

Chapter 2

Sensors for Air Monitoring

Rishi Kant and Shantanu Bhattacharya

Abstract Monitoring and diagnosis of air quality are essential for providing clean and safe air for breathing. In the current scenario, the air around us contains different types of pollutants such as CO (carbon monoxide), methane (CH₄), sulphur dioxide (SO₂), nitrogen oxides (NO_x), ammonia (NH₃), ozone (O₃), volatile organic compounds (VOCs), heavy metals [Pb (lead), Hg (mercury), etc.] and particulate matter [mixture of suspended particles in air (PM_{2.5} and PM₁₀)] leading to severe respiratory disorders within all age groups. These pollutants put threat to life in general by affecting living beings through respiratory system, digestive system, urinary system, nervous system, etc. Thus, it is important that proper diagnostic techniques to be developed for their quick identification and quantification in whole air samples and if possible their immediate remediation through air filtration methods. The present air monitoring stations (comprising sensors) are scattered and fixed in one area which are generally unable to detect most polluted area in one city. So, there is a lot of scope for the development of miniaturized air sensors based on MEMS/NEMS technologies. This chapter presents brief review on MEMS-/NEMS-based air sensors for collecting real-time data in quick time with higher sensitivity and selectivity. Apart from this, a summary of the various technologies like the semiconducting metal oxide, optical, calorimetric, surface acoustic wave, gas chromatography, chemiluminescence is presented in view of air sensor development.

Keywords Air pollutants • Air sensors • Diagnostics • MEMS/NEMS
Particulate matter • Human health

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1 Introduction

A healthy human inhales around 10^3 L of air every day. The clean air is a basic requirement for the survival of humans in this planet. The current trend of modernization and industrialization of human civilization has led the human life to go into a critical situation as air pollutants are increasing day by day. These air pollutants can go directly into human systems affecting the organs like lungs, kidneys, heart, nervous system. The pollutants can enter into blood–air barrier (alveolar–capillary barrier) creating deleterious effects to the human body which in turn may create respiratory diseases (Beelen et al. 2008), cardiopulmonary mortality (Filleul 2005), asthma exacerbations (Guarnieri and Balmes 2014), etc.

The surrounding air mainly consists of air pollutants like nitrogen oxides (NO_x), ammonia (NH_3), CO (carbon monoxide), methane (CH_4), sulphur dioxide (SO_2), ozone (O_3), cigarette smoke, volatile organic compounds (VOCs) and particulate matter (mixture of suspended particles in air ($\text{PM}_{2.5}$ and PM_{10})). Table 1 summarizes the effects of different air pollutants on human health. Since these air pollutants put a threat to human life, so their diagnostics and control become a grand challenge to scientists and technologists. In 2005, World Health Organization (WHO) has released guidelines on these air pollutants which are summarized in Table 1. Through a review conducted by WHO for air quality in 2015, it has been found that 92% of world population is currently living in polluted environment with respect to standard guidelines of the World Health Organization (WHO 2015). We can categorize environmental pollutants based on their physical and chemical characteristics as follows:

- (i) Air pollutants (such as NO_x , CO, O_3 , VOC, SO_2 , CO, NH_3).
- (ii) Persistent organic pollutants (such as dioxins).
- (iii) Heavy metals [such as Pb (lead), Hg (mercury)].
- (iv) Particulate matter (PM) (such as $\text{PM}_{2.5}$ and PM_{10}).

We will be focusing on the detection of air pollutants in this particular chapter. Air pollutants' sources and their effect on human body have been summarized in Table 1.

The air monitoring has now been primary task for human beings as air pollution has become threat to the whole human civilization. It is an urgency of today's world to monitor and control air pollutants precisely. For identification and quantification of air pollutants precisely, sensors must have high sensitivity, selectivity, response time, reversibility, low fabrication cost, low energy consumption, portability of instruments, etc. The monitoring of air quality by conventional techniques which commonly utilize networks of air monitoring stations is unable to detect most polluted areas in quick and real time with high sensitivity and specificity which create the need for the evolution of real-time monitoring micro-/nanosystems. Recently, MEMS (microelectromechanical systems)-/NEMS (nanoelectromechanical systems)-based technologies have shown promising outcome for the development of real-time-based sensors for air monitoring (White et al. 2012).

Table 1 Various air pollutants with their effect on human health (Kampa and Castanas 2008), effect on environment, source and WHO guidelines

Air pollutant	Effect on environment	Effect on human health	Source	WHO guidelines
O ₃	Greenhouse effect, damaging forest and crop growth	Asthma, pulmonary inflammation, lung disease, etc.	Photochemical reaction of VOC, NO _x and CO under the ultraviolet (UV) light illumination	100 µg/m ³ 8-h mean
CO	Causing effect on greenhouse gases	Can cause dizziness, headache, nausea and vomiting	Incomplete combustion of gasoline, charcoal, wood, coal, etc.	10 mg/m ³ 24-h mean
NO ₂	Causing acid rain and making hazy air	Can damage lung tissue and respiratory organs	Combustion using automobile engines, thermal power plants, chemical refineries, etc.	200 µg/m ³ 1-h mean
SO ₂	Causing acid rain and deforestation	Nose irritation, shortening of breath, coughing and wheezing, etc.	Combustion of coals and petroleum in power plants, refinery facilities and household fireplaces	20 µg/m ³ 24-h mean
NH ₃	Causing acidification of groundwater	Burning sensation in nose, throat and respiratory system. Can be cause of respiratory system failure	Agriculture-related chemicals, food industry and by dead animal's body decomposition, etc.	17 mg/m ³ 8-h exposure
PM _{2.5} (particle size less than 2.5 µm)	Causing depletion of nutrients in the soil, acidic rain, etc.	Can damage alveolar wall, lung and throat region of the respiratory track	Soil, rock, emission by automobile and burning plants	25 µg/m ³ 24-h mean
PM ₁₀ (particle size less than 10 µm)	Harmful to plants and soil, may cause global warming	Bronchitis, lung cancer, asthma and cardiovascular diseases	Construction sites, agriculture, landfills, motor vehicles and waste burning in open environment, etc.	50 µg/m ³ 24-h mean

Today, the pervasive air monitoring is being envisioned due to the developments that have taken place in the area of MEMS/NEMS technologies and wireless sensing network. The conventional air monitoring systems have kept challenges as they are bulky in size, remain fixed at one location, and contain heavy weight and higher price. In today's world of extreme human activities, the air monitoring in urban areas requires quick and reliable technological solution which can generate pollution maps in the real time. This enables the people to be more aware of surrounding air condition.

