

A Survey on VOC Monitoring and Detection Techniques

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Abstract— Wireless Sensor Nodes have found wide acceptance in field of environmental monitoring in both industrial and residential settings. Volatile Organic Compounds (VOCs), which are a major source of indoor pollution and health disorders, are also monitored using WSNs. This paper provides an overview of current as well as traditional techniques for monitoring VOCs and an outline of current scenario of technology regarding this subject. Different approaches to accomplish the system have been viewed unbiasedly to help understand the core of the matter and help build a more flawless system. After a detailed introduction containing points from reports of various Environmental agencies, different measurement techniques along with their and drawbacks are explained which includes Canister, Sorbent tube, DNPH and Photoionization detection techniques for VOCs. Notable related works and researchs are then covered in terms of infrastructure and architectures, sensing mechanisms and energy consumption and philosophies to manage energy consumptions to prolong lifetimes of the WSN systems. The report is concluded with future research directions and exploring trends in the field.

Index Terms— Air Quality, air sampling, indoor, monitoring, pollutants, VOCs, wireless sensor networks.

1 INTRODUCTION

INDOOR Air Quality (IAQ) has become a matter of concern due to findings related to health risks because of pollutants in indoor air such as the Sick Building Syndrome in which individuals may feel uncomfortable in particular buildings due to presence of pollutants. In India, it has become a major issue due to gigantic vehicle population and weak monitoring framework. The Environmental Protection Agency (EPA) identifies indoor air pollution as a greater risk to human health than outdoor air pollution, the reason being that people spend 80-90% of their times indoors [1]. VOCs (Volatile Organic Compounds) are a major source of pollutants in indoor air. VOCs are harmful organic chemical compound that can significantly vaporize under conditions of normal atmospheric temperature and pressure. They are also defined by European Union as organic compounds with boiling points below or equal to 250 °C (482 °F) measured at a standard atmospheric pressure of 101.3 kPa [2]. There are thousands of volatile organic compounds and only a few are regulated, but it does not mean that others are not harmful. Hence there still is a vast unexplored area in the field of VOCs.

VOCs are released from burning fuel such as gasoline, wood, coal or natural gas. They are also emitted from oil and gas field and diesel exhaust as well as solvents, paints, glues, nail polish, perfumes, hair sprays, dry cleaned clothes, PVC cement, moth balls, air fresheners, cosmetics, pesticides, plywood, furniture, carpets etc. [3]. Humans can be exposed to volatile organic compounds by breathing polluted air that contains them and they are more abundant in air in summer when sun and hot temperatures cause vaporization of VOCs.

Health effects of VOC are known to vary greatly according to the compound, level and length of exposure and can range from being highly toxic to having no obvious health effects at all. According to a report published by National Toxicology Program, benzene and formaldehyde are human carcinogens; perchloroethylene and styrene are "reasonably anticipated to be human carcinogens." Long term exposure to volatile organic compounds can cause damage to the liver, kidneys, and central nervous system. Short term exposure to volatile organic compounds can cause eye and respiratory tract irritation, headaches, dizziness, visual disorders, fatigue, loss of coordination, allergic skin reactions, nausea, and memory impairment [4]. Figure 1 shows sources of VOCs in general places. Besides being dangerous to human health, VOCs can also damage plants, destroying their natural processes, if exposed for long periods. Higher concentrations of VOCs can form an explosive mixture in air and can become a concern when they exceed the Upper Explosive Limit described by chemical specifications. According to the UK Environment Agency, total VOC emissions peaked in 1989 and fell by 38% by 2000. Road emissions fell by 55% over the same period, mainly as a result of the introduction of catalytic converters for petrol cars. Fuel switching from non-catalyst cars to diesel cars has also had a small beneficial effect. However, emissions from solvent use have changed little over the past 25 years.

In Western countries, monitoring VOCs is required by law in most cases. As a general rule the various industrial sources that emit VOCs are divided into Part A, Part A2 and Part B processes. Those that use the largest amount of VOCs and therefore

have the highest potential emissions are classed as Part A and Part A2 processes—these are regulated by Environment Agencies. Part B processes cover smaller operations and are

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regulated at a regional level by Local Authorities. For almost each process there is a Process Guidance Note that gives details on total VOC emissions allowed to be exhausted to atmosphere, usually quoted in mg/m³, ppm (parts per million) and ppb (parts per billion) [5].

