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## **Volatile Organic Compounds: Classification, Sampling, Extraction, Analysis and Health Impacts**

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**Abstract** Volatile organic compounds are those that are present in the air having the low boiling points and easily evaporated. These are classified into three categories: volatile, semi-volatile and very volatile compounds. They can be collected by the passive and air sampling or grab and integrated sampling. Mostly, they are collected in tedlar bags made up of Teflon or canisters or can be adsorbed on adsorption tubes. These organic compounds are characterized by the GC-MS, MS, thermal conductivity and electron impact ionization techniques. These compounds are very dangerous and cause many diseases in organisms like urine, blood, lung and skin irritation.

**Keywords** VOCs, Sampling, Extraction, Health impacts, Analysis

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### **Introduction**

Different scientists and organizations define the volatile organic compounds by the different ways and can be described as:

#### **Volatile Organic Compounds**

Those chemicals have hydrogen, oxygen, carbon and some gases. Another way of defining is those compounds which are highly photo-chemically reactive and volatile in nature.

#### **According to Lincoln (1998)**

"Volatile organic compounds are those which are released in air due to natural emission and anthropogenic. Due to their participation in photochemical pollution, these are very helpful." **According to Art (1993)**

"These are Hydrocarbons having low boiling points (less than 100 °C) and evaporated easily". Examples of volatile organic compounds are Benzene, propane, gasoline etc.

#### **According to World Health Organization (WHO)**

Definition of VOC by WHO is totally based on boiling points. "Any compound that have Carbon, Hydrogen and its boiling point is in the range of 0 °C to 50 °C called very volatile organic compound. Any organic compound that have boiling point in the range of 50-100 °C to 240-260 °C is called Volatile organic compound".

#### **According to International Standard Developing Organization (ASTM)**

Any organic compound that is evaporated under the specified set of test conditions is called VOC and other volatile solvents like *p*-chlorobenzotrifluoride, methylene chloride etc. and water are not incorporated in VOC [2-5].

#### **According to United Nations Economic Commission for Europe (UNECE)**

"All the organic compounds that are manmade are able to produce the oxidants products by the reaction of sunlight with nitrogen oxides are called VOC" (2-5).



**According to USEPA**

All those compounds that have carbon atom in their structure or those compounds which take part in photochemical reactions like Carbon dioxide, Carbon monoxide, Carbonates, Ammonium Carbonates and Carbides of metals (2-9).

**According to European Union**

This definition related to Indoor Air Quality. "Volatile organic compounds are those compounds that are produced by manmade activities other than those that produced the photochemical oxidants that are emitted by the reaction of sunlight with nitrogenous oxides" [2-9].

**International Organization for Standardization**

Those organic compounds those are present in offices, homes and in buildings that are under construction and emit the organic compounds [2-5].

**Sources of VOCs**

Solvents, wood preservatives, paints, paint strippers, cleansers, moth repellents, disinfectants, stored fuels, air freshners, dry cleaned clothing, automotive products etc [9]. In our homes, many products release the gases. Some examples of VOC's that are produced by the different sources are shown in the tables 1.

**Table 1:** Sources of volatile organic compounds

Description	Sources
Building materials	Solvents, Paints, Varnishes, Vinyl floors, Wood products, Carpets and Adhesives
Home and personal care products	Air cleaners, Air fresheners, Cosmetics, Moth balls, Vehicle exhaust, Fuel oil, Nail polish
Behaviours	Hobbies, Newspapers, Cooking, Smoking and Photocopiers

**Different types of VOC**

There are following different types of VOC's that are categorized by the two ways on the bases of boiling points of chemicals and that of sources.

**On the base of boiling points****Very volatile organic compounds (VVOOC)**

Very volatile organic compounds (VVOOCs) are very volatile and their measurement is so difficult and mostly found in atmosphere and not on surfaces and in materials. These having boiling point 0 to 50-100 °C. Examples are methyl chloride, propane etc [10].

**Volatile organic compounds: (VOC)**

Those compounds that include carbon having the boiling point less than 250 °C at the 101.3 kPa pressure. Examples are acetone, ethanol, toluene etc [10].

