What are VOCs?

Volatile Organic Compounds (VOCs) are the organic compounds which have high vapour pressure and emitted into atmosphere by natural as well as anthropogenic sources. Measurement of VOC concentrations in the atmosphere is important to understand several of chemical processes that take place in the atmosphere and their impact on air quality, climate and health. However, the accurate measurement of VOC concentration is a difficult task considering their high volatility and low atmospheric abundance. Different techniques have been adopted for the measurement of VOCs. Gas Chromatography with Flame Ionisation Detector (GC-FID), GC-Mass Spectrometry (GC-MS), High Performance Liquid Chromatography (HPLC) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS) are some of them to name. In this article, we provide general overview of importance of VOC measurements and different techniques to measure them.

Where are the VOCs come from?

VOCs are emitted by both natural (biogenic) and man made (anthropogenic) sources. Isoprene, mono-terpenes are the examples of biogenic VOCs (BVOCs) which are emitted from vegetation whereas benzene, toluene, xylene, etc. represent the anthropogenic VOCs emitted from vehicular exhaust and fossil fuel burning. Recent estimates show global VOC emissions of around 1200-1600 Tg/yr (Bon et al. 2011). Emission inventories show isoprene
and monoterpenes as the most prominent BVOCs. Alcohols and carbonyls follow the isoprenoids as the second most predominant group (Kesselmeier and Staudt 1999). Isoprene accounts for around 65% of the biogenic and 40% of the total VOC in the global scale. On a hot sunny day, emissions of BVOCs like isoprene and mono-terpenes can be very high. In the places where there is an abundance of vegetation, the BVOCs influence will be of higher importance, whereas in urban areas anthropogenic VOCs may take over the BVOCs.

**Why VOCs knowledge is important?**

VOCs play a vital role in the chemistry of the atmosphere (Goldan et al. 1995; Sahu and Lal 2006; Lal 2007). Many VOCs are potent ozone precursors and are important components of photochemical cycles in the atmosphere (U.S. Environmental Protection Agency 1996; Monks 2005; Sahu 2012). Figure 1 shows a general pathway of VOC oxidation initiated by OH radical. VOCs directly contribute to the formation of ozone through their oxidation initiated by hydroxyl (OH) radical. Ozone at lower atmosphere is harmful as it forms the photochemical smog, which affects the human respiratory and cardio systems. Since the VOCs are emitted in large amount, they have the strong influence on regional air quality, global tropospheric chemistry and balancing the global carbon cycle (Goldan et al. 1995). They also form the base for secondary organic compounds through different reactions and contribute to the secondary organic aerosol (SOA) formation.

**Figure 1:** General pathway of VOC oxidation initiated by OH radical.
Table 1: shows U.S. Environmental Protection Agency (EPA) published list of VOCs which are recognised to be the potential ozone precursors (U.S. Environmental Protection Agency 1996).

Table 1: U.S. EPA list of potential ozone precursor VOCs

<table>
<thead>
<tr>
<th>VOC</th>
<th>p-Ethyltoluene</th>
<th>o-Xylene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>n-Heptane</td>
<td>n-Hexane</td>
<td>1-Pentene</td>
</tr>
<tr>
<td>Benzene</td>
<td>n-Heptane</td>
<td>o-Xylene</td>
<td>1-Pentene</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1-Hexene</td>
<td>Propane</td>
<td>Propylene</td>
</tr>
<tr>
<td>1-Butene</td>
<td>Isobutane</td>
<td>1,2,3-Trimethylbenzene</td>
<td></td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>Isopentane</td>
<td>1,3,5-Trimethylbenzene</td>
<td></td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>Isopentane</td>
<td>2,3,4-Trimethylpentane</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Isoprene</td>
<td>2,3,4-Trimethylpentane</td>
<td></td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>Methylcyclohexane</td>
<td>trans-2-Pentene</td>
<td></td>
</tr>
<tr>
<td>n-Decane</td>
<td>Methylcyclopentane</td>
<td>n-Propylbenzene</td>
<td></td>
</tr>
<tr>
<td>m-Diethylbenzene</td>
<td>2-Methylheptane</td>
<td>Styrene</td>
<td></td>
</tr>
<tr>
<td>p-Diethylbenzene</td>
<td>3-Methylheptane</td>
<td>Toluene</td>
<td></td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>2-Methylhexane</td>
<td>1,2,4-Trimethylbenzene</td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>3-Methylhexane</td>
<td>2,2,4-Trimethylpentane</td>
<td></td>
</tr>
<tr>
<td>2,4-Dimethylpentane</td>
<td>2-Methylpentane</td>
<td>n-Undecane</td>
<td></td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>3-Methylpentane</td>
<td>Ethylene</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>n-Nonane</td>
<td>m-Ethyltoluene</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>n-Octane</td>
<td>n-Pentane</td>
<td></td>
</tr>
<tr>
<td>o-Ethyltoluene</td>
<td>m-Xylene</td>
<td>cis-2-Pentene</td>
<td></td>
</tr>
</tbody>
</table>

VOCs also play an important role in indoor air quality as they are emitted from cooking, wall paints, paint strippers, cleaning supplies, disinfectant sprays, mosquito repellents, air fresheners, furniture, wood preservatives, glues and adhesives, deodorants, body sprays, etc. Some VOCs (such as benzene, toluene etc.) can be dangerous to human health if inhaled in large amount or exposed for a prolonged time. They can be harmful to plants and other living organisms.

