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RESEARCH

Fluorimetric Reusable Polymeric Sensor for Hydrogen Sulfide Detection

Ayça Şeyma Ünaldı[1] · Soner Çubuk[1] · Aslı Beyler Çiğil[2] · M. Vezir Kahraman[1]

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Abstract
In this study, with the help of reactive monomers, crosslinkers, and photoinitiator that detect H_2S in various matrices, an H_2S sensitive fluorescence sensor polymerizes under ultraviolet (UV) light was developed. To this goal, a polymeric membrane was prepared, and the characterization of the membrane was carried out with Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) methods. Afterward, appropriate conditions were identified, the excitation wavelength was determined as 370 nm, and the emission wavelength was determined as 425 nm. It was established that the fluorescence intensity of the prepared polymeric membrane decreased in the presence of H_2S. A detailed analysis was executed to determine the sensor's most suitable pH value and time. It was found that the optimum pH was 8.0, and the optimal duration was 15 s. It has been calculated that the linear range of the developed method is 2.19×10^{-8}– 6.25×10^{-7} M, and the detection limit (LOD) is 7.37×10^{-9} M. The effect of some possible interfering ions was investigated, and it determined that the sensor had excellent selectivity. In addition, the sensor used to determine H_2S can be used at least 100 times. The recovery percentages were 102.1%–103.2%, and 104.6%, using tap water samples. In terms of providing reliable, fast results, high sensitivity, reusable, low cost, and ease of use, the developed fluorimetric sensor, compared to standard methods, has become more advantageous.

Keywords Fluorimetric sensor · Photo-curing · Polymeric membrane · Selective H_2S determination

Introduction

H_2S is a highly corrosive and toxic gas. It has harmful effects on the human nervous system in low concentrations, leading to death at high concentrations [1, 2]. H_2S has been regarded as an environmentally toxic gas for many years. It is colorless and flammable, with a rotten egg odor [3, 4]. It can be produced from the hydrodesulfurization of crude oil containing sulfur compounds and many natural gas fields [5]. Also, H_2S can be produced from different sources related to the petroleum industry, such as the thermochemical reduction of sulfate to H_2S, bacterial reduction of sulfate to H_2S, and thermal decomposition of kerogen and sulfides in oil, so H_2S has been regarded as a potential industrial hazard [6]. H_2S can cause damage to the human respiratory and nervous systems, leading to loss of consciousness even at concentrations as low as 500 ppm [7, 8]. Therefore, it is important to develop accurate, sensitive, selective, fast H_2S sensors to detect concentrations as low as ppm to prevent exposure to H_2S gas, especially in areas related to the oil refining industry.

Many analytical methods have been available for the measurement of H_2S, including electrochemical [9], gas chromatography (GC) [10], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [11], and electrogenerated chemiluminescence (ECL) [12] methods. However, the common disadvantage of these methods is that they require complex instrumentation and are not suitable for simple and rapid analysis. Among these methods, fluorescent sensors meet the requirements for commercializing gas sensors due to their high sensitivity, excellent selectivity, cost-effectiveness, and easy use. Therefore, many H_2S fluorescent analysis reagents based on various detection principles have been developed in the literature. For example, in addition to the reagents based on the ability of sulfur as a ligand to exchange with metal complexes in studies reported

✉ Soner Çubuk
sonercubuk@marmara.edu.tr

[1] Chemistry Department, Faculty of Science, Marmara University, 34722 Istanbul, Türkiye

[2] Dep. of Chemistry and Chemical Process Technology School, Amasya University Technical Sci. Vocational, Amasya, Türkiye

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in the literature in recent years [13–15], fluorogenic reagents using a sulfur-reducing ability or nucleophilicity have been reported [16, 17]. However, many of these methods suffer from using environmentally harmful organic solvents or toxic metals, the need for complex multiplex or expensive synthetic procedures for fluorescent probes, and the slow reaction time with H_2S [13, 15, 18–21].

The present study aimed to prepare a practical, fast, simple, and affordable polymeric membrane for H_2S determination, which does not contain toxic metals, does not require the use of environmentally harmful organic solvents and can be cured with UV rays in 3 min. An H_2S polymeric membrane prepared by UV curing has yet to be previously reported. It was determined that the prepared polymeric membrane showed high stability and selectivity against H_2S and could be used repeatedly. The prepared fluorimetric sensor provided a practical and realistic method for determining H_2S concentration in samples with its sensitivity, selectivity, reproducibility, ease of use, and low detection limit.

