A review of sensor-based methods for monitoring hydrogen sulfide

Sudhir Kumar Pandey, Ki-Hyun Kim, Kea-Tiong Tang

We review sensor-based methods commonly employed for monitoring hydrogen sulfide (H_2S), and recent developments in H_2S-sensing instrumentation.

We evaluate the basic quality-assurance parameters of different sensor types for quantifying H_2S in terms of major operational criteria (e.g., response time, limit of detection, common operating range of concentrations, and stability). We also describe the applicability of these sensor-based methods with respect to practicality in various environmental settings. Finally, we highlight the limitations and the future prospects of these sensor-based methods.

Keywords: Chemical sensor; Environmental analysis; Hydrogen sulfide; Limit of detection; Malodor; Nuisance; Real-time monitoring; Sensor-based method; Sensor response time; Toxicity

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1. Introduction

Hydrogen sulfide (H_2S) is a toxic gas with a characteristic malodor of rotten eggs [1]. It is also commonly referred to as sewer gas, stink damp, swamp gas, and manure gas [2]. It occurs naturally in crude petroleum, natural gas, hot springs, and foods. H_2S gas is commonly formed in nature and released during the decay of organic matter (e.g., human and animal wastes) in septic or sewer systems by bacterial breakdown [3]. Furthermore, it is also produced in large quantity from such industrial activities and places as petroleum/natural gas drilling and refining, wastewater treatment, coke ovens, tanneries, kraft paper mills, and landfills [4,5].

H_2S is rapidly absorbed by the lungs, once exposed via inhalation [2]. A variety of occupational epidemiological studies on humans has indicated that exposure to H_2S (at high concentrations) has profound health effects on the respiratory system, which could then lead to unconsciousness with attendant neurological sequelae and, sometimes, death [e.g., 6]. It has also been associated with cardiovascular related deaths [7]. Further, it can cause a malodor-nuisance problem even at relatively low concentrations [8].

As a first step towards the management of this gaseous pollutant, one has to monitor its behavior in various environmental settings. To determine this noxious gas in environmental samples, gas chromatography (GC)-based methods have been employed most frequently [9]. These quantification methods have proved their reliability in terms of high detectability and precision. However, application of these methods is not simple, as it involves a multi-stage protocol starting from sampling and going to final determination. As such, this approach is not convenient to track down short-term variations in behavior due to the dynamics of varying environmental conditions. Moreover, off-line analytical protocols of H_2S analysis can also suffer from a number of biases (e.g., sorptive loss in association with its high reactivity) [9]. Hence, it has always been a big challenge to measure H_2S accurately with the least amount of bias under field conditions.

Chemical sensors have been widely used in a number of applications (e.g., critical care, safety, industrial hygiene, process control, product-quality control, human comfort controls, emissions monitoring, automotive industry, clinical diagnostics, home-safety alarms, and homeland security) [10]. For real-time monitoring of harmful pollutants that can cause a nuisance, numerous chemical sensors have been developed and employed. These sensors have mainly been based on semiconducting metal-oxide, electrochemical

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(with both liquid and solid electrolyte) sensors, optical sensors, and sensor arrays. These sensor-based devices have shown several advantages in terms of high sensitivity, fast response, easy operation, and low cost. Depending on their material type and fabrication, their sensing principles can vary to a large extent. For example, semiconducting metal-oxide sensors mainly work on the principle of conductivity impedance, whereas electrochemical sensors rely on amperometry, potentiometry, cyclic voltammetry, and impedance measurements [11]. However, the detection principles for optical sensors are based on observation of fluorescence-labeled systems or direct optical detection in the heterogeneous phase [12]. To this end, most H_2S gas sensors are developed based on principles of colorimetry and spectroscopy (absorption and fluorescence).

The present review is made in an effort to describe the most up-to-date features of these emerging sensor-based methodologies for H_2S analysis in a practical sense. To this end, we first describe common sensor types after dividing them based on their material type and/or sensing principle (Fig. 1). Then, we evaluate their efficacy in terms of real-world applications by comparing their quality-assurance (QA) parameters (based on the compilation in Table 1). Finally, we summarize these sensor-based methods and discuss them with respect to their advantages, limitations, and future prospects.

2. Common sensor types employed for H_2S analysis

2.1. Semiconducting metal-oxide sensors

Sensors in the form of thin or thick films, based on metal-oxide semiconductors (e.g., tin oxide), are very advantageous because of their small size, simple construction, low weight, low power consumption, and low cost [13]. The heated metal-oxide sensor is the most commonly applied sensor for monitoring gases. As the reaction of a target gas on the metal-oxide surface alters its electronic properties, the resistance of the metal-oxide semiconductor also changes to operate the sensing system [10].

Although many metal oxides have been investigated for H_2S-gas sensing, SnO_2 (or doped SnO_2) has been used most widely {e.g., CeO-doped SnO_2 thin film (prepared by the sol–gel technique) was investigated for the detection of H_2S at room temperature [14]}. These authors showed that their sensing device could measure H_2S in the range 1–15 ppm under the laboratory conditions with response and recovery times of 20 s and 40 s, respectively.

Similarly, CuO was also tested as an outstanding promoter in enhancing the catalytic activity (and gas-sensing properties) of SnO_2 [e.g., 15–17] {e.g., SnO_2 film with CuO dotted islands was found to exhibit a moderate sensitivity (e.g., 20 ppm of H_2S) with a fast response time of 15 s compared to un-doped SnO_2 [18]}. These authors studied the response of this H_2S-sensing device in the concentration range 20–1200 ppm. Ultrahigh-sensitivity SnO_2-CuO sensors were also fabricated on Si (100) substrates for the detection of relatively low levels of H_2S [19]. Esfandyarpour et al. successfully tested this sensor against 0.1–10 ppm of H_2S test gas.

