Application of Gas Monitoring Sensors in Underground Coal Mines and Hazardous Areas

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Abstract—Underground mining requires equipment and manpower to operate under the earth surface. Subsurface atmosphere may be contaminated with poisonous gases that displace the necessary oxygen to support life or flammable gases that may cause explosion. Therefore, it is necessary to develop technologies and find ways to accurately measure concentration levels of toxic and flammable gases levels in subsurface atmosphere for safety of underground coal mines. Each sensor has its own advantages and constraints, like some sensors are better for sensing toxic gases and some are better for combustible gas detection. The paper enumerates operating principle, working procedure and application of different types of sensors for monitoring toxic and flammable gases in hazardous areas.

Index Terms—Gas sensors, MEMS, Nanotechnology, TLVs

I. INTRODUCTION

Underground coal mine is characterized by tough working condition and hazardous environment. Many accidents occur in underground coal mine which leads to fatal accidents and huge loss of properties. These accidents have variety of causes, including sudden rise in toxicants such as carbon monoxide (CO), dangerous flammable gases especially methane (CH₄) or firedamp and insufficient oxygen for mine workers to breathe. Therefore, for sustainable growth of coal mining industry and safety of miners, it is necessary to develop technologies and find ways to make mines hazard free [1].

To keep atmosphere just right in underground coal mine, the primary requirement is to regularly monitor the levels of gases, like oxygen, methane, carbon dioxide, carbon monoxide etc. This gives miners short and long term trending information in the subsurface atmosphere and allows early warning against explosive and toxic atmospheres at every place where miners normally work or travel. No mineworker should enter any underground work place, in particular those places with poor air circulation (e.g. blind headings), unless the air has been checked therein to ensure a safe breathable atmosphere free from levels of hazardous gases.

II. HAZARDOUS AREA

Fire, toxic atmospheric contaminant and dust or gas explosion are some critical hazards specifically linked to underground mining. It is necessary to figure out which area needs to be defined as hazardous area so that miners should be alerted in advance (Table I).

A. Combustible Gases

A hazardous area is defined based on three criteria, namely (i) depending upon type of gas, (ii) ignition temperature of the gas, and (iii) likelihood of gas being present in flammable concentrations. Flammability limit, thus defined, gives the proportion of combustible gases in a mixture, between which limits mixture is flammable.

- Lower Explosive Limit (LEL): The minimum concentration of gas or vapour mixed with air (percentage by volume, at room temperature) that will cause the propagation of flames when it comes in contact with a source of ignition. In common terminology, mixtures below the LEL are too lean to ignite.
- Upper Explosive Limit (UEL): The maximum concentration of gas or vapour mixed with air (percent by volume, at room temperature) that will cause the propagation of flames when it comes in contact with an ignition source. In common terminology, mixtures above the UEL are too rich to support combustion.

B. Toxic Gases

As toxic gases can cause harm in low levels over a long period of time (chronic exposure) or in higher concentrations over a short period of time (acute exposure), different countries have established threshold limit values (TLVs) for poisonous gases in order to advance worker protection by providing timely scientific information to occupational and environmental health professionals.

TLVs of airborne substances refer to those concentrations within which personnel may be exposed without known adverse effects to their health or safety. Followings are the three types of TLVs:

1. Time Weighted Average (TWA) is the average concentration to which nearly all workers may be exposed over given hours of work shift/week without known adverse effects. However, many substances are sufficiently toxic that short-term exposures at higher concentrations may prove harmful or even fatal.
2. Short-Term Exposure Limit (STEL) is a time-weighted average concentration occurring over a period of not more than few minutes. It is also recommended that such circumstances should not occur many times.
3. Ceiling Limit (CL) is the concentration that should not be exceeded at any time. This is relevant for the most toxic substances or those that produce an immediate irritant effect.
III. GAS DETECTING SENSORS

Gas sensors detect presence of various gases within an area, usually as a part of safety system. Sensors give a proportional electrical response depending upon the concentration of gas to be detected. If the concentration exceeds threshold concentration limit, the instrument containing it will provide an alarm to nearby personnel, or it may activate other remedial actions, such as increasing the ventilation, switching off the power supply etc. [3]. Different methods for detecting above gases are given in Table II and their operating principles are summarized in Table III.

<table>
<thead>
<tr>
<th>Name</th>
<th>Methods of detection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>Electrochemical, paramagnetic, flame lamp</td>
</tr>
<tr>
<td>Methane</td>
<td>Catalytic oxidation, thermal conductivity, optical, acoustic, flame lamp</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Optical, infrared</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>Electrochemical, catalytic oxidation, semiconductor, infra-red</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>Electrochemical, infra-red</td>
</tr>
<tr>
<td>Nitric oxide, Nitrous oxide, Nitrogen dioxide</td>
<td>Electrochemical</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>Electrochemical, semiconductor</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Catalytic oxidation</td>
</tr>
</tbody>
</table>

A. Catalytic Bead Sensors

Theory: Combustible gas mixtures will not burn until they reach an ignition temperature. However, in the presence of certain chemical media, the gas will start to burn or ignite at lower temperatures. This phenomenon is known as a catalytic combustion.