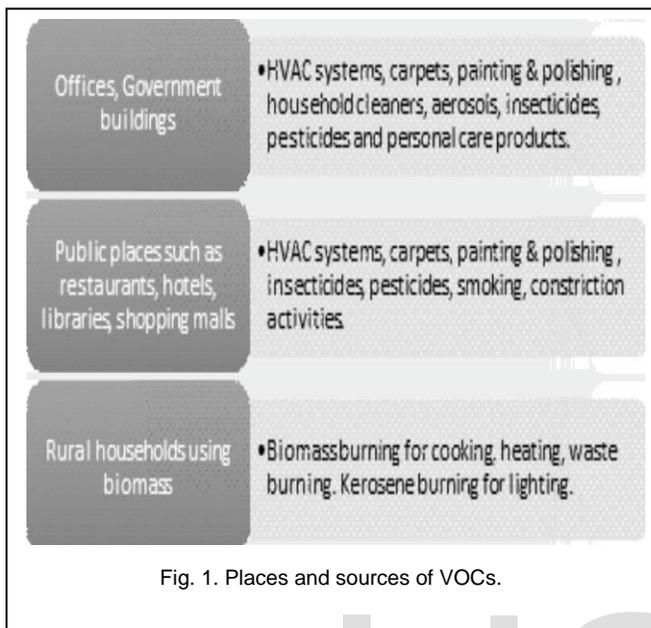


Fig. 1. Places and sources of VOCs.

The recommended limit for the presence of total VOCs in indoor environment have been published by many organizations and vary accordingly. Table 1 summarizes them.

Because of the health effects of VOCs in indoor environments, the need for a robust and non-obstructive automated system has become essential. There have been many attempts to measure VOC concentrations ranging from traditional methods to the use of ZigBee modules and sensors. The aim of

TABLE 1
TVOC LIMIT RECOMMENDATIONS [10].

Agency	Recommended Limit	
	µg/m ³	ppb
Scandinavian Construction Materials Assoc.	300-1300	~75-325
Japan Ministry of Health	400-1000	~100-250
AHRAE/ACGIH	<1000	~200
Texas General Services Commission	500	~100
Australian National Health & MRC	500	~100
Finnish Society of IAQ & Climate	200-600	~50-150
German Guideline (Seifert, 1999)	300	~75
Denmark Institute of Hygiene	250	~50

this paper is to reflect upon these methods in a constructive manner.

2 VOC MEASUREMENT TECHNIQUES

Judging VOC requires information about the compounds present in the air at any given location. The sampling or measurement method directly impacts the overall analysis, decisions and conclusion. Many countries have organizations (e.g. Environmental Protection Agency and the American Society for Testing and Materials) that publish standard protocols and procedures to be followed for measurements of VOCs. But the measurement of VOCs in India is not exercised widely. Measurement involves specifying methods, selecting location and times for sampling, monitoring conditions and complex evaluations and analysis. While using any of these techniques, we must ascertain that each method has its own advantages as well as drawbacks. To select proper method for measurement depends both on the individual and the prevailing conditions.

2.1 Canister Technique (CAN)

This is a whole-air sampling technique that can be used in field measurements. In canister sampling, two sampling techniques are commonly used: passive sampling and active sampling. Active sampling requires the use of a pumping device whereas passive sampling does not. In passive sampling, an air sample is pulled through a flow controller into an evacuated canister over a chosen period of time, ranging from 5 minutes to 24 hours. The sampling period and the flow rate determine the canister volume required. In active sampling, a pump is used to push the sample through a mass flow controller and into the canister. Although active sampling is very flexible, a drawback to using a pump is the need for additional quality assurance requirements for sample integrity. Additionally, a pump requires a battery or line power source, which may be difficult in remote field-site sampling [6]. A typical passive sampling train includes the following components: a sampling inlet, a particle filter, a critical orifice, a flow controlling device, a vacuum gauge and a canister (an example is shown in Figure 2).

