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Review Paper:

An Overview of VOC Sampling and Detection Techniques

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Abstract

Volatile Organic Compounds (VOCs) are the key air pollutants that act as precursors to major secondary pollutants including tropospheric ozone and secondary organic aerosols (SOA) and various health issues. Therefore, there is a need to have a simple, portable, reliable sampling method to quantify VOCs. This study reviews VOC sampling techniques based on feasibility, the material used, sensors and gas chromatographic instruments. A particular highlight on VOC sensors concerning their sensitivity, detection limit, response time and robustness has also been done.

Also, the study focuses on critical aspects of VOC characterisation in ambient air along with the advantages and challenges of the methods. Around 65% of researchers have used the gas chromatography-based FID technique (GC-FID) for VOC characterisation in India. The typical sampling methods used in India are sorbent tubes or cartridges, air sample bags (commonly Tedlar bags), glass air sampling units and canisters. The portable real-time method is also used. The most common sampling method is passive sampling with sorbent tubes with activated carbon. However, extensive research is required on more sophisticated and world-class sensors, sampling and detection techniques to reach safe and recommended targets.

Keywords: Air pollution**,** Gas Chromatography**,** Spectroscopy**,** Sensors, Volatile Organic Compound.

Introduction

Rapid and uncontrolled industrialisation and urbanisation have resulted in a significant increase in atmospheric pollution over the years. Volatile organic compounds (VOC) are one of the main air pollutants causing detrimental effects on health and the environment [43]. VOC emissions are broadly divided into biogenic and anthropogenic depending on their source. Biogenic VOCs are emitted from plants containing compounds such as monoterpenes and isoprenoids[35]. Prime sources of anthropogenic VOCs are vehicular exhaust and emissions from fuel evaporation, solvent usage, industrial processes, oil refining, waste landfills and dumpsites and material emissions from domestic painting[57,63,75,78].

VOCs are responsible for smog formation and act as precursors of secondary air pollutants, tropospheric ozone (O_3) and secondary organic aerosol (SOA) formed by photocatalytic oxidation[27,32,94]. SOA is the primary source of particulate matter (PM) formation[26,87]. Recent studies have also found associations between PM and SOA levels and the transmission of coronavirus disease of 2019 **(**COVID-19) suggesting that they can act as carriers of viruses and other micro-organisms[11,53,66].

Thousands of VOCs are produced and consumed in our daily life from indoor and ambient air and the standard U.S. Environment Protection Agency (E.P.A.) methods enlist hazardous air pollutants [88]. Benzene, toluene, ethylbenzene, (o,p,m)-xylene (commonly called BTEX) are the most toxic[7]. Studies reveal benzene and 1,3 butadiene to be carcinogenic whereas toluene and xylene [1, 30, 42] have shown teratogenic effects[19,95,97].

This review aims to impart a fundamental understanding and practical approach to acknowledge the different sampling methods for VOCs in the ambient air. The sampling methods prominently describe canisters, sorbent tubes and air sample bags. Moreover, lab-based and real-time analysis methods focus on analytical techniques. This study also highlights low-cost sensors and portable gas chromatography instruments, which are gaining popularity.

VOC Determination

VOC determination primarily includes sampling, detection and analysis. In addition, the aspects mentioned earlier have been studied in the context of India for the last decade (2011 - 2020). Here, we present an extensive review of sampling techniques available and their characteristics, highlighting the factors that make such methods or sensors suitable for these applications. A comprehensive study was interpreted with the help of graphs, tables and Microsoft tools for plotting the graphs and pie charts.

Manual Sampling: Air monitoring provides information on the concentration and nature of pollutants at the desired location over a specific duration. Various monitoring techniques such as manual or whole air sampling, accurate- or automatic-time analysers and wireless sensors are frequently used [13, 80]. Manual sampling (also known as entire air sampling) is the most common and popular method. The air is sampled, stored and later analysed in the laboratory by standard methods (e.g. EPA TO 15)[80,88]. Sampling is done in two ways i.e. active and passive sampling (Figure 1); active sampling is when air is mechanically forced into the sampling unit with a constant flow rate whereas passive sampling is based on the phenomenon of diffusion into the sampling adsorbents.

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The sampling of air is performed with the help of canisters, sorbent tubes, air sample bags (Polyvinyl fluoride filmed plastic air sampling bags), balloons, foam-based sampler (Polyurethane foam -PUF) etc. Table 1 and figure 2 depict and summarise the standard manual sampling techniques for VOCs.