In another application of CuO-modified SnO_2 films, Patil and Patil [20] were able to measure H_2S in a wide concentration range (1–300 ppm) with a fast response time of 15 s under the laboratory conditions. Lee et al [21] tested the response characteristics of CuO–SnO_2 composite thin films for H_2S gas in the concentration range 0.01–3 ppm range. As an alternative to Cu metal, Fe-doped SnO_2 nanomaterial was tested as an H_2S sensor at relatively low temperatures [22]. Based on this approach, Vaishampayan et al. were able to measure H_2S test gas in the concentration range 10–250 ppm with a fast response time of 5–15 s.

H_2S is catalytically oxidized (by O_2 in air) to yield intensive chemiluminescence (CL), when it passed over the surface of Fe_2O_3. Hence, using this property, an Fe_2O_3-based CL sensor was developed [23] and was found highly selective to the target gas without the effect of the common interfering gases (e.g., hydrocarbon, alcohol, and NO_2). When tested against laboratory-synthesized air, the response time of this CL sensor (to H_2S) was within 15 s with a linear range of 8–2000 ppm under optimal conditions. These authors were able to achieve a limit of detection (LOD) of 3 ppm. Stability of the sensor was demonstrated to be fairly good using a 100-ppm H_2S standard for 100 h.

Tanda et al. [24] developed a portable sulfide monitor with a zinc-oxide (ZnO) semiconductor sensor for daily field study. These authors were able to analyze H_2S in oral malodor samples with an LOD of 20 ppb along with other reduced sulfur compounds (RSCs). (One may thus easily notice superior detectability of this sensor relative to most metal-oxide sensors mentioned.) This can be ascribed to several factors [e.g., use of alumina-coated (as a catalyst) ZnO as sensor material and acidic silica-gel filter traps (to remove obstructive gases)].

Fu [25] developed a metal complex ($[Cu_5(bipyO_2)_6Cl_8]Cl_2$) as a potential gas sensor for H_2S and NO_2. They explained the sensing mechanism of this metal complex by using a double-energy-valley model. It showed a good reproducibility of below 4.4% [in terms of relative standard deviation (RSD)] with a very fast response of 8 s, when tested in the concentration range 100–540 ppm.

Use of nano-structured materials has great potential to improve the performance of gas sensors, especially in terms of their sensitivity [26]. Due to their much larger surface-to-bulk ratio relative to coarse micro-grained materials, nano-structured materials can attain a large interface between the oxide and the gaseous medium, and that ultimately helps raise sensitivity. For example, Ionescu et al. [27] tested a WO_3 nanoparticle gas sensor,

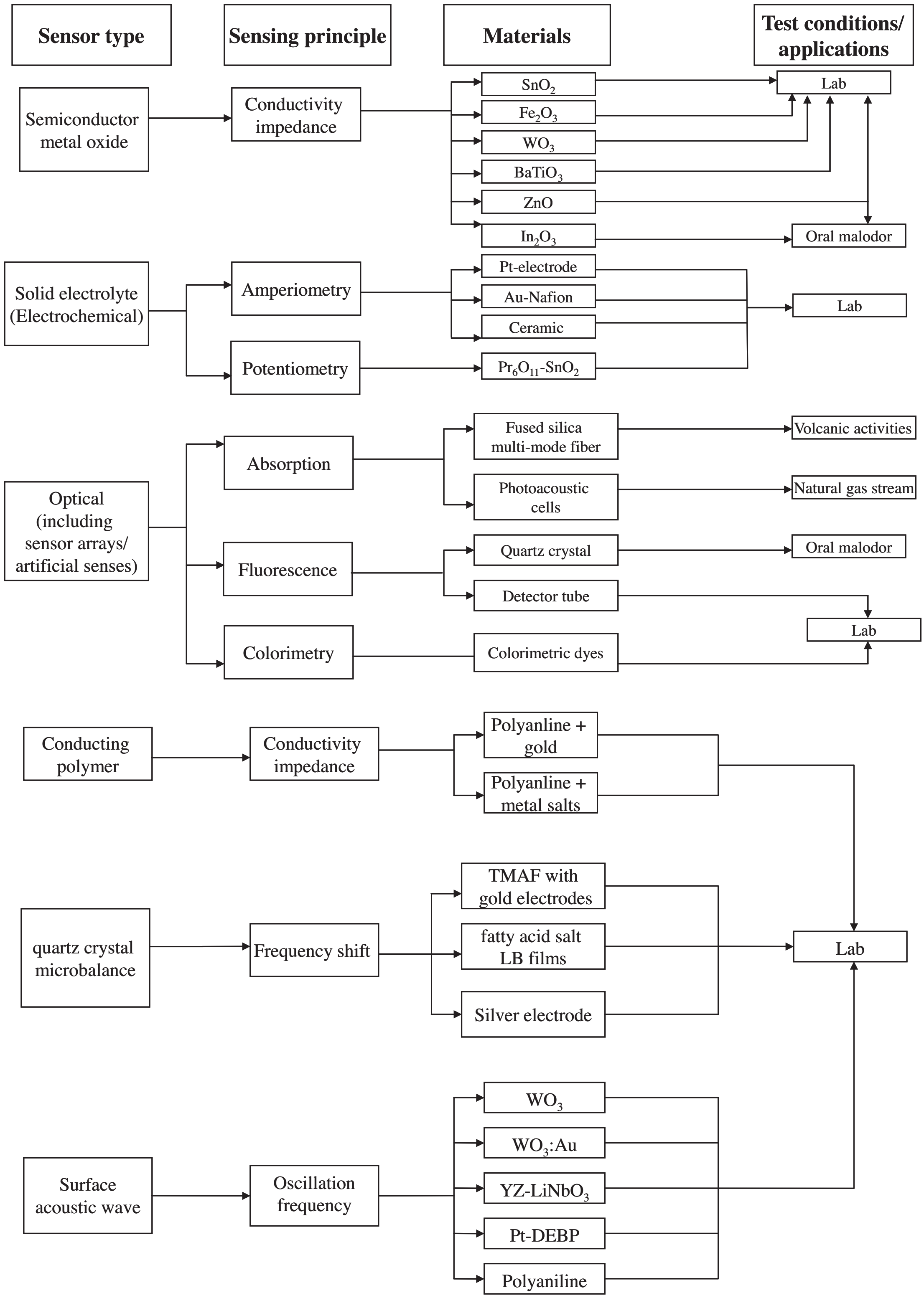

Figure 1. Common sensor types for real-time detection of H_2S gas.

which detected dry H_2S gas in the range 0.02–1 ppm, with a high detectability of 20 ppb.