A coil of wire is coated with glass or ceramic material which is coated with a catalyst. The coil is electrically heated to a temperature that will allow it to burn (catalyze) combustible hydrocarbon (CHC) gas being monitored.

Pellistors are miniature calorimeters used to measure the energy liberated by burning of a combustible (flammable) gas or vapor [6]. A pellistor consists of a coil of small-diameter platinum wire supported in a refractory bead coated with a layer of catalytic material (Fig. 1), on which the gas is burnt. The coil serves two purposes: firstly, it is used to heat the bead electrically to its operating temperature of around 500°C, and secondly it is used to detect changes in temperature produced by oxidation of flammable gas.

Working procedure: A Catalytic bead sensor is used in Wheatstone bridge (Fig. 2), a circuit for measuring an unknown resistance by comparing it with known resistances. A balanced bridge has no output signal. \( R_1 \) is trim resistor that keeps the bridge balanced.

Resistor value \( R_0 \) and trim pot \( R_1 \) are selected with relatively large resistance values to ensure proper function of the circuit. During its operation, a current is passed through the coil, which heats up the bead to a high temperature. The gas is burned when a flammable gas molecule comes into contact with the catalyst layer. The reaction occurs without a flame since the level is below the Lower Explosive Limit (or LEL) of the gas. However, during burning reaction, heat is released which increases the temperature of bead. This increase in temperature causes rise in electrical resistance of the coil.

There is another bead in the circuit which is identical to the detector bead, but does not contain any catalyst. This bead will react to changes in humidity, ambient temperature etc., but will not react to flammable gas. All that is required is a comparison of the resistance of one bead against another in a Wheatstone bridge type circuit in order to obtain a meaningful signal.

![Fig. 1: Catalytic bead](image1.png)

![Fig. 2: A catalytic bead sensor Wheatstone bridge](image2.png)

Reaction: Reaction takes place on the surface of catalytic bead is given as

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 8N_2
\] (1)

From the above reaction, one part of methane requires ten parts of air for complete combustion. For a sensor to detect methane, the signal output will respond linearly from 0–5% of methane. As the concentration reaches close to 9%, the signal increases very rapidly & peaks at around 10% (Fig. 3).
The signal starts to drop slowly as the concentration of gas passes approximately 20%; after 20% it drops sharply and at 100% sensor signal is zero.

![Sensor output vs. methane concentration](image)

Factors affecting the operations of catalytic sensors are as follows:

(i) Catalyst poisoning: Poisoning compounds cause a permanent reduction of the sensor sensitivity. The exact cause of poisoning is very difficult to identify. Tetraethyl lead, silicon compounds and sulphur compounds are among the most common poisons.

(ii) Sensor inhibitors: Inhibitors cause a temporary loss of sensitivity to sensor and may be partially or totally recovered after a short exposure to fresh air. The most common inhibitors are \( \text{H}_2\text{S} \), chlorine, chlorinated hydrocarbons and halogen compounds.

(iii) Sensor cracking: The sensor, when exposed to high concentration of gases, excessive heat and various oxidation processes that take place on the sensor surface, may eventually deteriorate its performance.

<table>
<thead>
<tr>
<th>Name of gas</th>
<th>Flammability limits in air (%)</th>
<th>Guideline for TLVs</th>
<th>Hazards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>&gt;19.5%</td>
<td></td>
<td>Oxygen deficiency, may cause explosive mixtures with reactive gases</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>CL = 81,000 ppm</td>
<td></td>
<td>Inert</td>
</tr>
<tr>
<td>Methane</td>
<td>5 to 15</td>
<td>At 1% isolate electricity, at 2% remove personnel.</td>
<td>Explosion</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>TWA = 0.5%, STEL = 3.0%, CL = 1.5%</td>
<td></td>
<td>Promotes increased rate of respiration</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>TWA = 0.005%, STEL = 0.04%, CL = 200 ppm</td>
<td></td>
<td>Highly toxic; explosive</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>TWA = 2 ppm, STEL = 5 ppm, CL = 10 ppm</td>
<td></td>
<td>Very toxic; irritant to eyes throat and lungs</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>TWA = 50 ppm</td>
<td></td>
<td>Oxidizes rapidly to ( \text{NO}_2 )</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>TWA = 50 ppm</td>
<td></td>
<td>Narcotic (laughing gas)</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>TWA = 3 ppm, CL = 5 ppm</td>
<td></td>
<td>Very toxic; throat and lung irritant; pulmonary infections</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>TWA = 10 ppm, STEL = 15 ppm, CL = 15 ppm</td>
<td></td>
<td>Highly toxic; irritant to eyes and respiratory tracts; explosive</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4 to 74.2</td>
<td></td>
<td>Highly explosive</td>
</tr>
</tbody>
</table>

Table III: Classification of sensors by transducer operating principle [5]

