DEVELOPMENT AND CHARACTERIZATION OF A PORTABLE APPARATUS FOR CONTINUOUS MEASUREMENT OF HYDROGEN SULFIDE IN GAS STREAMS

Bashar Yousef Abu Hattab

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United Arab Emirates University

College of Science

Department of Chemistry

DEVELOPMENT AND CHARACTERIZATION OF A PORTABLE APPARATUS FOR CONTINUOUS MEASUREMENT OF HYDROGEN SULFIDE IN GAS STREAMS

Bashar Yousef Salman Abu Hattab

This thesis is submitted in partial fulfilment of the requirements for the degree of Master of Science in Chemistry

Under the Supervision of Professor Sayed Marzouk

November 2018
Declaration of Original Work

I, Bashar Yousef Salman Abu Hattab, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "Development and Characterization of a Portable Apparatus for Continuous Measurement of Hydrogen Sulfide in Gas Streams", hereby, solemnly declare that this thesis is my own original research work that has been done and prepared by me under the supervision of Professor Sayed Marzouk, in the College of Science at UAEU. This work has not previously been presented or published, or formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

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A novel detection scheme for the hydrogen sulfide (H$_2$S) was described and patented recently by researchers at UAE University. This detection scheme and the described bench-scale analyzer offered the advantage of low-cost solution for real-time monitoring of percentile levels of H$_2$S with excellent signal stability. However, this previous work suffered from two major limitations, which are the relatively low sensitivity and slow response time, which mainly hindered its commercial utilization. Therefore, the aims of the present work were to enhance the detection sensitivity, decrease the response time, and develop a portable prototype of the H$_2$S analyzer based on the improved calorimetric detector. The calorimetric detection scheme was substantially improved by replacing the diffusion scrubber, reported previously, with a direct mixing of the H$_2$S containing gas stream with the sodium hydrogen and hydrogen peroxide reagents. Also, the heavy stainless steel mixing block was replaced with a carefully designed light-weight stainless steel alternative. The improved detector, two reagent pumps, two reservoirs, thermocouples-data acquisition card, compact PC and lithium ion battery were the main component used to construct a portable H$_2$S analyzer. The analyzer was optimized and fully characterized. The presented analyzer succeeded to lower the previously reported response time (i.e., 7 min) to 70 sec. and also the limit of detection was decreased from 200 ppm to 20 ppm. Additional advantages of the presented analyzer compared to the previous report include: (i) portable version with gross weight of approx. 8 kg; (ii) stand-alone operation for up to 4 hours at least, (iii) lower reagent consumption, (iv) single waste stream instead of two, (v) lower in cost (i.e., 2000 USD) compared with commercialized H$_2$S gas analyzer based on UV absorption detection (i.e., 23000 USD), (vi) ability to measure H$_2$S in liquid samples within 31 sec and with a LOD at 1 ppm, and (vii) capability to monitor the removal efficiency of H$_2$S from gas stream. Also, the reported advantages did not compromise the previously reported advantages such as the impressive signal stability or the low cost to any extent.

**Keywords**: H$_2$S Determination, thermometric detection, portable gas analyzer.
تطوير وتوصيف جهاز محمول لقياس المستمر لتركيز غاز كبريتيد الهيدروجين في تيار غازي

الملخص

قام باحثون من جامعة الإمارات حديثاً بتوصيف طريقة كشف جديدة لكبريتيد الهيدروجين اعتمدت على تفاعل طارد للحرارة وتميزت بالتكلفة المنخفضة وثبات الإشارة لتركيزات كبريتيد الهيدروجين في تيار غازي، ومع ذلك عانت تلك الطريقة من عيوب أساسيين وهما الحساسية المنخفضة نسبيا ووقت الاستجابة البطيء، وهو ما أعاق بشكل أساسي استخدام تلك الطريقة بشكل تجاري. ولذلك، كانت أهداف هذه الرسالة تعزيز حساسية الكشف، وتقليل زمن الاستجابة، وتطوير نموذج محمول ل محلل غاز كبريتيد الهيدروجين بعد تطوير أداء الكاشف الحراري. وقد اعتمدت طريقة تطوير أداء الكاشف الحراري على (أ) استبدال أغشية الانتشار التي تم وصفها سابقا بالخلط المباشر للغاز المحتوي على كبريتيد الهيدروجين مع كواشف هيدروكسيد الصوديوم وفوق أكسيد الهيدروجين و (ب) استبدال خلاط الساتانس ستيل النقي بخلاط ستانلس ستيل خفيفة الوزن ومصممة بعناية. هذا وقد تم استخدام الكاشف المحسن في بناء محلل محمول ل كبريتيد الهيدروجين مكون أيضا من مضخات، ورقائق، وكوارك وأدوات القياس الحرارية، وحاسوب صغير وطوارئ وتوربينات الليثيوم. تم توصيف أداء المحال بشكل كامل والذي أظهر نجاح في تقليل وقت الاستجابة الذي تم نشره سابقا (أي 7 دقائق) إلى 70 ثانية فقط، وكذلك تم تقليل حد الاكتشاف من 200 إلى 20 جزء في المليون. تشمل المزايا الأخرى للمحلل المحمول في هذه الرسالة مقارنة بالقرور السابق ما يلي (i) النسخة المحمولة ذات الوزن الإجمالي 8 كجم تقريبا، (2) تشغيل مستقل لمدة تصل إلى 4 ساعات على الأقل، (3) استهلاك أقل للكواشف، و (4) تيار نغبات واحد بدلاً من اثنين. ويجدر الإشارة أيضاً إلى أن المزايا التي تم الحصول عليها في هذه الرسالة عنها لم تؤثر على المزايا التي تم الإبلاغ عنها مسبقا مثل اثبات الإشارة المثير لإعجاب أو التكلفة المنخفضة إلى أي مدى. ويعتبر المحلل المحمول خطوة هامة نحو الجهود الجادة الرامية إلى تسويق محلل كبريتيد الهيدروجين على أساس الكاشف الحراري كمقياس منخفض التكلفة للمحلات المتاحة الأخرى ذات التكلفة العالية.

مفاهيم البحث الرئيسية: تقييم غاز كبريتيد الهيدروجين ، الكشف الحراري ، الجهاز المحمول
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I also express my gratitude to Dr. Nadia Abdullatif for her great assistance in getting me familiar with the commercial H$_2$S analyzer (OMA-300) which is part of my thesis.
Dedication

This thesis is dedicated to the memory of my parents
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<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BLS</td>
<td>Bureau of Labor Statistics</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer Numerical Control</td>
</tr>
<tr>
<td>FR</td>
<td>Flow Rate</td>
</tr>
<tr>
<td>GFR</td>
<td>Gas Flow Rate</td>
</tr>
<tr>
<td>HFMC</td>
<td>Hollow Fiber Membrane Contactor</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>Hydrogen Sulfide</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Sodium Sulfide</td>
</tr>
<tr>
<td>KMnO$_4$</td>
<td>Potassium Permanganate</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit Of Detection</td>
</tr>
<tr>
<td>MFC-4</td>
<td>4-Channel Computer Controlled Gas Mixer</td>
</tr>
<tr>
<td>MLPM</td>
<td>mL per minute</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>Na$_2$S</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>OSHA</td>
<td>Occupational Safety and Health Administration</td>
</tr>
<tr>
<td>ppm</td>
<td>Part Per Million</td>
</tr>
<tr>
<td>PWM</td>
<td>Pulse Width Modulator</td>
</tr>
<tr>
<td>P1/P2</td>
<td>Pump1 / Pump2</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to Noise Ratio</td>
</tr>
<tr>
<td>R1/R2</td>
<td>Reagent1 / Reagent2</td>
</tr>
<tr>
<td>TC</td>
<td>Thermocouple</td>
</tr>
<tr>
<td>TC-08</td>
<td>8-Channel Thermocouple Data Logger</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