ZnO nanorods were also used for ppb level (LOD = 50 ppb) detection of H_2S at room temperature in laboratory conditions [28]. Jain and Patil [29] developed CuO-doped $(Ba_{0.8}Sr_{0.2})(Sn_{0.8}Ti_{0.2})O_3$ BSST thick-film resistors for measuring H_2S. They were able to measure H_2S gas in the 1–100 ppm range (in the presence of air)

Table 1. Compilation of sensor-based methods applied for H_2S gas monitoring

Sensor type	Sensing device/Material	Analytical condition	Response time (s)	Recovery time (s)	LOD Concentration (ppb)	Reproducibility (% RSD)	Linearity range (ppm)	Recovery (%)	Concentrations (measured) ppm	Ref.
(1) Semiconducting oxide										
	CeO_2 –SnO_2 sol–gel thin films	Lab (at Room temp)	20	40	1000				1–25	[14]
	Cu-nanocrystal-SnO thin film		Less than 120							[26]
	In_2O_3 sensor-GC system	Oral malodor							0.05–1	[32]
	CuO–SnO_2 composite film microgas sensor	Not measured (Film test)							0.01–3 (Test range)	[21]
	CuO-modified SnO_2 films	Lab test gas	15	~240					1–300	[20]
	ZnO rods	Lab			50					[28]
	Fe_2O_3 (Chemiluminescence)	Lab synthesized air	15	120	3000		8–2000	94.4–104	80–213.4	[23]
	CuO-doped $(Ba_{0.8}Sr_{0.2})(Sn_{0.8}Ti_{0.2})O_3$ BSST thick film resistors	H_2S gas	10	60	4–10				1–100	[29]
	$[Cu_5(bipyO_2)_6Cl_8]Cl_2$	Lab (Test gas)	8	10		Below 4.4			100–540	[25]
	SnO_2-CuO micro sensor	Lab test gas							0.1–10	[19]
	Metal–dielectric–semiconductor (MDS) sensor	Lab							0.005–0.02	[30]
	ZnO semiconductor	Oral malodor			20					[24]
	$BaTiO_3$ thick film resistors	Lab test gas	3	9				80	100	[29]
	Cu-SnO_2 material	Lab	15	118					20–1200	[18]
	Fe-doped SnO_2 nanomaterial	Lab (Test gas)	5–15		10,00				10–250	[22]
(2) Electrochemical										
	Solid polymer electrolyte (SPE)-Pt electrode		10						0–100	[33]
	Sodium super ionic conductor (NASICON) combined with Pr_6O_{11}-doped SnO_2 electrode	Lab (Test gas)	4–8	12–30					5–50	[37]
	Nafion membrane (H_2SO_4 treated)	Lab (H_2S + N_2 mixture)	9		100				0.1–100	[35]
	Cermet sensors (Cyclic voltammetry)	Lab			Sub-ppm					[36]
(3) Optical										
	Microchannel scrubber + microfluoroscence detector	Lab test gas			1				0–0.02	[43]

Gas detector tube + optical sensor	Wind tunnel			below 19					[45]
Online diode laser (photoacoustic spectroscopy)	Natural gas stream			500				100	[40]
Plasma-polymerized film (PPF)-coated quartz crystal	Oral malodor			Sub-ppm				0.084	[47]
Gas detector tube	Lab (Test gas)			115				0.012–1	[46]
Colorometric sensor	Lab (Test gas)					0.05–50		0.05–5	[48]
Wireless electronic nose system(WENS) (Micro gas sensors)	Lab (Test gas)	0.2		50				0.15–1.5	[49]
(4) Conducting polymer									
Polyaniline nanowires-gold nanoparticles hybrid network	Lab	<120	<300	0.1				0.0001–0.1	[52]
Polyaniline nanofiber composites with metal salts	Lab	66						10	[51]
Screen printed silver IDE on a flexible PET substrate with inkjet-printed layers of polyaniline and copper(II) chloride	Lab		180					10–100 ppmv (parts per million volume)	[53]
(5) Quartz-crystal microbalance									
Tetramethylammonium fluoride tetrahydrate (TMAF) with gold electrodes Euroquartz	Lab (glass cell)		Reversible		Reversible		Reversible		[61]
fatty acid salt Langmuir–Blodgett (LB) films	Lab(glass-grounded stopper)	Response time: the 1st fast				(τ_1 = 61.1 ± 6.9) and the 2nd slow process (τ_2 = 3233.7 ± 376.8)	Irreversible		
irreversible	2.5 ∼360 mL (1.4∼100%)	Irreversible		[62]					
Nine MHz quartz crystals with AT-cut crystal plate (8 mm diameter) and silver electrode (5 mm diameter)	Lab (37°C for micro-organisms producing) H_2S		Irreversible		Irreversible		Irreversible		[63]
(6) SAW									
YZ-$LiNbO_3$ film	Lab test gas	240	360					1–10	[68]
WO_3 on $LiNbO_3$	Air/ H_2S gas							50	[65]

(*continued on next page*)

Table 1 (*continued*)

