CHAPTER 1
CHEMICAL SENSORS

1.1. INTRODUCTION:
The sensing of gaseous substances has become increasingly important in recent years for applications in environmental, industrial, and biomedical monitoring. A sensor is a device that is responsible to the value of a physical quantity or parameter. Sensors have many advantages, such as simple and low cost instrumentation, fast response times. It converts information from one energy domain into another\(^1\). Chemical sensor systems are capable of detecting a wide range of molecules in the headspace because they consist of an selective sensor elements with a different selectivity to each gaseous component. Such sensors or transducers play an important role in instrumentation and control. A general feature of modern industrial plants is the increased number and diversity of sensors installed for controlling the processes for reasons of economy, safety or reduction of environmental pollution. Sensors provide many of the functions of analytical instrumentation, but with reduced cost, size, and power consumption, along with the ability for real-time, in-situ measurements. These sensors should be linear and reversible over a wide range of concentration, should be highly reproducible over many cycles and should be selective i.e., sensitive to a single species or parameter.

A sensor can be viewed as a component of a system, which measures an input and provides an output independently of the state of the other parts of the system. As shown in Fig.1.1.chemical sensor\(^2\) consists of an active surface, a transducer, and electronics. A specific material is used in the sensor because of its specific advantage in dealing with a signal in that domain\(^3\). The sensing element selectively recognizes a particular molecule through adsorption process and the transducer converts the results of this recognition into a usable signal, which can be quantified. The sensing element is responsible for the selectivity of the sensor. Examples include polyethylene glycol, triethanolamine, Quadrol etc. The detector, which plays the role of the transducer, translates the physical or chemical change by recognizing the analyte and relaying it through an electrical signal. As shown in Table 1.1. sensors can have a global impact in many areas\(^4\) such as environmental cleanup, industrial process control, emission monitoring, aeronautical and
space systems, planetary exploration, nonproliferation of weapons. Screening for explosives and contraband, home and workplace safety, and medical diagnosis and care. Optimization of industrial processes using computer control algorithms requires real-time information of the various process parameters and to understanding and managing risks to human health and environment and for efficient process controls. The degree to which a process can be optimized depends upon the quality and quantity of information received, and this can be enhanced by development of efficient, advanced and cost-effective sensors. Over the past two decades, research and development in Sensors has increased significantly, as demonstrated by the growth in financial investment by the manufacturing sector, the number of papers published, and the number of active researchers worldwide. Some of the essential or desirable properties of the chemical micro-sensors are summarized as follows.

1. Selectivity
The chemical sensor must respond to a range of chemical species to be detected. The sensors should not have broadly overlapping sensitivities to discriminate between different chemicals.

2. Sensitivity
The chemicals to be detected may be present in the concentration range of ppm. The sensor should be sufficiently sensitive to detect small concentration level of gaseous species.

3. Speed of response
In order to be used for online measurements, the response time of the sensor should be in the range of seconds.

4. Reproducibility
The individual sensor element should be reproducible in their manufacture and response characteristics. This will reduce the task of calibrating each sensor element before use. Fabrication processes used to make a single sensor must be compatible with the manufacture of an array of reasonable size. Additionally, the sensors should have an inherently linear response characteristic.
Fig. 1.1 Principles of chemical sensors

Fig. 1.2 Classification of chemical sensors
### Table 1.1 Applications of chemical sensors

<table>
<thead>
<tr>
<th>Field of application</th>
<th>Typical example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>Engine control, air quality in car, emission</td>
</tr>
<tr>
<td>Aerospace</td>
<td>Engine control, air quality in cabin, emission</td>
</tr>
<tr>
<td>Agriculture</td>
<td>Fertilizer and pesticide control</td>
</tr>
<tr>
<td>Chemical analysis</td>
<td>Laboratory testing of materials</td>
</tr>
<tr>
<td>Safety (fire)</td>
<td>Fire warnings in mines buildings, houses etc</td>
</tr>
<tr>
<td>Process control</td>
<td>Production of chemicals, food stuffs etc</td>
</tr>
<tr>
<td>Environmental monitoring</td>
<td>Detection of pollutants in air, water and soil</td>
</tr>
<tr>
<td>Medicine</td>
<td>Anesthetic gases, diagnostics, biochemistry</td>
</tr>
<tr>
<td>Customs</td>
<td>Illegal and dangerous substances (explosion)</td>
</tr>
<tr>
<td>Quality control</td>
<td>Smell/ flavor of drinks, foodstuffs, tobacco</td>
</tr>
</tbody>
</table>

### Table 1.2 Major transducer principles and their transducing property

<table>
<thead>
<tr>
<th>Transducer property</th>
<th>Principle chemical sensor system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance, ΔR</td>
<td>Semiconductor gas sensors</td>
</tr>
<tr>
<td>Current, ΔI</td>
<td>Electrochemical cells</td>
</tr>
<tr>
<td>Capacitance, ΔC</td>
<td>Humidity sensors</td>
</tr>
<tr>
<td>Work function, Δϕ</td>
<td>Gas FETs</td>
</tr>
<tr>
<td>Mass, Δm</td>
<td>BAW and SAW sensors</td>
</tr>
<tr>
<td>Temperature, ΔT</td>
<td>Pelliostors and thermopiles, and</td>
</tr>
<tr>
<td>Optical properties</td>
<td>Optical sensors</td>
</tr>
</tbody>
</table>

