}C by 2 ^{0}C/min. Second, increased to 170 ^{0}C by 8 ^{0}C/min. Then to 220 ^{0}C by 15 ^{0}C/min, held for 10 min.	Varian Factor-Four VF-1 ms GC column (30 m x 0.25 mm x 1µm film)	-	[61]
VOCs (Hexane, Ethyl acetate, Toluene, Limonene)	200 mg Tenax TA (3.5 in x 0.25 in x 4mm) (35/60 mesh)	Markes International	Active (GilAir3 personal air sampler pump) in homemade exposure chamber	Desorption at 50 ^{0}C for 1 min, then raised to 260 ^{0}C for 7 min. Cold trap at -10^{0}C in 22 mg of Tenax TA and 34 mg Carbograph 1TD sorbent (v/v 50:50). Flashed heat at 270 ^{0}C during 3 min.	Oven temp. First, ramped from 35 ^{0}C to 60 ^{0}C by 2 ^{0}C/min. Second, increased to 170 ^{0}C by 8^{0}C/min. Then to 220 ^{0}C by 15 ^{0}C/min, held for 10 min.	Varian Factor-Four VF-1 ms GC column (30m x 0.25mm x 1µm film)	-	[61]
VVOCs (methanol & ethanol)	Carbotrap 300 (Carbopack C + carbopack B + Carbosieve SIII)	Supelco	Active	Desorption at 40 ^{0}C at 12 ^{0}C/min to 200 ^{0}C for 0.40 min. Cold trap at -100 ^{0}C for 0.7 min, at a rate of 12 ^{0}C/min to 200 ^{0}C for 3 min. 2nd Desorption at 40^{0}C at 20^{0}C/min to 220 ^{0}C for 5 min.	-	Zebron WAX Plus Column (30 m x 0.32 mm x 0.5 µm) for FID system. Restek Rxi 5 separation column (60 m x 0.25 mm x 0.25 µm) for MSD system.	For FID system LOD = 2 – 3 µg/m^3 LOQ = 8 – 15 µg/m^3 For MSD system LOD = 20 µg/m^3 LOQ = 60 µg/m^3	[62]
Odorous VOCs	Tenax TA (60/80 mesh)	Alltech	Active/diffusive sampling	Desorption at 300 ^{0}C for 5 min. Cryo trap at	Oven temp. 40 ^{0}C for 5 min. Raised to 200 ^{0}C	CP was (60 m x 0.25 mm ID x 0.25 µm)	Recovery = 75.8 – 83.9% for Tenax TA	[63]

				-10 ^{0}C and flashed heated to 320 ^{0}C for 20 min. Cold trap material = Carbopack B + Tenax)	by 10 ^{0}C/min, held for 4 min.			
Odorous VOCs	Carbopack X (40/60 mesh)	Supelco	Active/diffusive sampling	Desorption at 300 ^{0}C for 5 min. Cryo trap at -10 ^{0}C and flashed heated to 320 ^{0}C for 20 min. Cold trap material = Carbopack B + Tenax)	Oven temp. 40 ^{0}C for 5 min. Raised to 20 0^{0}C by 10 ^{0}C/min, held for 4 min.	CP was (60 m x 0.25 mm ID x 0.25 µm)	Recovery = 62.5 – 76.5% for Carbopack X	[63]
Odorous VOCs	Tenax TA (60/80 mesh) + Carbopack B (60/80 mesh) + Carboxen 1000 (60/80 mesh)	Alltech and Supelco	Active/diffusive sampling	Desorption at 300 ^{0}C for 5 min. Cryo trap at -10 ^{0}C and flashed heated to 320 ^{0}C for 20 min. Cold trap material = Carbopack B + Tenax)	Oven temp. 40 ^{0}C for 5 min. Raised to 200 ^{0}C by 10 ^{0}C/min, held for 4 min.	CP was (60 m x 0.25 mm ID x 0.25 µm)	Recovery = 81.0 – 82.8% for Tenax + Carbopack B + Carboxen 1000	[63]
VOCs (Liquid-phase standards)	Tenax TA + Carbopack B + Carboxen 1000	Carpoback X for lighter VOCs.sampling	Vaporized and Direct Injection into sorbent tubes	Cold trap (Tenax TA, Carbopack B) Desorption at 300 ^{0}C for 5 min. Cold trap at -10 ^{0}C, held for 1 min. Flashed heated to 320 ^{0}C for 20 min.	Oven temp. 40^{0}C, ramped by 10 ^{0}C/min to 200 ^{0}C and held for 4 min.	CP-WAX (0.24mm ID x 60 m x 0.25µm film).	Direct Injection Relative Recovery = 4.72 – 175%. Vaporization Relative Recovery = 5.66 – 266.	[64]

3. Conclusion

This paper carried out a comprehensive review of the detection of VOCs. The emissions of VOCs are a great concern due to the damaging impact on the human respiratory system. Moreover, the concentration of VOCs can influence the formation of ozone in the ambient air. The SEA region is already considered as a tropospheric ozone hotspot and the atmospheric pollution so that is why resultant chemical reactions need to be explored precisely. Therefore, the current review has given an emphasis on determining VOCs in the ambient atmosphere, indoor microenvironment, landfills, and workplace. From the above review, it can be seen that the initial considerations when selecting the best method are sorbent strength of the sorbent material, inertness, hydrophobicity, and artefacts. In the SEA region, the RH is relatively higher and exceeds the border of 90% during the northeast monsoon. Thus, the hydrophobic properties of the material need to be carefully considered. Further to the effect of RH, the artefact effect of the material itself is a challenge to be optimized and multi-sorbent material in a single tube could be a viable option to minimize the effect of unwanted signal in the spectrum. However, some of the key points important prior to deciding on a suitable material are: a) volatility range, quantitative retention and efficient desorption; b) the temperature range for conditioning thermally-stable sorbents must not exceed the temperature limit of the sorbents used; and c) loosely bound analytes may transfer from weak to strong sorbents during the preservation of the samples. This might lead to irreversible adsorption and incomplete recovery. The migration can be reduced by inserting a medium-strength sorbent in between the weak and strong sorbent.

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