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Types of devices</th>
<th>Physical change</th>
<th>Source of signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Catalytic gas sensors (pellistors), thermal sensors</td>
<td>Temperature or heat</td>
<td>Changes in resistance in wheat stone bridge</td>
</tr>
<tr>
<td>2</td>
<td>Optical sensors (infrared, laser, optical fiber)</td>
<td>Absorbance Luminescence Refractive index Scattering</td>
<td>Either caused by gas itself, or due to reaction with certain indicator. Emission, caused by chemical reaction For example, caused by change in solution composition. Caused by particles of definite sizes present in the sample.</td>
</tr>
<tr>
<td>3</td>
<td>Semiconductor (solid)</td>
<td>Electrical</td>
<td>Changes in work function</td>
</tr>
</tbody>
</table>
state) gas sensors conductivity
4 Electrochemical gas sensors (potentiometric or amperometric) Voltametric Changes in current between electrodes is measured
5 Piezo-electric sensors (quartz crystal microbalance) Mass Changes of resonant frequency of quartz oscillator plate due to adsorption of a gas on its chemically modified surface
6 Flame ionization detector, photo ionization detector Ionisation Amount of ionization

B. Infrared Gas Sensor

Theory: Gas molecules are made up of number of atoms bonded to one another. These interatomic bonds are similar to springs, connecting atoms of various masses together. This bonding vibrates with a fixed frequency called the natural frequency. When infrared radiation interacts with gas molecules as shown in Fig. 4, part of energy has the same frequency as the gas molecule’s natural frequency and it is absorbed while rest of the radiation is transmitted. As the gas molecules absorb this radiation, the molecules gain energy and vibrate more vigorously.

This vibration results in temperature rise of gas molecules. Rise in temperature is detected by the detector. On the other hand, the radiation absorbed by the gas molecules at the particular wavelength will cause a decrease in the original wavelength. This radiation energy decrease can be detected as a signal also.

Working of Non-Dispersive Infrared (NDIR): It is based on infrared absorption property of some gases which consists of a single IR source, a beam splitter and two detectors as shown in Fig. 5. One detector is used to monitor the characteristic hydrocarbon wavelength. The other is a reference that monitors an atmospheric “window” where no IR active gases are normally present. Infrared energy (2-5microns, where micron is a common unit to express wavelength in infrared range) is emitted from the source, passes through the gas cell, and is reflected back to the detectors. If no hydrocarbons are present within the gas sample, then energy reaching the detector is the same. However, if some combustible hydrocarbons are present, they will absorb some IR energy at that wavelength, thus reducing the amount received by the analytic detector. Gas concentration is determined by comparing the relative values between the two wavelengths (Fig. 6). This is called dual beam infrared detector [9]-[10].

$$I = I_0 e^{kp}$$

Where:
- $I$ — the intensity of light striking the detector,
- $I_0$ — the measured intensity of an empty sample chamber,
- $k$ — a system dependent constant, and
- $P$ — the concentration of the gas to be measured.

Infrared detectors convert electromagnetic radiation energy or temperature changes into electrical signals. Some of the detectors (Fig. 7) types are:

(i) Pyroelectric detector: Pyroelectric materials are crystals, such as lithium tantalite [14], which exhibit spontaneous polarization, or a concentrated electric charge that is temperature dependent. As infrared radiation strikes the detector surface, the change in temperature causes a current to flow. This current is proportional to the intensity of radiation.
This detector exhibits good sensitivity and good response to a wide range of wavelengths, and does not require cooling of the detector. It is the most commonly used detector for gas monitors.

![Image](a)

**Fig. 7:** Different detectors used for converting into electrical signals: (a) Pyroelectric, (b) Luft and (c) Photoacoustic detector [13]

(ii) Luft detector: A Luft detector consists of two chambers, either linked by a micro flow sensor or divided by a diaphragm [15]. The chambers are sealed with a target gas at a low pressure. IR transparent windows are fitted to seal the chambers and the same intensity of pulsed infrared radiation is received by both chambers when no target gas is present. When a sample containing target gas flows through the sample cell, reduced radiation energy is received by the detector chamber. This causes temperature and pressure to drop in the detector chamber. The amount of temperature or pressure drop is in direct proportion to the gas concentration. In the case of linked chambers, the pressure difference between the two chambers causes a detectable flow, which is measured as a signal. In the case where a diaphragm separates the two chambers, a movement of the diaphragm causes a measurable change in capacitance.

(iii) Photoacoustic detector: This detector is similar to Luft detector except that the pressure change is measured by a condenser microphone. The sample gas is passed through a chamber at a preset time interval and the chamber is sealed with a fixed volume of sample gas trapped inside. A specific wavelength of infrared radiation is pulsed into the chamber via an infrared transparent window. The pulsating pressure change is measured by the microphone as a frequency change which produces the signal [16]-[17].

Fourier Transform Infrared (FTIR): FTIR measuring principle is used for multi-gas detection (Figs. 8). The principle of FTIR is that the gas to be analyzed is led through a cuvette with an IR light source at one end (i.e. sending out scattered IR light), and a modulator that “cuts” the infrared light into different wavelength. At other end of the cuvette, a detector is measuring the amount of IR light to pass through the cuvette. By data processing, Fourier Transformation mathematics is used to turn the measured absorption values into gas concentration for the analyzed gases. As the light is modulated into many different wavelengths, it is possible to analyze many different gases in the same instrument, such as CO, H₂O, SO₂, NO, HF, NH₃ etc. [18].