Sampling time is limited by the combination of canister size and the flow rate at which the sample is to be collected. They are generally made of stainless steel so that the collected sample may not seep through the vessel wall or degrade due to exposure to light. It is also important to keep the inner surface of the canister inert to avoid any chemical interactions with the collected sample. Two types of canisters are available, the difference being the interior surface.

The traditional canister is the stainless steel SUMMA® or TO-Can® canister. The new generation of sampling canister is typified by the SilcoCan® canister. SilcoCan® comes with Siltek® treatment that makes the surface inert not only for relatively inactive organic compounds, but also for compounds that are highly reactive with metal surfaces, such as sulfur-containing compounds.

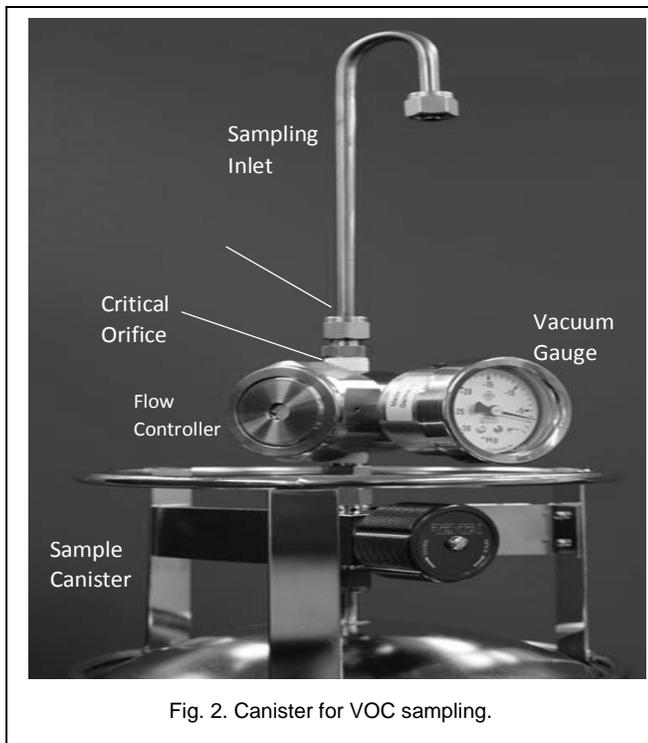


Fig. 2. Canister for VOC sampling.

2.2 Sorbent tubes

Sorbent tubes are stainless steel tubes used for organic compound monitoring having length generally 10cm. These tubes are designed for long term monitoring and sufficient concentrations of compounds are absorbed in the tubes. Samples may be collected over a duration of 8 hours to 4 weeks. The advantages of using Sorbent tubes stated by manufacturers include low cost, operation over a wide area for longer terms and non-requirement of a power source. Sorbent tubes work on principle of molecular diffusion (movement of molecules from area of high concentration to area of low concentration) [7]. The compounds in the air are at a higher concentration than those in the tube, so the compounds diffuse into the tube and collect on the absorbent inside. Because the compounds are absorbed, the low concentration at the sorbent surface is maintained, and therefore diffusion continues. The rate that the compounds move into the tube is called the uptake rate. This is a known rate and is used in the calculations during analysis.

After sampling, the tubes must be sealed and taken to a laboratory where analysis is done. In the laboratory, the sample is generally removed from the tube by a process called thermal desorption during which the sample is heated to allow it to be extracted from the absorbent. The sample is transferred to a GCMS (gas chromatography-mass spectrometry) where the lab determines the concentration of compounds on the tube. This is then used in a calculation with the pump flow rate or uptake rate to calculate the average concentration of compounds that were present in the air over the monitoring period. The results can be obtained in parts per billion (ppb) for passive sampling or micrograms per metre cubed ($\mu\text{gm-3}$) for pumped sampling. SGS India is a firm that provides VOC testing for products in India in receipt of fees [8].