Therefore, the measurement of VOCs in different environments will be of great importance for better understanding the air quality and their role in atmospheric chemistry. In particular, VOC data will provide better understanding of ozone production efficiency (OPE) and life time of radical species like OH. VOC measurements are also performed for reasons other than research interest such as regulatory compliance to decide the safe work place, assessing the health impacts, etc. Quality controlled VOC data in Indian region is a gap area in atmospheric chemistry research and needs more focus.

VOC measurement challenges and the methods commonly used

Most of the VOCs are in very low concentrations (pptv to ppbv) in the atmosphere. Therefore, the accurate quantification demands a specific technique, which has the required sensitivity to detect them at very low concentrations. It should also be selective to the target VOC, reliable and user friendly. First ever ambient VOCs measurement was ever made in
1956 (Kopppmann 2008) using a Gas Chromatography (GC) technique with Thermal Conductivity Detector (TCD). Since then different techniques have been used, among them Gas Chromatography with different detectors is one of the oldest and commonly used techniques. In recent years, other techniques which have gained significance include High Performance Liquid Chromatography (HPLC) and Proton Transfer Reaction-Mass Spectrometry (PTR-MS). Basic principles for the different analytical techniques commonly used for the VOC analysis are given below.

I. VOC analysis using Gas Chromatography coupled with Flame ionization detector (GC-FID) technique

VOC measurements using GC-FID is a two-step process. In the first step, air sample is prepared for analysis and in the second step, detection and concentration of VOCs is carried out. As mentioned before VOCs have tremendously varying volatility and low concentrations in the ambient air. Therefore, a pre-concentration is required to get their concentrations in the detectable range of the GC technique. The reduced trapping technique for pre-concentration of VOCs from ambient air has proven to be a viable approach to achieve optimum analytical sensitivity and selectivity for VOC monitoring. This is generally achieved through a cryo-trap or a thermal desorber (McClenny et al. 1984). They use specific adsorbent materials to trap and pre concentrate the VOCs from the air sample. Cryo-traps are mostly custom made according to the user needs. The sampling can be done on solid adsorbents, sample bags or canisters. Then the collected sample is drawn through the cryo-trap for the pre concentration before thermal desorbing it to the analytical instrumentation for analysis. An example has been demonstrated in Figure 2 which was used by Goldan et al. 1995. They drew ambient air using a sampling mast and then passed through ozone and water traps. Ozone and water free air sample was then passed through a cryo-trap sampling loop made of a 6-port valve kept in liquid nitrogen. After sampling a set volume, the pre-concentrated sample was injected to the GC-system using a transfer line kept at 50 °C for the separation and analysis of different compounds.

Irregular peak shapes are the results of improper injection, column overloading, gas leaks etc. Below is the comparison of different irregular peak shapes with good peaks.

<table>
<thead>
<tr>
<th>Good Peak Shape</th>
<th>Peak Tailing</th>
<th>Peak Fronting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Splitting</td>
<td>Peak Shouldering</td>
<td>Broad Peaks</td>
</tr>
</tbody>
</table>

![Comparison of different peak shapes](image-url)
The cryo-trap method is very efficient in trapping the VOCs as most of the VOC boiling points are higher than the liquid nitrogen temperature (~77 K). However, the method demands manual operation and handling of liquid nitrogen, which is risky for unskilled person. Availability of liquid nitrogen is another essential requirement to set up this method for the continuous use. Other cryogens like dry ice (solid CO2) can also be used in this method.