1.1 Overview

1.1.1 Chemistry of Hydrogen Sulfide

Hydrogen sulfide (H$_2$S) was discovered by C. W. Scheele in 1777 [1–4]. It is a poisonous, corrosive, flammable, explosive [5–8] dense, colorless, toxic and with a characteristic odor of rotten eggs [9–13]. It is also called sulfureted hydrogen, sulfane, swamp gas, marsh gas, sewer gas and sulfur hydride [14], [15]. H$_2$S is a weak acid [16] and it has a boiling point of -60.7 $^\circ$C and melting point of -85.5 $^\circ$C [17]. The dissociation constant ($K_a$) for the first proton is $1 \times 10^{-7}$ and the second proton’s $K_a$ is $1 \times 10^{-12}$, respectively [1]. The p$K_a$ values for the first and second dissociation steps are about 6.88 and 19, respectively [18]. It dissociates initially into hydrosulfide ion (p$K_a$ = 6.9) and sulfide ion (p$K_a$ = 11.96) [19]. Sulfur in H$_2$S has an oxidation state of -2 [20] and is surrounded by 2 lone pairs [21]. H$_2$S largely exists in two forms: the neutral molecular form (H$_2$S) and an ionic form (HS$^-$) while, S$^{2-}$ is a very minor component simply because of the second p$K_a$ being very high [16], [22]. Hydrogen sulfide exists as bent shaped molecule with tetrahedral electron geometry [23] and bond angle of 92° [24] as shown in Figure 1 [1], and due to its bent geometry, H$_2$S molecule is polar [1] (dipole moment of 0.97 D) [25]. It is slightly denser than air with density of 1.539 g/L at 0$^\circ$C [17] and 1.19 g/L at 15 $^\circ$C, respectively [26]. It is slightly soluble in water [27] (0.41 g/100 mL at 20 $^\circ$C) and forms hydrosulphuric acid which is a weak acid. Hydrogen sulfide remains in the atmosphere for approximately one day in the summer and 42 days in winter [28].
1.1.2 Health Aspects of H$_2$S

The emission of hydrogen sulfide to the atmosphere can reduce the quality of life, and cause health effects even at low concentrations (i.e., < 1 ppm) such as tumors [29], ischemia [30] headache, pulmonary, dizziness, nausea, edema and neurotoxicity [31], [32]. Human’s nose can smell hydrogen sulfide at low concentrations in the air, between 0.0005 and 0.3 ppm. According to available data from OSHA and the Bureau of Labor Statistics (BLS), H$_2$S is considered as one of the most dangerous gases in the workplace [26]. According to the safety standards established by American Conference of Government Industrial Hygienists, the threshold value defined for hydrogen sulfide is only 10 ppm, and over this concentration, the ability to sense H$_2$S declines because the human nose becomes desensitized. Such results recorded human death when the concentration of this gas is over 700 ppm [33], [34].

There are tragic consequences between 10 and 700 ppm that affect human body. At 30 ppm, H$_2$S begins to saturate the olfactory making it difficult to recognize the toxic gas, and close to 100 ppm, it is totally undetectable through smell alone.
Acute exposure to 400 ppm H₂S induced severe mitochondrial swelling in support cells and olfactory neurons, which progressed to olfactory epithelial necrosis and sloughing [36]. Table 1 represents dose related effects of hydrogen sulfide inhalation exposure [37].

Table 1: Dose related effects of hydrogen sulfide inhalation exposure

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>3–5 ppm</td>
<td>Offensive “rotten egg” smell</td>
</tr>
<tr>
<td>10–20 ppm</td>
<td>Eye irritation</td>
</tr>
<tr>
<td>50–100 ppm</td>
<td>Conjunctivitis, severe eye injury</td>
</tr>
<tr>
<td>100–150 ppm</td>
<td>Olfactory fatigue</td>
</tr>
<tr>
<td>150–250 ppm</td>
<td>Irritation of nose and lungs, dizziness, vomiting, headache, nausea</td>
</tr>
<tr>
<td>250–500 ppm</td>
<td>Severe respiratory irritation, pulmonary edema</td>
</tr>
<tr>
<td>500–1000 ppm</td>
<td>hyperpnoea, apnea, seizures, coma, death</td>
</tr>
<tr>
<td>1000 ppm and above</td>
<td>Sudden knockdown, death</td>
</tr>
</tbody>
</table>

Lambert et al. [38] revealed several studies regarding to H₂S effect on eye. They reviewed that acute H₂S exposure might produce eye irritation and toxic effects. A study showed a superficial inflammation of the cornea and conjunctiva due to the irritant effect of hydrogen sulfide which they called “gas eye”.

Furthermore, it was concluded that exposure to H₂S from crude oil among former workers and neighbors of a refinery might cause neurophysiological abnormalities [39]. Another study had investigated the cognitive functions among workers of sewer networks showed that exposure to H₂S was associated with cognitive impairment [40].
1.1.3 Environmental Aspects of H$_2$S

Hydrogen sulfide occurs naturally in crude petroleum, natural gas, other natural sources [41], [42] and from many industrial processes [43]. It forms from any source of sulfur-containing compounds that comes into contact with organic material, especially at high level of temperature by reducing sulfur or sulfate to hydrogen sulfide [44].

There are different environments where hydrogen sulfide is generated. Firstly, in swamps, and sewers, where sulfate-reducing bacteria break down organic substance in the absence of oxygen using anaerobic digestion process [45]. Secondly, in volcanoes when it comes out with the released gases [46], oil and gas industry as well [14]. Thirdly, it is also produced by human and animal wastes [47]. Fourthly, it is produced from industrial activities, such as Kraft paper mills [48]. Table 2 represents summary of occupational settings and other sources of hydrogen sulfide [37].
Table 2: Summary of occupational settings and other sources of hydrogen sulfide

<table>
<thead>
<tr>
<th>Petroleum refineries of crude oils with sulfur</th>
<th>Livestock farmers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas plants</td>
<td>Sewage plants and sewer workers</td>
</tr>
<tr>
<td>Coke manufacture from coal with sulfur</td>
<td>Animal manure disposal</td>
</tr>
<tr>
<td>Kraft wood pulp production</td>
<td>Pipeline maintenance</td>
</tr>
<tr>
<td>Tanneries</td>
<td>Food processing factories</td>
</tr>
<tr>
<td>Sulfur production</td>
<td>Production of deuterated water</td>
</tr>
<tr>
<td>Hydrogen sulfide gas production and storage</td>
<td>Construction industry (e.g., manhole workers, asphalt use and storage)</td>
</tr>
<tr>
<td>Viscose rayon production</td>
<td>Carbon disulfide production</td>
</tr>
<tr>
<td>Hydraulic fracking</td>
<td>Mixing household chemicals for suicide</td>
</tr>
<tr>
<td>Gypsum drywall</td>
<td>Carbonyl sulfide in vivo metabolism</td>
</tr>
</tbody>
</table>

1.1.4 Uses of H$_2$S

H$_2$S adopted into the family of endogenous gasotransmitters [49], [16] that regulate essential processes of mammalian physiology [50]. It is generated from an amino acid (l-cysteine) and H$_2$S synthetic enzymes which are expressed in most organs and tissues of the body [51], [52]. In brain, tissues, and blood in mammalian, the concentration of hydrogen sulfide ranging from 1 to 160 μM [53], [54]. H$_2$S plays key roles in the cardiovascular, endocrine, gastrointestinal, and central nervous systems [55]. Figure 2 shows H$_2$S as gas gasotransmitter for modulating several aspects of cellular physiology [15]. Also, H$_2$S is used to make sodium sulfide and
sodium hydrosulfide which then they used in the production of pharmaceuticals, dyes and pesticides [26].

Figure 2: Physiological processes modulated by H₂S
1.1.5 Hydrogen Sulfide in Wastewater

The most common malodorous component in wastewater treatment areas is hydrogen sulfide [56]–[59]. The rate of sulfide generation in wastewater depends on: temperature, pH, oxidation–reduction potential and nutrients [60]. The sulfide concentration in tannery wastewaters ranging from 1 to 500 mg/L [61] and the limit value for salt water is 0.5 mg/L [62]. Refinery wastewaters contain 2 mg/L of sulfide and exceed 150 mg/L in sour water strippers [63]. Concrete corrosion have been mentioned when the sulfide concentration lies between 0.1 to 0.5 mg/L and reach up to 2.0 mg/L [64] in some cases.