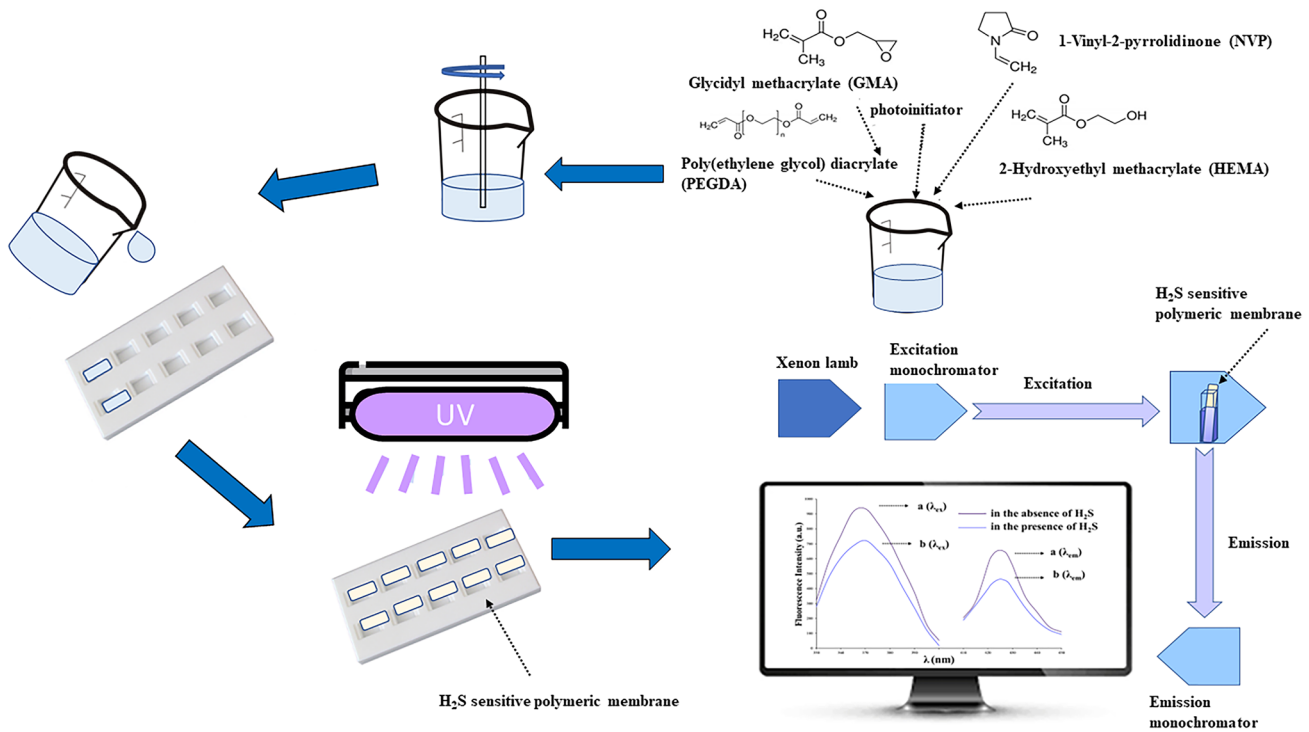
Experimental Section

Materials and Reagents

Glycidyl methacrylate (GMA), 1-Vinyl-2-pyrrolidone (NVP), poly(ethylene glycol) diacrylate (PEGDA), hydroxyethyl methacrylate (HEMA) and 2,2-dimethoxy-2-phenyl acetophenone (DMPA) were purchased from Sigma–Aldrich. Although other chemicals were purchased from Merck in this study, all chemicals used in all experiments were analytical reagent grade.

Preparation of Polymeric Membrane

The aim was to prepare a fast, practical, easy-to-prepare, UV-curable polymeric membrane for H_2S determination. Accordingly, GMA (1 wt%), NVP (20 wt%), PEGDA (30wt%), and HEMA (50wt%) were weighed in a precision balance and taken into a beaker, and stirred until becoming homogeneous. The beaker was covered with aluminum foil, and a photoinitiator (3 wt%) [2,2-dimethoxy-2-phenylacetophenone] was added in the dark. The prepared polymeric membrane formulation was poured into a Teflon® mold with dimensions D = 1.2 cm, L = 4.0 cm, and thickness 0.2 cm. The crosslinked polymeric membrane was obtained by keeping it under UV (OSRAM 300 W, λ_{max} = 365 nm) light for 3 min. Then, this membrane was set in a lyophilizer after soaking overnight in distilled water to remove the starting materials. The obtained polymeric membrane has a rigid, transparent, homogeneous, crack-free, fracture-free, and non-porous structure. Scheme 1 demonstrates the chemical structure, fabrication, and detection of the H_2S sensor.



Scheme 1 The schematic diagram of fabrication, and detection of the sensor

Characterization of the Polymeric Membrane

A Perkin Elmer Spectrum 100 attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectrophotometer was used to identify functional groups of the polymeric membrane. The FTIR spectrum of the polymeric membrane was recorded in the range of 4000–450 cm^{-1}.