Miniaturised air sampling techniques have also been developed to overcome problems such as bulky size, higher cost, longer sampling hours and complicated setup. These are also divided into active and passive sampling. Amongst sampling, the most common method is the Needle-Trap Micro-Extraction (NTME), In-Tube extraction and miniaturised sorption traps[37]. For miniaturised passive air sampling, Solid-Phase Micro-Extraction (SPME) and Solid-Phase Dynamic Extraction (SPDE) are used. SPME is utilised in the form of an arrow, fibre and thin film. Miniature sampling devices can also be installed on drones for quick analysis[40]. Active sampling is the preferred sampling technique to identify episodic emissions of VOCs but provides limited sample information due to the breakthrough volumes of the sorbent tubes.

Major drawbacks of passive sampling are: sampling over very long durations (e.g. three months, six months, one year). Less strongly sorbed compounds may not be well retained on passive samplers over such long intervals. In addition, longer sampling durations provide more time for the uptake of water to influence performance through competition for adsorptive sites for some sorbents (e.g. activated carbon), hydrolytic degradation of some chemicals (e.g. methyl ethyl ketone, 1,1,1- trichloroethane), or reactions with ground-level ozone[59].

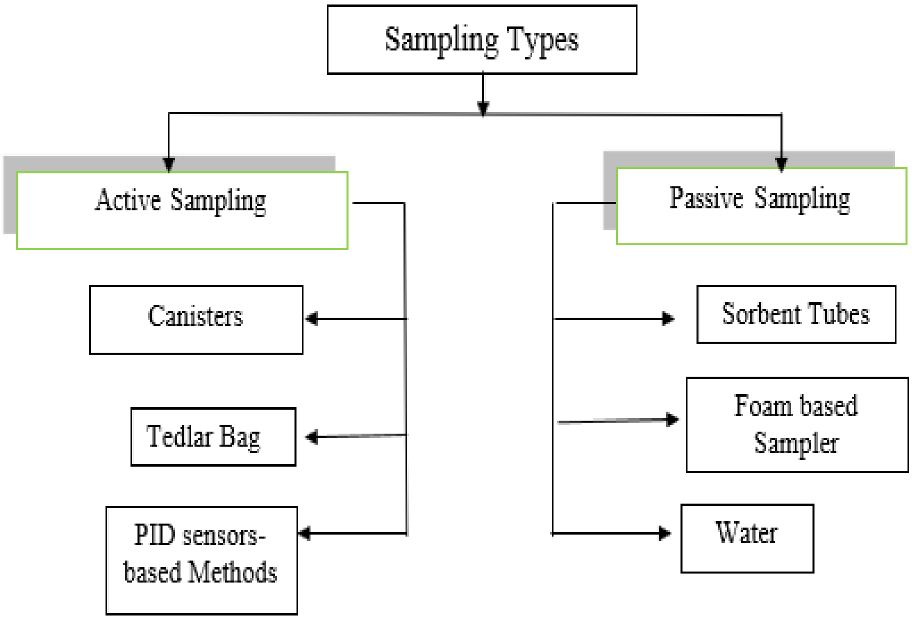


Figure 1: Various Sampling Methods

(a)
Single sorbent tube connected to a 60ml syringe for collection of vapor sample[40]

(b)
Canisters (spherical and cylindrical containers) with Flow Controllers (smaller gauges and blue box)

(c)
One-liter Tedlar Bag with Disposable Syringe and Three-way Valve for Filling

Figure 2: a) Single sorbent tube b) Canister in a spherical and cylindrical shape with flow controllers c) Tedlar bag with a disposable syringe and three-way valve[84]