In order to deal emerged problems, the researchers are trying to couple the portable air sensor and wireless sensor network. Combining these two components (portable air sensor and wireless sensor network) enables the person to visualize updated information at every second (Ma et al. 2008). The portability of low-cost

air sensors enables the large-scale arrangement of sensor nodes which in turn increase the spatial and temporal resolution of most polluted areas in the city. The real-time monitoring of air quality with good space and time resolution provides useful information to the people which enable them to take precautions as per their health condition.

In the present chapter, first, we will focus on various MEMS-/NEMS-based technologies that are being utilized for robust air sensor development and their mechanisms for diagnostics of different air pollutants. Further, we will discuss different air pollutant sensors and their capability to detect air pollutants which are presently available in the markets and their limitations.

2 Sensors Based on Various Sensing Techniques

A sensor essentially contains an element which can respond to any alteration in physical/chemical properties. Such response is recorded and then converted in the form of electrical signals with the help of transducers. There exist different techniques for the detection of air pollutants, based on which various sensors can be classified. The different sensor can also be categorized on the basis of sensing materials such as metal oxide semiconductor, nanostructured materials, graphene, carbon nanotube (CNT), polymers, nanofibres. The different sensing techniques can detect air pollutants by measuring the change in electrical conductivity, work function, optical parameters (such as absorption, refractive index, fluorescence, reflection), temperature and the electric current of the sensing material. These techniques have their advantages and disadvantages; for example, metal oxide-based technologies can provide portability to sensor but the same time, they have limitations on sensitivity and selectivity in comparison with optical-based technologies, while optical-based technologies such as Fourier transform infrared spectroscopy (FTIR), differential optical absorption spectroscopy (DOAS), non-dispersive infrared (NDIR) spectroscopy hinder the portability of air sensor. Figure 1 demonstrates various changes happening during sensing of air pollutant by metal oxide-based sensor. The different types of air sensor which can be categorized on the technological basis have been detailed in the following section.

2.1 *Semiconducting Metal Oxide Sensors (SMOS)*

Sensors based on semiconducting metal oxide find a wide range of applications (such as in automobile, gas sensing, biomedical research, electronic nose). These sensors are suitable candidates for commercialization as they possess high sensitivities, reversibility and have low fabrication cost and also provide ease of portability to instruments. Generally, metal oxide-based sensors include electrodes, sensing elements and the heating elements. For detecting air pollutants, the change

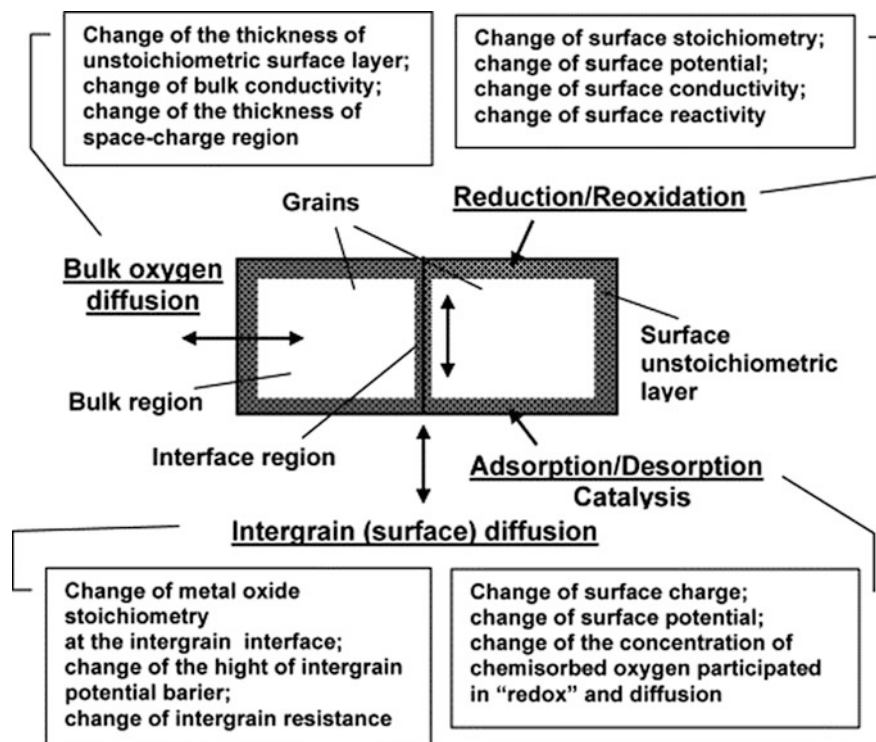


Fig. 1 Changes occurring in semiconductor metal oxides' properties during sensing. Reprinted with permission from Korotcenkov (2007)

of resistance of sensing elements is measured over electrodes. These sensors can perform the detection of air pollutants under adverse environmental conditions.

Their mechanism of sensing can be described in four steps which are as follows:

- (i) Pre-adsorption of oxygen on metal oxide surfaces.
- (ii) Air pollutant adsorption.
- (iii) Adsorbed air pollutant and oxygen reaction.
- (iv) Desorption of reaction products of reactions (i.e. previous step).

During above steps, the transfer of electrons between air pollutant and metal oxide yields higher sensitivity of the sensor. When the sensor's surface reacts with air pollutants, its conductivity increases due to the adsorbed surface oxygen which acts as acceptors while a decrease in conductivity of oxygen molecules occurs by virtue of their electron-donating capability (Gardner 1989). In the world of nanotechnology, the characterization of nanostructured metal oxide sensors is being carried out by FET (field-effect transistor), conductometric and impedometric sensors. These nanostructured metal oxides such as TiO_2 , Fe_2O_3 , GeO_2 , MoO_3 , Nb_2O_5 , CuO , Mn_2O_3 , Cr_2O_3 , Co_3O_4 , Ta_2O_5 , La_2O_3 offer their applicability for

sensing of air pollutants by conductive measurements (Kanazawa et al. 2001). In the literature, the numerous work for detecting NO₂ (air pollutants) has been reported by various researchers as NO₂ is considered to be a very dangerous gas for affecting the health of living organisms (Gardner 1989). A sensor based on WO₃ (tungsten oxide) fabricated with thin film deposition techniques (like electrostatic spray) was utilized to detect NO₂ at considerably lower amounts (below 1 ppm) (Ghimbeu et al. 2010). Heidari et al. (2010) reported the synthesis of WO₃ nanoparticles which were deposited over alumina substrates by AC electrophoresis methods. The fabricated sensor shows a response with NO₂ detection limit (~50 ppb) at 200 °C. ZnO (zinc oxide) has also shown its applicability as a sensing element for NO₂ detection, and the synthesis of ZnO nanopowder was performed by aerosol methods (Baratto et al. 2004). This sensor showed limit of detection for NO₂ up to 0.1 ppm at 200 °C.