The polymeric membrane's surface morphology was investigated using a Philips XL30 Environmental Scanning Electron Microscope with Field Emission Gun (Equipped with EDAX-Energy Dispersive X-ray Analysis Unit) (ESEM FEG/EDAX). The specimen was prepared for SEM by freeze fracturing in liquid nitrogen and applying a platinum coating.

Results and Discussion

Characterization of the Polymeric Membrane

In Fig. 1, the FTIR spectrum is shown as a result of the carried out in the wavelength ranges of 450–4000 cm^{-1} belonging to the polymeric membrane. The peaks around 1200–1000 and 1700 cm^{-1} in the spectrum of the polymeric membrane, respectively, were due to carbon–oxygen ether bond vibrations and carbonyl stretching in GMA, PEGDA, and HEMA. The broad band around 1250 and 950 cm^{-1} was associated with the vibration bands in the epoxy group found in GMA [22]. Also, the vibration of -CH_2- bonds in PEGDA was seen as a broad peak at 2869 cm^{-1}, and the vibrations of O–H groups in HEMA were seen at 3331 cm^{-1}. After crosslinking with UV rays, the absence of peaks at 1635 cm^{-1}, attributed to all acrylate groups, in the spectrum of the polymeric membrane indicates that the crosslinking has been carried out successfully [23].

The surface morphology of the polymeric membrane was characterized by SEM, and the resulting image, magnified 10000-fold, is given in Fig. 2. Examining the image, it was seen that the polymeric membrane has a homogeneous and non-porous structure and a smooth and unbroken structure. Therefore, the surface morphology of the polymeric membrane is an important factor for its use as a fluorescence sensor. As can be seen from the SEM image, the sensor provides the expected surface properties.

Spectral Characterization Studies

In the present study, all fluorescence measurements were performed using a Varian Carry Eclipse spectrofluorometer equipped with a Xenon short arc lamp as the light source. The spectrum given in Fig. 3 was obtained by scanning the