![Image](b)

![Image](c)

**Fig. 8:** FTIR infrared spectrum [19]

Infrared provides high accuracy, resistance to contamination and reliable measurements. Unlike catalytic bead sensor, gas sample enters and leaves the cell unchanged. Nothing is transformed, substituted or removed from it. As the IR source ages, its energy level decreases. But there is only one source. Therefore, the energy level reduction will equally affect both sensor tubes (reference and detection) and no imbalance is detected.
There is no need of extreme temperature for detection, resulting in less stress on construction materials. As there is no combustion, corrosive combustion by-products are not produced. All electronics and active components are sealed away from the combustible gas environment. So, there is no inhibitor, which helps in providing improved gas response [20].

However, close coupling of electronics to IR sensor limits operation at high temperature. Exceeding the operational temperature limit can cause IR sensor drift or failure. Due to component precision and assembly, IR sensors have higher initial cost than catalytic detectors. IR sensors do not detect all combustible gases (e.g. hydrogen). Humidity and water may affect the sensor. Dust and dirt can coat the optics and impair sensor response.

C. Electrochemical Sensors

Theory: Electrochemical sensors are fuel cell-like devices consisting of an anode, cathode, and electrolyte. The components of the cell are selected such that target gas is allowed to diffuse into the cell, which causes chemical reactions and generates current.

Working procedure: It (Fig. 9) consists of a sensing electrode (or working electrode) and counter electrode separated by a thin layer of electrolyte/catalysts. Gas that comes in contact with the sensor first passes through a small capillary-type opening and then diffuses through a hydrophobic barrier, and eventually reaches the electrode surface. This approach is adopted to allow the proper amount of gas to react at the sensing electrode to produce sufficient electrical signal while preventing the electrolyte leaking out of the sensor. The gas that diffuses through the barrier reacts at the surface of the sensing electrode involving either an oxidation (CO, H₂S, NO, SO₂ etc.) or reduction (NO₂ and Cl₂) mechanism. These reactions are catalyzed by electrode materials specifically developed for the gas of interest [21].

Fig. 9: Electrochemical gas sensor [22]

The counter electrode balances the reaction of sensing electrode – if the sensing electrode oxidizes the gas, then the counter electrode must reduce some other molecule to generate an equivalent current.

Reactions: The reaction kinematics is explained by the following reactions:
For working electrode: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \) (3)
For counter electrode: \( \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \) (4)
Overall cell reaction: \( 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \) (5)

The main responsibility of the potentiostat circuit is to ensure that adequate current is fed to the counter electrode and the counter electrode can operate at its preferred potential.

For a sensor requiring an external driving voltage, the sensing electrode potential does not remain constant due to the continuous electrochemical reaction taking place on the surface of the electrode. It causes deterioration of performance of the sensor over extended periods of time. To improve the performance of the sensor, a reference electrode is introduced. The reference electrode maintains the value of this fixed voltage at the sensing electrode. No current flows to or from the reference electrode. Sometimes a scrubber filter is installed in front of the sensor to filter out unwanted gases. [23]

Gas specific electrochemical sensors can be used to detect the majority of common toxic gases, namely CO, H₂S, Cl₂, SO₂ etc. in a wide variety of safety applications. They can be specific to a particular gas or vapour. They are typically very accurate. They do not get poisoned easily.

As disadvantages, electrochemical gas sensors have a narrow temperature range and a short shelf life; they are subject to several interfering gases such as hydrogen. Sensor lifetime will be shortened in very dry and hot areas.

D. Semiconductor Sensor

Theory: These sensors (also called solid state sensor) are primarily used for toxic gas measurements and limited use in CHC gas measurement. A semi conducting material is applied to a non-conducting substrate between two electrodes (Fig. 10).

Fig. 10: Schematic diagram of modern resistive semiconductor gas sensor [24]

The substrate is heated to a temperature such that the gas being monitored can cause a reversible change in the conductivity of the semi-conducting material. The target gas interacts with the surface of the metal oxide film (generally through surface adsorbed oxygen ions), which results in
change in charge carrier concentration of the material.

This leads to alter the conductivity of the material. An n-type semiconductor is one where the majority charge carriers are electrons, and upon interaction with a reducing gas an increase in conductivity occurs. Conversely, an oxidizing gas serves to deplete the sensing layer of charge carrying electrons, resulting in a decrease in conductivity. Opposite effects are observed with p-type semiconductor material (Table IV).

<table>
<thead>
<tr>
<th>Classification</th>
<th>Oxidizing gases</th>
<th>Reducing gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance increase</td>
<td>Resistance decrease</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance decrease</td>
<td>Resistance increase</td>
</tr>
</tbody>
</table>

Working procedure: The gas sensing film is located on a micro machined hotplate which operates at 100-400 °C. Under zero gas condition, it is assumed that O_2 molecules tie up free electrons in the metal oxide semiconductor material by absorbing on its surface, thereby inhibiting electrical flow [26]. The depleted layers are responsible for a high contact resistance. For conduction, electrons must cross over the surface barriers.

As reducing gases (CO, methane, H_2S or H_2 gases) are introduced, they replace the O_2, release free electrons and decrease resistance between the electrodes (Fig. 11). This change in resistance is measured electrically. It is proportional to the concentration of gas being measured [28]. The sensitivity of metal-oxide gas sensors can be substantially improved by dispersing a low concentration of additives, such as Pd, Pt, Au etc.