Sensor type	Sensing device/Material	Analytical condition	Response time (s)	Recovery time (s)	LOD Concentration (ppb)	Reproducibility (% RSD)	Linearity range (ppm)	Recovery (%)	Concentrations (measured) ppm	Ref.
	Polyaniline thin film On $LiNbO_3$ Y-Z substrate	Lab	300						25–500	[69]
	WO_3:Au Film On $LiNbO_3$ Y-Z substrate	H_2S gas							0.25–100	[67]
	WO_3 film on a single $LiNbO_3$ substrate	Lab	100		<10				0.01–30	[64]
	WO_3	Lab							0.0005–0.001	[66]

with an estimated LOD in the range 4–10 ppb with a 10-s response time. Hence, the sensitivity achieved by these two sensors appears to be superior over most sensors made of metal oxides. This enhanced sensitivity of certain sensor types can be attributed to modification or replacement of the sensing materials (e.g., nano-phase ZnO (or WO_3) and the thick film of $BaTiO_3$).

An H_2S-gas analyzer based on a metal–dielectric–semiconductor (MDS)-capacitor was developed for application in the range 5–200 ppb. This sensor was found to be highly sensitive and selective to H_2S in diverse applications (e.g., geological prospecting for fuel gas deposits, medical diagnosis of gastrointestinal diseases, ecological monitoring of water purity, and monitoring household wastes in communal economies) [30,31].

In addition to these miniaturized sensor devices, a portable oral malodor analyzer was also developed for quantitative detection of volatile sulfur compounds (VSCs) in mouth air using a combination of a semiconductor gas sensor (SGS) and a compact GC system [32]. These authors applied a specific column design, a simple sampling system, and a signal-processing method so that the analyzer could be operated without a pressurized carrier-gas standard. They used In_2O_3 doped with Au as the optimum sensing material of the gas sensor. Such modification was necessary to measure all the VSCs in mouth air at fairly low concentrations (i.e. 50–1000 ppb). Based on the aforementioned studies, many efforts were made to overcome the major limitation of metal-oxide sensors by extending their detectability from the ppm range to at least the sub-ppm (or ppb) range. This improvement in the detectability of sensing techniques could not have been possible without advancement in certain semiconductor materials and catalysts. However, their performance still needs proper validation for practical application. In addition, it should be noted that the dramatic shift in detectability from ppm to ppb is a great improvement for measuring most problematic sources and their associated samples. However, it is still not sufficient to cover the entire range of ambient air, as RSCs are typically present at the sub-ppb range in a clean atmosphere.

2.2. Electrochemical sensors

Based on electrolytes, electrochemical sensors can be divided into liquid and solid electrolyte sensors. For H_2S-gas analysis, solid-electrolyte sensors are commonly applied. These sensors can be further divided, based on their working principle (i.e. amperometric and potentiometric).

Amperometric approach produces current signal, which is related to the concentration of the analyte by Faraday's law and the laws of mass transport. This method has been used to cover a wide range of analytes [e.g., CO, nitrogen oxides, H_2S, O_2, glucose, unique gases (e.g., hydrazine), and many other vapors]. More specifically, a solid-polymer electrolyte (SPE)-Pt electrode was tested for quantitative determination of gas-phase H_2S

(in an $H_2S + N_2$ mixture) in laboratory conditions [33]. This electrode system, when operated in a controlled potential mode, showed a low LOD, good reproducibility (±1 ppm), fast response (10 s), and satisfactory linearity (0–100 ppm). Thus it was proved to have the potential for practical application in the field.

Similar to this effort, an SPE hydrophobic gas-diffusion electrode comprising small Pt particles distributed in a porous structure was used for quantitative determination of H_2S [34]. Based on this method, they were able to measure H_2S in the range 0–100 ppm. The stability of the SPE-H_2S sensor was also tested consecutively over 7 months in ambient temperature with the introduction of 100-ppm H_2S into the sensor for 4 h per day. During this period, they observed performance deteriorate. After careful investigation, it was inferred that deposition of elemental sulfur played a major role in reducing the performance of this sensor.

As another application of an electrochemical sensor, Yu et al. [35] used H_2SO_4 pre-treated Nafion membrane as a solid-electrolyte sensor for H_2S gas. Moreover, because of concern about the interaction between Pt and many gases, an Au catalyst was used as an alternative electrode to improve selectivity toward H_2S. In line with the principle of cyclic voltammetry, Yu et al. could measure H_2S in the range 1–100 ppm with a 9-s response time. The detectability of this sensing device was found to be 0.1 ppm. Considering the level of performance, it was also recommended for practical application to H_2S analysis.

Electrochemical sensors comprising a ceramic–metallic (cermet) solid electrolyte were examined for detection of H_2S and other gaseous sulfur compounds (SO_2 and CS_2) emitted from industrial processes [36]. This sensor was driven by cyclic voltammetry to produce a current–voltage profile for each analyte. Based on this approach, they were able to detect H_2S along with other gaseous components in the ppm range, with low cost and reusability.

Apart from the amperometric methods mentioned above, the potentiometric method has also been explored for H_2S monitoring. In contrast to amperometric sensors, potentiometric sensors can measure electrical potential (voltage). As an example of this application, Liang et al. [37] developed a compact tubular sensor based on sodium super ionic conductor (NASICON) and Pr_6O_{11}-doped SnO_2 sensing electrode for the detection of H_2S. This sensor was capable of detecting H_2S in the 5–50 ppm range with a fast response of 4–8 s. Moreover, the sensor showed a good selectivity to H_2S among the common interferences (e.g., SO_2, NO_2, CH_4, and CO), while exhibiting an excellent resistance to water vapor. As such, this approach also showed a great potential for practical applications. In summary, electrochemical sensors appear to be feasible for H_2S gas sensing in the ppm range. Nonetheless, as most previous studies were basically confined to laboratory-scale testing, they need validation for real-world applications.