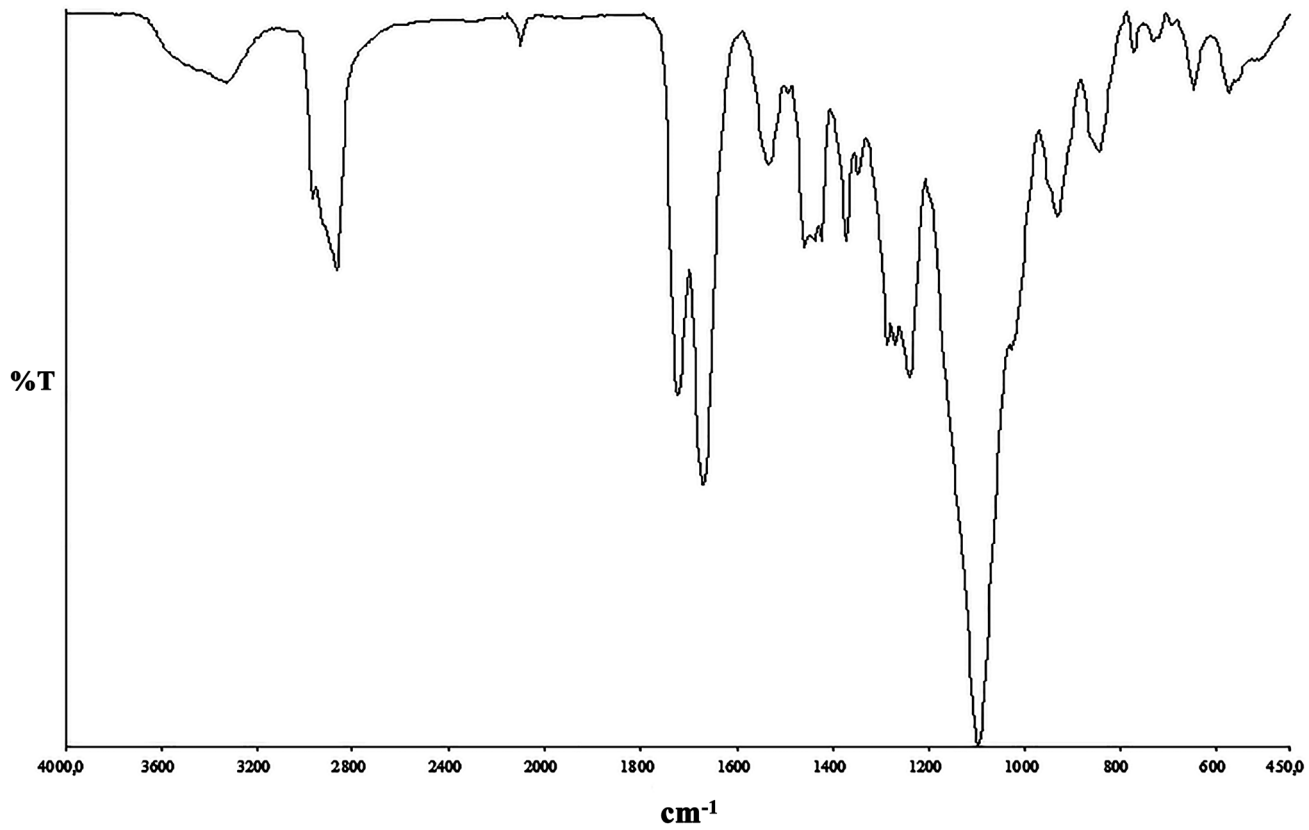


Fig. 1 FTIR spectrum of H_2S polymeric membrane

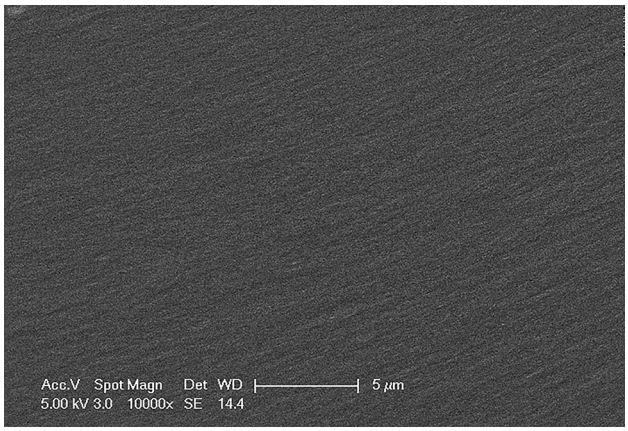


Fig. 2 SEM micrograph of H_2S sensitive polymeric membrane at 10000 × magnification

spectrum in the presence and absence of 1.56×10^{-7} M H_2S to determine the excitation ($\lambda_{ex.}$) and emission wavelengths ($\lambda_{em.}$) of the polymeric membrane. Different slit widths and photomultiplier tube voltages were used during the spectrum scanning.

As a result of the study, the excitation wavelength ($\lambda_{ex.}$) was determined to be 370 nm, the fluorescence wavelength ($\lambda_{em.}$) was found to be 425 nm, the slit width of 5 nm, and the photomultiplier tube voltage was 600 V. Furthermore, the fluorescence intensity of the prepared polymeric membrane decreased in the presence of H_2S. The color of the prepared membrane was colorless before and after the addition of H_2S solution.

Optimization of the Parameters for H_2S Detection

To examine the pH effect of the obtained polymeric membrane on the fluorescence intensity, as a result of the studies carried out with separately prepared solutions containing 1.56×10^{-7} M H_2S in the pH 1.0–10.0 range, the pH value increased in the range of 1.0–8.0, and it was observed that at pH higher than pH 8.0. It was also determined that there was a decrease again, and the most suitable pH was 8.0 (phosphate buffer solution). The results obtained are shown in Fig. 4. It was seen in Fig. 4 that the pH reaches its maximum fluorescence intensity at pH 8.0.

Determination of Response Time

To assess the changes in fluorescence intensity of the polymeric membrane against H_2S depending on time, measurements were carried out at 5-s intervals for 5 min, and it was observed that there were no significant changes in fluorescence intensity exceeding 5% until the 30th second, and then it started to decrease. Figure 5 shows the time-dependent changes in the fluorescence intensity of the polymeric membrane. From the test results, the response time of the sensor was decided to be 15 s.

Regeneration and Reusability

The initial fluorescence intensity could be reached with a 2-min wash with distilled water to regenerate the polymeric membrane. As a result of the regeneration process, it was determined that the polymeric membrane could be reused