### Table 1.3 Principles, measurand and typical examples of chemical sensors

<table>
<thead>
<tr>
<th>Principle</th>
<th>Measurand</th>
<th>Typical sensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductometric</td>
<td>Resistance/conductance</td>
<td>Tin oxide gas sensor</td>
</tr>
<tr>
<td>Potentiometric</td>
<td>Voltage/e.m.f</td>
<td>Ion selective FET</td>
</tr>
<tr>
<td>Capacitive</td>
<td>Capacitance/charge</td>
<td>Polymeric humidity sensor</td>
</tr>
<tr>
<td>Amperometric</td>
<td>Current</td>
<td>Electrochemical cell</td>
</tr>
<tr>
<td>Calorimetric</td>
<td>Heat/temperature</td>
<td>Pelliostor gas sensor</td>
</tr>
<tr>
<td>Gravimetric</td>
<td>Mass</td>
<td>Piezoelectric or SAW sensors</td>
</tr>
<tr>
<td>Optical</td>
<td>Path length/absorption</td>
<td>Infra red detector for methane gas</td>
</tr>
<tr>
<td>Resonant</td>
<td>Frequency</td>
<td>Surface plasmon</td>
</tr>
<tr>
<td>Fluorescent</td>
<td>Intensity</td>
<td>Fibre-optic</td>
</tr>
</tbody>
</table>
5. Reversibility

The sensor should be able to recover after exposure to gas. If the process of absorption of gas in the polymer film is completely reversible, the sensor will not degrade and the response will not drift in the subsequent cycles.

6. Portability

Devices should be small so that small sample volumes can be used. The power consumption should be low so that the device can be operated with a battery, making the sensor portable.

1.2. Review of sensor types for the measurement of gaseous pollutants:

Sensor science and technology are growing rapidly in response to an ever increasing demand for faster, cheaper, smaller and more sensitive means to monitor the chemical, biological and physical world around us. The traditional use of chemical sensors focuses at the output of an individual chemical sensor with its single sensor signal (feature), e.g. a specific current at a fixed potential of an electrochemical cell or a resistance change of a metal oxide semiconductor, etc. In principle available and easily measurable transducer properties of chemical sensors are changes of transducer properties as is shown in Table 1.2.

The sensors can be categorized into three general groups (Fig. 1.2) based primarily on the principal physics and operating mechanisms of the sensor: (1) Electrochemical sensors; (2) mass sensors; and (3) optical sensors as shown in Table 1.3. Electro-chemical sensors, include sensors that detect signal changes (e.g., resistance) caused by an electrical current being passed through electrodes that interact with chemicals. Mass sensors rely on disturbances and changes to the mass of the surface of the sensor during interaction with chemicals. Optical sensors detect changes in visible light or other electromagnetic waves during interactions with chemicals.

1.2.1 Electrochemical Sensors

Electrochemical sensors can be categorized into three groups: (1) potentiometric (measurement of voltage); (2) amperometric (measurement of current); and (3) conductometric (measurement of conductivity). These types of sensors appear to be most relevant for detecting and monitoring gaseous pollutants.
1.2.1.1. Conductometric Sensors

Three different types of conductometric sensors 1) a polymer-absorption sensor that indicates a change in resistance in the conductive polymer electrode when exposed to chemicals. 2) the catalytic bead sensor, which requires elevated temperatures to burn combustible hydrocarbon vapors and change the resistance of an active element. 3) the metal-oxide semiconductor sensor, which responds to changes in the partial pressure of oxygen and requires elevated temperatures to induce combustion of chemical vapors that change the resistance of the semiconductor.

1.2.1.1.1. Polymer-Absorption Chemiresistors

The concept of using polymeric absorption to detect the presence of gaseous pollutants in the ambient atmosphere has existed for several decades. These polymer-absorption sensors (Chemiresistors) consist of a chemically sensitive absorbent that is deposited onto a solid phase that acts as an electrode. When pollutant of interest come into contact with the absorbent, the chemical absorb into the polymers, causing them to swell. The swelling changes the resistance of the electrode, which can be measured and recorded. The amount of swelling corresponds to the concentration of the chemical in contact with the absorbent. The process is reversible, but some hysteresis can occur when exposed to high concentrations.

Several companies and organizations have developed Chemiresistors, but the specific attributes and types of absorbents, which are generally proprietary, vary among the different applications. As shown in Fig. 1.3. chemiresistors are small, low power devices that have no moving parts and have good sensitivity to various chemicals. As a result, they are amenable to being placed in situ in monitoring wells. Another big advantage for Chemiresistors in comparison to the standard electrochemical sensors is that they don't require liquid water to work properly. That liquid (usually water with controlled ionic strength and pH buffers) must be supplied by the sensing medium (like a well) or a reservoir in the sensor package, which can dry out. These sensors may not be able to discriminate among unknown mixtures of chemicals. Some polymers react strongly to water vapor.
Uncertain durability of polymers in subsurface environments; need to develop robust packaging, may need pre-concentrator to detect very low limits (for regulatory standards). Although reversible, signal may experience hysteresis and a shift in the baseline when exposed to chemicals.

1.2.1.2. Catalytic Bead Sensors
Catalytic bead sensors are low-power devices (50-300 mW) that have been used for many years in the detection of combustible gases and other toxic gaseous species like CO, NO₂, SO₂, etc in air. They are used widely in portable gas detection instruments. The catalytic bead sensor is comprised of a passive and active element, both made from an embedded coiled platinum wire in a porous ceramic. The active element is coated with a catalyst such as platinum, and the passive element is coated with an inert glass to act as a reference element to compensate for environmental conditions. Both elements are heated to a prescribed operating temperature ranging from 300°C to 800°C. When a combustible gas contacts the elements, the compound combusts on the active element and the active element increases in temperature. As a result, the resistance of the platinum coil changes, the changes in resistance are measured as a change in voltage.
1.2.1.1.3. Metal-Oxide Semiconductor Sensors

The metal-oxide semiconductor (MOS) sensor is comprised of a tin oxide that is sintered on a small ceramic tube. As shown in Fig. 1.4, a coiled wire is placed through the center of the ceramic tube to act as the sensor heater. Metal wires provide electrical contact between the tin oxide and the rest of the electronics. The MOS sensor requires power between 300 mW and 600 mW to operate the sensor at elevated temperatures between 200°C and 450°C. The combination of the sensor operating temperature and the composition of the metal oxide yields different responses to various combustible gases. When the metal oxide is heated, oxygen is adsorbed on the surface with a negative charge. Donor electrons are transferred to the adsorbed oxygen, leaving a positive charge in the layer. Inside the sensor, electrical current flows through the grain boundary of metal oxide micro crystals. Table 1.4 displays some common materials used in chemical microsensor.