**Semi volatile organic compounds: (SVOC)**

Those organic compounds which having higher boiling point than water (240- 400 °C) and vapourized in air at room temperature. Examples are polynuclear aromatic hydrides, phenol etc [10]. These categories are shown in table 2:

**Table 2:** Classification of VOCs

Types	Boiling points (°C )	Examples
VVOOC	< 0 to 100	Propane, methyl chloride
VOC	< 250	Ethanol, methanol, toluene
SVOC	240 to 400	Phenol, pesticides (DDT), cosmetics

**Different types of VOC on the bases of sources****Natural VOC's**

These compounds are essential part of life. These are emitted from the oxidation of organic matter by bacteria or the biodegradation process and produced carbon dioxide and methane. These are obtained by the gaseous emission by the conifers and deciduous trees, flower perfume and from our own respiration. Isoprene, terpenes, molds, microbes, fungi are important VOC's in large amount at biological level.



**Human-made or Anthropogenic VOC**

Volatile organic compounds are also produced by the human activities. These are emitted by the production of hydrocarbons such as solvent evaporation, industrial combustion, painting and oil refining etc.

**Air Samples**

Air samples and sampling methods can be categorized by the type of pollutant, emission source or by the air. Air sample sources have five types: mobile sources, soil sources, indoor air, stationary sources, ambient sources, Indoor air samples. Indoor air samples are collected from homes, office buildings, industrial facilities and work place environment.

**Ambient Air Samples**

Ambient samples are collected at ambient temperature and humidity from suspected sources, outdoor locations, manufacturing facilities and soil remediation sites.

**Stationary Samples**

Stationary source samples are collected from indoors and outdoors locations in industrial settings. But they may be collected from the single point source emission like exhaust stock, manufacturing facilities, soil vapour extraction and power plants.

**Soil Vapor Samples**

The samples are collected in fixed and field based laboratories. Soil vapour samples are mostly used by engineers in investigations. Ambient air and soil vapour method of sampling are mostly used for air sampling.

**Sampling Techniques**

There are different techniques of sampling but active and passive method of sampling are very important for the collection of air samples. Collection of whole air samples can be taken as a grab sample (taken over short period of time, usually < 5 minutes) or as an integrated sample (taken over a longer period of time, usually ½ hour to 24 hours).

**Grab Sampling**

Collection of sample can be taken as Grab Sample in which sample is taken over a small time of period usually it will be less than 5 min. Grab sampling is required in those conditions when sample collected quickly or in which the composition of gases that are present in air and does not changes over time. Grab sampling is mostly used for the analysis of particular interest of contaminants during short period of time and provides the limited qualitative information about absence or presence of interested particles. Draeger tubes, tedlar bags are mostly used for this process. It is also called short term sampling. This type of sampling is performed over 15-30 minutes and described about exposing peaks within a shift. Passive dosimetry, direct reading instruments are used for the grab sampling of air.

**Integrated Sampling**

In this type of sampling, sample is taken over large time periods but this is preferred when the composition of samples changes over time. In this, sample handling is required. It is also called full-shift term sampling. Full-shift sampling is performed over 8 hours shift or 10-12 hours shift and used to describe the average contaminants concentration. This type of sampling is completed with multi media and passive dosimetry, integrated air sampling equipment and direct reading equipments are used for the study of full-shift exposure sampling. Integrated sampling includes amount of contaminants and extraction is based on condensation, adsorption, and absorption principles.

**Condensation**

This process is used for the collection of gaseous materials in the form of solids or liquids for the identification process. It is also used for the collection of those samples which cannot be collected by other techniques like sulphur dioxide [11]. The collectors or collection traps are double walled collectors and air is passing between the walls and analytes are immersed in acetone, liquid nitrogen and in ice bath. During the sampling periods of condensation of gas vapours, pressure (1mmHg) and temperature should be lowered. The advantage of this method is to prevent the sample from chemical reaction with other species and condensation of sample analytes. The main



disadvantage of this method is the condensation of other contaminants with major specie or contaminants and these adsorbed contaminants are extracted by different techniques [12].

### **Adsorption**

This is most common air sampling method which is used for the collection of unreactive and trace amount of gases adsorbed on solid absorbent bed. Some solid absorbents are charcoal, porous polymer beads, molecular sieves and activated alumina [13].