Furthermore, there exist a wide variety of air pollutants (NO₂, CO, NH₃, SO₂ and CH₄) sensors which were reported time to time in the literature. They have been summarized in the following section in tabular form (Tables 2, 3, 4, 5 and 6). The tabular form consists of the details about sensing element, fabrication method limit of detection, etc.

In current practice, there has been more attention to explore the possibility of sensing through nanostructured sensing elements such as graphene (Yuan and Shi 2013), ZnO nanobundles (Gupta et al. 2014), TiO₂ (Kirner et al. 1990) to provide a large surface area for coming air pollutant molecules. Recently, inkjet printing has been heavily utilized to fabricate graphene-based flexible NH₃ sensor which contained poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)-grapheme (PEDOT: PSS) film for sensing. Fig. 2 shows different steps for fabricating graphene-based air sensor which contains (a) an electrode fabrication process, (b) inkjet printing process, (c) deposition of graphene-based sensing film and (d) real picture of the fabricated sensor.

Table 2 Summary of different reported semiconducting metal oxides for NO₂ detection

Sensing element	Fabrication method	Limit of detection/ range (ppm)	References
WO ₃	Electrospinning of PVP/TiO ₂ /Pd composites and calcination	0.8–2.8	Moon et al. (2010)
WO ₃	Screen printing	Up to 300	Jo et al. (2009)
ZnO	Hydrothermal	1	Cho et al. (2006)
WO ₃	Evaporation of W filament	Up to 1	Meng et al. (2009)

Table 3 Summary of different reported semiconducting metal oxides for CO detection

Sensing element	Fabrication method	Limit of detection/range (ppm)	References
ZnO	Sputtering (via DC magnetron)	1.2–100	Min et al. (2003)
TiO ₂	Electrospinning of TiO ₂ /PVP composites and its calcination	2.6–15	Park et al. (2010)
In/ Pd-doped/ SnO ₂	Solgel	1–10	Zhang et al. (2009b)
ZnO	Evaporation	7.8–100	Lin et al. (1998)
Pt/WO ₃	Solgel	1–400	Srivastava and Jain (2008)

Table 4 Summary of different reported semiconducting metal oxides for NH₃ detection

Sensing element	Fabrication method	Limit of detection/range	References
TiO ₂	Sputtering (via DC magnetron)	500 ppm	Karunagaran et al. (2007)
CNT/SnO ₂	Heat treatment and spin coating	27–200 ppm	Park et al. (2010)
ZnO	Thick films	7.9 ppm	Zhang et al. (2009a)
WO ₃	Thick films	0.5 ppm	Sberveglieri et al. (1995)
Graphene	Inkjet printing	25 ppm at room temperature	Seekaew et al. (2014)

Table 5 Summary of different reported semiconducting metal oxides for SO₂ detection

Sensing element	Fabrication method	Limit of detection/range (ppm)	References
WO ₃	Pyrolysis	35	Shimizu et al. (2001)
Pt/WO ₃	Heat treatment and spin coating	1	
WO ₃	Electrostatic spray	3	Ghimbeu et al. (2009)
Ni/SnO ₂	Pechini method (based on solgel chemistry)	0.95	Hidalgo et al. (2005)

Table 6 Summary of different reported semiconducting metal oxides for CH₄ detection

Sensing element	Fabrication method	Limit of detection/ range	References
Pt/SiO ₂ /SnO ₂	Etching and thin film deposition	100 ppm	Friedberger et al. (2003)
WO ₃	Sputtering	0.5 ppm	Sberveglieri et al. (1995)
Pt/SnO ₂ , Mo/SnO ₂ , Cu/SnO ₂ and Rh/SnO ₂	Chemical vapour deposition and evaporation method	NA ^a	Sauvan and Pijolat (1999)

^aNA stands for data not available

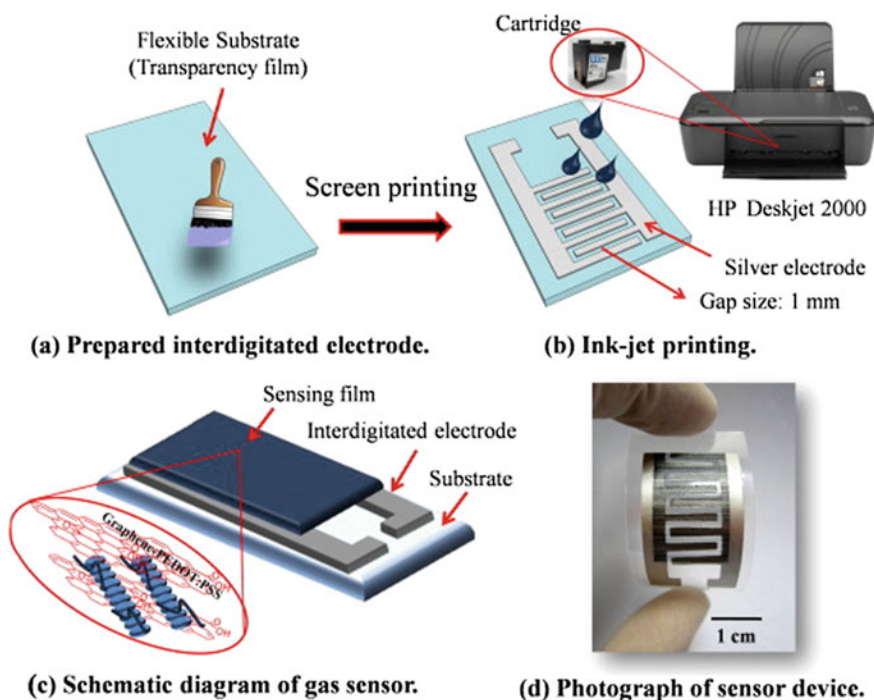


Fig. 2 Schematic representation of steps involving in fabrication of sensor device. Reprinted with permission from Seekaew et al. (2014)

2.2 Optical Sensors

Optical sensor majorly utilizes absorption and emission measurement through different techniques such as surface plasma resonance (SPR), differential optical absorption spectroscopy (DOAS), Fourier transform infrared (FTIR) spectroscopy, laser diode absorption spectroscopy (LDAS), cavity ring down spectroscopy

(CRDS), non-dispersive infrared (NDIR) spectroscopy, light detection and ranging (LIDAR), UV fluorescence and chemiluminescence for the detection of air pollutant in air samples. Optical sensors are well known for their selectivity as they do not depend on any chemical reaction or catalytic activity.