Table 1.4. Some common materials used in chemical microsensor

<table>
<thead>
<tr>
<th>Active material</th>
<th>Examples</th>
<th>Sensing principles</th>
<th>Measurands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin oxide layer</td>
<td>SnO(_2), ZnO</td>
<td>Surface conductance</td>
<td>Combustible gases</td>
</tr>
<tr>
<td>Thick porous oxide layers</td>
<td>SnO(_2), ZnO, TiO(_2)</td>
<td>Bulk conductance</td>
<td>Combustible gases</td>
</tr>
<tr>
<td>Catalytic metals</td>
<td>Pd-TiO(_2), Pd-MOS</td>
<td>Surface potential</td>
<td>H(_2), CO</td>
</tr>
<tr>
<td>Ion selective devices</td>
<td>AgCl, AgBr</td>
<td>Electrochemical potential</td>
<td>Cl(^-), Br(^-)</td>
</tr>
<tr>
<td>Catalytic coating</td>
<td>ThO(_2)/Al(_2)O(_3)</td>
<td>Heat of combustion</td>
<td>H(_2), CH(_4)</td>
</tr>
<tr>
<td>Organic films</td>
<td>Substituted phthalocyanines</td>
<td>Bulk conductance</td>
<td>NO(_x)</td>
</tr>
<tr>
<td>Langmuir -Blodgett films</td>
<td>Steric acid</td>
<td>Piezoelectric /SAW</td>
<td>Various polar molecules</td>
</tr>
<tr>
<td>Conducting polymers</td>
<td>Poly (pyrrole)</td>
<td>Bulk conductance/mass</td>
<td>Polar compounds, NH(_3)</td>
</tr>
</tbody>
</table>
Resistance to this electrical current is caused by negatively charged oxygen at grain boundaries. In the presence of a reducing gas, a surface catalyzed combustion occurs and the surface density of negatively charged oxygen decreases, thereby decreasing the resistance of the sensor. The relationship between the amount of change in resistance to the concentration of a combustible gas can be expressed by a power-law equation. The MOS sensors have high sensitivity to combustible gases (e.g., hydrogen, carbon monoxide, methane, ethane, propane, alcohols, etc.). They are compact and durable and the cost is also relatively inexpensive. The MOS sensor has a fair amount of sensitivity to water humidity, which may be problematic in subsurface environments.

1.2.1.1.4. Potentiometric and Amperometric Sensors

Potentiometric and amperometric sensors employ an electrochemical cell consisting of a casing that contains a collection of chemical reactants (electrolytes or gels) in contact with the surroundings through two terminals (an anode and a cathode) of identical composition. For gas sensors, the top of the casing has a membrane which can be permeated by the gas sample. Oxidization takes place at the anode and reduction occurs at the cathode. A current is created as the positive ions flow to the cathode and the negative ions flow to the anode. Gases such as oxygen, nitrogen oxides, and chlorine, which are electrochemically reducible, are sensed at the cathode while electrochemically oxidizable gases such as carbon monoxide, nitrogen dioxide, and hydrogen sulfide are sensed at the anode. Potentiometric measurements are performed under conditions of near-zero current. Amperometric sensors are usually operated by imposing an external cell voltage sufficiently high to maintain a zero oxygen concentration at the cathodic surface; therefore, the sensor current response is diffusion controlled.

Sensitivity of amperometric sensors is better than potentiometric sensors. A common application for potentiometric and amperometric sensors is for water analysis. The most common is the pH sensor system. The basic principal of these devices is that they require two separated, carefully controlled liquid reservoirs with two different chemically unstable electrodes (called reference electrodes), for example a silver wire with a coating of silver chloride. The pH is measured by the voltage difference between the two reference electrodes, so the unknown sample must be in electrochemical connection with
both solutions through a glass membrane. However, these thin porous membranes can break, the solutions can leach out or dry out, or the chemistry of the reference electrode itself can change giving a slightly different voltage. Small changes in the chemistry can result in large changes in output voltage. Consequently these systems require constant attention and calibration against known pH solutions. Many ion selective electrodes for particular ions are sold using basically the same system described in (Fig. 1.5) above but with special membranes taking the place of the pH-sensitive glass that give potential differences for different ions. The same maintenance and calibration problems exist, as well as interference problems from other ions. Some gases that can be detected using potentiometric methods include Sulphur dioxide, carbon dioxide, oxygen, carbon monoxide, hydrogen, chlorine, arsenic oxides, and oxidizable pollutants. To speed up the diffusion process, the working electrode is placed virtually on top of the gas-permeable membrane. These devices can be specific for a particular gas or vapor and are typically very accurate. They do not get poisoned and can monitor at ppm levels. But the Primary sensitivity is for toxic gases and oxygen, not amenable for in-situ applications. Membranes are sensitive and may degrade with time. Devices are not very durable and have short shelf lives. Subject to interfering gases such as hydrogen.