The principle of adsorption is that air (gas) is passing through the packing tube having the sorbent material and the molecules of contaminants are chemically adsorbed on the surface of sorbent material. The adsorbents have polar and non-polar properties and polar sorbents are considered mostly because they have attraction for polar and non-polar contaminants. Silica gel is a polar sorbent and formed by the reaction of sulphuric acid and sodium silicate. It is amorphous form of silica. It attracts the charged particles towards itself and having the polar characteristics. The main advantages for silica gel are that it is important for the collection of inorganic contaminants that are present in air and also, it is useful for desorption of contaminants in solvents. The disadvantage of silica gel is its polarity, due to the polarity of silica gel, water is remaining adsorbed on its surface and moisture will be present in desired analyte [14].

Charcoal is formed by the burning of animal bones, woods etc. and it is amorphous form of carbon. It is most common solid sorbent. It has large internal surface area and non-polar in nature and adsorbed the only organic molecules in large amount. Inorganic and organic molecules like hydrogen sulfide, amine, ozone, nitrogen sulphide and oxides are easily adsorbed on it [15]. Impregnated solid sorbents are used for the collection of soluble, reactive and polar types of contaminants. The principal of impregnated solid sorbent is that collection of gases in special solid sorbent tubes and changes into ions. Ionic form of vapour and gas can be analyzed through the ion chromatography. In this technique, contaminated sample is passed through ion exchange column in which contaminants are adsorbed. To remove the unwanted contaminants, eluent is passed through the second ion exchange column and desired ions were detected through detector. Passive dosimeters: A new technique that is used for the collection of inorganic and organic samples. This method has low cost and unit, require no sample pump and sorbent tubes are used for the collection of sample. GC technique can be used for the analysis of sample. Passive dosimetry used the first law of diffusion of Fick's law. The basic condition is production of concentration gradient [16]. The concentration of contaminants on the edges is ambient and on the surface is zero then concentration gradient produces and diffusion occurs at constant rate [17]. Passive dosimeter is used for the collection of nitrogen oxide, aniline and sulfur dioxide [18].

### **Absorption**

In this method [19], gas contaminants are collected from atmosphere and formed the solution of the gas contaminant with absorbing reagent. Spiral and helical absorber, simple gas-wash bottles, glass beaded columns and fritted bubblers are used. Spiral type absorbers are similar to gas wash bottles that are used for the collection of gaseous sample. The efficiency of spiral type absorber is higher due to the spiral or helical structure of design. It takes 5-10 times more than simple wash bottles and the retention time is of gas with absorber solution is also higher. Simple wash bottles are used for the collection of nonreactive vapours of gases that are soluble in absorbers and formed the soluble solution. Examples are midget impinger and green berg smith. Efficiency of simple wash bottles can be achieved by the reactivity of sample with absorbing liquid [20]. Glass beaded column scan be used in those conditions in which higher concentration of gaseous sample is required. These columns are coated with special absorbing medium. A bead provides the large surface area for the collection of large volume of air contaminants. This method is used for the collection of hydrocarbon and benzene vapours in nitric acid solution [21]. Fritted bubblers are used in ambient atmosphere condition for the collection of air samples. They have greater efficiency for collection than all other absorbers [22].

### **Active Sampling**

This is also called solid sorbent sampling. In this type of sampling, gas or air sample is actively drawn into sampling media or pumped into sampling media. This sampling is important for semi volatile and volatile compounds like PCBS or pesticides, polycyclic aromatic hydrocarbons (PAHs), ammonia, aldehydes, carboxylic acids and amines.



Sampling media can be adsorbent tubes (thermal desorption tubes and solvent desorption tubes), cassettes and filters. For the capturing of desired analyte, this sampling type guaranteed low interference and sufficient capacity. ATIS adsorbent tube injector, tubes for mercury vapor sampling and DNPH sampling products are the complete range products of this sampling. Electricity pumps are used in it. So, it is more costly sampling [3, 23-24].

### **Passive Sampling**

Passive sampling is also called diffusive sampling. In this type of sampling, gaseous molecules are adsorbed on adsorbent through diffusion. This sampling type is cheaper due to simpler use and requiring no electricity pumps and moving parts and its results are comparable to active sampling [3, 24].