![Schematic Diagram](image)

**Figure 2:** Schematic diagram of the system used to measure VOCs (adapted from Goldan et al. 1995).

In the recent past, commercially available automated thermal desorption (TD) techniques becoming more and more prominent. The TD system uses a cryogen free peltier technique and offers a computer controlled operation. The computer controlled peltier heating and cooling system provides better control on cooling and heating cycles. However, the limitation is trapping temperature could not be achieved as low as liquid nitrogen temperature. Typical temperatures that can be achieved by the peltier cooling technique is around -30 to -40 °C. To overcome this limitation, the system uses modern adsorbent materials such as glass beads (or glass wool), silicon beads, selected polymers, etc. (Zlatkis et al. 1973) depending on the requirement of the analysis which allow efficient trapping even at higher temperatures. The combined effect lead to the enhanced sensitivity of the analytical system and better peak shape (Woolfenden 2012). In the process, ambient air (or collected sample) is continuously drawn through a cold trap kept at -30 to -40 °C. Once the user set volume of the gas is collected, the cold trap will be heated rapidly to release the analyte to the
GC system for the analysis. A schematic diagram of sampling and desorption phases in TD system (Broadway and Tipler 2012) is shown in Figure 3.

**Figure 3:** Schematic diagram of Thermal Desorption system: Upper part is the trapping configuration and bottom part is the desorption configuration.

The TD system is capable of trapping VOCs with chain length $C_2$-$C_{12}$ and support the real-time online analysis in the field. Following paragraph gives a brief description about the basic working principle of the GC instrument.

Gas chromatography (GC) is a well-established analytical technique generally used for separation of a mixture of chemical species and to test the purity of a particular species. The technique relies on differences in viscosity of gases to the walls of tube known as stationary phase (column). This technique is also called as gas-liquid partition chromatography and based on the column chromatography principle with a gas as the mobile phase. The sample to be analysed is introduced to the instrument in the gas or liquid phase (the “mobile phase”) through a tube that is either packed with, or coated with a material called the “stationary phase.” A stationary phase can be either a polar or non-polar material depending molecules of interest for separation. Chemical species are separated as the sample moves in the tube according to their polarity/viscosity and temperature of the column which decides their retention time of an eluted species. The temperature of the column is increased in a programmed manner (referred as analysis method) such that separation of low boiling to high boiling VOCs is achieved. Different detectors are coupled with GC to detect the separated chemical species according to the need. Flame Ionisation Detector (FID) is a
commonly used detector owing to its relatively low cost, easy maintenance and wide range of linear response. Figure 4 shows a basic schematic of GC-FID system.

![Figure 4](image)

**Figure 4:** Basic principle of GC-FID measurement (Source, Wikipedia 2015).

The analysis method in the GC system is optimized by the users according their need. Some of the recent developments have introduced a two column separation of VOCs (Broadway and Tipler 2012). In this configuration, the GC system simultaneously uses two different types of columns for the VOC separation. A basic design of two columns GC system is shown in Figure 5. Typically, VOCs of chain length C₂ to C₆ come out of primary column first but have less separation among them and are directed to the secondary column using a switching valve.

![Figure 5](image)

**Figure 5:** Basic design of the heart cut device used to separate the analyte into two columns (adapted from Agilent Technologies 2003).

The device works by the simple switching of solenoid valve mounted outside the GC oven. The analyte is injected onto the primary column. The effluent from this column normally goes to the primary Detector via the restrictor, a length of deactivated tubing. When the solenoid valve is activated to position ‘A’, gas pressure from the Pressure Control Module (PCM) switches to the ‘A’ side of the pneumatic coupler, forcing the effluent of the primary
column to go to the secondary column. This column has different separation properties, so that compounds that do not separate on the primary column may separate on the secondary column.

**Figure 6:** The separation and detection of USEPA listed ozone precursor VOCs on two different columns using Perkin Elmer ozone precursor analyser (adapted from Broadway and Tipler 2012).
Typically, the primary column is a packed column consisting dimethyl siloxane used for the heavier VOCs like hexane and higher hydrocarbons. The secondary column is a retentive Porous Layer Open Tubular (PLOT) capillary column made out of alumina material, used for the separation of highly volatile compounds such as ethane, ethylene, acetylene etc. Figure 6 shows a general example for the chromatographic separation of USEPA listed ozone precursor VOCs on two different columns using Perkin Elmer ozone precursor analyser using a standard VOC mixture (Broadway and Tipler 2012).

II. VOC analysis using High Performance Liquid Chromatography (HPLC)

HPLC is an improved form of liquid column chromatography. In traditional liquid column chromatography, the solvent is allowed to drip through a packed column under gravity, instead in HPLC it is forced through under high pressures of up to 400 atmospheres. This results in much faster elution, better separation and detection. Figure 7 shows a schematic diagram of HPLC. Instrument contains a solvent reservoir (mobile phase), pump to generate high pressure, a HPLC tube packed with adsorbent material (stationary phase), detector and computer for signal processing. Different compounds have different retention times depending on the pressure used (because that affects the flow rate of the solvent), the nature of the stationary phase (not only what material it is made of, but also particle size), solvent mixture composition and column temperature. Ultra Violet (UV) detector is the most commonly used detector because most of the organic compounds absorb UV radiation.