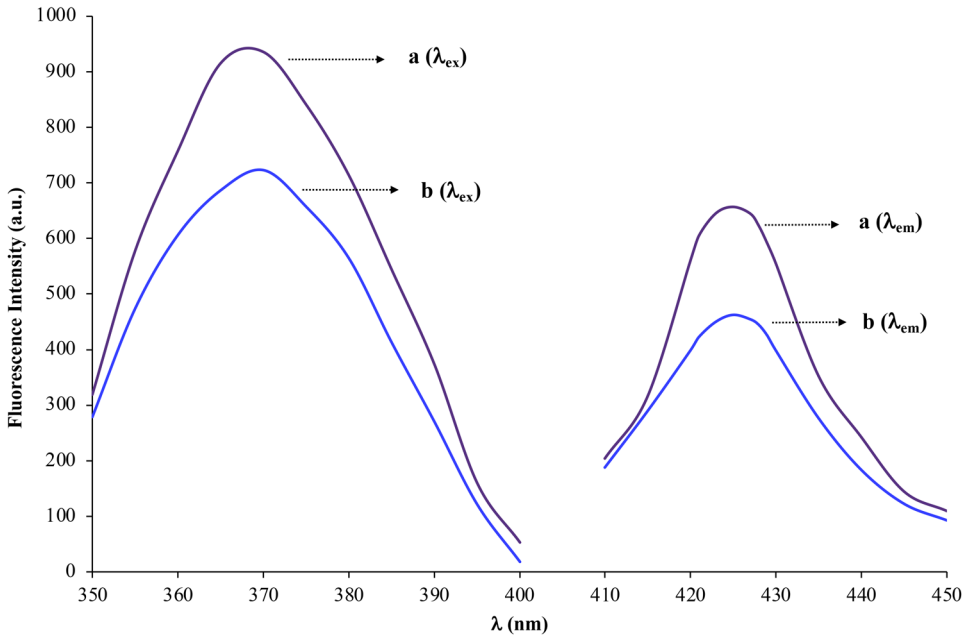


Fig. 3 Excitation and emission spectra of the polymeric sensor in the **a** absence and the **b** presence of 1.56×10^{-7} M H_2S. (λ_{ex} = 370 nm, λ_{em} = 425 nm, pH: 8.0, t: 30 s.)

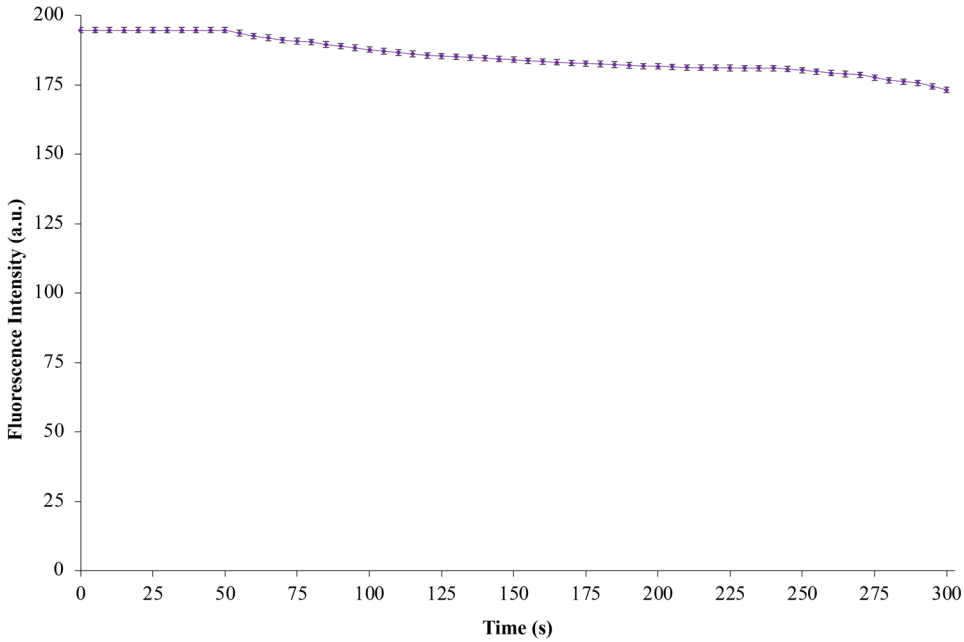


Fig. 4 Effect of pH on fluorescence intensity of the polymeric membrane

at least 100 times. The graph showing only 30 regeneration results of regeneration results is in Fig. 6. The standard deviation of the fluorescence intensities of the polymeric membrane between the 1st and 100th reading values was calculated to be ± 1.64.

Linear Range, Detection Limit

Using pH 8.0 phosphate buffer solution at concentrations between 2.19×10^{-8} M – 6.25×10^{-7} M at an excitation wavelength (λex.) of 370 nm and fluorescence wavelength (λem.) of 425 nm for 15 s under the conditions determined as a result of the studies using a pH 8.0 standard solution. The calibration curve obtained using 370 nm excitation wavelengths of H_2S standard solutions is given in Fig. 7. Fluorescence quenching efficiencies ($I_0 - I$) for the membrane at ex/em = 370/425 nm are plotted as functions of the logarithm of the H_2S concentration at pH 8.0, where I_0 and I are the fluorescence intensities of the sensing polymeric membrane in the absence and presence of H_2S. To determine the developed method's LOD value, five solutions were completed to the final volume with a pH 8.0 phosphate buffer solution system containing 2.19×10^{-8} M H_2S, and measurements were made with these solutions. The detection limit was calculated as 7.37×10^{-9} M, three times the standard deviation value obtained from the measurement results.