Optical detection of air pollutants follows the Beer–Lambert law which is as follows:

$$I = I_0 * e^{-\alpha l}$$

where

I is the light transmitted through the sample, I_0 is incident light, α is absorptivity, l is path length.

The detection of chemical species by spectral transmission method is widely accepted. The detection of air pollutants is realized by utilizing species' optical characteristics such as absorption, Raman scattering. There have been numerous attempts in the literature to carry out optical sensing of air pollutants. Some of them have been discussed below.

Mihalcea et al. (1998) developed a laser diode absorption spectroscopy (LDAS)-based gas sensing system to measure combustion gases (NO, CO, O₂, CO₂ and N₂O). They were able to measure NO in a spectral range 5556–5572 cm⁻¹ (at 296° K, 1 atm), N₂O in 6535–6600 cm⁻¹ (at 297° K, 272 Torr), H₂O, CO and CO₂ in 6250–6666 cm⁻¹ (at 296° K, 1 atm). The limit of detection was found to be 20 ppm for NO, 6 ppm for N₂O, 9 ppm for CO, 7 ppm for CO₂ and 43 ppm for O₂. Archenault et al. reported a low-cost optical fibre chemical sensor for CH₄ gas detection, in which refractive index of medium (acting as the cladding layer) was measured. Their apparatus was able to perform remote sensing of liquid (Archenault et al. 1992). The experimental set-up used by them has been schematically represented in Fig. 3. Further, a sensor based on optical fibre technology was presented, in which the detection of gas and chemical vapours is carried

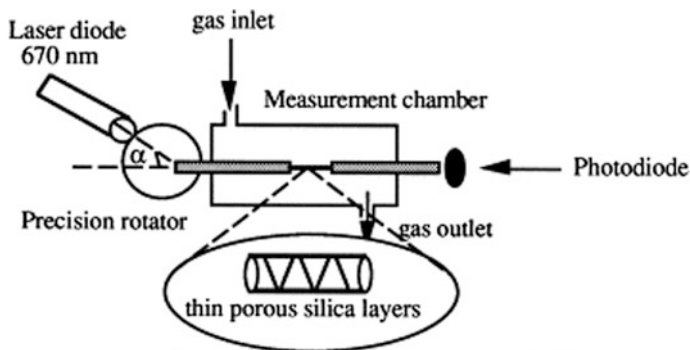
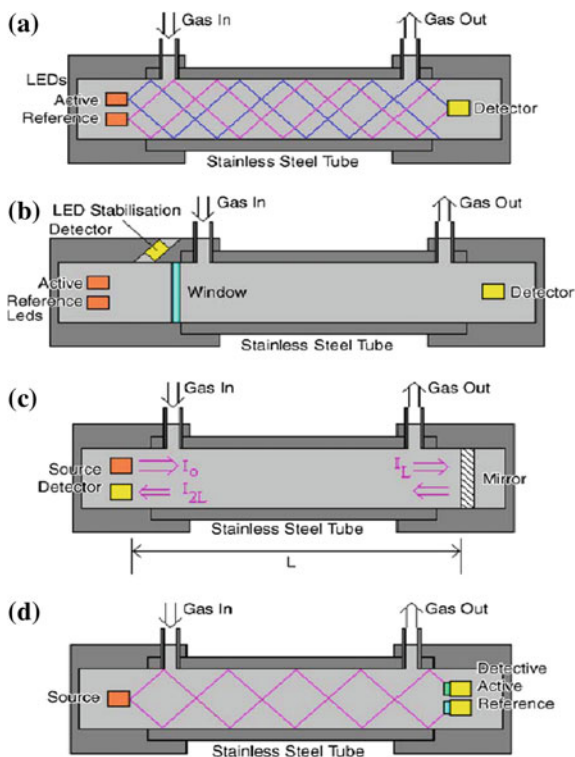


Fig. 3 Schematic representation of used experimental set-up. Reprinted with permission from Archenault et al. (1992)

Fig. 4 Different configurations for source and detector of sensor **a** dual source and single detector; **b** dual source and stabilization detector; **c** folded path; **d** single source and dual detector. Reprinted with permission from reference Massie et al. (2006)



out for alkanes and chlorinated hydrocarbons. The detection range varied between 0.6 and 25%. They used a silica fibre with a coating of porous silica fabricated through solgel method (Abdelghani et al. 1997).

For sensing of NH_3 , Kondratowicz et al. (2001) demonstrated the detection of ammonia by utilizing electrochromic polymers with fibre optic apparatus in the range of 0–1000 ppm of NH_3 with humidity range (0–100%). Later, Massie et al. presented a portable and low-cost optical sensor for CH_4 sensing with sensitivity up to 1% of the lower limit of exposure (500 ppm). They used near-IR LEDs which were operating on absorption lines of CH_4 . They tried different configurations of source and detector in a steel tube (Fig. 4) for getting the enhancement in the sensitivity of the sensor and found out that dual detector system was best suited for providing optimized performance (Massie et al. 2006).

Recently, a LED (light-emitting diode)-based CH_4 gas sensing was performed at minimum explosion limit (4.4 vol.%) (Wittstock et al. 2017). MEMS-based photoacoustic detectors were utilized to monitor methane gas inside an elliptic cell (Fig. 5a). The elliptical cell was designed in such a manner so that whole light could fall (at focal point) onto the detector. The elliptical reflector was made of half ellipsoids which were overlapped (Fig. 5b). The complete sensor design consists of microcontroller coupled with amplifier for controlling LED (mid-IR range), LED