![Schematic diagram of HPLC](image-url)
HPLC is generally used to measure oxygenated VOCs (OVOCs) such as aldehydes, ketones, esters, enones and carboxylic acids (also called carbonyl compounds) (Zielinska et al. 1996). The ambient air sample is drawn through a sampling tube containing 2, 4-dinitrophenylhydrazine (DNPH). The carbonyl compounds present in the air sample will react with DNPH to produce corresponding derivative. The resulted derivative is eluted out of sampling cartridge using a solvent such as acetonitrile and injected into HPLC system for the detection of VOCs (Kesselmeier et al. 2000). The general reaction scheme of DNPH with carbonyl compounds is given below.

III. VOC analysis using Proton Transfer Reaction Mass Spectrometry (PTR-MS)

There are some key disadvantages of using GC based techniques. The GC requires relatively large amount of sample and long analytical time and hence may not reflect the fast changes in the air composition. Alternatively, the proton transfer reaction-mass spectrometry (PTR-MS) technique is very sensitive and used for rapid online measurements of VOCs in laboratory and fields. PTR-MS technique is a relatively new technique commonly used for the online measurements of VOCs analysis. The technique first developed at Institute of Ion Physics of Innsbruck University in 1998 by Lindinger et al. 1998. This has the some advantages over the other methods like no pre-concentration requirements, direct on-line sampling, rapid response time, soft chemical ionisation, absolute quantification and very high sensitivity. The detection limit can be in the order of few pptv (parts per trillion by volume) (Lindinger and Jordan 1998; Taipale et al. 2008). A standard PTR-MS instrument consists of an ion source, a drift tube and mass detection system. Figure 8 shows a schematic representation of the configuration of PTR-MS instrument.
Figure 8: PTR-MS schematic representation (adapted from Takita et al. 2007).

Chemical ionisation method is much softer compared to the traditional electronic ionisation and hence eliminates the need of prior separation of VOCs with techniques like GC/HPLC. To achieve the chemical ionisation, first the hydronium (H$_3$O$^+$) ion is produced in a hollow cathode tube by ionising the water vapour. The resulted H$_3$O$^+$ ion then reacts with VOCs resulting in the ions of respective VOCs (VOC + H$_3$O$^+$ -> VOCH$^+$+H$_2$O) which is called the proton transfer reaction and takes place in the drift tube. Resulted ions will then travel to mass detector through a Quadrupole (Quad) or Time of Flight (ToF) mass spectrometer (MS) at different speeds according to their molecular weight. In the quadrupole mass analyser there are four parallel metal rods making two electronically opposing pairs.

The electric field oscillates between the opposing pair. Ions with a certain m/z ratio make a stable trajectory for a given ratio of voltages and pass through to the detector (more details on quadrupole ion trapping can be found in Rao et al. 2001). Others will collide with the rods. In case of ToF the ions are accelerated with a known strength electric field. This brings the ions with the same charge on same kinetic energy. Then they are allowed to travel through a flight tube where the velocity of each ion determined by its m/z ratio. The time taken by the ion to reach the detector is used to calculate the m/z of that ion and hence the detection. This technique is well adapted now and can be used for monitoring a variety of VOCs. Figure 9 shows an example PTR-MS spectrum of a laboratory air sample.
Figure 9: Example PTR-MS spectrum measured at PRL, Ahmadabad using IONICON PTR-TOF 8000 instrument.

Except for isomers, each mass-to-charge ratio (m/z) corresponds to different compounds. For example, in PTR-TOF-MS, m/z values of 59.0497 and 69.0704 correspond to acetone and isoprene, respectively (Sahu and Saxena 2015). Operational complications are very less in PTR-MS because it needs only small amount of distilled water and electrical power to operate. This is also a compact and portable instrument. The PTR-TOF-MS are capable to separate the contributions of isobaric pairs such isoprene and furan owing to the high mass resolution of PTR-TOF-MS. It is an important advantage of TOF compared to PTR-Quad-MS based measurements of VOCs (Sahu et al. 2016)).

Epilogue

To summarise, in the present paper we have made an attempt to highlight the importance of VOCs in the atmosphere. The role of VOCs in atmospheric chemistry, measurement challenges and different methods are discussed. Quality controlled VOC analysis is one of the challenges atmospheric science community is yet to find the complete answer. For example, Renuka et al. 2014 using a box model have shown that, observed ozone concentrations are higher for a rural atmosphere which can only be explained by the inclusion of BVOC concentrations in the model. Further, they have also found that ozone concentrations over last decade have not increased in spite of increase in population and other activities over large part of Southern India. This could be related to the changes in vegetation cover and emission of BVOC from them. However, in the absence of accurate BVOC measurements from rural atmosphere this would be just a speculation. This makes it a very interesting gap area and encourages more and more research especially in Indian tropical region.
Suggested Readings


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