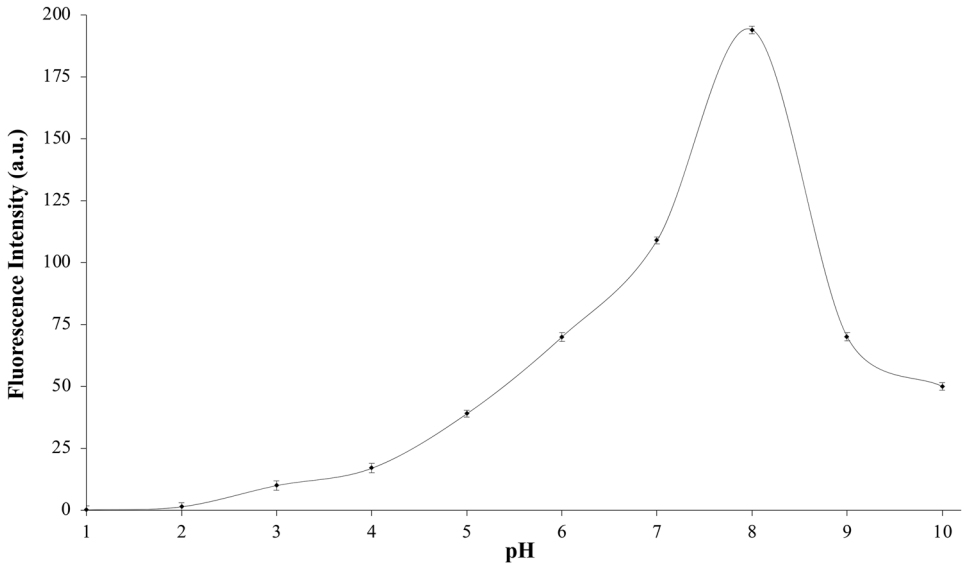


Fig. 5 Effect of time on fluorescence intensity during 5 min ($C_{H_2S} = 1{,}56.10^{-7}$ M)

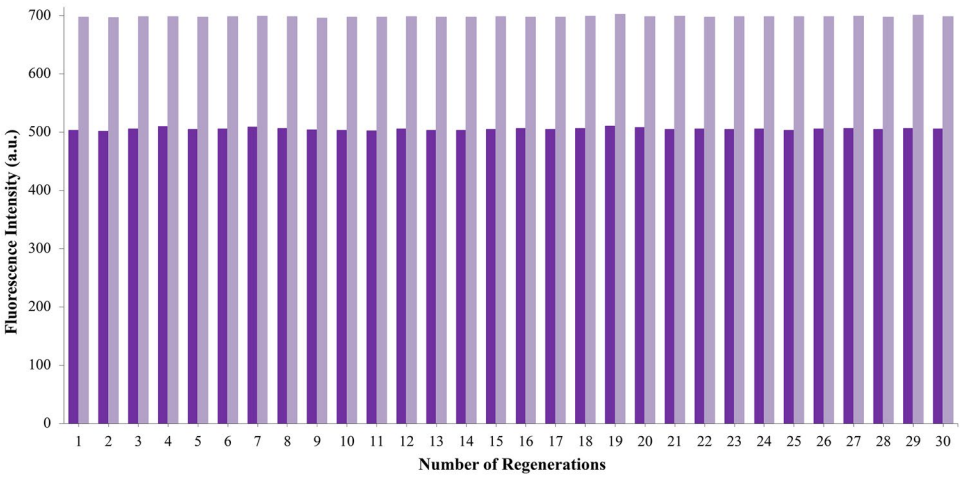


Fig. 6 Regenerability of the polymeric membrane

Reproducibility, Reversibility, and Stability of the Polymeric Membrane

The reversibility of the polymeric membrane, which was kept in the dark environment prepared for H_2S determination, was evaluated by repeatedly examining the fluorescence intensity of the polymeric membrane in the presence of 1.56×10^{-7} M H_2S solution. Before all measurements, the polymeric membrane was regenerated with distilled water. As a result of the measurements, it was observed that there were no changes in the fluorescence intensity of the polymeric membrane exceeding ± 5% of the first measurement result for six months. The prepared membrane was stable for at least six months when kept in a desiccator in the dark.

To determine the short-term stability of the polymeric membrane, the fluorescence intensity was measured every 15 min for 10 h in the presence of 1.56×10^{-7} M H_2S solution under the previously determined conditions. It exhibited good stability with a standard deviation as low as ± 2.01.