Table 1
Details of manual sampling technique

Sampling instrument	Material	Sample holding duration	International method	Flow rate
Canisters	Stainless steel[7,13,15,16,87,92]	Up to 30 days	EPA TO-15 EPA TO-14A	100-200 mL/min
Sorbent tubes	Inorganic sorbents like silica gel. Organic sorbents like activated carbon Organic polymers are also used[7,9,18,52]	Maximum 14 days	EPA TO -17, C.P.C.B. (Central Pollution Control Board)	50-200 mL/min
Air Sample bags	Polyvinyl Fluoride film-coating, Teflon and flex foil[7,16,31]	Less than 24 hrs	EPA TO-14A	100-200 mL/min
SPME	Polydimethyl siloxane, Divinyl benzene,Carboxen[5]			70mL/min
Foam-based sampler	Nylon or Foam[99]	Upto 24 hours		2000-2500 mL/min
Passive Sampling	Tenax TA, Chromosorb 106 ,Carbopack B, Carbograph 1TD, Anasorb GCB1, Carbograph 4TD, Carbopack X, Carbograph 5TD , Carboxen 1016[49,59,90]			Varies according to the sorbent material

Table 2
Types, principles and detection limit of detectors in Instrumental analysis

Detectors	Principle	Detection Range	Type	Compounds detected
FID	The ionisation of organic compounds by igniting the compounds in the hydrogen-air flame[14,31,77]	ppm or ppb	Universal detector	Organic compounds, such as hydrocarbons.
TCD	The difference of thermal conductivity properties between the carrier gas and the target is being detected[14]	ppm or ppb	Universal detector	All the compounds i.e. organic, inorganic except carrier gas
ECD	Some electrons of individual molecules which pass through the detector are captured and the current being measured reduces, which results in a positive peak being recorded[14,65]	ppt	Selective detector	Halogenated compounds
MS	Ions produced from inorganic or organic compounds are separated by their mass-to-charge ratio (m/z) that can be detected qualitatively and quantitatively by their respective m/z and abundance[14,19,23,98]	ppb	Universal detector	Maximum number of compounds
PTR-MS	VOC molecules in gas-phase get ionised by the proton transfer from H_3O^+ to the VOC molecules: $VOC + H_3O^+ \rightarrow VOC \cdot H^+ + H_20$[2,8,14,33,56,81] A mass analyser subsequently detects the VOC ions ($VOC \cdot H^+$) generated during this reaction.	ppt	Selective detector	Maximum number of compounds

Lab-based instrumental analysis of VOCs: Samples collected through manual sampling are generally analysed to detect, identify and quantify various VOCs at the laboratory using analytical instruments. Gas chromatography (GC) is the most common separation technique used for VOC analysis[51,54]. Different detectors like Flame ionisation detector (FID), Photoionization Detector (PID), Electron capture detector (ECD), Mass spectrometry (MS) and Thermal conductivity detector (TCD) can be used for VOCs (Table 2). Another instrument used for separation is Proton-Transfer-Reaction Mass Spectrometry (PTR-MS). The detectors that detect each compound present in the column, excluding the mobile phase, are considered Universal detectors [28].

The PTR-MS carries the limitation possessed by mass spectrometry, as it is challenging to separate e.g. a couple of compounds, it may work by reagent ions switching and or by varying the reduced electric field strength in the drift tube. A vast range of compounds such as VOC (e.g. BTX), hydrocarbons such as propene, isoprene, oxygenated compounds for example formaldehyde, acetone and nitrogen-containing compounds (for example acetonitrile) can be measured for real-time monitoring[44,86]. Some of the technique's disadvantages are that all the molecules are not detectable, maximum measurable concentration is limited and it acts as a real-time trace gas analysis method featured on mass spectrometry. Also, gas-phase of the sample is mandatory. PTR-MS is used to monitor traffic emissions (e.g. Benzene, Toluene, Xylene (BTX), Alkylbenzenes) with different sampling times varying between 3 to 10 s/mass.[4]

VOC Determination at Real-Time: For VOCs, real-time analysers consist of different sensors such as photoionization detector (PID), metal oxide (MOx)[17], amperometric[25] etc. Among these, PID-based sensors are designed for measuring the low concentration levels of VOCs, therefore they are most widely used[79]. With the advent of the internet of things (IoT) and Artificial Intelligence (AI), a wireless network of such sensors can be deployed and programmed to provide real-time or near-real-time data over an area (e.g. an industry or gas station) or region (e.g. neighborhood or a city) – thus creating a geo-tagged hyperlocal database.

The reason to use more than one type of detector for GC is to achieve selective and/or susceptible detection of specific compounds encountered in particular chromatographic analyses. The selective determination of aromatic hydrocarbons or organo-heteroatom species is the job of the photoionisation detector (PID), which uses ultraviolet light as a means of ionising an analyte exiting from a GC column. The ions produced by this process are collected by electrodes. The current generated is therefore a measure of the analyte concentration. If the energy of an incoming photon is high enough (and the molecule is quantum-mechanically "allowed" to absorb the photon), photoexcitation can occur to such an extent that an electron is wholly removed from its molecular orbital i.e. ionization.