### **Whole Air Sampling**

This type of sampling is simplest; it means to collect the air sample in bags and is required in those conditions when air has much contaminant. The desired particles are collected directly from vessel. Vapour pressure, surface area of vessel, matrix effect and chemistry of contaminants are factors that influence the collection rate. Bulbs, Gas sampling bags, Summa canister and tedlar bags are used for this purpose [23].

### **Impinger Sampling**

This is similar to solid sorbent sampling and by liquid impingers airborne contaminants are sampled. It is commonly used for the determination of various stationary contaminants sources (ammonia, aldehydes, halogen and halogen halide etc.) at high temperature and moisture level.

### **Filter Sampling**

Aerosol contaminants or vapour phase samples are collected by using filter cassettes. In this type, the filter media chemically reacts with vapour phase contaminants to form stable products. This is mostly used for the inorganic species and particulate matter like metals that is similar to filter solid sorbent sampling. Instruments for whole air, active and passive sampling are shown in Figure 1.



*Figure 1: whole air sampling, passive sampling, active sampling instrument*

## **Air sampling Medias**

### **Introduction to Canisters**

For air sampling, containers are used for sample collection. The containers are made up by stainless steel and have cylindrical or spherical shape. Valves are used for the regulation of air samples. Flow controllers are used for the collection of desired samples. Valves are closed after the collection of sample. Almost 1-6 liter sample has collected in the container. For the ambient air sample, 6L containers are used. For soil vapor, 1 liter containers are used.

### **Summa Canister**

Summa canisters are formed by Summa process in which electro polishing step combined with chemical deactivation step to produce a chemically inert surface having bright, shiny and smooth surface. Summa canisters are constructed by stainless steel. Certain gases like CO, CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> are collected in it. Stability of analytes and gases in it for 30 days. Summa has wide size range (400 ml to 6l). They can be used for grab and integrated sampling [25-27].

### **Introduction to Bags**

Air sampling bags are used to collect sample for soil gas, stationary source and landfill gas samples. They are formed from different materials that have different stability properties. They are helpful for those analysis in which the range of sample is in ppm. They are specially used for the sulphur containing compounds.



**Tedlar bags**

It is a polyvinyl fluoride film formed in 1960's and helpful due to various applications [6]. Nalofan is formed by polyterephthalic ester and Teflon is formed by propylene copolymer and fluorinated ethylene. It has mechanical properties, flexible, tough over 200 °F. It shows good chemical inertness, good resistance and low permeability. Tedlar bags requires pump for sampling. They can be used for the collection of various samples like hydrocarbons, solvents, atmospheric and biogenic gases and chlorinated solvents etc. Naphthalene that has low vapour pressure cannot be collected in these bags due to their low recovery in short time period. Hydrogen and Helium have low molecular weight so they can also be diffused from them and bags show the low storage stability. Stability of analytes and gases is 1-3 days in it. Tedlar bags are easy for handling and transportation and are less expensive (10, 28). Table 3 shows the different properties of summa canisters and tedlar bags:

**Table 3:** Differentiate between the Summa canisters and Tedlar bags

Properties	Summa canisters	Tedlar bags
Analysis holding time	1-30 days	1-3 days
Surface inertness	Excellent	good
Volume of Sample	400 ml to 6 liters	ppm
Advantage	Long holding time	cheap

**Sorbent tubes**

Sorbent tubes are used for the collection of ambient and indoor air. These tubes are made up from glass and stainless steel and save the time and cost. These are suitable for the pumping and diffused sampling. For the long storage stability of samples and product, they are very important and helpful. These are reusable sampling devices. Sample collected in the amount of ppt to ppm in desorption tubes. These desorption tubes are useful for the analysis of large amount of sample (>100 ppb). So, these have greater efficiency (>99.95%) than canisters. Due to absorption ability, they removed the moisture and helpful before the GC injection (29). Table 4 shows the different properties of desorption tube and canisters:

**Table 4:** Difference between the canisters and desorption tube

S. No.	Desorption tubes	Canisters
1	They contain the sample volume ppt to ppm.	They contain the sample volume 400ml to 6 liters.
2	They save the sample and product up to 30 days.	They save sample volume for 30 days.
3	They are made up from glass and stainless steel.	They are made up from stainless steel.
4	They are suitable for diffused and pumped sampling.	They are suitable for grab sampling.
5	They have maximum inertness surface due to the glass surface.	They have less inertness than desorption tubes due to the stainless steel.
6	They can be cleaned automatically.	They cannot be cleaned easily. Their cleaning requires air purges and evacuation at elevated temperature.
7	Desorption tubes are used for the collection of less volatile (polar and non-polar) compounds.	Canisters are used for the collection of non-polar and very volatile compounds.
8	They saves the time and cost. ( \$50-130 each)	Canisters are costly. (\$200-700 each )
9	They are reusable and having more efficiency.	They are less efficient for collection.
10	Only single sample injection is used for analysis.	Multiple sample injection is used for analysis.

**Sampling analytes from atmospheric air**

For the improvement of air sampling analytes, there are three main principle methods for the collection of sampling analytes from the atmospheric air:

- Passive technique



- Denuder technique
- Dynamic techniques

### **Passive techniques**

The first passive technique was conducted in 1973 that having the two types:

- Permeation is for the detection of Sulfoxides analytes in air [30].
- Diffusion is used for the detection of nitrogen analytes in air [31].

Passive technique was introduced in 1873 by Swiss analyst Schoenbein when he is analyzing the ozone particles in atmospheric air. In the diffusion process, the absorption of analyte occurred on the sorbent bed in the passive dosimetry as a function of exposure time and concentration of analyte. Passive dosimetry technique can be used to monitor the analyte in soil, air and water. The process of migration takes place due to the difference of potential between the interior dosimeter and retention medium [32]. The analyte transport to the interior of dosimeter due to the process of permeation by the semi-permeable membrane and through free diffusion layer. Chemical or physical sorption takes place for the retention of analytes on sorption bed. Chemical sorption takes place by the process of thermal desorption. 2,4-dinitrophenylhydrazine is the example of chemical adsorption used in HPLC. The rate of Physical adsorption is greater than chemical adsorption [5].

### **Denuder techniques**

This type of technique is used to determine the diffusion coefficient of sulphur dioxide in 1971 and this technique is also used to determine the organic and inorganic pollutants in air. It consists the features of passive and dynamic sampling. Denuder wall is coated with sorption medium and a flow of gas is applied for the diffusion of air analytes on the walls of the denuder and continues to the process of equilibrium. The process of diffusion depends on the type of denuder and intensity of air flow. Cylindrical denuder is commonly used and is simplest. Another type is suspended-drop denuder in which solvent drops are used for the retention of analytes. It forms a needle like syringe for the diffusion of solvent to VOC. The advantage of denuder sampling is filtration of contaminants and exact amounts of contaminants or matter is obtained [5, 33].

### **Dynamic techniques**

In this sampling analyte technique, flow of gas is passed in the course of tube having the sorbent bed with the help of calibrated pump instrument [34]. In this method, flow of gas is used to disperse the analyte particles. Mostly graphitized carbon black, porous polymers, activated carbon [35]. Sphero-carb, carbopack B, Tenax TA etc. are used as sorbents. Sulphur compounds are not sorbed on this sorption beds due to their decomposition. Solvent extraction or thermal desorption techniques are used for the release of retained analytes. It depends upon the enrichment of analyte molecules, volume of gas and can taken few minutes to 24 hours. Target analytes that are basically volatile unsaturated hydrocarbons can be lost due to the presence of water. Sometimes sorption bed containing the desiccant like magnesium carbonate ( $MgCO_3$ ),  $CaCl_2$ ,  $K_2CO_3$  etc. are used for determining the organic compounds in air. Benzene can be determined in air by using the silica gel as desiccators [36]. There are two basic types of desiccators that are inorganic and organic and used as air driers: first is the Permeation and second is Membrane.