2.3. Optical sensors

The application of an optical sensing technique, based on the attenuation of light waves, can be made one of the most effective chemical sensors (i.e. optical sensors). Optical chemical sensors commonly employ optical transduction techniques to yield analyte information [38]. Design for these sensor types frequently uses a waveguide (or optical fiber) and a coating. When the analyte is placed at the interface of the fiber and a coating, it interacts with the light. The experimental signal for quantitative and/or qualitative analysis can thus be recorded due to absorption or emission phenomenon.

Optical chemical sensors can generally be categorized into two types (i.e. direct and reagent mediated) [38]. In direct sensing, the analyte is detected directly via its intrinsic optical property (e.g., absorption or luminescence). However, for reagent-mediated sensors, a change in the optical response of an intermediate agent (e.g., analyte-sensitive dye molecule) is considered for measurement. We provide information on these two principles below.

2.3.1. Direct sensing. The techniques used for direct sensing of analytes include infrared (IR), Fourier transform infrared (FTIR), non-dispersive infrared (NDIR), diode laser sensing, and ultraviolet (UV) absorption.

A compact, rugged and portable fiber-optic evanescent-field laser sensor was developed for simultaneous detection of H_2S, CO_2, and H_2O in the gas streams of volcano fumaroles located at Solfatara, Italy [39]. Willer et al. used an uncoated fused-silica multi-mode fiber (as sensor material) and a single-mode DFB laser diode operating around 1.5705 μm as a light source. They were able to detect H_2S and other gases (CO_2 and H_2O) in the gas streams of volcano fumaroles. Although their effort was basically intended to do qualitative analysis, it showed potential for developing new, rugged and compact fiber-optic sensors as warning devices for volcanic activities.

In other research, a dual-channel H_2S sensor was developed on the basis of photoacoustic spectroscopy [40]. The system was built with a single-mode, fiber-coupled, room-temperature-operated, telecommunication-type diode laser (with a wavelength of 1574.5 nm and an output optical power of 40 mW), and two identical resonant photoacoustic cells. By employing this sensor system to monitor natural gas streams, Varga et al. [40] were able to achieve an LOD of 500 ppbv for H_2S. They also pointed that their systems, even when operating in harsh industrial environments, recorded excellent performance (in terms of long-term stability and unattended automatic on-line monitoring).

2.3.2. Indirect sensing: Sensor arrays and artificial sensors (Electronic noses). Sensors are also being used in the form of arrays, most frequently based on an optical technique with the aid of some sampling system [41,42]. Considering their remarkable ability to mimic the mammalian senses, sensor arrays are often called electronic noses (or electronic tongues), when combined with sampling systems [10]. As sensor arrays have diverse features with numerous specifications, they are now applied extensively (e.g., diagnosis of disease, the quality of meats and fruits, smart fire detection, homeland security, wine, perfume, and coffee analysis). We describe some examples of these sensor arrays developed for gaseous H_2S quantification in the following section.

Indirect optical sensing technique requires the reagent (the intermediate agent to modulate the optical response of analyte) to be immobilized in solid or liquid matrices. Although both reagent types can be used, optical sensing has most commonly been practiced with solid-phase immobilization matrices [38]. For example, based on micro-fluorescence detection, a miniature gas-analysis system (μGAS) was developed for continuous on-site measurements of atmospheric trace gases with high sensitivity [43]. A thin gas-permeable membrane (made of polydimethylsiloxane) was fabricated on a shallow channel for efficient accumulation of analyte into the absorbing solution. Koda et al. [43] demonstrated the performance of this μGAS as a H_2S-gas sensor that consumed only 1 mL of the reagent solution in 8 h of operation. This sensor system was successfully tested with a H_2S test gas in the 0–20 ppbv range with an LOD of 1 ppbv.

The gas-detector-tube technique is well known as a simple method for gas measurement that relies on the chemical reaction between the analyte and the reagent system to form colored compounds [44]. The concentration of the target gas is visually readable by the length of the color change. By taking advantage of this property, Tanaka et al. [45] developed a malodor sensor that combined a conventional gas-detector tube and an A4-size optical scanner. Based on their sensor system, they were able to detect H_2S gas with an LOD of 19 ppbv along with other compounds [e.g., methyl mercaptan (29 ppbv) and propionaldehyde (46 ppbv).

They also noticed that the sensitivity of this method was increased by 10 times compared to a conventional detector tube. They further studied distribution of a bad smell in a wind tunnel using a sensor network comprising six portable sensors. Although the experimental results have not been described on a quantitative basis, Tanaka et al. were able to detect the changes of the plume shape as a function of the wind speed with the aid of the proposed bad-smell sensor network.

Similar to this effort, a bad-smell sensing network was also developed using gas-detector tubes and mobile phones with digital cameras [46]. For this system, the estimated detectability of H_2S corresponded to 115 ppbv. Ninh et al. [46] tested their system to trace the changes of gas distribution for xylene and ammonia at a paint factory, although H_2S was not quantified, probably because its presence was below the LOD range.

In order to trace the progress of periodontitis (through human breath or oral malodor), a plasma-polymerized organic film-coated quartz-crystal-resonator sensor (PPF sensor) array was tested to detect a VSC mixture [47]. The PPF-sensor array was tested against a humid air sample with a VSC mixture analogous to human breath (RH = 97% and temperature = 24°C). The sensor array was able to discriminate methanethiol and H_2S in the VSC mixture, thus indirectly supporting its applicability to real samples.

Recently, many efforts have been directed to the development of a simple, rapid, and low-cost method to detect gaseous H_2S, which can differentiate over a wide range of concentrations (50 ppb–50 ppm) [48]. This sensor device worked at ambient temperature using a colorimetric sensor array comprising chemoresponsive dyes coupled to a commercially-available 8-bit flatbed scanner. The quantification of this method was based on kinetics of color change through which the array of chemoresponsive dyes spots, specifically the portion of reacted H_2S at different detection thresholds. Sen et al. [48] explained that the low-cost, disposable nature of chemical sensor array (CSA) technology is incisive enough for environmental monitoring in sub-ppm to ppm range. However, the current response time of CSA at the sub-ppm level (30 min) needs to be improved for practical application.