A photoionization reaction is:[61]

$$R + h\nu \longrightarrow R^{+} + e^{-}$$

If the amount of ionization is reproducible for a given compound, pressure and light source, then the current collected at the PID's reaction cell electrodes is proportional to the amount of that compound entering the cell (Figure 3). The compounds are routinely analyzed and are either aromatic hydrocarbons or heteroatom-containing compounds (like organ sulfur or organ phosphorus species). These species have ionization potentials (IP) that are within reach of commercially available U.V. lamps. The available lamp energies range from 8.3 to 11.7 eV, that is, lambda max ranging from 150 nm to 106 nm. Although most PIDs have only one lamp and depending on the compound, selectivity lamps can be exchanged for the analysis.

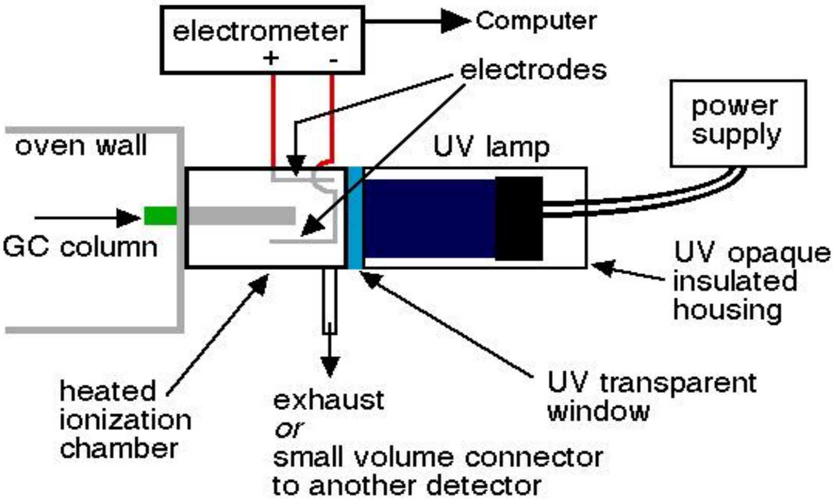


Figure 3: PID Internal construction[61]

Since only a tiny (very reproducible but basically unknown) fraction of the analyte molecules is actually ionised in the PID chamber, this is considered to be a nondestructive GC detector. Therefore, the exhaust port of the PID can be connected to another detector in series with the PID. In this way data from two different detectors can be taken simultaneously and selective detection of PID responsive compounds is augmented by the response from like a FID or ECD. The major challenge here is to make the design of the ionisation chamber and the downstream connections to the second detector so that peaks that have been separated by the GC column, do not broaden out before detection.

Sampling and Analysis methods in the context of India

Passing over the decades, VOC pollution in the ambient air has raised unavoidable environmental problem in urban areas, prominently in the developing countries like India[68], China[93], Iran[29], Vietnam[10], Thailand[89], Brazil[12], Chile[71], Indonesia[60], South Korea[36], Poland[38], Turkey[96] and the Arabian Peninsula[82]. With increasing pollution concerns, India, being amongst the most polluted countries globally, has not undermined their significance and started its path for VOC monitoring. Also, some of the industrial disasters add to these increased emissions such as the recent Vizag gas tragedy (7th May 2020) in India that led to a styrene gas leak, one of the VOCs [62, 85].

The conventional methods for VOC sampling and analytical techniques used in India have been studied from 2011 to 2020[3,4,6,20-22,24,34,39,45-48,50,55,58,64,67,69,70,72-74,76,83,91] available within the literature and are summarised in figure 4. The usual sampling methods used in India are with sorbent tubes or cartridges, air sample bags (commonly Tedlar bags), glass air sampling units and canisters.

VOC monitoring is tedious due to its nature. Also, different methods and protocols are proposed in the literature which might be confusing. Comprehensively, a summary can be offered to understand the VOC monitoring, to begin with which can increase the efficiency of sampling (Figure 2). The first and foremost step in the monitoring is to target the VOCs to be measured as they are many and source-specific. It is rare to find all the VOC at one source. Once decided, choose the suitable technique for sampling without ignoring the cost, source location, meteorological factors and distance. Then according to the method selected and the nature of VOC, the analytical techniques are to be opted (Figure 5). It will also help us to crosscheck the limitations, if any, while planning the procedure for monitoring.