Permeation driers are constructed from Nafion, used as nafion tubes and they remove water in the form of water of hydration through absorption. It is a synthetic material of tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid copolymer. This is particularly chemically inert, having excellent hydration properties due to the presence of sulfonic groups and like a Teflon. It can absorb 22% water which means that there are 13 water molecules for each sulphonic group. Nafion tubes remove the water molecules selectively and continuously from gas samplers. Liquid nitrogen is used to remove the interference of water and increased cryogenicity and takes place at  $<150$  °C. So, analytes sorbed on solid sorbent takes place at low temperature. When the dew point (the point or temperature at which the water vapour condenses) is lowered then desiccation occurs in membrane driers, a compressed flow of gas (air) is passed through the microfiber membranes and water vapours diffuse through these membranes and collected on the outer surface (5).

### **Direct-reading instruments for VOC's**

There are three types of direct reading instruments that are used for the analysis or detection of VOC's:

- PID ( Photoionization detector)



- PAS ( Photo-acoustic sensors)
- FID ( Flame-ionization detector)

### **Principles of measurement**

#### **Photoionization detector (PID)**

In the PID, UV radiations are used for the ionization of volatile organic compounds. UV lamps emits the energy that is enough to ionize some molecules of VOC's but mostly are not ionized that are chlorinated molecules. Due to the order of magnitude, PID is more sensitive than FID. PID showed the response in the form of total volatile organic compound (TVOC). So, it is less stable than FID. It is simple to use and sample will not be destroyed. The disadvantages of PID are highly variable responses and contamination present.

#### **Photo- acoustic sensors (PAS)**

It is also called photo-acoustic infrared detector. In this detector, infrared radiations are absorbed by volatile organic compounds and variation in pressure of organic compounds is detected and acoustic signal is observed by microphones and the resultant temperature. This is obtained by the variation of acoustic frequency with intensity of infrared radiation. PAS response is dependent upon the infrared radiation and entrance of vapours of methane and water with response. This is non-destructive technique because it does not change the sample into gas.

#### **Flame ionization detector (FID)**

In this type of detector, ions are produced by the burning of volatile organic compound with hydrogen flame. Ions are produced by this burning and attracted towards the collector electrode. Due to the production of ions, electric current generated. Number of carbon atoms and structure of volatile organic compounds influence the signal intensity. It is most commonly used detector and detects the large number of volatile organic compounds. It is stable detector. The advantages of FID are insensitive to carbon dioxide, carbon monoxide and water. It is very costly due to hydrogen as a fuel, rugged and gives linear response over a wide range.

#### **Electron capture detectors (ECD)**

In this type of detector, low energy beta emitter  $^{63}\text{Ni}$  is present. Molecules that are present in sample absorb the electrons and electron attracted towards the positive electrode and current reduces. This is important for the nitrogen containing and halogens compounds. The advantage of electron capture detectors are femtogram is in ppt level and more sensitive than FID. The major draw backs are oxygen contamination issues, give the strong response for temperature, pressure and have limited linear range than FID.

#### **Advantages of direct reading instruments**

- These instruments are easy to use and in handling.
- They detect the rapid changes concentration of analyte.

#### **Limitations of direct reading instruments**

- They can response only for VOC and VVOC and other contaminant species.
- The signal obtained from these detectors explain only quantitative information and does not explain the qualitative information [5].

#### **Method of extraction**

The methods of extractions are performed for the further analysis of volatile organic compounds. These methods of extractions are: Thermal desorption, Solvent extraction, Solid phase micro-extraction etc.

#### **Thermal desorption method**

Thermal desorption, a method of extraction is very effective method from solid sorbent. It is a non-destructive method in which solid sorbent is exposed to sampling tube at high temperature (200 to 380 °C). This all process depends upon the properties of solid sorbent and desired volatile organic compounds are desorbed on the solid sorbent and collected. This collected desired VOC's are used for further analysis. Cryogenic focus trap is a type of thermal desorption method of extraction [3].

#### **Solvent extraction method**

In this method, volatile organic compounds are dissolved in liquid solvent for pre-concentration. For the conversion of analytes into products, derivatization reagents are used for further detection. This method is very important for the separation of carbonyl compounds and converted it into hydrazone, in which (DNPH) 2,4-diphenylhydrazide is used



as derivatization reagent. These hydrozones can be analyzed through Fluorescence, UV-Vis and HPLC techniques. Florisil, silica gel are widely used instead of DNPH for the collection of these carbonyl compounds. This method has limited sensitivity due to time consumption [37].