1.2 Statement of the Problem

The improvement of the detector design is based on the previous version as shown in Figure 3[65]. This previous work suffered from two major limitations, these are the relatively low sensitivity (i.e., LOD 200 ppm) and slow response time (i.e., 7 min), which mainly hindered its commercial utilization.
Figure 3: Construction of the previous detector
1.2.1 Purpose of this Work

To the best of our knowledge, no researchers continuously improve the previous report (Sensors and Actuators B 2012, 162, 377-383). The major objectives of this work are: enhancing the response time form 7 min to 2 min, lowering the limit of detection from 200 pm to 20 ppm, and developing a novel portable design from bench-scale size. These objectives can be approached by (i) evaluating some novel detector design, (ii) optimizing the various parameters (such reagent concentrations and flow ratio) to maximize the S/N ratio, and (iii) construction of the portable analyzer which proposed to contain two reservoirs for the two liquid reagents, waste reservoirs, H$_2$S bubbler reservoirs, dual-channel peristaltic pump, pump controller, battery, detector, Tablet PC, thermocouples data acquisition interface, and a power switches. The design and the construction material will be carefully optimized to minimize the analyzer weight and footprint. The characterization of the developed portable gas analyzer will include: (i) signal stability, (ii) signal repeatability and reproducibility, (iii) linearity, (iv) sensitivity, (v) response time, (vi) response time, and (vii) applications. More details of its principle operation, optimization, and characterization are described.

1.3 Relevant Literature

1.3.1 Analytical Methods and Techniques Available for H$_2$S Detection

Sulfide can be determined by different technique methods. The term “sulfide” includes hydrogen sulfide, sulfide and bisulfide [66]. There are various methods to quantify hydrogen sulfide analytically. Figure 4 summarizes various methods used for hydrogen sulfide determination [67].
Figure 4: Various methods for the detection of sulfide

1.3.1.1 Titrimetric Method

There are different quantitative analyses methods for measuring sulfide by titrimetric analysis which include potentiometric [68]–[70] volumetric [71], iodometric (appearance or disappearance of elementary iodine indicates the end point) [72], redox [73] and Argentometric [74].

The most used titrimetric method is iodometric method [75] which does not require a sulfide standard [76]. This is based on preserving the sulfide sample by
addition of zinc acetate and sodium hydroxide for maintaining the pH to be above 9. The precipitated zinc sulfide is oxidized to sulfur by the addition of iodine in the acidic medium. Then, a standard solution of sodium sulfate is titrated with the remaining of the iodine until the disappearance of the iodine-starch complex. The methylene blue method of colorimetric determination is based on the reaction of dimethyl-p-phenylenediamine, ferric chloride, and sulfide which results in the formation of methylene blue (colored). This method is used for samples which contain a concentration of sulfide between 0.1 and 20 mg/L. The potentiometric titration method is based on utilizing silver/silver sulfide electrode in titration of dissolved sulfide and it is applicable for contamination that exceed 0.03 mg/L [75].

However, the titrimetric technique is insufficiently sensitive and little selective [72]. Iodometric method has a drawback that it is not sensitive enough for solutions less concentrated than 1 mg/L of sulfide [76]. Later on, direct titration with iodine is avoided because of the loss of the sample through aerial oxidation and/or volatilization [73]. Redox titration suffers from interference from other oxidizable materials, such as sulfite and thiosulfate through competing side reactions thus can cause apparently high results for sulfide [67].

1.3.1.2 Spectrochemical Methods

1.3.1.2.1 Spectrophotometric Methods

The determination of H$_2$S in spectrophotometric techniques by the methylene blue method (a reaction of hydrogen sulfide and N,N-dimethyl-p-phenylenediamine in the presence of hydrochloric acid and oxidizing agent) has been widely used since
its introduction by Fischer in 1883 [77]. Fogo-Popowsky method is one of the general standard reference methods used spectrophotometric techniques for the determination of hydrogen sulfide [78]. Methylene blue method has been the general standard reference method used for the determination of hydrogen sulfide by spectrophotometric method [79]. Ghadiri et al. [80] were able to detect sulfide by spectrophotometric method based on peroxidase inhibition of sulfide by detection of purpurogallin formation in the concentration range of 0.6–7.0 μM with a detection limit of 0.4 μM. Silva et al. were used methylene blue chemistry, based sequential injection analysis by using N,N dimethyl-p-phenylene diamine hydrochloride and FeCl₃ for H₂S determination with a detection limit of 40 μg/L, and linear dynamic range from 0.05 to 2 mg/L [81],[82].

Spectrophotometric methods revealed number of limitations include (i) lack of controlling factors influencing sulfide stability such as pH [83], which leads to release of acid-labile sulfide and false quantitation as free sulfide as a result [84] (ii) the limited extent for such techniques to detect levels of sulfide for tissue, blood and other biological specimens, and (iii) long time dependent nature of color production and the intensity which requires precise monitoring [83].

1.3.1.2.2 Luminescence Methods

There are several methods reported for the determination of sulfide based on fluorimetric [85], [86] and chemiluminescence techniques [87], [88]. Fluorimetric method have been investigated with methylene blue [85], thionine [89] and 2,7-dichlorofluorescein [90]. A common approach for fluorescent labels employing fluorescein–mercuric acetate complexes that are quenched [85] by the presence of
sulfide [67]. Main disadvantage of such a system is the poor selectivity when other thiol compounds are present which result by causing a significant interference.

1.3.1.3 Chromatographic Method

Gas chromatography techniques have been applied to the detection of sulfide including soil sampling [91], pharmaceutical preparations [92] and body blood [93]. Several detection methods that are both sensitive and selective to sulfur compounds were used by gas chromatography such as atomic emission [94], flame photometric [95], [96], pulse flame photometric [97], [98], and sulfur chemiluminescence [99]. Pulse flame photometric detection provides improved detection sensitivity and much higher selectivity for sulfur compared to flame photometric detection [100]. Ion chromatography is a process that allows the separation of ions from the mixtures based on their charge [101], and it is implemented to detect sulfur compounds such as sulfide [102], [103].

On the other hand, some drawbacks were noticed of these methods such as the difficulty of miniaturization and field usage, bulkiness, time consuming, instrumentation is expensive, automation mandatory when used in harsh environments, and large quantities of toxic reagents are used [104], [105].

1.3.1.4 Electrochemical Methods

1.3.1.4.1 Potentiometric Methods

Potentiometric method is an electrochemical technique which measures the electrode potential and utilizes the galvanic cell concept [106]. A pair of electrode is immersed and the potential of one of the electrodes is measured relatively to the
other. Such examples include pH meters [107], and ion-selective electrode [108]. The most commonly exploited potentiometric systems tend to involve silver sulfide as the main sensing element [109].

Richter et al. were able to detect sulfide based on potentiometric method within range between 0.1–30 μg/mL and 0.3–50 μg/g for liquid and solid samples, respectively [110]. Another study showed a sulfide-selective electrode based on surfactant modified zeolite particles into PVC membrane exhibited linear response range to sulfide in the range of $1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$ mol/L with detection limit of $6.3 \times 10^{-8}$ mol/L [111]. Hoffmann was able to oxidize hydrogen sulfide to sulfur by hydrogen peroxide and studied potentiometrically [112]. Lawrence et al. [113] were able to used carbon nanotube modified glassy carbon electrodes for measuring sulfide with a detection limit of 0.3 μM and linear dynamic range from 1.25 to 112.5 μM. There are some disadvantages to the potentiometric method such as a response is dependent to the oxygen concentration and poor of the selectivity [67].

1.3.1.4.2 Amperometric Methods

Amperometric detection is based on oxidation/reduction of a sample at a working electrode which held at a potential. Several approaches for determination of sulfide by glassy carbon electrode were studied [114], [115]. Lawrence et al. were used a boron doped diamond (BDD) electrode for oxidation the sulfide and detected [116]. Giuriati et al. [104] were able to detect the free sulfide by pulsed amperometric detection (PAD) at a silver-working electrode with a detection limit of 1.0 μg/L. Some of silver electrodes were suffer from drawback such as short operational life time (5-7 days) [117].
1.3.1.4.3 Conductometric Method

Conductivity is the measurement of water’s capability for passing electrical flow. This ability is directly related to the concentration of ions in the water [118]. Miah et al. [119] they were able to study the concentration of the sulfide on the commercial charcoal by conductometric techniques. The conductivity of the sulfide solution took place in a range of 0.00005 – 0.02 M.

1.3.1.5 Calorimetric Method

Calorimetric is a measurement of the amount of heat absorbed (endothermic) or released (exothermic) in a chemical reaction. The calorimetric detection is widely used in thermal engineering and science [120]–[122]. Marzouk et al. [65] they were only be able to detect hydrogen sulfide based on thermometric detection. Furthermore, no researchers continuously improve the previous report (Sensors and Actuators B 2012, 162, 377-383).