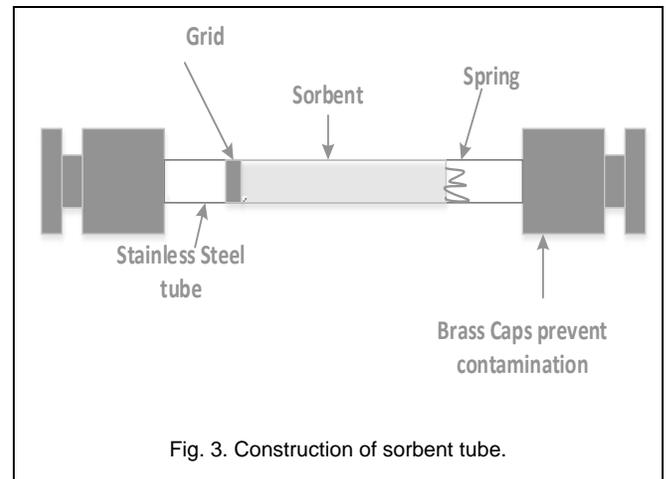


Fig. 3. Construction of sorbent tube.

We can find the procedure of sampling through Sorbent tubes, followed by thermal desorption and gas chromatography/mass spectrometry, documented in EPA compendium method TO-17. In both cases (Canister and Sorbent tube), the samples must be sent to certified laboratories for analysis. The costs of analysis vary in different regions but are known to be rather high.

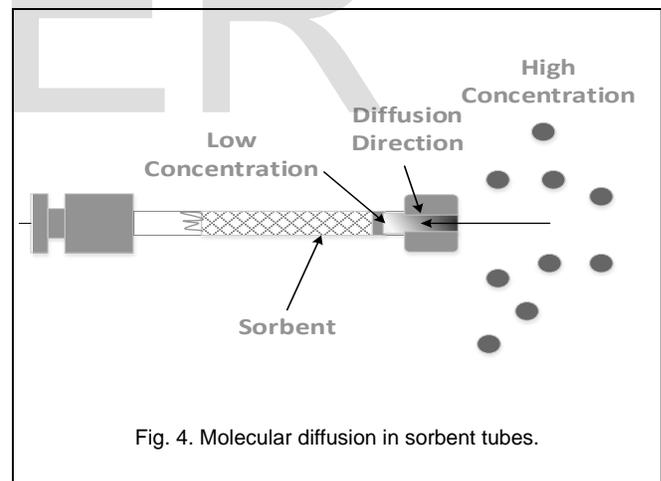


Fig. 4. Molecular diffusion in sorbent tubes.

2.3 DNPH Tubes

DNPH tubes are a variant of sorbent tubes and consist of adsorbent cartridges that are coated with 2,4- dinitrophenylhydrazine to collect light chemical compounds. Analysis involves separation and examination of the chemical compound by high performance liquid chromatography with ultraviolet (UV) detection. Carbonyls are trapped on a sampling cartridge containing high purity silica adsorbent coated with 2,4 dinitrophenylhydrazine (2,4-DNPH), where they are converted to the hydrazone derivatives [9].

In a study made in [2], fourteen retail stores in the U.S were

studied for concentrations of VOCs over a year in regions of Pennsylvania and Texas. A permanent indoor sampling location was selected in each store where instruments were set-up for continuous monitoring. The instruments used, along with their detection limits and uncertainty and resolution are summarized in table 2.

2.4 Photoionization detectors

Photoionization detectors are sensors that have resolution of few ppb and can distinguish different levels of VOCs. They