Reactions: Atmospheric oxygen molecules are adsorbed on the surface of semiconductor oxides in the form of O^+, O^- or O_2-. The reaction kinematics is explained by the following reactions:

\[
\text{O}_2 (\text{gas}) + e^- \rightarrow \text{O}_2 (\text{ads})^- \\
\text{O}_2 (\text{gas})^- + e^- \rightarrow 2\text{O} (\text{ads})^-
\]

The presence of chemically adsorbed oxygen causes electron depletion in the thin film surface and building up of Schottky surface barrier. Consequently, the electrical conductance of thin film decreases to a minimum. The SnO_2 thin film interacts with oxygen by transferring the electron from the conduction band to adsorb oxygen atoms. The response to H_2S can be explained as a reaction of gas with the O_2 (ads)^-:

\[
\text{H}_2\text{S} + 3\text{O} (\text{ads})^- \rightarrow \text{H}_2\text{O}(g) + \text{SO}_2(g) + 3e^-
\]

With this reaction, many electrons are released to thin film surface. This decreases the Schottky surface barrier and makes depletion layer thinner; consequently, the electrical conductance of the thin film increases. Metal oxide semiconductor (MOS) sensors may be used for toxic as well as combustible gas monitoring.

Tungsten oxide semiconductor is somewhat rugged, sensitive to parts per million (ppm) levels, flood-proof and less expensive. The major disadvantage of the sensor is that the sensor is sensitive to humidity and temperature, but not specific to gases and vapors.

E. Laser Sensor

1) Tunable diode laser absorption spectroscopy

Theory: Tunable diode laser absorption spectroscopy (TDLAS) is a technique used for measuring concentration of gases (methane, water vapour etc.) in a gaseous mixture based on the characteristic of the distributed feedback (DFB) diode laser with narrow line width and tenability. This makes it possible to obtain the spectroscopy of single molecule absorption line in the characteristic absorption spectrum region [29].

The focus here is on a single absorption line in the absorption spectrum of a particular species of interest [30]. TDLAS sensors commonly exploit the laser’s fast tuning capability to modulate the wavelength, causing it to sweep back and forth across an absorption feature at a precise modulation frequency. When narrow-band light passes a gas cell, Beer’s Law describes the exact relationship between IR light intensity and gas concentration same as Infrared gas
sensor.

Working procedure: Most of gaseous materials show characteristic optical absorptions, especially in the mid-infrared (2–25 μm) band. The optical fingerprints of different gases have made the spectral absorption a unique method of gas analysis [31]. In TDLAS, a diode laser emits light at a well-defined but tunable wavelength over the characteristic absorption lines of a target gas in the path of the laser beam. This causes a reduction of the measured signal intensity, which can be detected by a photodiode, and then used to determine the gas concentration (Fig. 12).

![TDLAS gas detector system](image)

**Fig. 12: TDLAS gas detector system** [32]

Different diode laser are used based on application and the range of tuning required. Typical examples of laser diode are InGaAsP/InP (tunable over 900 nm to 1.6 μm), InGaAsP/InAsP (tunable over 1.6 μm to 2.2 μm) [33]. Varying the quantum cascade laser (QCL) temperature and/or laser injection current provides wavelength tuning of the emitted laser radiation from DFB devices within a limited spectral range (~10 cm-1). The external cavity configuration, EC-QCL approach allows tuning over a range of >200 cm-1 [34]. Wavelength modulation spectroscopy (WMS) is based on the modulation of the light emitted by a laser that is slowly tuned through an absorption feature of the species to be detected. The signal of second harmonic can be measured with lock-in amplifier and it is proportional to the concentration [35]. In different temperature conditions, for the same concentration of gas, the amplitude of second harmonic detected by lock in amplifier fluctuates with the variation of ambient temperature. WMS measures faster response and can provide parts per million (ppm) to parts per billion (ppb) chemical detection limits, depending on the spectroscopic properties of the target gas and the sampling path length. WMS is thus a highly sensitive and gas-specific form of spectroscopic gas analysis [32].

**Advantages:**

a. TDLAS has been widely employed in detecting atmospheric trace gases due to its high sensitivity, high selectivity, and fast time.

b. TDLAS method uses a compact single mode diode laser tuning over an interested wavelength range swiftly to fulfill the function of spectroscopy scan, may overcome the drawback of FTIR, especially in field on-line applications where fast response needed [29].

c. A further advantage of near infrared TDLAS is compatible with optical fibers for optical communication, which makes it easy to realize multipoint remote sensing.

d. The laser emission line-width is narrower than gas absorption line-widths. This may be contrasted with near-IR (NIR) absorption techniques that sample with broadband sources and measure absorption from multiple lines across a fairly broad range of frequencies. TDLAS thus offers the advantage of selectivity for a target trace gas absent spectral interferences from other background gases.

**Disadvantages:**

a. In different temperature conditions, for the same concentration of gas, the amplitude of second harmonic detected by lock in amplifier fluctuates with the variation of ambient temperature. For the retrieval of the trace gas concentration, the influence of temperature fluctuations must be taken into account.

b. Any noise introduced by the light source or the optical system will deteriorate the detectability of the technique.