The analyzer was based on absorbing the hydrogen sulfide from the sodium hydroxide through hollow fiber membrane (HFM) contactor (diffusion scrubber) followed by oxidation of sulfide ions by hydrogen peroxide which resulted by generating of heat. This exothermic reaction is measured and proved as useful analytical signal for H$_2$S detection. This method was capable of detecting H$_2$S in the range of 200 ppm – 5 % with a response of 7 min.

The advantages of this calorimetric analyzer include good low cost of construction, linear response (i.e., 0.05 - 5 %), excellent selectivity in the presence of several gases (i.e., N$_2$, O$_2$, CH$_4$, CO$_2$ and CO), and signal repeatability and stability.
1.3.1.6 H₂S Sensors

Different sensors in the form of thin or thick films based on semiconducting metal-oxide [123], electrochemical [124]–[127], optical [128]–[132], surface acoustic wave [133], [134], and conducting polymer [135] were used to detect sulfide. These sensors suffered from some limitation such as lack of field validation [105], limited selectivity, high operation temperature, poor stability, high energy consumption, dependence on relative humidity under varying environmental conditions, and difficult to reproduce [135], [136].

1.3.1.7 H₂S Analyzers

Wright et al. [137] They were constructed an analyzer that able to measure H₂S in waste water stream. The analyzer is limited for measuring purgeable hydrogen sulfide in the liquid sample. Neihof et al. [138] they were also built an H₂S analyzer based on the colorimetric indicator. Takashi-Ihara et al. [139] measured quantitatively sulfur content in a sulfurous sample by burned it in combustion chamber. Leco sulfur analyzer was used by Jones and Issac [140] for determination of sulfur in plant in addition of magnesium oxide, iron and tin accelerator followed by titration procedure. However, a drawback of the Leco sulfur analyzer was noticed i.e., the result obtained from soil samples had not proven to be acceptable especially with low sulfur concentration (i.e. < 30 micro mol/g) [141].
Chapter 2: Experimental Work and Set-up

2.1 Materials

Stainless steel tubes (2.4 mm ID and 2.6 mm OD) were purchased from MicroGroup (USA). Tygon tubing. Type-T thermocouples with miniature flat pin plug were received from TC Direct (UK), Model 401-324. Two-part thermal adhesive, model ASTA-7g was received from Arctic Silver (USA). Quick epoxy (Devcon®) and Multi-purpose polyurethane foam spray (USPRO ™) were purchased from the local market.

An 8-Channel thermocouple data logger (Model TC-08) was purchased from Pico Technology (UK). An OEM 7-inch Industrial Computer 4GB RAM & 64 GB SSD with Windows 7 Operating System, 32 bit was purchased from the local market. Dual-channel peristaltic pumps from Jihpump (model 101K/ZL-S-16) (www.aliexpress.com). Digital Display Pulse Width Modulator (PWM) for DC Motor Speed Control Controller 12-80 V and 30 A was received from Electronic World (www.aliexpress.com). 24 V 10 Ah Lithium ion battery (model 6S5P 18650) was received from Surplus Xin battery store (www.aliexpress.com). Digital thermometer digital voltmeter were purchased from the online stores (www.aliexpress.com). Illuminated push-button metallic switches (12 mm and 16 mm dia, 24 V) of different colors were purchased from the online stores (www.aliexpress.com). A 24 VDC-0.15 A cooling fan (5 cm x 5 cm) was purchased from the local market. Acrylic sheets (4 mm and 6 mm thick) were purchased from Signtrade, UAE.
Gas cylinders containing standard H$_2$S (5.00 % in N$_2$), N$_2$ (99.99 %) and CO$_2$ (99.99 %), respectively were received from Air products (United Arab Emirates). Hydrogen peroxide (34.5-36.5 %), sodium hydroxide, sodium sulfide, potassium permanganate and sulfuric acid were obtained from Sigma-Aldrich. All solutions were prepared using deionized (DI) water.

2.2 Experimental Setup

A 4-CH computer controlled gas mixer (Model MFC-4, Sable Systems, USA) was used to control four Mass flow controllers (Sierra Instruments, USA) to prepare gas stream of variable compositions for calibrations and characterization purposes. The MFC-4 utility software (Sable Systems) was used to run a given preset program of required steps of variable gas composition.

2.3 Preliminary Investigation to Improve the Detector Design

2.3.1 Investigation to Improve the Pre-Mixer Design

At the earlier stage, several trials to improve the mixer design (mixing NaOH and H$_2$S) were investigated. Figure 5 shows the multi attempts (fabricated in local CNC. market) of mixing these two compounds.
Figure 5: Preliminary investigation to improve the detector’s mixer design
2.3.2 Investigation to Improve the Detector Design

Several trials to fabricate a reliable detector were examined. Some detectors were designated to be in flat shape and others designated to be in helical. Figure 6 shows several trials for fabricating different detectors geometry.

Figure 6: Preliminary investigation to improve the detector design
2.3.3 Final Fabrication of the Detector Design

The new reaction compartment mixer design was fabricated from a tube of stainless steel consist of 75 cm in length, weighted 13 g and has a 2.4 mm in inner diameter and 2.6 mm in outer diameter, respectively. The mixer was constructed to be in helical shape (15 mm in inner diameter) consisting of two layers, each layer has six coils as shown in Figure 7. The outer surface of each layer of the mixer was coated by thermal epoxy as well as the thermocouples were stick on it as shown in Figure 8. The detector was covered by foam and inserted into a transparent acrylic tube as shown in Figure 9.

![Fabrication the detector](image)

**Figure 7: Fabrication the detector**
Figure 8: Detector coated by thermal epoxy

Figure 9: Detector covered by foam
2.4 Concept Design of the Portable H\textsubscript{2}S Analyzer

The concept design of the portable H\textsubscript{2}S analyzer is illustrated by the block diagram showing the main components of the analyzer as presented in Figure 10. The analyzer is constructed from two DC-peristaltic pumps (P1 and P2) which are dedicated for the two reagents (R1 and R2), respectively. The two reagents are mixed together and with the analyte gas stream and fed through the detector. The ambient temperature and the detector temperature were continuously measured by one and three thermocouples, respectively. The thermocouple signals were recorded using an 8-Channel data acquisition interface card (model TC-8, Pico Technologies). A battery operated compact PC was used in data acquisition, data display and storage. A 24-V lithium ion battery (10Ah) was used to power the PC and the pumps as well as other electrical components as will be presented in the detailed construction below. The waste solution was stored on-board in a waste reservoir and the excess gas stream was vented through a sodium hydroxide bubbler to trap the residual H\textsubscript{2}S.
Figure 10: The block diagram showing the main components of the portable H\textsubscript{2}S analyzer.
2.5 Detailed Construction of the Portable H₂S Analyzer

2.5.1 CNC Machining

The Minitron D-23 Desktop CNC (Computer Numerical Control) router machine (Figure 11) was received from CanCam. A sheet of 6 mm was used to fabricate the portable H₂S Analyzer (Figure 12) by using different milling cutters (end mill 2, 3 and 6 mm) as shown in Figure 13. The CNC utility Vectric software (Version 9.0) was used to draw and design for cutting parts on CNC router. More specifications are shown in Table 3.

![Figure 11: CNC. machine](image-url)
Figure 12: White sheet 6mm

Figure 13: End mills cutters (2, 3 and 6 mm)
2.5.2 Construction the Base Part

The analyzer body was constructed from white acrylic sheet (6 mm thick). The base was constructed from two layers of identical footprint and glued together by chloroform. Such two-layer structure allowed the creation of internal conduits for the two reagents. The Design and the dimensions as well as the photo of the as-cut by the CNC machine of the lower and the upper layers are presented in Figures 14, 15 and 16, respectively. The depth of the conduits machined in the lower layer was 3 mm.