![Fig.1.5. Ion selective field effect transistor](image)

1.2.1.1.5. Microcantilever sensors

Micro electromechanical systems can be composed of multiple micron-thick cantilevers (visualize miniature diving boards) that respond by bending due to changes in mass. Appropriate coatings are applied to the cantilevers to adsorb chemicals of interest. This particular technology has been used for developing infrared sensors to “see” images in
darkness\textsuperscript{24} but commercial devices using Microcantilever sensors to detect gaseous pollutants were at research level.

1.2.2. Optical Sensors
Fiber optic sensors are a class of sensors that use optical fibers to detect chemical contaminants. Light is generated by a light source and is sent through an optical fiber. The light then returns through the optical fiber and is captured by a photo detector. Some optical fiber sensors use a single optical fiber while others use separate optical fibers for the light source and for the detector. There are three general classes of fiber optic sensors. The first type is completely passive. A spectroscopic method can be used to detect individual types of contaminants. This method involves sending a light source directly through the optical fiber and analyzing the light that is reflected or emitted by the contaminant. The refractive index of the material at the tip of the optical fiber can be used to determine what phases (vapor, water) are present. A second class of fiber optic sensors consist of a fiber optic sensor with a chemically interacting thin film attached to the tip. This film is formulated to bind with certain types of chemicals. Contaminant concentration can be found by measuring the color of the thin film, the change in refractive index, or by measuring the fluorescing of the film. The third type of fiber optic sensors involves injecting a reagent near the sensor. This reagent reacts either chemically or biologically with the contaminant. The reaction products are detected to give an estimate of the contaminant concentration. Low power; several types have no moving parts; can detect various chemicals at very low concentrations. Limited ability to transmit light through the optical fiber over long distances. Some pollutants are not easily differentiated using UV-visible spectroscopy. Concentration range sensitivity may be limited. Sensors that use chemically sensitive coatings may degrade with time.

1.2.2.1. Colorimetry
Pocket colorimeter test kits can be used to measure trace levels of contaminants. They work by analyzing the color of reagent that has been mixed with a particular chemical analyte. To test water samples, the pocket colorimeter compares a reacted sample with a sample blank and yields results in concentration units. Portable, simple to use. Visual evidence of gas detection event. Not prone to interferences. Limited chemical sensitivity
to individual pollutants, needs actual samples (cannot be used in situ); most kits do not meet USEPA method requirements and may not be used for compliance monitoring. Requires visual inspection and is not amenable to long-term in-situ applications.

1.2.2.2. Infrared Sensors

Infrared sensors can be used to detect gases, which, in general, have unique infrared absorption signatures in the 2-14 nm range. The uniqueness of the gas absorption spectra enables identification and quantification of chemicals in liquid and gas mixtures with little interference from other gases. These devices are typically comprised of a source of infrared radiation, a detector capable of seeing the infrared radiation, and a path between the detector and source that is exposed to the gas being detected. When gas in the path absorbs energy from the source, the detector receives less radiation than without the gas present, and the detector can quantify the difference. These devices can be made to identify specific gases; they require less calibration than other sensors; good durability with minimal maintenance. They can only monitor specific gases that have non-linear molecules; they can be affected by humidity and water; they can be expensive; dust and dirt can coat the optics and impair response, which is a concern in in-situ environments.

1.2.3. Mass Sensors

1.2.3.1. Surface Acoustic Wave Sensors/Portable Acoustic Wave Sensors

Acoustic Wave Sensors are sensors used to detect gaseous pollutants. A SAW device consists of an input transducer, a chemical adsorbent film, and an output transducer on a piezoelectric substrate. The piezoelectric substrate is typically quartz. The input transducer launches an acoustic wave which travels through the chemical film and is detected by the output transducer. The device runs at a very high frequency 100MHz. The velocity and attenuation of the signal are sensitive to the visco-elasticity as well as the mass of the thin film which can allow for the identification of the contaminant. Small, low power, no moving parts other than the high-frequency excitation, good sensitivity to various chemicals can detect chemicals in very low concentrations. Some polymers react strongly to water vapor; uncertain durability in subsurface environments.
1.3. Status of national and international sensor market:

Market studies determine needs and present usage of chemical sensor systems for Environmental analytical applications have been carried out by various workers. Sensors have been developing over many years and new designs continue to come into the market. The technology of sensors has gone through several stages and its evolution is continuing. Mechanical sensors have been superceded by electrical, electrical by electronic and so on. In addition to the basic technology of detecting, the sensor is having more intelligence built into it. In a smart sensor, the detector, microprocessor and memory are interconnected using hybrid micro circuits technology. Software is an important input. Such sensors are able to take decisions based on data stored in its memory as per its programmed logic. Overall Sensors are not a standardized product with clear-cut and widely accepted specifications. There is enormous variety available. In fact, sensors from different companies for the same application may not only look different, but may even use different technologies.

1.3.1. Market picture:

Market can be broadly divided into two groups. One group buys sensors as a sub-system from any one of different sources. Chief among this sector are IC&A where the industrial plant engineer, in consultation with process control equipment manufacturer selects the most suitable sensors. At the other extreme are OEM manufacturers who want sensors that exactly suit their application to the point – sometimes – of being proprietary. Such sensors have to be designed in close association with the equipment manufacturers. Study of International data revealed that volume sensor usage was restricted to certain area such as the following:

a. Industrial control and automation (IC&A)
b. Medical equipment
c. Automobiles
d. Environment and pollution control
e. Security
f. Consumer items
g. Office automation
One surprising finding of the BEHRAM WADIA & ASSOCIATES, Consultants in Electronics\textsuperscript{16} was that users are quite unconcerned about the technology used in a particular sensor. End user treats the sensors as a black box. The black box has to sense the parameter and produce the output. The sensitivity, accuracy, precision, reliability, size and cost of the black box is what concerns the end user. Coupled with the limited standardization, this gives considerable flexibility to a sensor designer to develop entirely new sensing techniques.