Conclusion and Recommendations

Recognising the complexity of high reactivity and challenges in the detection of trace levels of VOCs in air, the selection of adequate and appropriate sampling techniques is necessary for accurate and reliable measurement. There is a need for a thorough determination of VOCs by lab-based method and therefore careful manual sampling is essential. Instrument type should be selected by considering the factors like the distance of the sample site, cost involved, weather conditions, the time-scale of the sampling and the purpose. Understanding the pros and cons of each of the analysis method types, advanced, easy yet cost-effective hand held instruments capable of active and passive measurement should be developed.

More sensitive PID sensors that are commercially available, should be chosen as per the demand and need of compounds to be detected. Intrinsically, limiting its use as they ionise all the compounds possessing ionisation energy, is less than or equal to the output of the lamp.

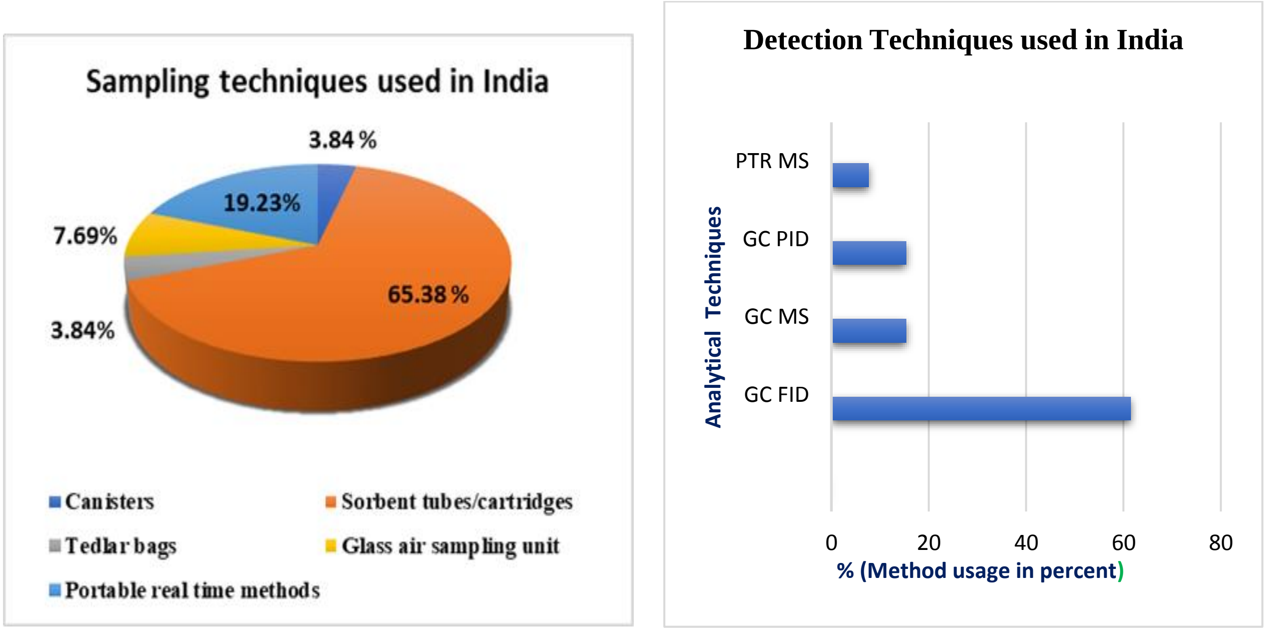
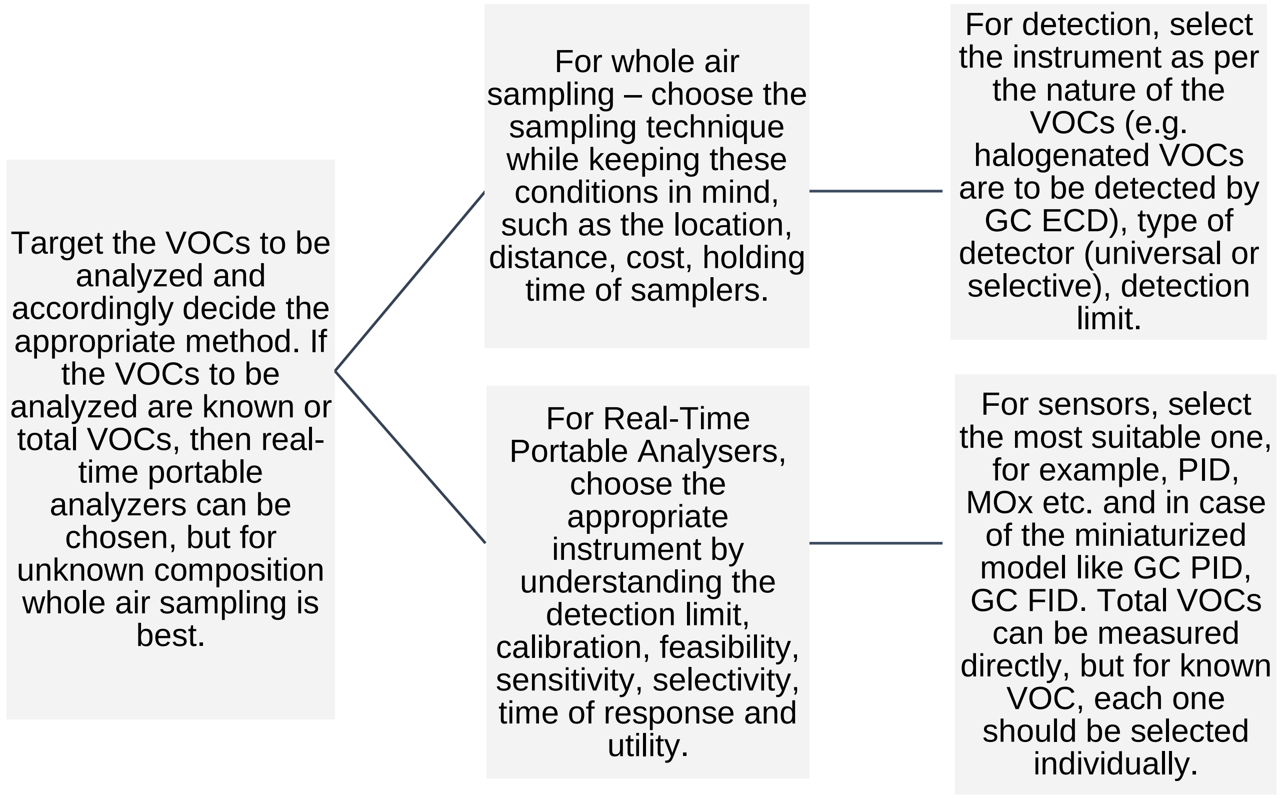