### Table 3: CNC. Specification

<table>
<thead>
<tr>
<th>Specification</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machining Bed</td>
<td>63.5 cm x 93.98 cm</td>
</tr>
<tr>
<td>Weight</td>
<td>150 kg</td>
</tr>
<tr>
<td>Color</td>
<td>White/Blue</td>
</tr>
<tr>
<td>Power</td>
<td>2.2 kW / 3 HP</td>
</tr>
<tr>
<td>Max Speed</td>
<td>24000 RPM</td>
</tr>
<tr>
<td>Rapid Speed</td>
<td>315 IMP</td>
</tr>
<tr>
<td>Max Cutting Speed</td>
<td>240 IMP</td>
</tr>
</tbody>
</table>
Figure 14: Design and dimensions of the lower layer of the analyzer base (A) and the as cut acrylic piece in the CNC machine (B)
Figure 15: Design and dimensions of the upper layer of the analyzer base (A) and the as cut acrylic piece in the CNC machine (B)
Figure 16: The reagent flow within the base conduits (A) and the upper view of the combined base (B) showing the footprint grooves of the reagent and water reservoirs, bubbler, battery and the pulse width modulator.
2.5.3 Construction the Front and Sides Panel Part

The front and two sides’ panel view of the analyzer were cut from one piece of acrylic sheet (6 mm) and the V shapes were grooved as shown in Figures 17 and 18, respectively to allow easily bending the piece by using a heat gun.

Figure 17: Front and sides panel view of the analyzer
Figure 18: Front and sides panel view of the analyzer
2.5.4 Assembling the Front/Base Parts

The two reagent bottles, waste bottle and bubbler bottle were integrated on the base piece. The base piece was glued with the front piece as shown in Figure 19. The piece of 6 mm was used as a border of the reagent.

Figure 19: Both of bottom piece and front piece
2.5.5 Construction the Analyzer Upper Part

The upper side view of the Analyzer was cut to fit with whole analyzer as shown in Figures 20 and 21, respectively.

Figure 20: Top view of the analyzer
Figure 21: Top view of the analyzer
2.5.6 Construction the Analyzer Rear Part

The rear view of the Analyzer was cut to be fit with whole analyzer as shown in Figure 22.

Figure 22: Rear view of the analyzer (A), photo of the rear view of the analyzer (B)
2.6 Assembly of Portable H₂S Analyzer

The portable analyzer consists of several components, i.e., thermometric detector, two peristaltic pumps, PWM with its screen, tablet PC, fan, On/Off switches, temperature gauge meter, thermocouples data acquisition interface TC-08, thermocouples (type T), two reservoir bottles for reagents, waste bottle, H₂S bubbler bottle, waste pump and a battery with its screen as shown in Figures 23-26.

Figure 23: Top view of the analyzer
Figure 24: Front view of the analyzer
Figure 25: Rear view of the analyzer
Figure 26: Side view of the analyzer
2.7 Electric Circuit Diagram for H₂S Portable Analyzer

The electric circuit for the portable analyzer was designated in which consist of four switches, each one is responsible for a certain purpose. The first switch was related to the main power in which feed all electrical devices. The rest of the switches were responsible for the PC device, reagent pumps and waste pump individually as shown in Figure 27. The utilizing of four switches will facilitate the treating the portable analyzer.

![Electric Circuit Diagram for H₂S Portable Analyzer](image)

Figure 27: Electric circuit diagram for H₂S portable analyzer
2.8 Gas Mixing System

The flow range of the mass flow controllers (MFC) were 0 - 10, 0 - 100, 0-1000, and 0-5000 mL/min, respectively. The PC 1 was responsible for controlling and programmed the MFC as well as the PC 2 was integrated to the portable analyzer for data display and storage as shown in Figure 28.

Figure 28: Experimental setup for gas mixing system
2.9 Calibration and Measurements

The first step of the analyzer measurements was to create a baseline. The baseline can be approached by pumping the two reagents in the presence of the nitrogen gas until the baseline be stabilized. The X axis represents the time in sec and the Y axis represents the temperature in Celsius (which is proportional to the H$_2$S concentration) as shown in Figure 29. The two detectors and two reagents with analyte gas are joining by means of Tygon tubing.

Figure 29: Baseline stabilized at the beginning of each experiment
2.10 Waste solution Treatment

The waste streams (liquid and gas phase) were collected regularly and kept in a reservoir bottle. The remaining gas phase from the waste bottle will be collected again in another bottle (bubbler) that contains concentrated NaOH to eliminate the residual of H$_2$S. The remaining alkaline sulfate solution can be neutralized and disposed safely.

2.11 Experimental Setup for Application of H$_2$S Analyzer in Gas and Liquid Treatment

2.11.1 Experimental Setup for Monitoring H$_2$S in Gas Treatment

To set up an application for monitoring H$_2$S in gas treatment, the hollow fiber module (Figure 30) was used to absorb the hydrogen sulfide gas analyte in the presence of sodium hydroxide. The different concentrations of the sodium hydroxide were injected gradually inside the HFM. The rest of the hydrogen sulfide concentrations were measured by the portable analyzer. The experimental setup for monitoring H$_2$S in gas treatment system was shown in Figures 31 and 32, respectively.
Figure 30: Hollow fiber membrane module (HFM)

Figure 31: Experimental setup for monitoring H₂S in gas treatment system
Figure 32: Photo of the same experimental setup without gas system
2.11.2 Designing System for Monitoring \( \text{H}_2\text{S} \) in Liquid Phase

To set up an application for measuring \( \text{H}_2\text{S} \) in liquid phase, a sample container which contains sulfide solution was used. The experimental setup for monitoring \( \text{H}_2\text{S} \) in liquid phase was shown in Figures 33 and 34, respectively. The hydrogen sulfide in liquid sample was produced from the reaction between sulfuric acid and sodium sulfide.

To allow safe opening of the sample container after \( \text{H}_2\text{S} \) evolution and attainment of the peak maximum, potassium permanganate solution (1.0 M) was injected to oxidize the residual soluble \( \text{H}_2\text{S} \) in the already acidified solution into elemental sulfur.
Figure 33: Experimental setup for monitoring H₂S in liquid phase
Figure 34: Top view for monitoring H$_2$S in liquid phase
Chapter 3: Results & Discussion

3.1 Improving the Detector Design

The previously described analyzer [65] was based on a diffusion scrubber and a relatively heavy stainless steel block with helical geometry which also served as a mixer to suppress the noise caused by the turbulent gas/liquid hot mixture. Although this design proved suitable to produce reproducible analytical signals, it suffered from two major limitations, i.e., (i) the slow response time (~ 7-8 minutes) and (ii) the relatively low sensitivity (~ 200 ppm H$_2$S). To address these two limitations, two changes were suggested. These are eliminating the diffusion scrubber to allow direct mixing of the gas stream with the liquids reagents, and improving the detector design by reducing the weight of the reaction compartment mixer which should reduce its heat capacity. Both of these suggestions should impart the desired reduction of the response time and enhancement of the detection sensitivity. Moreover, the suggested configuration offers the advantage of producing a single waste stream compared to the previous configuration [65], which produces the regular gas/reagent mixture waste as well as the gas stream which contains the residual H$_2$S.

Eliminating the diffusion scrubber should remove the dependence of the gas mass transfer on the membrane resistance and also eliminates the time needed to carry the absorbed H$_2$S from the diffusion scrubber unit to the detector downstream. A comparison between the previous and the present configurations are shown in Figure 35. It is important to emphasize that the reaction compartment mixer and the thermocouples attached to it constitute together the analyzer detector.
Figure 35: A comparison between the previous and the present configurations

The prediction of the effect of removing the diffusion scrubber on reducing the overall response time was straightforward. However, its impact on the sensitivity cannot be readily predicted because of the two opposing operating factors, i.e., the negative cooling effect of the larger proportion of the inert gas component (nitrogen in this case) in the analyte gas stream and the positive effect caused by the decreased resistance of H₂S transfer to the liquid phase.

To improve the detector design, several aspects should be taken into consideration: (i) to retain the stainless steel as the construction material for the reaction compartment mixer which previously proved as the most suitable material
for this purpose because of its chemical compatibility with the corrosive reagents, (ii) to minimize the overall weight of the reaction compartment mixer to minimize its heat capacity, (iii) to keep the overall volume of the reaction compartment mixer to the minimum, not only for the sake of compactness but also to avoid the cooling effect by the radiative heat loss, (iv) to attach the TC to the outer surface of the stainless reaction compartment mixer using thermally conducting epoxy to ensure the efficient heat conduction, (v) to use more than one TC to average their signal readings to further improve the S/N ratio and (vi) to thermally insulate the reaction compartment mixer and the attached thermocouples.