#### **Solid phase micro-extraction techniques: (SPME)**

In this technique, partitioning equilibrium is established between the stationary phase and sample matrix. The stationary phase is usually used like fiber or fused silica and stationary phase existed in wide variety of polarity. For the determination of chlorobenzene in air, adsorbent cartridges are used by Barro *et al.* [38]. This method gives the high output for the analysis of VOC at sub level ( $\text{ngm}^{-3}$ ). It is an important technique, in which pre-concentration of analytes and sampling takes place in one step. Adsorption takes place on fine fiber. This fiber is transported to the syringe needle. The fiber is coated with the sorbent material and used for the recovery of volatile organic compounds. Addition of reactive chemicals like amines and formaldehyde form the derivatives. Then this fiber can be injected into the heated zone of the injector port, where the analytes are adsorbed thermally. This is used for the determination of hydrocarbons from mixtures. This technique is very important for the following advantages, reagents are not required for desorption. Sensitivity is very good, sampling device is compact and light weight shows the linear response with concentration, independent of humidity, expensive thermal desorbers are not required. The major draw backs are that samples are not time integrated, gas standard are required for calibration, whole sample is used and storage stability is poor [39-40].

#### **Membrane extraction**

This technique is mostly used for the monitoring of indoor analytes or for passive sampling. Single and multi-membrane devices are used for the transfer of desired analytes from the donor phase to acceptor phase [41-42].

#### **Chemical desorption**

In the chemical desorption, activated charcoal is used with appropriate solvent in solid sorbent. Acetonitrile, carbon disulphide and methanol are mostly used for this purpose. For the desorption of VOC's on the sorbent 1-2ml solvent is used and kept for 45-60 minutes for desorption [43-44].

#### **Method of analysis**

These are following methods that are used for the analysis of volatile organic compounds. Like gas chromatography that is commonly used for the analysis of compounds. In this technique, Stationary phase is adsorbed on the inner side of the column and target molecules or analytes are adsorbed on it and separated by the inert mobile phase. Controlling the column temperature, separation of VOC's is done better and volatile organic compounds are separated by their structure, polarity and molecular based physical properties.

#### **Gas chromatography-mass spectrometry**

In this technique, a fused silica column is used and temperature of detector and injector is 260 °C. All the carrier gas is constructed from copper tubing and stainless steel. For this purpose, Buna-rubber or Non-polytetrafluoroethylene is used. In the chromatographic columns, 5 % phenyl, 95 % methyl silicone or 100 % methyl-silicone are used as absorbent. The capillary columns has diameter of 0.25-0.53 mm and non-polar compounds can also be separated by this technique. In mass spectrometry, linear quadrupole or ion trap mass spectrometer is used for the separation of volatile compounds. They have capability of scanning from 35 to 300 amu in every one second by using the 70 volts. The quadrupole consists of four electrodes like rods placed in square structure. Direct current and radiofrequency potentials are used between the electrodes. Ions are generated and moves in parallel way under the production of generated field and their  $m/z$  values are calculated. Only 0.1-0.2 % ions are detected through the detector [45-46].

#### **Mass spectrometry**

When high voltage is applied on the gas molecules then the ionization takes place in which the gas molecules changes into ions or fragments. These ions are entrapped and flow in a beam. This ion beam is subjected to the magnetic field and deflected from their path. The degree of deflection shows the charge to mass ratio of the fragments. This technique requires the sample in small size (microliters). Hydrocarbons, ozone, carbon monoxide, carbon dioxide, nitrogen oxide, nitrogen dioxide and sulphur dioxide are detected by this technique [45-46].



**Voltammetric**

A potential difference is produced between the reference electrode and sensing electrode. The gas molecules carried the current and linked between these electrodes. The gas molecules have charges or ionic and migrate towards the sensing electrode. Then current is flowed between the electrodes or through the system. This flowing of current shows the amount of contaminant or volatile organic compounds. Hydrogen sulphide, carbon monoxide and sulphur dioxide are detected by this technique [45-46].