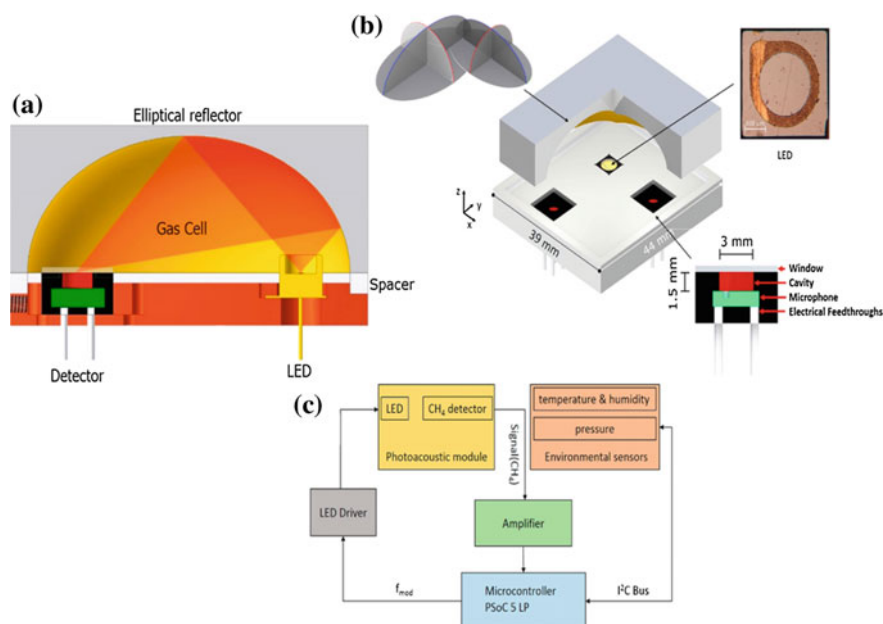


Fig. 5 **a** Schematic representation of single-channel gas sensing set-up of the single-channel sensor set-up for demonstrating focusing of emitted light on photoacoustic detector; **b** schematic representation of sensor design containing photoacoustic detector; **c** schematic diagram for complete set-up consisting of microcontroller, LED driver, photoacoustic detectors and sensors for temperature, humidity, environment and pressure measurements. Reprinted with permission from reference Wittstock et al. (2017)

driver, photoacoustic detectors and sensors for temperature, humidity, environment and pressure measurements (Fig. 5c). The sensor was able to detect methane gas at 2500 ppm detection limit with 12-mm optical path length. The sensor design offered its suitability for working as sensor node in wireless gas sensing network. This would allow real-time monitoring of methane in particular zone of interest.

There have been several other techniques based on optical gas sensors which are utilized for detecting gases like CO₂, CH₄, CO, NO, SO₂, NO₂, N₂O, NH₃ in the literature. A summary has been presented in Table 7, which comprises different techniques, detectable gases and their limit of detection.

2.3 Calorimetric Sensors

The calorimetric sensors utilize change in temperature (due to chemical reaction) of a catalytic surface to perform any sensing event. Their sensing element has the capability to carry out signal transduction, in which any temperature change is converted into readable electrical signals. Even today, these sensors are best suited

Table 7 Summary of different optical detection techniques with their detection capability and limit of detection

Optical detection techniques	Detectable gases	Limit of detection
SPR	N ₂ , CO ₂ , NH ₃ , Cl ₂ , CH ₄ , H ₂ S	N ₂ , CO ₂ , NH ₃ [(2×10^{-7}) (refractive index units)] (Phan et al. 2015), CO ₂ , NH ₃ , Cl ₂ , CH ₄ , H ₂ S(10 ppm) (Mishra and Gupta 2015)
LIDAR	O ₃ , CO ₂ , NO ₂ , N ₂ O, NO, CH ₄ , H ₂ S, SO ₂	Low ppb range (Bogue 2015)
FTIR	CO ₂ , CH ₄ , CO, NO, SO ₂ , NO ₂ , N ₂ O, NH ₃ ,	CO (13 ppb), N ₂ O (3 ppb), CH ₄ (24 ppb) (Grutter 2002)
NDIR	CO ₂ , N ₂ O, NH ₃ , CO and CH ₄	CO ₂ (70 ppb), N ₂ O (20 ppb), NH ₃ (40 ppb), CO(100 ppm), CH ₄ (100 ppm) (Dinh et al. 2016)
CRDS	C ₂ H ₂ , CH ₄ , CO ₂ , CO, NH ₃ and other greenhouse gases	C ₂ H ₂ (0.37 ppbv), CO ₂ (10 ppbv), CO (174 ppbv), NH ₃ (1.0 ppbv ^a) (He and Orr 2006), CO ₂ and other greenhouse gases (Fiddler et al. 2009)
DOAS	NO ₂ , O ₃ , SO ₂ , NH ₃ and NO	SO ₂ (5 ppb), NH ₃ (0.7 ppb), NO (2.8 ppb) (Edner et al. 1993)
LDAS	NO, N ₂ O, O ₂ , CO and CO ₂	NO (20 ppm), N ₂ O (6 ppm), CO (9 ppm), CO ₂ (7 ppm), O ₂ (43 ppm) (Mihalea et al. 1998), CO (0.1 ppm) (Wang et al. 2000)

^appbv parts per billion by volume

for carrying out the measurement of combustion products. A lot of attempts have been made in the development of calorimetric sensors in the literature. Bartlett and Guerin (2003) demonstrated micromachined calorimetric gas sensors for the detection of CH₄, whose detection limit was in the range of 0–2.5%. The sensors were developed using KOH etching route to fabricate the sensor diaphragm made up of a thin Si₃N₄ (silicon nitride) deposited layer which was added through chemical vapour deposition technique (Fig. 6). They utilized surfactant C₁₆EO₈ (octaethyleneglycol monohexadecyl ether) and (NH₄)₂PdCl₄ (ammonium tetrachloropalladate) for the deposition of a nanostructured palladium thin film electrochemically (Bartlett and Guerin 2003). Later, Park et al. reported a miniaturized calorimetric sensing device for sensing CH₄, H₂ and other mixed gases. They used different catalysts on hot side (Pd/θ–Al₂O₃) and cold side (Pt/α–Al₂O₃) of the device for getting accurate temperature measurements. The sensor had a thermoelectric gas sensing element combined with a catalytic combustion technique (Park et al. 2014).

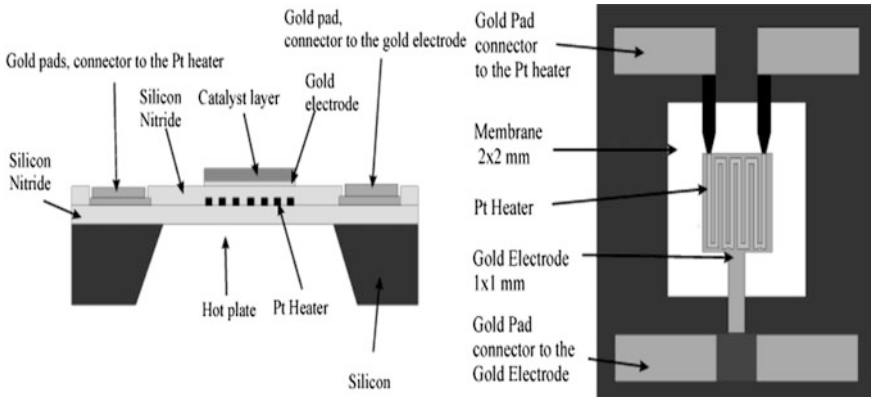
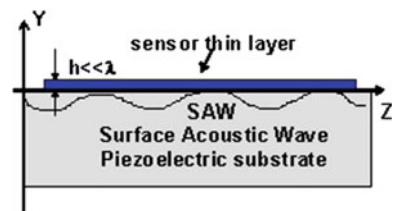