Thin-walled stainless steel tubes are commercially available at relatively low cost and seemed as very suitable candidates for simple and straightforward construction of the reaction compartment for direct mixing of the gas stream and the two liquid reagents. The thin-walled stainless steel tubes pretty much satisfy all the construction consideration mentioned above. Shaping the long straight tubes into a compressed coil shape can also provide the needed compactness. In the present work, several geometries were tested and the best geometry (based on the highest S/N ratio) was based on a SS tube (75 cm long, ID 2.4 mm and OD 2.6 mm) coiled into a double coil geometry (6 turn each) which has an ID of 15 mm and the OD of 25 mm, as shown in Figure 7.

To enhance the thermal conductivity of the entire double coil, the grooves between the turns were filled with a thin layer of thermally-conducting silver epoxy from the inner side, between the two coils as well as the outer side. The thermally conducting epoxy also served to fix the two TCs to the double coil. The first TC was sandwiched between the inner and the outer coils and the second was fixed at the
outer surface. In such a way, the small active part of each TC can be reasonably assumed to respond to the average surface temperature of the entire double coil rather than to its local point temperature. The detector construction was completed by thermally insulting the double coil and the attached TCs with polystyrene foam molded in acrylic tube as shown in Figure 9.

To eliminate the effect of ambient temperature fluctuations on the calorimetric signal, differential temperature measurements were used throughout. The ambient temperature (T1) was measured continuously by means of a TC connected to the outer surface of a coil constructed of a thin-walled SS tube (similar to that used in the detector construction). This coil was placed before the detector as shown in Figure 25. The analytical signal was the difference between the average temperature recorded by the detector TCs (T2) and the ambient temperature (T1). In the absence of H₂S, the (∆T) will be around 3 °C which was attributed to the heat of mixing of the NaOH with H₂O₂ (with noise level ~ ±0.06 °C). In all situations, the baseline value was very stable for a given set of conditions.

3.2 Evaluating the Importance of a Prior Absorption of H₂S from the Gas Stream

Preliminary investigations were conducted to evaluate the concern against direct mixing of the H₂S in the gas stream with the two reagents which could result in a partial absorption of H₂S and subsequent exothermic reaction. The anticipated initial increase in temperature could inhibit further absorption of H₂S and lowers the detection sensitivity. Some mixers were used for initial absorption of H₂S in sodium hydroxide directly prior to its reaction with hydrogen peroxide. However, such pre-
absorption step was excluded since it caused an increase in response without any significant increase in sensitivity.

3.3 Construction of the Portable H$_2$S Analyzer

The most immediate requirement for a portable device is the power source. This is normally achieved with a rechargeable battery of adequate voltage, that suits the individual electric components (i.e., PC, pumps, cooling fan and switches), and power for the intended standalone operation time prior to the need for recharge. In the present work, a 24-V lithium ion battery (10 Ah) was utilized to provide a standalone operation for at least 4 hours which was one of the set targets for the present portable analyzer.

The standalone operation is not only determined by the battery but also with the volume of the reagents’ reservoir capacities. In the present analyzer, the consumption rates of the two reagents are equal. Hence, the two reservoirs were of the same capacity (~ 750 mL) which should provide continuous operation for up to 4 hours at flow rate of 3 mL/min. Due to the nature of the calorimetric detection of the present analyzer, it was also important to consider a good thermal insulation of the reagents’ reservoirs from the hot waste solution to avoid unnecessarily drift in the reagents’ temperature.

In addition to the above basic requirements, several design needs were also identified. These include: (i) the need for two dual-channel peristaltic to pump the two reagents, respectively (ii) the need for two individual reagent reservoirs with convenient reagents refill and visual monitoring of the reagents’ level; (iii) the need for a waste solution reservoir with a mean for convenient discharge; (iv) need for an
on-board bubbler; (v) the need for gas line inlet port; (v) the need for a data acquisition interface for thermocouples and compact PC for data display and storage, (vi) the need for individual electric switches to allow individual powering of the PC, liquids; peristaltic pumps, waste pumps, and the cooling fan; (vii) the need for monitors for ambient temperature, and battery voltage; (viii) the need for user friendly interface/panel and convenient maintenance to replace parts if needed; and finally (ix) the need for a compact design with gross weight less than 10 kg for a true standalone portable device.

The upper layer of the base part served three purposes: (i) as a ceiling for the conduits grooved in the lower part, (ii) as a footprint groove for some analyzer components such as reagent and waste reservoirs, battery, and the bubbler and (iii) as inlets/outlets for the reagent conduits as shown in Figure 16.

The analyzer body was fabricated from acrylic (6 mm thickness) as a good compromise between the needed strength and the weight. The analyzer base design (described in section 2.5.2) contributed significantly to the overall compact design of the analyzer.

All the above requirements were taken into consideration and the design process of a prototype has gone through several iterations for stepwise refinement and improvement of the portable analyzer as presented in Figures 23-26 to successfully meet all the design requirements.
3.4 Characterization of the Portable H₂S Analyzer

3.4.1 Effect of NaOH and H₂O₂ Reagents Flow Rate

The relative amount of NaOH and H₂O₂ can be varied by changing their flow rates and/or concentrations. To investigate the effect of flow rates, the concentrations of the reagents were kept constant at 1.0 M and 18.5 % (w/w) for NaOH and H₂O₂, respectively. Pumping the two reagents at the same flow rate resulted in a minimum noise which was attributed to the maximum mixing efficiency of the two reagents and the maximum thermal homogeneity. Therefore, the effect of different relative flow rates was attempted [65]. The effect of reagents flow rate was studied and the obtained results were presented in Figure 36. The sensitivity was increased by 60 % upon decreasing the flow rate from 4.0 to 2.0 mL/min but on the expense of increased the response time, i.e., from 42 to 64 sec at 0.25 % H₂S. Such an enhancement in sensitivity was attributed to the longer contact time between the gas stream and the reagents which was also responsible for the longer response time. The baseline was stable due the constant heat of mixing of the reagents and fixed gas flow rate.

Linear responses were obtained for all tested flow rates as shown in Figure 37 which suggested the analytical suitability of all tested flow rates. However, the lower flow rates will offer the advantages of the higher sensitivity and longer standalone operational time (due to the lower consumption of the reagents) on the expense of longer response time. Whereas the high flow offer the advantage of faster response on the expense of lower sensitivity and shorter operational time. These two extreme scenarios could be advantageous for different applications when sensitivity or response is more important, respectively.
Figure 36: Effect of reagents flow rate on the analyzer response to percentile concentrations of H₂S in the gas stream. 1.0 M NaOH, 18.5 % H₂O₂, gas flow rate 1000 mL/min. The H₂S concentration steps correspond to 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 % (v/v), respectively. The baseline corresponds to N₂-stream
Figure 37: Linearity test of the effect of reagent flow rate
3.4.2 Effect of NaOH and H\textsubscript{2}O\textsubscript{2} Reagents Concentration

The individual effects of NaOH and H\textsubscript{2}O\textsubscript{2} concentrations were investigated at constant reagents and gas flow rates. The sensitivity was increased by 23 % upon increasing the H\textsubscript{2}O\textsubscript{2} concentration from approximately 9 % to 37 % (w/w), respectively, at constant NaOH concentration as shown in Figure 38. Slight increase in the baseline was attributed to the increased heat of mixing of more concentrated H\textsubscript{2}O\textsubscript{2}. Linear responses were also obtained for the tested concentrations as shown in Figure 39.