In other research performed recently, a wireless electronic nose system (WENS) was designed for real-time quantification of H_2S and NH_3 along with their mixtures [49]. The performance of the proposed WENS was also assessed with reference gas in the concentration range 0.15–1.5 ppm with an excellent response time of 0.2 s. The detectability of this WENS system was approaching 50 ppb. Although these sensor arrays and/or electronic noses are still at the development stage, they seem to be an attractive option for real-time monitoring of H_2S at fairly low concentration levels (sub-ppm range) for various purposes.

2.4. CPSs

Conducting-polymer sensors (CPSs) have been widely applied to gas sensing because of their easy fabrication, high reproducibility, rapid reaction rate, and affordable price. The basic idea is to mix conducting materials [e.g., carbon black, carbon nanotubes (CNTs), single-walled carbon nanotubes (SWCNTs), and multiple-walled carbon nanotubes (MWCNTs)) with polymers selected for the target gas to form a conducting-polymer-composite sensing material. This composite material, once deposited on a sensor substrate, can be applied as a chemiresistive sensor. The conducting materials serve as a conduction path, while the polymers provide selectivity to the target gas. When the concentration of the conducting materials exceeds the percolation threshold of the polymer, an electrical resistance value can be measured by a multimeter through the newly formed conduction paths. As the target gas contacts the composite material, the polymer swells via reaction with the gas. It then induces some of the conduction paths to break and the electrical resistance to increase. Because most CPSs are generally built to operate at ambient temperature, they do not require heater units. The electronic interface for CPSs is very straightforward to enhance portability. The sensitivity of CPSs is in the range 0.1–100 parts per million (ppm) [50]. The main drawback of CPSs is their high sensitivity to humidity, so it is desirable to tune out background humidity and associated sensor drift.

Researchers have used different composite materials to sense H_2S. Metal salts and polyaniline nanofibers were used to form a new composite material to enhance the sensing response [51]. The metal salt reacted with H_2S to form corresponding metal sulfide, whose response was correlated with the K_{sp} value. Recently, a polyaniline nanowire-gold-nanoparticle hybrid network was reported for application to the detection of H_2S [52]. The sensor was fabricated by a simple electrochemical technique. Initially, polyaniline nanowires (diameter 250–320 nm) for bridging the gap between a pair of microfabricated gold electrodes were synthesized using a templateless electrochemical-polymerization base in a two-step galvanostatic technique. Polyaniline nanowires were then electrochemically functionalized with gold nanoparticles using the cyclic voltammetry technique. These chemiresistive sensors showed an excellent LOD (0.1 ppb), wide dynamic range (0.1–100 ppb), high selectivity, and good reproducibility. A response time of less than 120 s was reported.

A fully printable polyaniline-copper(II)-chloride sensor was also reported to detect H_2S gas [53]. The sensing device comprised a screen-printed silver interdigitated electrode (IDE) on a flexible PET substrate with inkjet-printed layers of polyaniline and copper (II) chloride. The modified polyaniline sensors were fabricated using a Dimatix materials printer (Fujifilm Dimatix, Inc.). This chemiresistor sensor showed changes in measured current with corresponding changes in concentration. On exposure to H_2S, as little as 2.5 ppmv was clearly detectable with a linearity range of 10–100 ppmv.

2.5. Piezeoelectric sensors

There are two types of piezoelectrics {(QCM) [54,55] and surface acoustic wave (SAW) devices [56,57]}. They are both configured as mass-change-sensing devices.

The QCM device is a resonating polymer-coated disk with metal electrodes, each side of which is connected to a lead wire. In operating mode, the device resonates at a characteristic frequency via excitation by a specific oscillating signal. When the odor is adsorbed by the polymer, the resulting increase in the mass of the device reduces the frequency of resonance. The reduction in frequency is inversely proportional to the odorant mass adsorbed by the polymer. QCM usually has sensitivity up to 1 ng mass change. One of its disadvantages, however, is that the system becomes noisier as dimension reduces due to instability with increasing surface-to-volume ratio.

Another type of piezoelectric sensor is the SAW device. Unlike QCM, SAW is based on the principle that a Rayleigh wave travels over the surface of the device instead of its volume. SAW sensors can operate at much higher frequencies than QCM sensors. As SAW sensors can exhibit larger frequency changes, it is sensitive enough to track changes of up to 1 pg mass. However, both SAW and QCM devices need more complicated interface electronics than CPSs.

2.5.1. Quartz-crystal microbalance (QCM) sensors. Tetramethylammonium fluoride tetrahydrate (TMAF) was initially introduced as an excellent coating material applicable to the detection of carbon dioxide [58,59]. It was also reported to react with H_2S [60]. A single coated piezoelectric quartz crystal with TMAF and gold electrodes was used to detect H_2S with a center frequency of 9 MHz [61].

It was reported that fatty acids (FAs) (e.g., stearic, arachidic, and behenic acid salts) can react easily and quickly with H_2S (or H_2Se) molecules by forming metallic nanoparticles of sulfide (or selenide) in an FA Langmuir–Blodgett (LB) film matrix. Recently, researchers deposited different FA salts (e.g., cadmium arachidate, lead arachidate, and zinc arachidate) on an LB film matrix. These films can be coated on piezoelectric QCM-electrode surfaces to detect H_2S [62]. Gas molecules are allowed to diffuse into the bulk of LB films with an ordered structure much more easily because of their high surface area to bulk volume ratio. The reaction kinetics of the LB films with H_2S molecules was monitored using the nanogravimetric technique. Upon exposure to the LB films, H_2S showed a fast response manifested by a dramatic change in the frequency of QCM (at the initial stage). The findings of the fast, irreversible reaction between LB films and H_2S gas suggested that FA salt LB films should be a potential candidate for sensing the target H_2S.