1.3.2. Sensor Technology changes:
Even though sensors of traditional design was said to be getting superseded by more modern technologies, this is at the design level. Traditional types of sensors continue to be made and to be used even though no developmental work to improve their performance is being done. Production caters to replacement markets and to traditional industries which are quite satisfied with the performance of these sensors. Developmental work, on the other hand is directed towards advanced types of sensors. Such sensors are used in modern plants where traditional sensors may be inadequate.

1.4. Summary and Need for new sensor systems:
The competitive environment India is facing is to a certain extent, a function of the technological environment and the degree of technological innovations attributed to the competitive environment. Technological change and worldwide flow of information are fundamentally reshaping how companies and nations do business. With the increasing awareness for the pollution free or cleaner environment in India the demand for the reduction of pollutant gases emitted by combustion processes and efficient process controls is more pressing. The pressures of technological competition increasingly drive corporations towards global strategies while stimulating nationalistic impulses to protect and secure the national technology base from international competition Chemical sensors are increasingly being viewed as low cost, compact, robust and versatile alternatives to large analytical tools such as optical spectrophotometers, gas chromatography etc. A wide variety of field deployable sensor techniques that could be applied to environmental measurements are available commercially, but they are not without limitations\textsuperscript{17}. Table 1.5 shows the different sensor technologies and their major limitations.
The analysis of scientific and patent literature shows that electrochemical-semiconductor- and catalytic-semiconductor-type sensors mostly used in gas-analytical devices for the oxides of nitrogen and Sulphur and for ammonia have a number of shortages, among them lowered sensitivity. Several brands of Electrochemical and catalytic instrument sensors use liquid electrolyte that must be refilled at regular intervals. Paper tape instruments can only be used for toxics because of their high cost and significant lag times exist between a leak and its detection as these instruments are typically kept in a central location and connected to multiple detection points.

Solid-state sensors can detect a wide range of gases but when they have not been exposed to gas for sometimes sensors oxidize. FTIR instruments are prohibitively costly and mechanical failure is also an issue with these instruments. The detection of special analytes plays an important role in many fields of the chemical industry, biotechnology and environmental technology. Complex and very expensive methods of spectroscopy and chromatography have been used for these applications for many years now. Although these methods are relatively rapid and inexpensive, sensitivity and accuracy are often lower than what we have come to expect with classical laboratory techniques. New generations of sensors able to provide directly immediate information on the composition of their surroundings are promising tools in the area of environmental monitoring. Among them piezoelectric crystal based sensors which can be thought of as highly sophisticated chemical sensor system incorporating quartz crystal electrodes as sensing element and a specific coating materials for the gas of interest is very attractive.
Table 1.5. Different sensor technologies and their limitations\(^{17}\)

<table>
<thead>
<tr>
<th>Sensor Type</th>
<th>Mode of Activity</th>
<th>Fabrication Method</th>
<th>Sensitivity ppm</th>
<th>Limitations</th>
</tr>
</thead>
</table>
| Metal Oxide            | Sensors pass an electrical current causing oxidation of gas molecule leading to change in the resistance | Microfabricated    | 5.0 to 500      | 1. Less selective than other sensor types  
2. Can be subject to poisoning  
3. Response can be affected by the presence of solvents. |
| Conducting polymer (CP)| In the presence of gas molecule a change in voltage across the polymer such as Polythiophene, Polypyrrole, Polyanilines occurs | Microfabricated    | 0.1 to 100      | 1. Sensitivity is achieved by controlling surface functional groups by varying anion chemistry during the growth  
2. Reproducibility is good  
3. Returns to baseline resistance in short time |
| Quartz Crystal Microbalance (QCM) | The oscillating frequency of the quartz crystal changes in the presence of a gaseous species | Screen printing  
Wire bonding  
MEMS       | 1.0 ng                       | 1. Problems of reproducibility in commercial production of QCM |
| MOSFET                 | In presence of gaseous species the MOSFET changes its Capacitance charge coupling | Microfabrication  
Screen printing  
MEMS       | Ppm                          | 1. Can achieve good sensitivity  
2. Problems of sensor reproducibility in commercial production  
3. Can easily be integrated with electronic interface circuits  
2. Gaseous pollutant must penetrate the gate to cause a measurable change in capacitance |
| Fiber optic sensors    | Change in fluorescence is measured from the photo deposited polymer/fluorescent dye on bundles of fiber optics | Dip coating  
MEMS, Precision matching  
MEMS, Precision matching |
| Colorimetry            | Transmitted light spectrum changes in the presence of volatile organic compounds | MEMS, Precision matching  
MEMS, Precision matching | Low (ppb) | 1. Sample not consumed  
2. Requires tunable quantum wave devices |

MEMS: Microelectrochemical system  
Besides the classical analytical methods measuring technologies are desirable which offer high selectivity, sensitivity and stability and allow on-line or in-situ measurements. They are also very favorable in price. This is the research field of modern chemical sensors. Due to the piezoelectric properties of a quartz, a voltage between the electrodes of a quartz leads to a shear deformation of the crystal. Since Sauerbrey described the relationship between a mass deposition on the quartz surface and the resulting shift in the fundamental oscillation frequency of the quartz the QCM-principle has been widely used for many applications. The interaction processes between a number of coordination compounds and gaseous analytes by means of piezo-quartz micro balance technique shows possibilities of using coordination compounds as components of the sensing coverings for sensors, which works on the principle of the correspondence of the analytical response to the change in the mass of the covering on the account of the analyte chemosorbtion with its surface.