Figure 38: Effect of H\textsubscript{2}O\textsubscript{2} concentrations on the analyzer response to percentile concentrations of H\textsubscript{2}S in the gas stream. 1.0 M NaOH, gas flow rate 1000 mL/min, reagents flow rate 3.0 mL/min. The baseline corresponds to N\textsubscript{2}-stream.
Figure 39: Linearity test of the effect of H₂O₂ concentration

The effect of NaOH concentration was somehow different than the observed effect of H₂O₂ as shown in Figure 40. Increasing the concentration of NaOH did not result in significant enhancement in sensitivity due to progressively higher heat of mixing. Linear responses were also obtained (with similar slopes) for the tested NaOH concentrations as shown in Figure 41.
Figure 40: Effect of NaOH concentrations on the analyzer response to percentile concentrations of H₂S in the gas stream. 18.5 % H₂O₂, gas flow rate 1000 mL/min, reagents flow rate 3.0 mL/min. The baseline corresponds to N₂-stream.
The obtained results suggested that 16 % (w/w) H$_2$O$_2$ and 1.0 M NaOH were the most suitable concentrations as good compromise between high sensitivity, good linearity and reagent consumption. Therefore, all subsequent measured were conducted with these two concentrations at flow rate of 3.0 mL/min.
3.4.3 Effect of Gas Stream Flow Rate

The effect of gas flow rate was tested by changing the gas stream flow rate from 250 to 1000 mL/min. The obtained results were presented in Figure 42. The sensitivity was increased with increasing the GFR. Linear response was obtained for each tested gas flow rate as shown in Figure 43. To quantify the effect of GFR on sensitivity, the sensitivity (slope of the calibration plot) was plotted vs. the GFR as shown in Figure 44. The direct proportionality between the sensitivity and the GFR was attributed to the proportional increase in the flux of H\textsubscript{2}S with GFR. The linear response also indicated that the H\textsubscript{2}S was the limited reagent up to 2.0 % (v/v) for all tested GFR. The rest of the experiments were conducted with GFR 1000 mL/min, unless otherwise stated.
Figure 42: Effect of gas flow rate on the analyzer response concentrations of H$_2$S in the gas stream. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3.0 mL/min. The baseline corresponds to N$_2$-stream
Figure 43: Linearity test of the effect of gas flow rate

Figure 44: The effect of GFR on sensitivity
3.4.4 Response and Recovery Times of the Portable Analyzer

The response time was estimated by step change in H$_2$S concentration from zero to 0.5 % (v/v). The analyzer exhibited acceptable response time i.e., $t_{0.95} = 70$ sec as shown in Figure 45. The overall analyzer response time was a sum of the residence time of the mixing reagents with H$_2$S inside Tygon tubings and the residence time within the detector. The recovery time, which was measured by switching to nitrogen stream at the same flow rate, was 55 sec as shown in Figure 46.

Figure 45: The analyzer response to H$_2$S concentration in the gas stream within 70 sec. 1.0 M NaOH, 18.5% H$_2$O$_2$, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream
Figure 46: The analyzer response to the recovery time in the gas stream within 55 sec. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream

3.4.5 Response Repeatability of the Portable Analyzer

The analyzer repeatability was tested carefully in series of experiments under different challenging conditions. In these experiments, different programs of step H₂S concentrations were used. The analyzer response repeatability was estimated by comparing the response to the same concentration step at different times. Also, the programs were designed in such a way to allow (i) adequately long experiment times, e.g., from 4000 to 7000 sec; (ii) different time separation to repeat the same concentration step; (iii) different number of steps at a given concentration; (iv) to evaluate the repeatability and different concentration; and (v) to allow base line recovery between concentration steps or to move directly from one H₂S concentration to the next. The obtained results were presented in Figures 47, 49-52.
The response repeatability was estimated by calculating the coefficient of variation (CV) for the 9 steps presented in Figure 51. The excellent CV (0.55 %) was attributed to (i) the excellent chemical compatibility of the SS detector to the reaction mixture, (ii) reliable thermocouples and robust detector design; (iii) the chemical stability of the reagents; and (iv) reagents’ flow rate stability.

Figure 47: The analyzer response to percentile H₂S concentration in the gas stream in the step mode where baseline is obtained between measurements. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream
Figure 48: Linearity test of the analyzer response in both upwards and downwards step H$_2$S concentrations

\[ R^2 = 0.9997 \]

\[ R^2 = 0.9998 \]
Figure 49: The analyzer response to percentile H$_2$S concentration in the gas stream in the step mode where baseline was continuous changes. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream
Figure 50: Three-point calibration repeated four times as a test for analyzer response repeatability. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream
Figure 51: Repeatability test for analyzer response. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, respectively, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream.
Figure 52: Repeatability of the H₂S analyzer response evaluated at two different H₂S concentrations. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min; gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream.
3.4.6 Response Stability of H$_2$S Portable Analyzer

The long-term signal stability is one of the important criteria for analytical devices designed for real-time monitoring. Therefore, the long-term stability of the presented portable H$_2$S analyzer was also evaluated for approximately one hour and the obtained result was presented in Figure 53. The signal response to 1.0 % H$_2$S was impressively stable and did not show any sign of significant drift (0.19 °C/h which is equivalent to 1.2 % of the signal). Moreover, a series of small concentration steps (i.e., 5.0 % changes in concentration) in H$_2$S were introduced to show the analyzer ability to detect such small changes and to restore its high signal level for extended period of time. Finally, the analyzer successfully restored its perfectly stable baseline when the gas stream was switched to nitrogen.

![Figure 53](image.png)

Figure 53: Real time recording showing the long-term stability of the analyzer response to 1.0 % H$_2$S and the analyzer sensitivity to slight changes in H$_2$S concentration in the gas stream. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream.
3.4.7 Response Sensitivity of H₂S Portable Analyzer

One of the major advantages of the analyzer setup is the convenience with of tuning the sensitivity and linearity. This was achieved by changing the reagents and gas flow rates.

Measuring H₂S at ppm levels require lower amounts of reagents flow rates on the expense of the response time to prevent any excess of them during the reaction process and to allow more pre-concentration. Also, an increasing in gas flow rate will enhance the gas fluxing inside the reaction compartment mixer. The effect of gas flow rate at ppm level of H₂S concentration was tested as shown in Figure 54. Gas flow rates at 4000 and 5000 mL/min did not showed a significant changes comparing with gas flow rate at 3000 mL/min. The total amount of gas flow rate was increased from 1000 to 3000 mL/min and the reagents flow rate was decreased from 3.0 to 0.5 mL/min. The minimum concentration of H₂S that can be detected by this analyzer was reached to 20 ppm (S/N = 3) as shown in Figure 55. Good linear response was obtained for the H₂S concentrations from 20 to 100 ppm as shown in Figure 56.
Figure 54: Effect of gas flow rate on the analyzer response concentrations of H$_2$S in the gas stream. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 0.5 mL/min. The baseline corresponds to N$_2$-stream.
Figure 55: The analyzer response to ppm levels of H$_2$S in the gas stream. The flow rate of each reagent was reduced to 0.5 mL/min and the gas flow rate was increased to 3000 mL/min. 1.0 M NaOH, 18.5 % H$_2$O$_2$. The baseline corresponds to N$_2$-stream.

Figure 56: Linearity test for the analyzer response to ppm levels of H$_2$S
3.4.8 Response Linearity of H₂S Portable Analyzer

Since we set 5.0 % H₂S as the targeted limit of linearity, the flow rate was selected in such a way that the highest possible temperature (i.e., ~70 °C) above ambient which is close to the boiling temperature is obtained at 5.0 % H₂S. The linearity test of H₂S can be tuned by changing the gas flow rate (from 1000 to 400 mL/min) which results in changing of the signal (more linear) as shown in Figure 57.

Good linear response was obtained for the H₂S concentrations from 1 to 5 % as shown in Figure 58. Applications that may require continuous monitoring of more concentrated gas streams are still possible by lowering the sensitivity and decreasing the gas flow rate.
Figure 57: The analyzer response to high percentile levels of H₂S in the gas stream. The gas flow rate was decreased to 400 mL/min. 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min. The baseline corresponds to N₂-stream.
Figure 58: Linearity test for the analyzer response to high percentile levels of H$_2$S concentration

$R^2 = 0.9996$
3.5 Performance Comparison with a commercial H\textsubscript{2}S Analyzer

The performance of the presented H\textsubscript{2}S portable analyzer was compared with the commercial H\textsubscript{2}S gas analyzer. The commercial analyzer is based on the ultraviolet absorption spectrometry (Model OMA-300, Applied Analytics, USA) and photodiode array spectrometer. In contrary to the presented H\textsubscript{2}S analyzer, the OMA-300 is nondestructive. Therefore, the two analyzers were connected in series in such a way that the H\textsubscript{2}S gas stream was first supplied to OMA-300 and then into the presented analyzer. The responses of the two analyzers to series of step changes in H\textsubscript{2}S were simultaneously recorded at four different concentration levels (i.e., 0.25, 0.5, 1.0 and 2.0 \% H\textsubscript{2}S) as shown in Figures 59-62, respectively. The close similarity between the presented portable H\textsubscript{2}S analyzer and the OMA-300 commercial analyzer was evident for all tested concentrations. The two analyzers showed identical response time (i.e., 14 sec) up to \( t_{0.5} \). However, OMA-300 showed faster response (i.e., 18 and 40 sec) compared to that obtained with the presented analyzer (i.e., 25 and 70 sec) for \( t_{0.75} \) and \( t_{0.95} \), respectively. Other relevant comparisons are presented in Table 4.