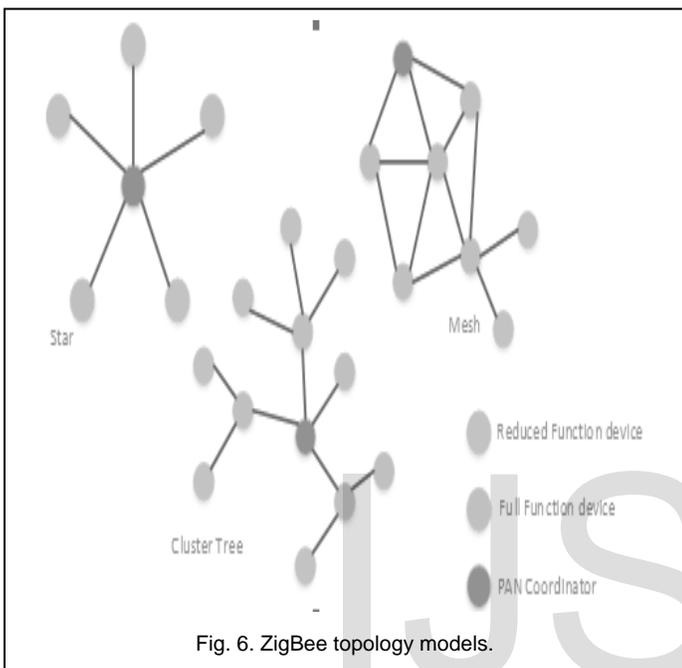


Fig. 6. ZigBee topology models.

TVOC	uous 5 min	Systems ppbRAE Plus PGM- 7240	UV Absorption	1 ppb	1 ppb
	Integrat ed 4 hrs.	DNPH tubes, analyzed by Labs	High- performance liquid chromatograp hy	100 ng	
Formal dehyde	Contin uous 30 min	Shinyei Formaldehyd e Multimode Monitor	UV absorption	20 ppb	1 ppb

are most easy to use sensors with no requirement for lab analysis and their features include speed and high sensitivity and are known to be of intermediate cost. They provide direct measurement of VOCs for quick identification. They can measure concentrations in a wide range of 0.01 to 10,000 parts per million (ppm). PIDs became more optimized for sensing low levels of VOC with advances in miniaturization and sensitivity made recently and have become powerful tools for measurement in all general environments. As the name suggests, these sensors work on principle of photoionization.

The PID consists of a short-wavelength ultraviolet(UV) lamp

that shines onto a small cell containing the gas sample. The UV light photoionizes the organic compounds, but not the air, which results in ejection of electrons and formation of positively charged molecules. The resulting current in the sensor is proportional to the concentration of compounds present [10].

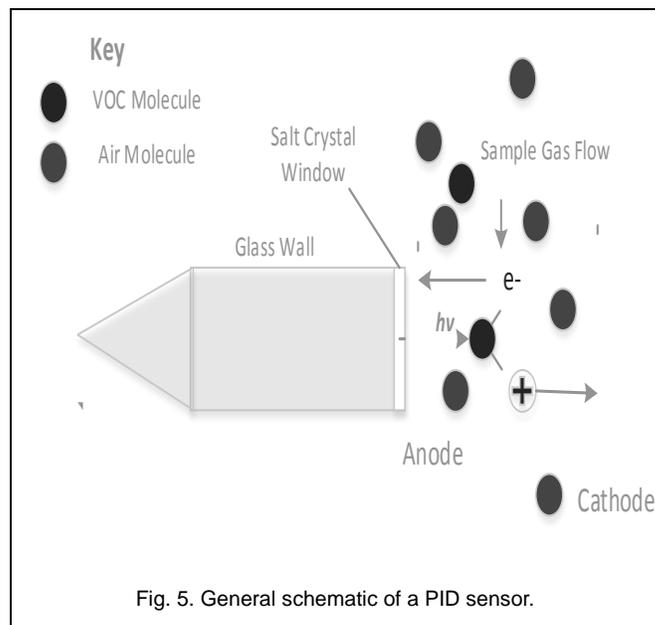


Fig. 5. General schematic of a PID sensor.

3 RELATED WORK

There is a large number of sensor systems that have been evaluated for sensing and monitoring of VOCs, some of them focusing on particular VOC such as benzene, acetone, formaldehyde etc. Some of the early works included radio frequency identification technology (RFID) as sensors for detecting vapors. There is also a variety to be seen in the sensing media technology over the time. Journal papers and online articles were studied to perform a survey into current progresses in this field and are related below.