2) **Differential Absorption Light Detection and Ranging**

**Theory:** Simple TDLAS measures the presence/concentration of a particular gas based on receiver measuring wavelength not absorbed by the target gas whereas differential absorption light detection and ranging is based on returning backscattered signal intensity absorbed by target gas as shown in Fig. 13. This system can detect and measure the presence of CO₂, CO, CH₄ etc. LIDAR (Light Detection And Ranging) operates in the ultraviolet, visible and infrared portion of the spectrum [36].

![Differential absorption LIDAR concept](image)

**Fig. 13: Differential absorption LIDAR concept** [36]

**Working procedure:** The laser source emits a laser beam in tune with molecular absorption line of a target gas and receives a reflected signal affected by gas absorption of the target gas in the atmosphere [37]. Near the optimum wavelength for the particular gas to be measured, the amount of absorption of the transmitted light varies strongly according to the wavelength for each particular molecule, and this creates unique molecular “signatures” for these gases. Therefore, the method called “Differential Absorption LIDAR” (DIAL) can be used to determine the concentration.
The large dust particles also backscatter radiation, but their scattering is much less wavelength dependent [38].

F. Fiber Optic Sensor

Theory: Two distinct approaches used in fiber optic sensors are: Firstly, by directly probing the spectrochemical changes, when interrogating wavelength coincides with the absorption band of the analyte. Such direct spectroscopic measurement is observed in near infrared TDLAS. Secondly, by utilizing an analyte specific reagent transducer converts analyte concentration into an optical signal. Majority of this involve an intermediate sensor element, which undergoes chemical changes initiated in the presence of the specific analyte [39].

In second method, sensor works based on modified cladding approach [40]. The cladding of the optical fiber is removed and the gas sensitive material (the conducting polymer film) is coated on a small section of the fiber (sensing probe). The sensing probe length, source intensity and source wavelength, indicates influence on the sensor response.

Working procedure: Optical fiber sensor uses a light modulation, i.e. one of the light parameter changes according to the analytes presence. Organic conducting polymer such as polypyrrole, polyaniline, polythiophene shows a reversible change in their resistance when exposed to certain vapors [41]. The change in conductivity changes permittivity, which leads to change in the refractive index. The analytes reacts with the coating to change the optical properties i.e. refractive index, absorbance, and fluorescence which is coupled to core to change the transmission properties through the optical fiber. An extrinsic fiber-optic evanescent wave chemical sensor is developed by replacing a certain portion of the original cladding with chemically sensitive material [42]. The sensor structure in which small section of cladding is replaced with chemically sensitive layer is shown in Fig. 14.

Advantages of fiber optic sensor are geometrical flexibility, remote sensing capability, small size and lightweight. It offers complete electrical isolation.

G. Thermal Conductivity

The principle of thermal conductivity is very similar to that of the pellistor. Two platinum coils are arranged in a Wheatstone bridge circuit. One coil is in contact with the gas stream and other is sealed into a separate chamber, used for temperature compensation (Fig. 15). All the gases have different thermal conductivity’s and so will conduct heat away from the coil in the gas stream at different rates. The change in temperature of the coil is directly proportional to the change in thermal conductivity of the gas mixture flowing past it [43].

The major drawback of the sensor is that it is less selective and sensitive. This technique for detecting gas is suitable for the measurement of high (%V/V) concentrations of binary gas mixes.

H. Ionization Detector

Photo ionization (Fig. 16) and flame ionization (Fig. 17) are common detection techniques used for gas chromatographic (GC) systems in laboratory environments. Both have very good sensitivity and large linear dynamic range.

Both techniques measure the current generated by the ionized species sensed by ion collector. The photoionization technique ionizes molecules using a high energy photon source, such as ultraviolet (UV) radiation [45], while flame
ionization technique burns organic molecules in a hydrogen flame [46]. The ions generations are detected similarly in both PIDs and FIDs. When electric field gradient is applied across the ionization region to drive the ions to the electrodes, the ions release their charges to produce signals that can be processed.

**Flame Ionization Detector (FID)**

The main differences between these two techniques are their ionization source and mechanism. The photoionization technique is a nondestructive method whereas the gas sample is destroyed in flame ionization method.

1. **MEMS Technology**

Micro-electro-mechanical systems (MEMS) are three-dimensional, electro-mechanical devices, which are made by micromachining silicon wafers using standard microelectronic fabrication and post-process techniques [49]. MEMS have been used to reduce the size, power consumption and cost of gas sensors while improving overall performance [50]. MEMS can be used in different innovative ways by combining the existing proven technologies as described herewith.

MEMS based array of sensor (work function based): Micromachining processes have enabled designers to place arrays of sensors on a single chip that can be mass-produced at reduced cost. SnO$_2$/Pt, WO$_3$/Au and ZnO/Pd sensing films were found sensitive to the target gases NH$_3$, H$_2$S and CH$_4$, respectively. Sensing pastes are deposited on the outside of a ceramic tube with a heater on the inside (Fig. 18). But these sensors have some cross-sensitivity. Further, this technique suffers from baseline drift, and high resistance and recovery time. However, sensor array response to the gases is unique, which allows selectivity by pattern recognition [51].