**Electron impact ionization**

It is also called the electron ionization and it is oldest method. In this technique, an electron beam (70eV, Rhenium or Tungsten) is passed through the sample. These electrons colloid with the sample molecules in the form of positive ion or molecular ion, called the fragment ion and detected by the means of photomultiplier tubes. The amount of sample is taken less than 1000 Da. This method is important due to determining of volatile organic compounds, fragmentation structural information and well understood. The major draw backs of this method are that the molecular ion peak may be present or absent in volatile organic compounds and sample must be stable and thermally volatile. Methane, CO, CO<sub>2</sub> etc. are detected by this method [45-46].

**Thermal conductivity**

Current is passed through a wire and wire is heated. A carrier gas stream is passing over the heated wire and the rate of current is equal to the amount of heat produced. At this process, the wire temperature and resistant will be constant. If volatile organic compounds will be added in the carrier gas stream then the amount of heat will be change and as a result the resistance and temperature will also change. From this, change in resistance will be measured and concentration of volatile organic compounds will be determined. Helium, oxygen, carbon monoxide, methane, aromatics, chlorine, hydrocarbons are analyzed by this method [45-46]. Some analytes and analysis techniques are summarized in Table 5.

**Table 5:** Analytes and their analysis techniques

S. No.	Analytes	Sampling media	Analysis technique	References
1	Vehicle exhaust, (benzene, toluene, m,p-xylene etc.)	Glass linked stainless tubes		[10]
2	Air of residences and buildings		SPME, GC-MS	[47]
3	C1-C6, C5-C10	Sorbent tube	Gas chromatography	[48]
4	C5-C10, C2-C6	Sorbent tube	Programmed Temperature Vaporization Injection	[49]
5	Sulphur dioxide	Absorbing reagent...sodium tetrachloromercurate...	colorimetric	[50, 51]
6	Nitrogen oxides	Midget impinger	Volumetric method	[52]
7	Benzene, toluene and xylene	Sorbent tubes	Gas chromatography	[53]
8	formaldehyde, methanol, acetaldehyde, acetone, isoprene/methylbutenol fragment, methylbutenol, hexanal, hexenal and monoterpenes	Sorbent tube made up from Teflon	disjunct-eddy-covariance (DEC), surface-layer-gradient (SLG), and surface-layer-profile (SLP) methods with proton transfer reaction mass spectrometry (PTR-MS)	[54]
9	isoprene, monoterpenes, homoterpenes, and sesquiterpenes	Sorbent column	GC-MS	[55]
10	Per chloroethylene in air	Canisters	GC-MS, MS	[56]
11	VOC materials from indoor and building materials	Charcoal absorbent tubes	GC-MS	[57]
12	VOC from paint industry	Column	GC-FID	[58]



**Effects of VOCs**

Volatile organic compounds are mostly present in external environment and inhaled by the human and other organisms. So they cause serious diseases of liver and lungs. For example, in early age, acetone and methylmercaptan were given to the patients for diabetes and liver diseases but these chemicals cause the foetor hepaticus, lung cancer and liver cancer in them [59]. Human urine contain the various volatile organic compounds like pyrroles, alcohols, ketones and these chemicals produces the scent in human and cause the uremic scent in them. Organism sweat can also have the scent of volatile organic compounds, so bacterial action can cause the disease in them. High concentration of these files leads to the Nausea, Dizziness, Headache and Necrosis. Chlorinated volatile organic compounds can lead to the diseases of irritation in respiratory system, liver and kidneys, in skin and in eyes [60-61].

**Conclusion**

VOCs are organic compounds that have the low boiling points and present in air and can be collected by the active, passive, integrated and grab sampling techniques. They are extracted by the different techniques like extraction, SPME, Thermal desorption etc. These VOCs are analyzed by the different techniques like Mass spectrometry, Voltammeters, Conductometry. Proper monitoring of air for VOCs is highly recommended for betterment of worldwide health and fitness and biosafety of environment

**Main challenges and future perspective**

- Low and very low concentration level of analytes.
- Differences in concentration levels of analytes belonging to the same group or class of compounds.
- Time and space fluctuations of the analyte concentration.
- Interferences from other constituents of a sample.
- Problems with availability of suitable reference materials.

**Conflict of Interest**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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