The estimated cost of the presented analyzer was based on the retail prices of the individual components. However, the overall cost can be substantially reduced by instrumentation manufacturing companies by custom design and fabrication of data acquisition interface, dedicated software for calibration and finally simplified screen display to eliminate the need of the PC.
Figure 59: The analyzer response (Black Peaks) compared with commercial H₂S gas analyzer OMA (Red Peaks). 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream.

Figure 60: The analyzer response (black Peaks) compared with commercial H₂S gas analyzer OMA (red Peaks). 1.0 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream.
Figure 61: The analyzer response (Black Peaks) compared with commercial \( \text{H}_2\text{S} \) gas analyzer OMA (Red Peaks). 1.0 M NaOH, 18.5 \% \( \text{H}_2\text{O}_2 \), reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to \( \text{N}_2 \)-stream.

Figure 62: The analyzer response (Black Peaks) compared with commercial \( \text{H}_2\text{S} \) gas analyzer OMA (Red Peaks). 1.0 M NaOH, 18.5 \% \( \text{H}_2\text{O}_2 \), reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to \( \text{N}_2 \)-stream.
Table 4: Comparison between OMA-300 analyzer and the presented H$_2$S analyzer

<table>
<thead>
<tr>
<th></th>
<th>OMA-300</th>
<th>Presented H$_2$S Analyzer</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Detector type</strong></td>
<td>UV-Absorption</td>
<td>Calorimetric</td>
</tr>
<tr>
<td><strong>Gross weight</strong></td>
<td>15 kg</td>
<td>8 kg</td>
</tr>
<tr>
<td><strong>Dimensions</strong></td>
<td>610<em>508</em>203 mm</td>
<td>407<em>210</em>173 mm</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>&gt;23,000 USD</td>
<td>~2000 USD</td>
</tr>
<tr>
<td><strong>Portability</strong></td>
<td>Wall-mount</td>
<td>Portable</td>
</tr>
<tr>
<td><strong>t$_{0.5}$ (sec)</strong></td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td><strong>t$_{0.75}$ (sec)</strong></td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td><strong>t$_{0.95}$ (sec)</strong></td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td><strong>Sensitivity</strong></td>
<td>Depends on the optical path length of the flow cell</td>
<td>20 ppm (depends on the operating conditions)</td>
</tr>
<tr>
<td><strong>Limit of Linearity (LOL)</strong></td>
<td>Depends on the optical path length of the flow cell</td>
<td>5 % (v/v) (depends on the operating conditions)</td>
</tr>
<tr>
<td><strong>Operating Cost</strong></td>
<td>Yearly maintenance i.e, lamp and electronics</td>
<td>3 USD/Hour</td>
</tr>
</tbody>
</table>
3.6 Application of the Portable H₂S Analyzer

3.6.1 Monitoring of H₂S in Gas Treatment System

The removal of gas contaminants from gas streams using hollow fiber membrane modules has been an active area of research over the past 2 decades [142]–[146]. The removal efficiency of a particular contaminant is typically monitored in the exit gas by gas chromatography or more suitably by gas analyzers which offer the advantage of real-time monitoring [147]–[149]. Therefore, the presented H₂S analyzer could also be a suitable candidate for such important application for continuous monitoring of the removal efficiency of H₂S from synthetic gas streams using a hollow fiber membrane modules and an appropriate absorption solvent.

The presented H₂S was used in the experimental setup described in section [2.11.1] to allow real-time monitoring of the treated gas stream using different concentrations of sodium hydroxide solutions. The obtained results were presented in Figure 63. The removal efficiency of H₂S increased upon increasing the sodium hydroxide concentration. This observation [149] was explained by the enhanced mass transfer of H₂S from the gas to the liquid phase due to the decreased liquid film resistance.
Figure 63: Testing the efficiency of the module to absorbing hydrogen sulfide pumped by 30.0 mL/min in membrane by keep increasing the NaOH concentrations starting from water up to 0.3 M NaOH. 1 M NaOH, 18.5 % H₂O₂, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N₂-stream.
3.6.2 Measuring Sulfide in Liquid Samples

The presented portable H₂S analyzer was designed, fabricated and tested primarily for continuous monitoring of H₂S in gas streams. However, the applicability of the analyzer to liquid samples was also evaluated. The simple experimental setup described in section [2.11.2] allowed the conversion of sulfide ions into the gas phase which was then carried to the analyzer by a nitrogen gas stream.

Due to the batch nature of the sulfide sample treatment, the analyzer response was in the form a peak which corresponded to the transient evolution of H₂S as shown in Figure 64. The peak height showed linear dependence on the sulfide ion concentration ($R^2 = 0.9958$) from 1 to 400 ppm as shown in Figure 65. The response time of H₂S in liquid stream (i.e., 31 sec) as shown in Figure 66 was faster than gas stream (i.e., 70 sec) while, the dynamic range of measuring H₂S in gas streams (from 20 ppm to 5 %) gives better scale than liquid streams (from 1 to 400 ppm).

The higher sensitivity of sulfide detection obtained with liquid sample was obtained by the relatively large volume of the sample (i.e., 500 mL) and the sudden conversion of the sulfide content into a concentrated burst of H₂S in gas phase. The exothermic effect of the addition of sulfuric acid as a releasing agent helped also in the expulsion of H₂S from the hot mixture because of the reduced solubility at high temperature. The peak response obtained with 1 ppm sulfide was presented in Figure 67. The high S/N ration (i.e., 10) suggests that even lower concentrations could be detected.
Figure 64: The analyzer response to the evolved H$_2$S from aqueous solution containing different concentrations of sulfide ions in 500 mL distilled water. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream
Figure 65: Linearity test of the analyzer response to the evolved H$_2$S from aqueous solution containing different concentrations of sulfide ions

Figure 66: The analyzer response to H$_2$S concentration in the liquid streams within 31 sec. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream
Figure 67: The analyzer response to the evolved H$_2$S from aqueous solution containing 1 ppm H$_2$S concentrations of sulfide ions in 500 mL distilled water. 1.0 M NaOH, 18.5 % H$_2$O$_2$, reagents flow rate 3.0 mL/min, gas flow rate 1000 mL/min. The baseline corresponds to N$_2$-stream
Chapter 4: Conclusions

The presented improved calorimetric detection scheme and the detector design proved successful to (i) lowering the limit of detection from 200 to 20 ppm, (ii) decreasing the response time from 7 min to less than 1.5 min and (iii) almost complete removal of H$_2$S in the detection step which eliminated the need for special gas treatment. These major improvements were obtained while maintaining all the advantages offered by the previous bench-scale analyzers.

The improved detector was integrated and successfully used in the construction of portable H$_2$S analyzer which is suitable for stand-alone continuous operation for up to at least 4 hours.

The presented portable analyzer was successfully applied in the continuous monitoring of H$_2$S in a treated gas stream. In addition, a simple experimental setup was suggested and allowed a convenient, rapid and sensitive determination of sulfide ions in liquid samples.

To promote the commercial potential of the presented portable analyzer, a comparison with a commercial H$_2$S analyzer was conducted and showed excellent comparability which suggests the high potential of the present analyzer to get commercialized in the near future.

To prove the usability and applicability of the presented portable analyzer, it was used as candidate for such important application for continuous monitoring of the removal efficiency of H$_2$S from gas streams by using a HFMM.
The portable analyzer has an ability to measure the \( \text{H}_2\text{S} \) in liquid samples by generating the hydrogen sulfide from the reaction of sulfuric acid and sodium sulfide and it was showed an excellent in response time (i.e, \( t_{0.95} = 31 \text{ sec} \)) with a LOD at 1 ppm.

We seek in future to address some improvements such as (i) obtaining a handheld \( \text{H}_2\text{S} \) gas analyzer, (ii) enhancing the sensitivity to be in ppb range, and (iii) decreasing the response time to be less than ten seconds.
References


[111] A. Nezamzadeh-Ejhieh and E. Afshari, “Modification of a PVC-membrane electrode by surfactant modified clinoptilolite zeolite towards potentiometric