1.5. Review of Sulphur dioxide monitoring methods:
Sulphur dioxide, one of the most harmful air pollutants, is widely used as a fungicide, preservative and bleaching agent and in the pharmaceutical preparations because of its toxic action upon vegetative organisms. Burning Sulphur bearing coal and oil and smelting of ores etc, are the main sources of its presence in the environment. The threshold limit value as fixed by American Conference of Governmental Industrial Hygienists is 5ppm, but lower values of 2 - 3ppm have been reported to be toxic to plants and corrosive to metallic construction materials.

Current Sulphur dioxide concentrations monitoring methods can be divided into six basic classes upon the basis of the type of sampling conducted and analysis employed: passive indicator methods, passive sampling and analysis methods, active sampling and direct measurement methods, active sampling and analysis methods, automatic local monitoring and integrated path monitoring.

1.5.1. Passive Indicator Methods
Passive indicators are materials that react with analyte species upon exposure and can be used to provide 'on the spot' information about air quality or individual airborne
Passive indicators are most commonly used qualitatively or semi-quantitatively, to indicate the presence of given pollutants at hazardous concentrations (e.g., household carbon monoxide detector tabs). Passive indicators are simple to deploy and are commonly used in a wide range of non-research applications, including commercial and domestic site monitoring and personal exposure assessment. However, passive indicators typically have low sensitivity, by comparison to the other classes of air pollutant monitoring methods discussed here. Furthermore, there are some concerns regarding the accuracy and reliability of such ‘wet chemical’ methods. Consequently, their use tends to be restricted to situations where unusually high pollutant concentrations are the focus of concern and immediate information is required (e.g., occupational health exposure). Passive indicators have to be deployed for long periods of time (i.e., >1 day for most pollutants) to achieve detection limits required for reliable routine ambient air quality monitoring. Passive indicator deployment and pollutant concentration measurement are typically manual operations as these are not readily automated procedures.

1.5.2. Passive Sampling and Analysis Methods
Like passive indicator methods, passive sampling and analysis methods employ materials that react with analytic species upon exposure to provide a measure of airborne pollutant concentrations. However, unlike passive indicator methods, these materials can not provide an ‘on the spot’ measurement as they require laboratory-based analysis to determine the amounts pollutants retained. Passive sampling and analysis methods are commonly used quantitatively, especially in large scale, short time period air quality studies (e.g., initial site screening exercises and annual surveys). Passive sampling and analysis methods are typically low-cost and simple to deploy.

Separate laboratory-based analysis means that these methods tend to be more sensitive and accurate than comparable passive indicator methods. A number of commercial contract laboratories offer convenient ‘by mail’ passive sampling devices (preparing, supplying and analyzing samplers tubes or badges after sampling at a fixed per sampler cost). However, passive sampling and analysis samplers typically require long sampling times (i.e., > 1 day for most pollutants) to provide reliable ambient air quality information.
and very few procedures are readily automated. Furthermore, for many of the priority pollutants considered here, significant doubts still exist regarding the specificity, accuracy and precision of such methods.26-29.

1.5.3. Active Sampling and Direct Measurement Methods
Like passive indicator methods, active sampling and direct measurement methods employ materials that react with analyte species upon exposure to provide an ‘on-the-spot’ measure of airborne pollutant concentrations.21 However, unlike passive indicator methods, in this case sampling is achieved by passing a fixed volume of air through the sampler. Like passive indicator methods, passive sampling and direct measurement methods are commonly used either qualitatively or semi-quantitatively.

Active sampling and direct measurement is likely to be more accurate than passive indication as the exact volume of air sampled is defined by the operators rather than local atmospheric conditions (that can vary considerably over the sampling period). Consequently, results obtained from active sampling methods tend to be more reproducible than those obtained from comparable passive sampling methods. Furthermore, analytical sensitivity is a function of air sampling volume rather than exposure time. Consequently, active sampling procedures typically require shorter sampling periods than comparable passive sampling methods. However, active sampling procedures are likely to be more expensive than comparable passive sampling procedures, due to the additional requirement for accurate air sampling equipment (e.g., calibrated large volume gas syringes or air pumps). Like passive indicator methods, active sampling and direct measurement methods are typically manual operations that are not readily automated.

1.5.4. Active Sampling and Analysis Methods
Active sampling and analysis methods use a prime mover, such as gas syringe, air pump or vacuum pump, to draw a fixed volume of air through an analyte trap, which is subsequently retained for analysis. Like passive sampling and analysis methods, these methods are commonly used quantitatively, especially in large scale, short time period air quality studies (e.g., initial site screening exercises and annual surveys).29-31 Active
Sampling and analysis methods offer a number of advantages over similar passive sampling and direct measurement methods: (i) active sampling provides higher sensitivity and reproducibility and requires shorter sampling times, and (ii) separate analysis provides further improvements in sensitivity and reproducibility, as well as an increased level of specificity. Sampler deployment periods vary significantly depending upon the analyte, although most are of the order of 1 hour to 1 day. However, sampling equipment and analytical procedures are typically more sophisticated. Consequently, both financial costs and the degree of skill, and therefore training, required to employ such methods are likely to be significantly higher than in the case of passive sampling methods and/or direct measurement methods. Furthermore, most of these procedures are not readily automated.