Fig. 6 Micromachined pellistor substrate: cross-sectional image (right side) and top view image (left side). Reprinted with permission from reference Bartlett and Guerin (2003)

2.4 Surface Acoustic Wave-Based Sensors (SAW)

The wave travelling on a material surface which exhibits elastic properties changes the wave properties due to surface adsorption, while the wave reflects off the surface during its traverse. This is generally termed as surface acoustic waves. This phenomenon was first described by Lord Rayleigh. If the absorption of air pollutants by the sensor's thin film occurs during travelling of surface wave in the nearby region then whole wave characteristics changes and this change can be detected with proper instrumentation. Figure 7 shows a schematic piezoelectric substrate on which a thin film of sensor is deposited interacting with the gas molecules. The literature shows that there have been a lot of efforts in the realization of SAW-based gas/air pollutants sensor. Jakubik et al. carried out H_2 detection on a bilayer structure of copper phthalocyanine (CuPc) and a thin palladium (Pd) film using SAW sensors. The working frequency range of the sensor was 200–400 kHz, while oscillator (made of $LiNbO_3$) had frequency range 0.5–43.6 MHz. They were able to detect 0.5–3% hydrogen concentration in nitrogen (Jakubik et al. 2002). Further, Varghese et al. presented a NH_3 sensor by utilizing surface acoustic wave principle. They used alumina nanoporous film to create pores (size 13.6–48 nm) for sensing ammonia

Fig. 7 Principle of surface acoustic wave-based sensor (h —layer thickness and λ —wavelength of travelling wave). Reprinted with permission from Jakubik (2011)



from gas samples. The alumina films were deposited over the surface having travelling wave of frequency 98.5 MHz. They were able to find a frequency shift by 0.001% per ammonia unit percentage increase (Varghese et al. 2003).

2.5 Gas Chromatography (GC)-Based Sensing

The principles of chromatography rely on physical equilibrium between movable sample and stationary phase (solid surface containing particulate). The movable sample can be either gas or liquid. While passing through solid phase, the sample (containing mixture of different components) interacts with stationary phase in different manner which results in the separation of different components (Fig. 8) as each component possesses different distribution coefficients which are the ratio of solute's molar concentration in solid phase to movable phase's molar concentration. Gas chromatography is a most common technique for gas sensing with more sensitivity and selectivity, but still it is at laboratory scale with higher cost.

Although the efforts have been made in the past decade towards its miniaturization, Terry et al. (1979) first presented fabrication of miniaturized GC on silicon wafer with three times size reduction in comparison with laboratory GC. They were able to separate hydrocarbon mixtures within 10 s via thermal conductivity detection system, but detection limit is not high enough as compared to conventional GC instrument. Since then people are trying to fabricate portable GC by utilizing different sensing techniques. In such quest, Zhong et al. (2009) reported a portable GC (Fig. 9) with chemiresistor sensor array for detecting volatile organic compounds (VOCs) mixture (31 different VOCs) in the ppt range. This sensor was able to perform sensing of VOCs within 7 min.

Recently, Akbar et al. (2015) fabricated chip-scale GC (Fig. 10) utilizing MEMS technologies (micropump and valve) for detecting dangerous VOCs (toluene, chlorobenzene, bromobenzene, *p*-xylene, *n*-dodecane, etc.). The miniaturized fabrication contained micromachined separation column (1 m $\times$ 190 μ m $\times$ 240 μ m deep with 20 μ m circular pillars), sample injection section (2 mm $\times$ 250 μ m),

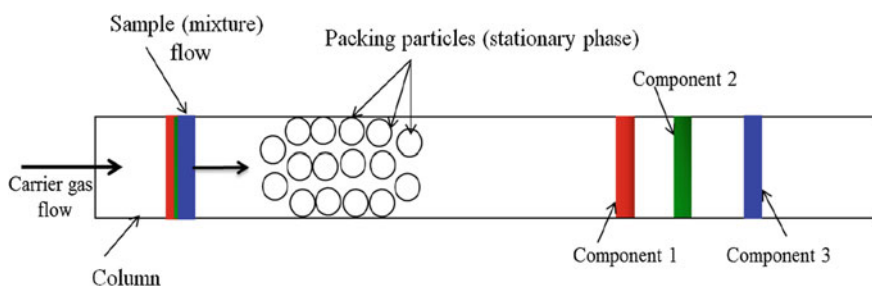


Fig. 8 Schematic representation of basic principle of gas chromatography

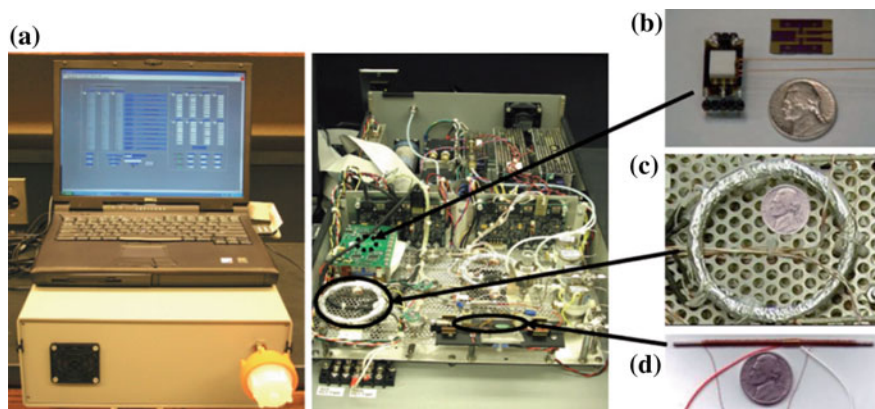


Fig. 9 **a** Portable GC prototype with computer (left) and prototype's cover removed (right); **b** chemiresistive sensor array without assembling in prototype; **c** GC column with heating coil and thermocouple; **d** multistage adsorbent injector with thermocouple and heater. Reprinted with permission from reference Zhong et al. (2009)

microdischarge photoionization detector (μ DPID) for helium discharge, T-shaped microchannel, micropump and valves. In order to quantify flow rate fluctuations and estimate loading time (in few seconds), the sample injection unit was characterized in terms of FWHM (full width at half maximum), at different pressure conditions. The μ GC laboratory on chip device was able to detect different VOCs (in lower ppm range) having boiling point in a range (110–216 °C) within one minute at optimized flow and temperature conditions. Such robust laboratory on chip device could be directly applied for real-time monitoring of VOCs at industrial or residential sites.