A silver electrode was proposed as a gas-permeable membrane of the piezoelectric crystal sensor for the detection of H_2S produced by microorganisms [63]. The detection theory was based on the adsorption of H_2S onto the silver electrode of the piezoelectric crystal sensor due to affinity of H_2S on a silver electrode, which decreases the resonant frequency of QCM to a large extent. A 100-Hz frequency shift was chosen as the criterion value to judge the presence of microorganisms producing H_2S. Such a design can overcome most factors influencing detection of targets in the liquid phase.

2.5.2. Surface acoustic wave (SAW) sensors. SAW sensors have been applied to the detection of H_2S for many years. An H_2S detector comprising twin SAW delay lines was fabricated on a single $LiNbO_3$ substrate [64]. Each delay line was configured as an oscillator. The propagation path of one delay line was coated with a sputtered film of activated tungsten trioxide (WO_3), while the other (uncoated) was used as a stable reference. Its detection range was reported as 0.01–30 ppm. Later on, it was reported that an activation process could increase sensitivity [65]. To enhance the sensitivity of the sensor, the deposited film was exposed to H_2S at elevated temperatures (above 300°C). This activation process was reported to decrease the sheet conductivity of the WO_3 film in air, while increasing the changes in sheet conductivity with exposure of the film to H_2S.

The use of WO_3 films for the sensing membrane was explored by Smith et al. [66]. The basic principle of this application was to transform the as-deposited films from an amorphous to a polycrystalline structure through heat treatment or an ''activation'' process, which also dramatically improved the response time and the sensitivity of the films to H_2S gas to allow its detection below 1 ppb with good reproducibility. In addition, a semiconducting metal-oxide film (WO_3) doped with gold was also examined with the gas-sensitive film, which was deposited on a Y-cut Z-propagating lithium niobate ($LiNbO_3$) substrate [67]. H_2S detection was made in the range 0.25–100 ppm.

A 27^o Y-cut of quartz was reported to provide a better match of conductivity for WO_3 film between substrate resonance and the operation [68]. In the case of YZL-iNbO_3-based sensors, the dielectric properties of the film are used to derive the sensor response because the film does not closely match the resonant conductivity of the substrate. The detection of H_2S was 1–10 ppm with the sensor response time of 4 min.

More recently, a thin film of polyaniline ($\sim$100 nm) was also applied as a toxic gas sensor in a SAW system [69]. This thin film was made by a vacuum deposition technique in one of the dual delay-line systems on a $LiNbO_3$ Y-cut Z-propagating substrate. Uncoated reference was used to permit easy detection of the differential frequency, Δf. The detectable concentration was 25–500 ppm.

3. Evaluation of basic QA in H_2S sensing

In order to assess the pragmatic utility for H_2S sensing, the basic QA criteria (e.g., LOD and response time) for each common sensor type are plotted for purposes of comparative evaluation. To this end, mean values for particular sensor types were derived across different studies (refer to Fig. 1 for classification). Although the basic QA data cannot be extracted consistently from all of these studies, this comparison is still meaningful to offer a general idea for each sensor category.

As shown in Fig 2, the response times (s) for major sensor types, if compared with each other, averaged 213 ± 103 (SAW), 93 ± 38.2 (conducting polymer), 26 ± 38 (metal oxide), 10 ± 0.8 (electrochemical) and 0.20 (optical sensors, sensor arrays). The response time for metal-oxide sensors generally lay in a wide range (i.e. 8–120 s), due to basic differences in sensor materials and/or modifications. By contrast, electrochemical and optical sensors showed comparatively superior response times. Likewise, the LOD patterns derived for these sensor types also showed good similarities so that both optical and electrochemical sensors exhibited the best performance. For example, the LOD values (ppb) for metal oxide, SAW, conducting polymer, electrochemical, and optical sensors (sensor arrays) averaged 715 (± 1181), 360, 240 (± 84.9), 100, and 46 (± 50), respectively (Fig. 2).

Many sensors are developed and tested under laboratory conditions, but only a limited fraction of them are employed in real situations. If the reported sensor techniques are examined across different studies, only a few studies are found to yield data sets under real-world conditions (Fig 1). These cases include measurements of oral malodor, warning indicators for volcanic activities, and natural gas-stream monitoring. After testing several basic QA parameters under laboratory conditions, many of these studies claimed that their sensors have a great potential for practical applications in many areas (e.g., clinical diagnostics, health-care, geological prospecting, warning indicators, malodor nuisance, environmental and health regulation). However, most of those sensor techniques need to be validated further in many respects.

4. Summary and future prospects

Because of toxicity, nuisance, and wide occurrence under various environmental settings, H_2S has often been targeted as one of the key pollutant gases for regulation. As an initial step in its regulation, an accurate tool for its quantitative analysis is required to operate reliably under real situations. For this purpose, several real (or near-real) time gas-sensing techniques have been developed. These sensor devices can be divided in to three major categories including semiconductor metal oxide, electrochemical, and optical sensors. Moreover, the emerging sensor arrays and electronic-nose techniques, derivatized or modified from those main sensing principles, are very attractive in drawing a great deal of attention from scientific community.

In metal-oxide sensors, SnO_2 (or doped SnO_2) films have been most commonly used for H_2S-gas sensing.