3.1 Infrastructure

Although most favored technique for sensing and monitoring is through wireless networks such as ZigBee or Bluetooth, monitoring has also been performed without these. But wireless networks provide a promising infrastructure for capturing information from monitoring areas and transmitting them back to the server for processing and actions. Three types of networks – wireless local area networks (WLAN), mobile networks and wireless sensor networks (WSN) – have been adopted widely for indoor air quality monitoring. The reason behind this is the fact that they are wireless and hence easily

deployable. A personalized mobile sensing system, MAQS, was proposed in [19] to monitor indoor air quality because it is inexpensive, portable and energy efficient. The system integrates smartphones with portable sensing devices, M-pods, to deliver personalized air quality information. According to the authors, it may lead to redundant information when users are

located near each other, and may lead to coverage gaps when users are not carrying sensing devices. A WSN with star architecture is also a widely adopted choice in indoor air quality monitoring.

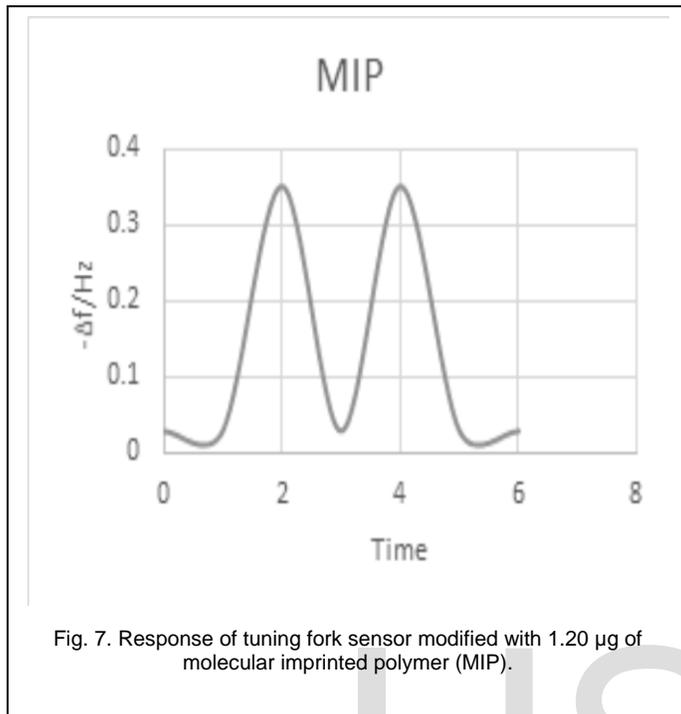


Fig. 7. Response of tuning fork sensor modified with 1.20 µg of molecular imprinted polymer (MIP).

Such systems require base station or ZigBee coordinator that receives data at regular time intervals from the ZigBee end nodes. The end nodes may be any nodes available in market such as the Liium Waspnote with gas sensor board for sensing data and in or the XBee and XBee pro module by Digi International Inc. [20] proposes a hybrid sensor network architecture which contains stationary sensors for accurate reading and calibration purposes as well as mobile sensors for overall coverage. According to authors, two main problems persisting in the system are selecting and placing the stationary sensors which requires exhaustive search from all possible schemes and the allocation and assignment of the mobile sensors using a heuristic approach. Overall based on parameters such as power, cost, ease of deployment, intrusiveness and environment dependency, it can be said that WSN based on the ZigBee standard is an appropriate or good option for indoor air quality monitoring.

3.2 Sensor nodes

A sensor node or array with multiple sensors is used to collect air pollution readings, from which the overall air quality level can be derived. Several standard methods have been established for analysis of VOCs in air. One of the most widely used methods, as mentioned above, uses an absorption tube or a canister with GC/MS equipment to collect the sample on the field, and then send the tube or canister to a lab, where a trained technician analyzes the sample using GC/MS equipment [21]. However, these methods are labor intensive and time-consuming, involving multiple steps, typically including