2.6 Chemiluminescence-Based Sensing

The concept of luminescence relies on spontaneous emission of radiation produced from a vibrationally or electronically excited species. Chemiluminescence obtains its energy from the chemical reactions of two chemicals which react to each other to achieve an excited state and emits the light. The popularity of chemiluminescence-based gas sensing is quite obvious from some of reviews (Aboul-Enein et al. 2000), (Zhang et al. 2005) and (Toda and Dasgupta 2007). The gases such as CO, NO₂, NO, H₂S, Cl₂, NH₃ and gas vapour (acetone, methanol, ethanol, benzaldehyde, acetic acid) can be detected using chemiluminescence-based techniques. Table 8 summarizes detection limit of some gases which can be sensed by chemiluminescence-based techniques.

Further, miniaturization of chemiluminescence-based sensor has been envisioned. In this regard, Gao et al. (2008) have reported microfluidically inspired gas

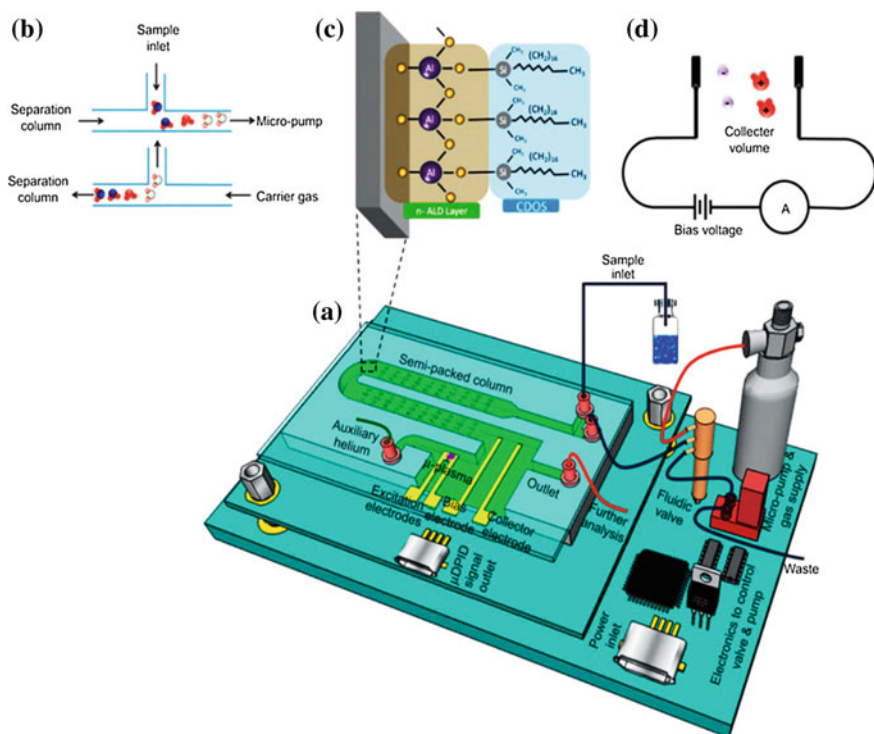


Fig. 10 Schematic representation of miniaturized gas chromatography platform on chip: **a** complete set-up for fluidics (valve and micropump) on chip with carrier gas; **b** loading phase and injection phase; **c** depiction of coating mechanism of microscale semi-packed separation column; **d** electrical interconnects for signal measurement of VOCs' ionization. Reprinted with permission from reference Akbar et al. (2015)

Table 8 Summary of gas sensing by chemiluminescence techniques and limit of detection

Sensing gas	Detection limit	Technique	References
CO	1.0 ppm	Cataluminescence-based sensing	Sadanaga et al. (2008)
NO ₂	5.5 pptv (parts per trillion by volume)	Ozone-induced chemiluminescence	Lee et al. (2009)
NO	1.8 pptv	Ozone-induced chemiluminescence	Lee et al. (2009)
NH ₃	14 ppb	Cataluminescence-based sensing	Shi et al. (2003)
H ₂ S	3 ppm	Cataluminescence-based sensing	Zhang et al. (2004)
Cl ₂	0.2 ppm	Chemiluminescence sensing	Gao et al. (2008)

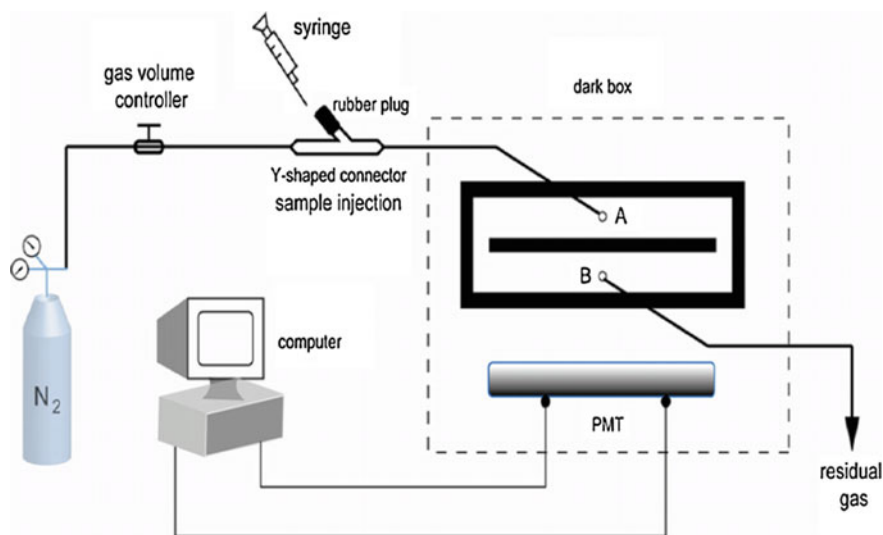


Fig. 11 Schematic representation of miniaturized chemiluminescence-based sensing system. Port A used for sample injection and Port B for residual gases after detection. Reprinted with permission from reference Gao et al. (2008)

sensor for chlorine detection using chemiluminescence technique. They used luminol ($C_8H_7N_3O_2$) solution which was mounted on microchannel [containing two parts (upper and lower)]. After insertion of Cl_2 in the microchannel utilizing surface tension, the luminol solution transmits ClO^- ion and emits chemiluminescence which was further detected by photomultiplier tube (PMT). Fig. 11 represents complete set-up used for chlorine detection utilizing microfluidic platform which consisted of N_2 gas, PMT coupled with computer and microfluidic device.