Figure 4: Classification of (A) sampling and (B) analytical techniques used in India respectively for the determination of VOCs



Target the VOCs to be analyzed and accordingly decide the appropriate method. If the VOCs to be analyzed are known or total VOCs, then real-time portable analyzers can be chosen, but for unknown composition whole air sampling is best.

For whole air sampling – choose the sampling technique while keeping these conditions in mind, such as the location, distance, cost, holding time of samplers.

For detection, select the instrument as per the nature of the VOCs (e.g. halogenated VOCs are to be detected by GC ECD), type of detector (universal or selective), detection limit.

For Real-Time Portable Analysers, choose the appropriate instrument by understanding the detection limit, calibration, feasibility, sensitivity, selectivity, time of response and utility.

For sensors, select the most suitable one, for example, PID, MOx etc. and in case of the miniaturized model like GC PID, GC FID. Total VOCs can be measured directly, but for known VOC, each one should be selected individually.

Figure 5 :Proposed prerequisite steps to be followed before VOC monitoring

Unfortunately, none of these sensors is careful to a distinct VOC In India. A commonly used method for VOC sampling is sorbent tubes. The need for R and D on more sophisticated procedures and techniques is required to enhance detection limits and to reduce the cost. The development of miniature, handy and portable instruments should be prioritised.

GC-MS provides the most reliable data compared to others; hence it should be used for more accurate results. However, portable GC is not cost-effective. Also, one can enlist the potential commercially available low-cost sensors based on the above review. A more detailed study of VOCs is needed and efforts should be made to carry out a complete analysis of VOCs along with source apportionment studies.

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