Fig. 18: CMOS based micro hotplate design of gas sensor array [50]

The resistance of a metal oxide film varies depending on the type of gas exposure. Combustible gases such as CH$_4$, H$_2$S and NH$_3$ act as reducing agents thereby adding electrons to the metal oxide, which increases conductivity (decreases resistance). Metal oxide sensing films have been doped with noble metals to increase sensitivity and reduce response time. Dopants such as Pt or Pd are catalysts that promote chemical reactions by reducing the activation energy between the film and test gas without being consumed by them. This allows the reaction to occur at a faster rate and lower gas concentrations.

Cantilever based sensor (piezoelectric based): Piezoelectric power generator made by MEMS technology can scavenge power from low-level ambient vibration sources. The developed MEMS power generators are featured with fixed/narrow operation frequency and power output in microwatt level [52]. These devices can be used as sensing platforms. Molecular adsorption of target gas onto the sensing element, a cantilever, shifts its resonance frequency and changes its surface forces (surface stress). Adsorption onto the sensing element (composed of two chemically different surfaces) produces a differential stress between the two surfaces and induces bending. The analyte that induces the mechanical response is chemisorbed onto the cantilever in a reversible or irreversible process. Devices that respond to chemical stimuli in this manner are referred as micro-cantilever sensors [53].

Cantilever based hydrogen sensor uses piezoelectric principle for gas sensing. This sensor uses stress-sensitive, palladium coated micro-cantilevers to detect hydrogen (Fig. 19). Absorption of hydrogen into palladium is fully reversible, at any given moment the cantilever capacitance indicates the current hydrogen concentration [54].

Fig. 19: Cantilever based hydrogen gas sensor [54]

J. **Nanotechnology**

Applications of nanotechnology in gas sensors are still in the preliminary stage of development. Presently, metal oxide 1-dimensional (1D) nanostructure as gas sensors are most promising area for nanotechnology. Some other 1D nanostructure gas sensors operation is based on changes in the photoluminescence spectroscopy and the mass of sensing
element, which accurately uses a quartz crystal microbalance [55].

1D nanostructure has advantages over conventional metal-oxide-based sensors in terms of power consumption, sensitivity, miniaturization and large surface area to volume ratio [56]. The change in the electrical conductivity caused by chemisorption of gas molecules on the surface of 1D nanostructure metal oxides is measured by electro-transducers. The main structures of the electro-transducers are field effect transistors (FET), resistive gas micro-sensors, and resistive gas sensors [57]. 1D nanostructure FET is fabricated using a single nanowire bridge between two metal electrodes on a heavily doped silicon substrate covered with SiO₂ acting as insulating layer between the nanowire/electrode combinations and the conducting silicon (Fig. 20).

Resistive gas micro-sensors are manufactured by MEMS technology in which a film composed of nanowires is contacted by pairs of metal electrodes on a substrate (Fig. 21). The measurement is performed by monitoring the changes in current or resistance of the device. The other one is resistive gas sensor, the channel length between the two electrodes for resistive sensor is usually in the millimeter scale within a ceramic tube.

For photoluminescence measurement, nanowire samples are mounted in a small vacuum chamber with ports to pass gasses and provide optical access. Photo-desorption and photo-adsorption of gases are found to affect the intensity, indicating the participation of free carriers. The time dependence of the changes in the spectral peak intensity is compared for measurement of gas concentration.

Quartz crystal microbalance (QCM) is an extremely sensitive measurement device. The principle of measurement is based on mass change as the gas adsorbs on the surface of the sensing material. It is quantitatively measured based on change in frequency rate (Sₚ) given by:

$$ S_p = \frac{|\Delta f/\Delta t|}{|am/A|/\Delta t|} \quad (9) $$

Where,

- Δf — response frequency shift within the time interval of Δt,
- a — constant,
- f — fundamental frequency of the unloaded piezoelectric crystal,
- Δm — mass loading on the surface of the crystal, and
- A — surface area of the electrode.

Ceramics such as zinc oxide (ZnO), tin oxide (SnO₂), indium oxide (In₂O₃), and titanium dioxide or titania (TiO₂) are used as nanowires/nanobelts for gas sensing. Carbon nanotubes (CNTs) have many distinct properties that may be exploited to develop next generation sensors. Single walled nanotubes (SWNTs) have been highlighted as gas-sensing elements due to the 1D structure with all the atoms residing only on the surface.

CNTs can be designed to have specific properties by changing the ratio of diameters of linearly joined CNTs, which in turn can be used in fabrication of FETs. The untreated SWNT-FET typically shows a p-type behavior, with threshold voltages being shifted upon gas exposure [58]. The inlet and outlet valves allow gases to flow over the carbon nanotubes of FET. Gas flow increases conductance of the carbon nanotubes. This can be obtained using current-voltage relationship before and after exposure to the gases. The effect occurs because when the gas molecules bond to the carbon nanotubes, charge is transferred from the nanotubes to the gas molecules, which increases hole-concentration in the carbon nanotubes and enhances the conductance (Fig. 22). The carbon nanotubes are covered with an insulating protection film [59]. CNTs show almost threefold sensitivity and efficiency compare to other metal oxide gas sensors available in the market, such as tin oxide sensor [60].

**IV. CHARACTERISTICS OF GAS SENSORS**

Performance of sensors is characterized by the following parameters [62]:

- Sensitivity is a change of measured signal per analyte concentration unit, i.e. the slope of a calibration graph.
This parameter is sometimes confused with the detection limit.