3 Commercially Available Sensor for Detection of Air Pollutants

Apart from high sensitivity, selectivity, response time, recovery time and low cost, the portability of air monitoring sensor has been the main concern for commercialization. SnO_2 -based sensors are available in the market with the capability of detecting CO_2 , CO , NH_3 , O_3 , H_2 gases in the environment. For example, MQ-135 sensor (of Air Quality Click™ and mikroBUS™) operable at 5 V DC provides the detection of NH_3 , C_6H_6 , NO_x , smoke, CO_2 (Fig. 12a). It can detect NH_3 and C_6H_6 in the range of 10–300 ppm. Another sensor (MG-811) has the capability of detecting CO_2 , CO , CH_4 and C_2H_5OH in 350– 10^3 ppm range (Fig. 12b). The sensor works on principle of solid-state cell electrolyte which is operable at 6 V DC. Moreover, there are sensors available in the market which do not require any additional circuitry to



Fig. 12 **a** Air pollutant sensor for NH_3 , NO_x , smokes, CO_2 detection, and model: MQ-135 **b** sensor for detecting CO_2 , model: MG-811; **c** VOC formaldehyde and $\text{PM}_{2.5}$ Air Quality Monitoring Tester. *Courtesy BSIDE EET100*

operate, i.e. they have in-house PWM (pulse width modulator), analog or digital signal for connection to microcontroller. Although, the sensitivity and selectivity of these sensors are not high enough to get accurate results in real time environment testing, yet they can provide a rough approximation of air pollutants.

Automobiles generate $\text{PM}_{2.5}$ particles in air which are responsible for damaging human respiratory track, and BSIDE's tester is commercially available in the market which can measure VOC and $\text{PM}_{2.5}$ particles in air in the range of 0–10 ppm and 0–500 $\mu\text{g}/\text{m}^3$, respectively. It is operable at 3.7 VDC battery (Fig. 12c). An Indian product (Fig. 13) for monitoring VOC gases (formaldehyde (HCHO), benzene (C_6H_6), toluene ($\text{C}_6\text{H}_5\text{CH}_3$), petrol/diesel and smoke, etc.) up to a range of 0–5 ppm is available in market, and its specification are depicted in Fig. 13.

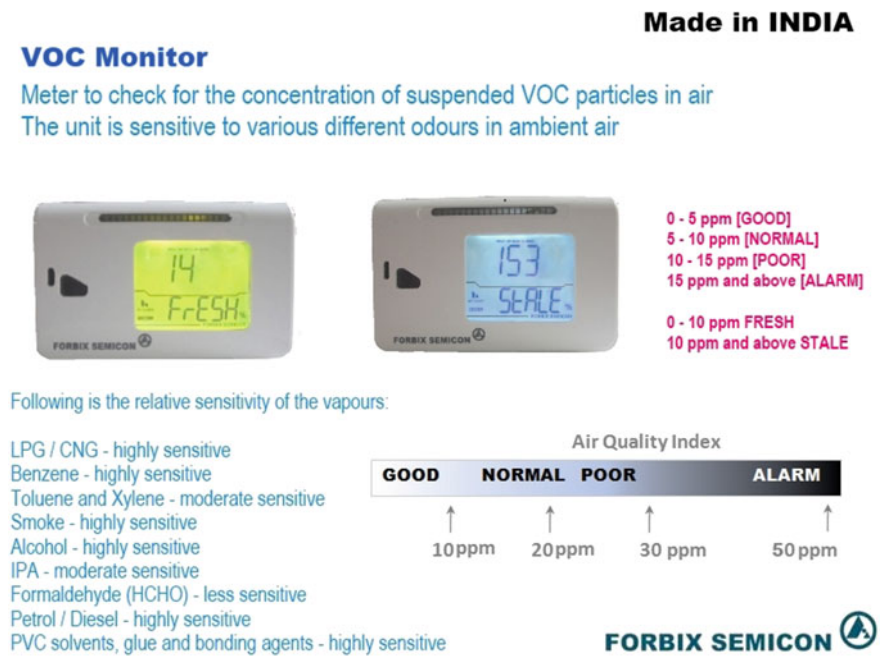


Fig. 13 Detection of VOC gases (formaldehyde, benzene, toluene, petrol/diesel and smoke, etc.) up to a range of 0–5 ppm. *Courtesy* FORBIX SEMICON Co.

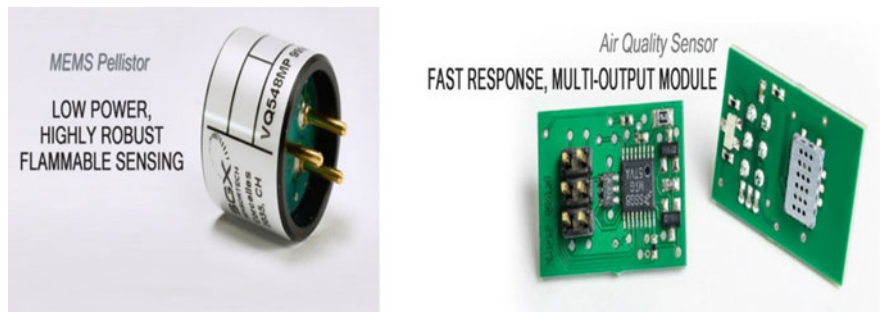


Fig. 14 Model: EC4-500-CO detector. *Courtesy* SGX Sensortech

For CO detection, SGX Sensortech provided infrared-based gas sensor, which can detect carbon monoxide, in the range of 0–500 ppm limit of detection (Fig. 14), while its limit of detection is 0.1 ppm. And it can also detect sulphur dioxide (5 ppm), nitric oxide (25 ppm), nitrogen oxide (5 ppm) and hydrogen (100 ppm).

4 Conclusion

We have outlined the need for air monitoring by sensors coupled with wireless sensing networks. The effects of air pollutants (CO, NH₃, NO₂, SO₂, CH₄, etc.) on human health and environmental condition are discussed in detail with prescribed guidelines provided by WHO. Further, different types of sensor based on various MEMS/NEMS technologies such as semiconducting metal oxide, optical fibre, calorimetric, gas chromatography have been discussed in depth with supporting literature. By keeping the view of miniaturization of sensors for air monitoring, the commercialized air sensors have also been discussed. Despite technological development of robust sensors presented in this chapter, there is utmost need for the development of portable air sensor combined with wireless sensor networks which could give real-time air pollutants' data in selective space and time with high sensitivity and selectivity. MEMS-/NEMS-based technologies are envisioned to fulfil these requirements.

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