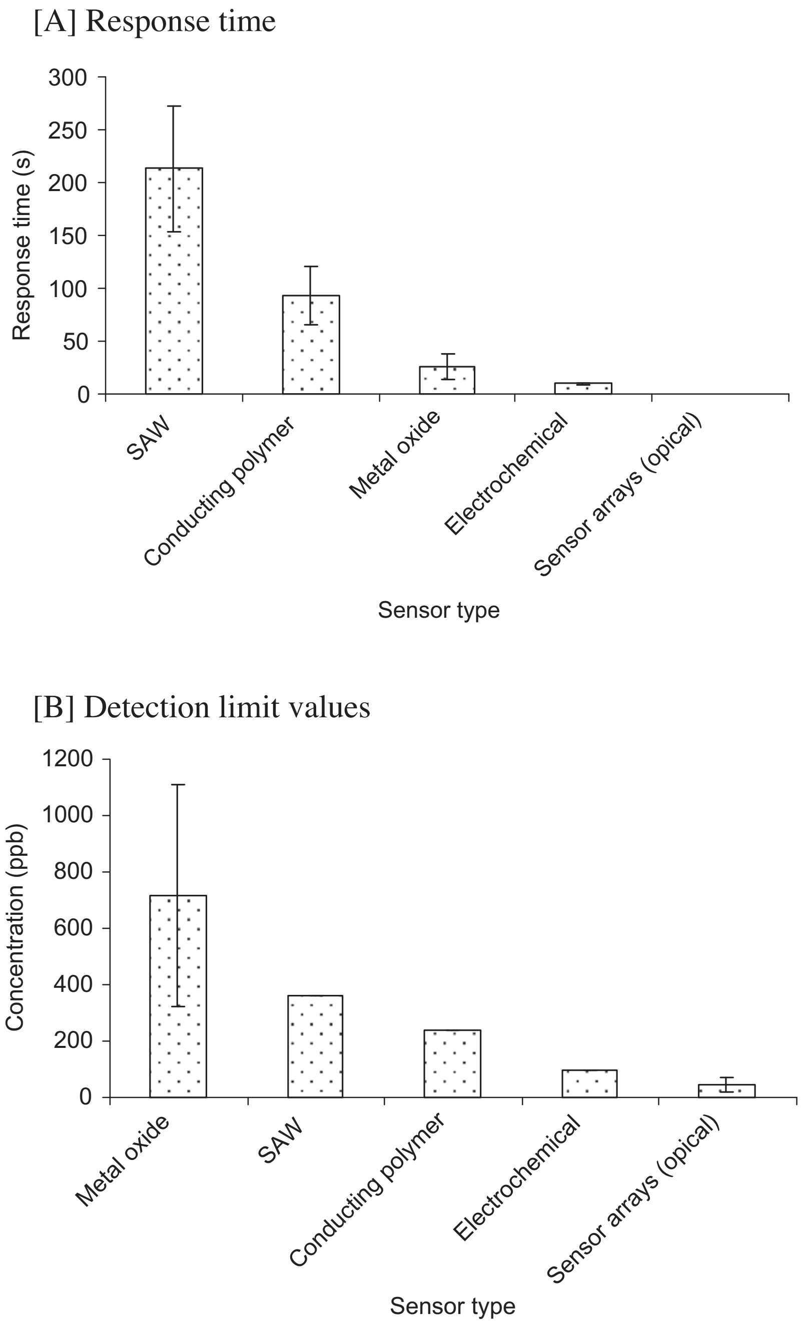

Figure 2. Comparison of two basic operating criteria across different sensor types for H_2S (The error bars represent ± standard error (SE); number of data for the above-listed sensor types (metal oxide, surface acoustic wave (SAW), conducting polymer, electrochemical, and sensor arrays) are 9, 3, 2, 4, and 4, respectively).

However, the potent role of alternative metal-oxide films has also been explored, including Fe_2O_3, WO_3, $BaTiO_3$, ZnO, and In_2O_3. In general, the detectability of these sensing devices falls in the ppm range. However, the detectability of sensing techniques has improved greatly to allow detection of H_2S at the sub-ppm range by certain modifications (e.g., use of catalyst and nanophase material-oxide films). The major advantages of these metal-oxide sensors are their small size, simple construction, low weight, low power consumption, and low cost. By contrast, their disadvantages include limited selectivity (against interfering gases) and dependence on relative humidity under varying environmental conditions. There has nonetheless been progress in meeting the challenges of developing more sensitive, more selective, and more stable sensors to cover H_2S levels in ambient air up to the sub-ppb range.

In electrochemical sensing techniques, solid-polymer-electrolyte sensors are commonly selected based on the principle of amperometry. Furthermore, other materials (e.g., H_2SO_4 treated Nafion membrane and ceramic metallic relying on cyclic voltammetry detection) have also been employed. Also, a Pr_6O_{11}-doped SnO_2 electrode was used for potentiometric detection of H_2S.

The performance of these electrochemical sensor devices has been proved with good detectability (a few hundred ppb) and response times (at or below 10 s). Their major advantages include economic cost, linear output, and being miniaturizable. The disadvantage is that they are readily affected by temperature, although such effect can be corrected.

Another important category of sensor technique for H_2S-gas detection is the optical method (either direct or indirect approach). To modulate the optical response of H_2S, a number of intermediate reagents are immobilized in sensor platforms. These include optical fibers, photoacoustic cells, quartz crystals, detector tubes, and colorimetric dyes. When these sensing materials are employed in the form of a sensor-array system, the sensitivity improves greatly to measure a few tens of ppb routinely. Hence, the enhanced sensitivity obtained by these sensor-array systems involves their application to H_2S monitoring near its odor threshold value (i.e. ppb). These sensor-array systems can be employed in smart techniques (e.g., WENSs and mobile-phone-based gas-sensing networks), which are among the hot, emerging areas in sensor technologies.

Future research warrants development of more sensitive, more robust, and more stable sensors for H_2S and other important trace pollutants that can operate consistently in harsh environmental conditions. As most of these sensors have been tested in laboratory conditions, they need to be validated more systematically to overcome harsh environmental conditions. After all, cost effectiveness will be one of the major issues in the practical application of H_2S-gas sensors.

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