- Selectivity refers to characteristic that determines whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte.
- Stability is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response and recovery time.
- Detection limit is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- Dynamic range is the analyte concentration range between the detection limit and the highest limiting concentration.
- Linearity is the relative deviation of an experimentally determined calibration graph from an ideal straight line.
- Resolution is the lowest concentration difference that can be distinguished by sensor.
- Response time is the time required for sensor to respond to a step concentration change from zero to a certain concentration value.
- Recovery time is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.
- Working temperature is usually the temperature that corresponds to maximum sensitivity.
- Hysteresis is the maximum difference in output when the value is approached with an increasing and a decreasing analyte concentration range.

- Life cycle is the period of time over which the sensor will continuously operate.

V. COMPARISON OF VARIOUS SENSORS

An ideal sensor would possess: (i) high sensitivity, dynamic range, selectivity and stability; (ii) low detection limit; (iii) good linearity; (iv) small hysteresis and response time; and (v) long life cycle. However, no single gas sensor is perfect in all the above parameters. Combination of appropriate detectors and sampling techniques help in reliable measurement of the target gas based on ambient conditions of the measuring area. Selection of right sensor is important for mitigating the impending hazard.

One sensor can be evaluated and compared against other sensors. Selection of sensors depends on various parameters, namely physical properties of target gases, ambient conditions, required sensitivity, maintenance cycle, method of operations etc. Given the large number of variables, it is tempting to either oversimplify the selection process to a few rules. Three qualities are essentially required in a sensor for gas monitoring, i.e. simple, reliable and easy to maintain. Simple means not much complicated, adapted to user’s requirement and backed by strong technology. Reliable indicates always “alarm” when required and “never” when should not. Easy to maintain specifies calibration is not required often, lifespan is long and troubleshooting is simple. Advantages and disadvantages of different types of sensor are summarized in Table V.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic</td>
<td>Simple, robust and inexpensive.</td>
<td>Sensor poisoning, sensor inhibitors and sensor cracking</td>
</tr>
<tr>
<td>Infrared</td>
<td>Immune to poisons and contamination, fail-safe operation, no routine calibration is required, and ability to operate in continuous presence of gas.</td>
<td>Flammability detection is only in %LEL range, high to medium power consumption, and the gas must be infrared active.</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>Reliable, fast response, low power, measures toxic gases in relatively low concentration, and wide range of gases can be detected.</td>
<td>Limited to operate at low ambient temperature and narrow pressure range, unsuitable for use in dry atmosphere and not fail-safe.</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>Robust, long operating life, wide operating temperature range, detect wide range of gases.</td>
<td>Commonly poor selectivity causing ‘false’ alarm, high power consumption and response drift problem.</td>
</tr>
<tr>
<td>Laser</td>
<td>No interference from other gases, high speed, high selectivity, low maintenance and operating cost, and self-calibration.</td>
<td>Only one gas can be measured with each instrument; heavy dust, steam or fog blocks laser beam.</td>
</tr>
<tr>
<td>Flame ionization detector</td>
<td>Best for CHC compounds.</td>
<td>Not used in explosive areas, destroy the sample, responds poorly to halogenated hydrocarbons, and non-specific response.</td>
</tr>
<tr>
<td>Photo ionization detector</td>
<td>Good method for organic compound detection at low level.</td>
<td>Non-specific response, and responds only to ionizable gases.</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>General applicability, large linear range, simplicity and non-destructive.</td>
<td>Low sensitivity</td>
</tr>
</tbody>
</table>
VI. CONCLUSIONS

Sensors help in maintaining safe and healthy environment in the underground mines by continuous monitoring of ambient air and taking appropriate control measures. Several promising new sensors have been developed, but no single sensor is reliable enough to detect every gas accurately. Catalytic bead sensor is simple but always not reliable and often calibration is required. However, IR sensor is reliable and easy to maintain, but it is expensive.

When toxic gas sensors are compared, there are apparent design weaknesses in the semiconductor sensors as compared to the electrochemical sensors. The biggest drawback is response time. Traditional electrochemical sensors too have disadvantages, but new developments in electrochemical technology have removed many of those shortcomings. Among many developments, MEMS is an emerging technology which uses the tools and techniques that were developed for the integrated circuit industry to build microscopic sensors. These sensors are built on standard silicon wafers. However, one of the disadvantages of the traditional semiconducting metal oxide gas sensors is low gas sensitivity due to the limited surface-to-volume ratio. In addition, many of the ceramic and thin film gas sensors must be operated at temperatures exceeding 500 °C in order to improve the sensitivity.

Nano-materials offer new possibility for improving solid state gas detection. Nanostucture sensing materials such as nanowires, nanotubes and quantum dots offer an inherently high surface area. In fact, carbon nanotubes have one of the best available surface-to-volume ratios. The increased surface area leads to high sensitivity, fast response and often allows lower operating temperatures. In addition, different types of nano-materials have different sensitivity. By applying different nano-materials on the same MEMS platform more gas mixtures can be detected.

The future of gas sensor is determined to a great extent by new detection principles, new or enhanced sensors, sophisticated evaluation algorithms and latest communication technologies. Equally, new demands arising from unconventional applications have stimulated new solutions, combining proven technologies in novel and innovative ways.

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