The repeatability of the polymeric membrane was studied using five different membranes of the same formulation treated with 1.56×10^{-7} M H_2S solution. The standard deviation value of the prepared membrane was calculated as ± 4.22, indicating that the repeatability of the membrane is satisfactory.

Selectivity Studies

High selectivity is an important requirement for any sensor. To examine the selectivity and specificity of the prepared polymeric membrane against H_2S, the effect of SO_3^{2}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_5^{2-}$, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+},

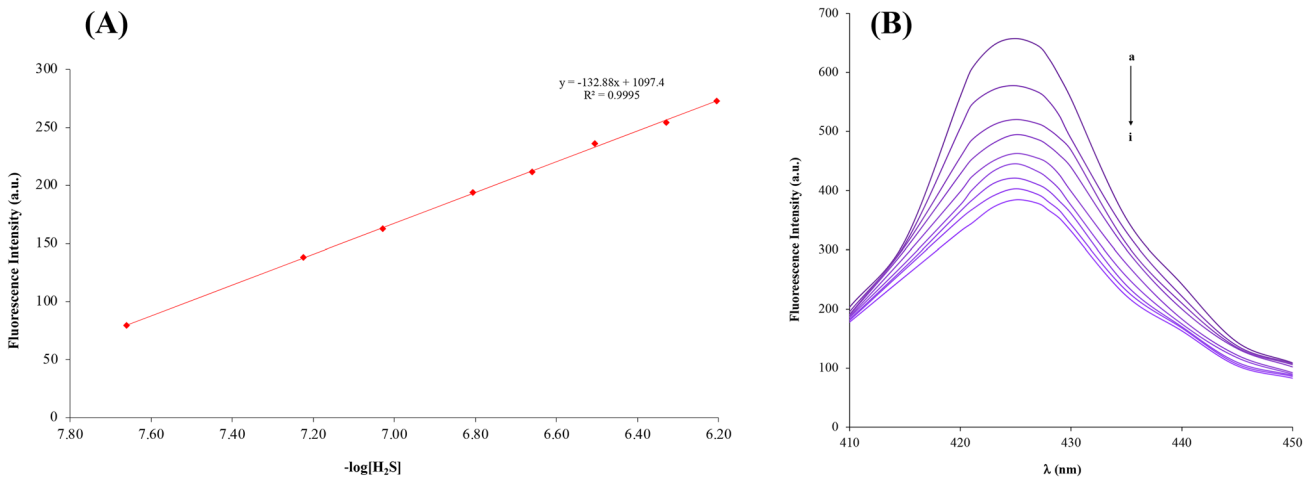


Fig. 7 **A** Calibration curve for H_2S using the fluorescence assay condition. **B** Fluorescence emission spectra of the sensing membrane in the presence of different concentrations of H_2S at pH 8.0. (**a**) 0, (**b**) 2.19×10^{-8} M, (**c**) 5.96×10^{-8} M, (**d**) 9.38×10^{-8} M, (**e**) 1.56×10^{-7} M, (**f**) 2.19×10^{-7} M, (**g**) 3.13×10^{-7} M, (**h**) 4.69×10^{-7} M, (**i**) 6.25×10^{-7} M, λex = 370 nm)

Cd^{2+}, Mn^{2+}, and Fe^{2+} ions, which may interfere during the measurement, on the fluorescence intensity was investigated. Accordingly, the number of foreign ions was increased starting from 1000 mol times 1.56×10^{-7} M H_2S ion in the medium until the concentration with a maximum ± 5% change in initial fluorescence intensity. The permissible concentration limits of foreign ions are given in Table 1.

As seen in Table 1, the gas detection potential of the prepared polymeric membrane did not change even in the presence of foreign ions of 800 times sulfide (SO_3^{2-}), 570 times sulfate (SO_4^{2-}), 440 times thiosulfate ($S_2O_3^{2-}$), 650 times metabisulfite ($S_2O_5^{2-}$), 1500 times Ni^{2+}, 1780 times Mn^{2+} as a mole of H_2S together with H_2S.

Analytical Applications of the Polymeric Membrane

To evaluate the actual applicability of the prepared polymeric membrane, Seronorm Trace Elements Serum Level-1 and Seronorm Trace Elements Serum Level-2 certified reference solutions were used. In addition, reference solutions were diluted with pH 8.0 buffer solution and used. It was observed that the results were compatible with the certificate values of the analyzed solutions. As seen in Table 2, H_2S levels in all samples were measured, and relative error values were calculated.

Also, upon adding Na_2S to tap water as an H_2S source, recovery studies were carried out with tap water samples with three different concentrations, and the results are given in Table 3. Recovery values were 102.1%, 103.2%, and 104.6%, showing that this proposed method is applicable and reliable for the sensitive and accurate determination of H_2S in environmental samples. The results supported that the present study's method can be a good alternative to H_2S determination methods.