sample collection, shipping and storage, use of costly equipment, and data analysis. An alternative approach aiming at overcoming the difficulties of these standard reference methods is to use real-time detection devices. One of such device is the photo ionization detector (PID), which is a broadband detector that detects ionized species with a UV lamp. For selective detection of many toxic chemicals, such as benzene (a carcinogen), the PID is inadequate since it monitors total VOCs. Although the approach offers real-time results, the selectivity and practical detection limits are limited, making PID devices suitable for indoor applications. Another real-time detection approach is the use of colorimetric tubes, which rely on a specific binding or reaction between an analyte and an appropriate sensing material. The specific binding leads to a change in the color of the sensing material, which is detected optically. Because the reaction is irreversible, this approach is for one-time use only and not suitable for continuous monitoring of analytes in the environment. A more serious limitation of the colorimetric approach is that it cannot be applied to chemicals that do not react to generate color changes. One such example is benzene, which is carcinogenic but does not interact strongly with common sensing materials.

Some authors [17], [21] have also used tuning fork sensors which are commercially available in large quantities. They are enclosed in a sensing cartridge which itself is an array of modified tuning fork sensors. The use of a sensor cartridge enables the sensor device to adapt to different applications according to the situation. Essentially, a different cartridge allows the sensor to detect different molecules or to improve sensitivity, response time, etc., by using different tuning fork sensors. In addition, it allows a worn out or damaged tuning fork sensor array to be replaced without having to replace the entire sensor system. Basically, the sensor cartridge gives the sensor device more flexibility, lower maintenance cost, and upgradeability. The tuning forks are coated with polymers or functional molecules to give it different detection properties depending on the interaction between the sensing layer and the targeted analyte(s).

Responses of tuning fork sensors modified with 1.20 µg of molecular imprinted polymer (MIP) and 3.10 µg of wax are shown in the graphs below. They show that MIP modified tuning fork has a bigger response even with a smaller coating mass. MIP can be further shaped in form of micro particulates to get even better sensitivity and responses. As the polymer coating is exposed to the analytes and the analytes interact with the polymer, the mass of the tuning fork sensor changes, resulting in a change in resonant frequency. If this change in resonant frequency is detected and if the sensor is properly calibrated, the concentration of the analytes the tuning fork

sensor is exposed to can be determined.

A more versatile approach is based on portable gas chromatography (GC) technologies [22]. High performance portable GCs have been developed, but the instruments are bulky and expensive, which seriously hinder their applications. In addition, the portable GCs often use carrier gas in cylinders, further limiting their portability and usability. In order to minia-

turize GCs, various novel detectors, such as arrays of chemiresistor, surface acoustic wave (SAW) and metal oxide-based sensors combined with microfabricated pre-concentrators and/or GC separation columns have been developed.

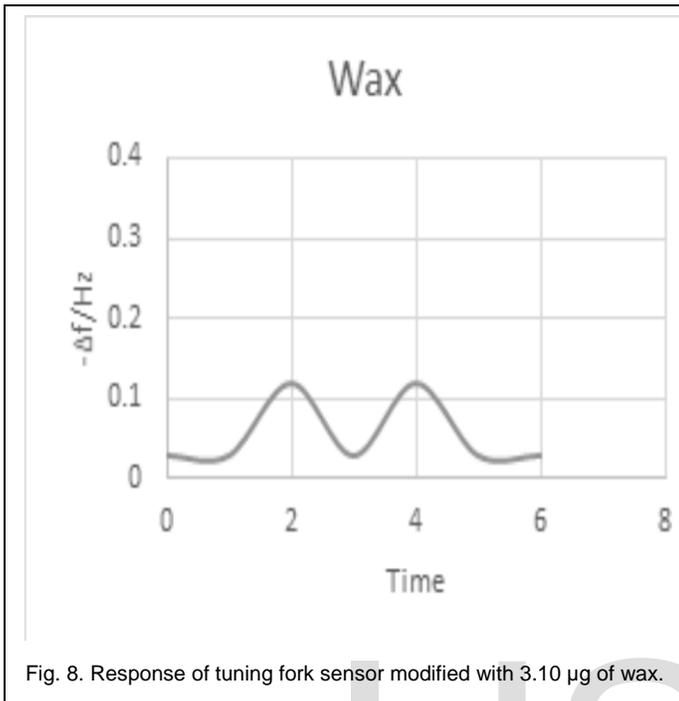


Fig. 8. Response of tuning fork sensor modified with 3.10 µg of wax.