1.5.5. Integrated Path Monitoring

Integrated path instruments can measure the 'integrated' concentration (i.e., average concentration) of airborne species between a light source unit and a detector unit. Most systems can be used to study a wide range of chemical species (often simultaneously) including Carbon Monoxide, Oxides of Nitrogen, Ozone, Sulphur dioxide, Benzene and 1,3-butadiene. Early instruments required long path-lengths (e.g., 1 to 10 km) to achieve high sensitivity, and are consequently often referred to as 'remote' or 'long path-length' methods. However, recent improvements in light source and detector technology have resulted in the development of 'short path-length' instruments. Unfortunately, these instruments are highly expensive and significant skill is required to interpret the data they provide.

1.5.6. Automatic Local Monitoring

Automatic local monitors can routinely measure analyte concentrations within operator input (i.e., automated active sampling and analysis methods) or instruments capable of direct measurement of analyte levels via the exposure of a sensor.
Such automatic monitoring systems are typically highly accurate, precise and reliable. Automatic monitoring systems can generally produce hourly-average, minute-average or even real-time data. Consequently, they can be deployed at a given sampling point to provide continuous site data. However, the automatic local monitoring systems used in conventional monitoring programmes are significantly more expensive than either passive or active sampling procedures.

A number of alternative technologies are now becoming available that can provide low-cost, real- or near-real-time air quality data (e.g., solid state sensors and related technologies). Furthermore, some existing analytical techniques have undergone significant technical improvements (e.g., electrochemical sensors). These developments mean that some of these alternative technologies may now be suitable for use in routine air quality monitoring programmes.

Several methods have been reported for its determination of Sulphur dioxide in air\textsuperscript{15}. the method based on the Schiff reaction\textsuperscript{36} proposed by West and Gaecke\textsuperscript{17}, using sodium tetrachloromercurate (TCM) as absorbing reagent for Sulphur dioxide and acid bleached pararosaline and formaldehyde for color development, for the measurement of ambient Sulphur dioxide is the method of choice for environmental chemists. Several modifications of this method have been suggested, which include improvement in the purity of dye\textsuperscript{38}, temperature dependence and stability of the colored product\textsuperscript{19} and studies on interferents\textsuperscript{40 - 41}. the method is still retained because of sensitivity, simplicity, specificity and easy adaptability.

Most of the methods for determination of Sulphur dioxide have two stages: absorption of Sulphur dioxide from air in a suitable medium and subsequent determination by using a suitable reagent to liberate the trapped Sulphur dioxide.

Aqueous iodine solution\textsuperscript{42}, hydrogen peroxide\textsuperscript{43}, glycerol-alkali\textsuperscript{44} and EDTA solution\textsuperscript{45} have been used by earlier workers. West and Gaecke recommended TCM as an efficient absorber for atmospheric Sulphur dioxide\textsuperscript{37}. The major disadvantages with this method are the instability of sulphite solution on storage (1% per decay at room temperature)\textsuperscript{40}
and the use of toxic and expensive mercury(II) chloride. To remove these defects, a modified West and Gacke method has been proposed in which formaldehyde\textsuperscript{46} and triethanolamine\textsuperscript{47} are recommended as the absorbing medium for Sulphur dioxide. Owing to large variation in purity and selectivity of pararosaline dye Kinsley and Throop\textsuperscript{48} recommended a reagent pair of p-aminoazobenzene and formaldehyde. P-aminoazobenzene gives more reliable and reproducible results as it is available in a pure form and can be synthesized in the laboratory\textsuperscript{49}.

A solid phase Spectrophotometric method for the determination of sulphite and its application to the determination of atmospheric Sulphur dioxide is described by Juan M.Bosque-Sendra et al\textsuperscript{50}. In this method Sulphur dioxide is trapped with morpholine to form an adduct which reacts with pararosaline and formaldehyde, and the reaction product is sorbed on Dowex-1-x8 resin. The absorbance of the resin phase at 565 and 700nm is measured directly allowing for the determination of Sulphur dioxide in the range of 4 – 56\textmu g l\textsuperscript{-1} in a solution, with a relative standard deviation of 2.1%.

Numerous absorption/extraction/ion chromatography analysis methods have been published for Sulphur dioxide\textsuperscript{51-57}. Although exact detection limits varied from procedure to procedure, typical quantification ranges were of the order of 15 to 3000 ppb, 2 to 400 ppb and 0.5 to 100 ppb for 1 day, 1 week and 1 month sampling periods, respectively\textsuperscript{58,54}. In field validation exercises, passive Sulphur dioxide samplers were reported to provide consistent data when compared with other techniques, such as active sampling procedures (ca. 10\%)\textsuperscript{86}, and fluorescence Sulphur dioxide analyzers (78-85\%)\textsuperscript{84}. However, diffusion tube Sulphur dioxide samplers may over-estimate gas-phase Sulphur dioxide levels as the result of particulate sulphates accumulation within the entrance region of the sampler. The experimental precision of Sulphur dioxide diffusion sampler procedures typically reported to be of the order of 5 to 15\%. Most of these procedures have been rigorously assessed under laboratory conditions and/or undergone field trials. However, relatively few passive Sulphur dioxide sampler procedures appear to have been employed in air quality surveys or general environmental research.
Conventional fluorescence Sulphur dioxide monitors have detection limits of the order of 1 to 1 mg/m³ and a dynamic quantification range in excess of 200 mg/m³. Reductant-sensitive electrochemical cells have been developed for gas-phase Sulphur dioxide monitoring. Electrochemical Sulphur dioxide cells are not widely used in environmental monitoring as 'best case' detection limits are often not sufficient for routine air quality monitoring, i.e., about 100 mg/m³.

Furthermore, some commercial systems are highly susceptible to significant interference from other airborne reducing species, most notably carbon monoxide. Of the above technologies, electrochemical sensors are undoubtedly the best developed and various commercial systems are readily available for air quality monitoring. Some future electrochemical sensor improvements are still likely, such as miniaturized 'on-chip' electrochemical sensors. However, further improvements in electrochemical cell sensitivity and specificity are probably only likely through the use of complimentary technologies (e.g., new or improved in-line sample clean-up, analyte derivation or analyte concentration).

1.6. Organization of thesis
Chapter 2 of this thesis presents the principles involved in the operation of the quartz crystal microbalance (QCM) sensor in which the operation of the QCM as a balance is described in detail. The mass sensitivity of the QCM is discussed along with parameters that may affect it. A historical review of different theories describing the mass sensitivity of the QCM is also given. Different models used to predict the oscillatory behavior of a coated QCM as the viscoelastic property of the coating may change are introduced. In addition, Chapter 2 includes a discussion of piezoelectric materials and their applications in monitoring of gaseous pollutants, and a comprehensive literature review of related research topic i.e. analytical applications of piezoelectric crystals in environmental analysis are provided.

Chapter 3 describes the Quartz crystal microbalance apparatus and its components. The development of the QCM and major improvements over time are described. Different film application and preparation methods were explored for making thin and uniform
films over the entire QCM surface. The film applications methods were discussed as part of the experiments where they were used in the subsequent chapters. This chapter also includes a discussion of the test rig design and the validation tests performed on the test oscillator circuitry. In addition, this chapter describes the gas generation system used for carrying the experiments.

Chapter 4 presents coating characteristics and measurement of sorption/desorption studies of different polymeric coating materials. The Chapter focuses on presenting the results obtained for the response of various coating materials used as gas sensing materials. Experimental results such as stability studies, cut-off studies, optimization of coatings, response versus chemosorbtion and suitability for detecting Sulphur dioxide under varying flow rates are presented in the chapter. This chapter describes the effect of various operating parameters on the efficiency of the detector.

Chapter 5 presents the development of a signal processing architecture for processing signal from the sensor is also discussed. Circuits have been designed and fabricated that are intended for collective implementation in the sensing plane that effectively processing of the sensor signals to generate a more robust aggregate output for subsequent signal processing stages. High accuracy frequency to voltage converter (FVC) circuit component, which is capable of maintaining a monotonic 0.01% linearity error over a 60dB range of 9.7KHz to 9.7MHz are studied for the fabrication of piezoelectric crystal analyzer. These circuits have been designed and fabricated so as to operate over the rage of 12 to 36V power supplies. Because synchronous VFC’s such as IC4 use an external timing element to define the full scale output frequency they achieve both greater linearity (<0.005%) and temperature stability than do non-synchronous charge balanced VFC’s or a sTable – multivibrator.

The presence of water significantly competes for adsorption sites on the coating and quartz piezoelectric crystal, thereby reducing the detector sensitivity. Hence removal of moisture is required for the successful measurement of Sulphur dioxide. Two hydrophobic membrane layers of PTFE 0.45µm thickness are found to reduce moisture reaching the coated piezoelectric crystal detector cell.
The response time and recovery time became quite slow, as the flow rate decreased below 40ml/min. As the flow rate increased from 40ml/min to 120ml/min, the response time decreased from 60s to 35s. Faster response and recovery can be obtained by increasing the flow rates but it will affect the baseline of the sensor. As the sampling time is increased the sensitivity will become better while the linear range is narrower. The linear range is from 0.01ppm to 30ppm for the Propyl Quadrol, 0.01 to 20ppm for Ethyl Quadrol and 0.01ppm to 15ppm for Polyethylene Glycol and 0.1to 5ppm for Silicone Oil.

Development of the portable instrument capable of detecting, identifying, and monitoring Sulphur dioxide gases at and above the parts-per-million levels developed are presented in this chapter. The instrument is small, microprocessor-controlled device composed of a compact piezoelectric crystal gas sensor. The analyzer comprising of the following options: 1) LCD display, 2) Reset button, 3) Select button, 4) Decrement button, 5) Increment button, 6) Set parameter button 7) Calibration button 8) Reset button 9) and 10) mode keys, 11) air pump, 12) Solenoid valves 13) Sensor for Sulphur dioxide i.e. piezoelectric crystal sensor has been fabricated and tested. The analyzer is highly flexible and can be operated continuously in real-time process and environmental monitoring. The piezoelectric quartz crystal analyzer coated with the amino functional polymeric coating material is found to have outstanding advantages such as higher sensitivity and long lifetime.

In Chapter 6 the main findings of the study on the Quartz crystal microbalance apparatus in which different Sulphur dioxide specific polymeric substances tested as adsorbents are summarized. The recommendations for the future work in the area piezoelectric crystal chemical sensors and commercial applications are also provided at the end of the chapter.

1.7 Concluding remarks:
Chapter 1 of the thesis dealt with the general categories of chemical sensor technologies and their potential application for real-time, in-situ chemical sensing applications. The first category reviewed was electrochemical sensors, which included conductometric, amperometric, and potentiometric sensors. The amperometric and potentiometric devices traditionally are used to monitor oxygen, carbon monoxide, chlorine, and other
constituents for air quality purposes. The conductometric sensors reviewed include polymer-absorption Chemiresistors, catalytic bead sensors, and metal oxide semiconductors. These devices are sensitive to VOC exposure, resulting in large changes to resistance in the device. The second type of technology reviewed was the mass sensor. These devices typically absorb the chemical of interest onto a surface, and the device detects the change in mass. The detection can be accomplished through changes in acoustic waves propagation. The chapter also presented national and international sensor market picture and the various sensor technology changes concluding with the need for the new sensor systems. The chapter concluded with a brief review on the existing methods of Sulphur dioxide monitoring.