3.3 Energy consumption and management

WSNs which use more number of sensors will have high power consumption. Of course, if we use less number of sensors, the rating will be lower. To proper manage energy, energy management scheme such as data aggregation algorithm are preferred. Data aggregation is defined as the process of aggregating the data from multiple sensors to eliminate redundant transmission and provide fused information to the base station. Data aggregation usually involves the fusion of data from multiple sensors at intermediate nodes and transmission of the aggregated data to the base station (sink) [23]. Clearly there are three major modes of operation for any wireless node. It is either transmitting, receiving, or simply "on." In the last mode it typically "listens" but is not actively receiving. In the transmitting mode energy is spent in two major ways. The first is in the front-end amplifier that supplies the power for the actual RF transmission. This includes the radiated energy as well as the internal heat losses in the antenna and the amplifier itself. The second is in the node processor that implements all the signal generation, formatting, encoding, modulation, memory access, and other signal processing functions. We call the first transmission energy and the second processing energy. In the receiving mode, energy is consumed entirely by the processor. In many applications (especially in sensor networks), a node may spend most of its lifetime simply in the "on" position without actually receiving or transmitting, this mode may represent the lion's share of the total consumed energy. Thus, to reduce the amount of energy needed to achieve a given communication task it is necessary to examine the role of every one of these components. Energy expenditures are af-

ected by design choices made at every one of these levels. For example, the selection of batteries is crucial. They determine the total amount of energy that is available to the node. Next, energy can be saved by proper selection of hardware. The circuit layout of every chip has notorious energy consumption effects so it is important to be careful on every step [24].

Studies show that there are three possible ways to address the problem of powering the wireless networks: 1. Improve the energy density of storage systems, 2. Develop novel methods to distribute power to nodes, 3. Develop technologies that enable a node to generate its own power. Research to increase the storage density of both rechargeable and primary batteries has been conducted for many years and continues to receive substantial focus. The past few years have also seen many efforts to miniaturize fuel cells which promise several times the energy density of batteries. The most common method (other than wires) of distributing power to embedded electronics would be through the use of RF (Radio Frequency) radiation. Many passive electronic devices, such as electronic ID tags and smart cards, are powered by a nearby energy rich source that transmits RF energy to the passive device, which then uses that energy to run its electronics. However, this method is not practical when considering dense networks of wireless nodes because an entire space, such as a room, would need to be flooded with RF radiation to power the nodes. The third method mentioned, in which the wireless node generates its own power, has not been explored as fully as the first two. The underlying idea in this method is that a node would convert "ambient" sources of energy in the environment into electricity for use by the electronics. This method is known as "energy scavenging", because the node is scavenging or harvesting unused ambient energy. It is potentially the most attractive as well as difficult method to exploit because each use environment will have different forms of ambient energy, and therefore, there is no one solution that will fit all, or even a majority, of applications.

4 CONCLUSIONS

A comprehensive survey of VOC monitoring techniques, methods and concerns have been presented with special focus on wireless sensor networks, important performance measures such as energy consumption, network topologies and sensing techniques. The main points and matters of concern have been described in a precise manner covering crucial information. The various advances in the field of sensors as well as traditional ways of sensing VOCs along with their benefits and shortcomings have been elaborated. The ZigBee standard 802.15.4 is maintained by the ZigBee alliance and undergoes constant advances and refinements in terms of coverage, data rate and power consumption as well as network formations. Although many approaches may seem research and enhancement. Combining aspects such as different types of air pollutant sensors and latest notes for monitoring is a good field for exploration. Analytical results on the bounds for lifetime of sensor networks is another area worth exploring. Existing work has provided bounds on lifetime for networks with specific network topologies and source behaviors. It would be

interesting to extend this work to more general network topologies such as cluster based sensor networks. Security is another important issue in data aggregation applications and has been largely unexplored. The sensor data are usually highly correlated and energy efficiency can be achieved by joint source coding and data compression. Although some research has been pursued in this direction, there is significant scope for future work.

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