Table 1 Various potential interferent species effect on the fluorescence intensity of 1.56×10^{-7} M H_2S solution at optimum conditions

Species	Concentration of the interferents species (M)	[Species] / [H_2S] (mol/mol)
Sulphite (SO_3^{2-})	1.25×10^{-4}	800
Sulfate (SO_4^{2-})	8.91×10^{-5}	570
Thiosulfate ($S_2O_3^{2-}$)	6.88×10^{-5}	440
Metabisulfite ($S_2O_5^{2-}$)	1.02×10^{-4}	650
Cu^{2+}	2.78×10^{-9}	50
Zn^{2+}	2.48×10^{-9}	50
Ni^{2+}	3.90×10^{-10}	1500
Co^{2+}	2.57×10^{-9}	250
Cd^{2+}	3.90×10^{-11}	100
Mn^{2+}	3.90×10^{-11}	1780
Fe^{2+}	2.57×10^{-9}	1600

Table 2 The data of the accuracy and precision study of the H_2S determination proposed method

Sample	Certificate Value (M)	Studied concentration (M)	Precision (RSD[a]) (%)
Seronorm Trace Elements Serum Level-1	$(3.33\pm0.03)\times10^{-2}$	$(3.47\pm0.32)\times10^{-2}$	4.20
Seronorm Trace Elements Serum Level-2	$(4.10\pm0.04)\times10^{-2}$	$(4.25\pm0.17)\times10^{-2}$	3.65

[a] RSD relative standard deviation

Comparison of the Proposed Method with the Previously Reported Ones for Monitoring of H_2S

Examining the literature is reviewed; due to the vital importance of H_2S, various measurement methods have been developed for its determination in biological systems and water. In contrast to chromatographic, ion-selective electrodes, and colorimetric methods, fluorescence is an attractive and promising approach given the significant increase in the number of newly developed fluorescent in recent years. Colorimetric assays are some of the oldest and most common methods used for in vitro H_2S detection, but their use for in vivo-H_2S measurement is not yet possible for rapid and accurate detection of H_2S in plasma, even after the incorporation of metal nanoparticles, which provides a fast route. Separation techniques such as gas or liquid chromatography offer higher selectivity than direct spectrophotometric or fluorescent H_2S measurements but cannot be used for real-time tracking of H_2S. Therefore, despite the many analytical procedures developed for the determination of H_2S, there is a need for highly selective, sensitive, reusable H_2S measurement methods that solve the unresolved disadvantages of existing methods. The recently published comparisons of the prepared polymeric membrane and the H_2S gas sensors are given in Table 4. It was seen that the prepared polymeric membrane was sensitive and usable for H_2S determination.

Table 3 Recovery data of H_2S in tap water samples

Added S^{2-} concentration (M)	Found concentration (M)	Recovery (%)
9.39×10^{-8}	$(9.59\pm0.23)\times10^{-8}$	102.1
1.57×10^{-7}	$(1.62\pm0.16)\times10^{-7}$	103.2
3.13×10^{-7}	$(3.27\pm0.14)\times10^{-7}$	104.6

Table 4 Comparison of the proposed method with the previously reported ones for measurement of H_2S

Method	Sensing compound	Reaction time (min)	LOD (µM)	Matrix	Ref.
Fluorescent chemodosimeter	2-formylphenyl moiety and a benzyl pyridinium substituted porphyrin fluorophore	none	0.046	red wine 1 & 2; beer 1 & 2; human serum	[24]
Fluorescent assay	6-azido-2-(pyridin-2-ylmethyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NPN-N3)	0.16	1.2	tap water, lake water, distilled water, red wine, and beer	[25]
Fluorescence assay	(E)-6-(4-(diphenylamino) benzylidene)-5-oxo-5,6,7,8-tetrahydronaphthalen- 2-yl 2,4-dinitrobenzenesulfonate (BOTD)	0.5	27.3	living cells	[26]
Microplate fluorescence assay	2-(4-hydroxyphenyl)-4,5-di(2-pyridyl)imidazole-copper(II) complex	none	0.16	River water	[27]
HPLC	none	4.5	~0.0002	blood serum and plasma samples	[28]
UV-microplate assay	ethyl propiolate	15	2.8	wastewater	[29]
Fluorescence assay	dicyanoisophorone azide	25	0.13	river water	[30]
ICP-AES	none	none	0.16	mineral water	[11]
Spectrofluorimetric	GMA/NVP/PEGDA/HEMA polymeric membrane	0.25	0.00737	tap water	This work

Conclusion

The present study produced a polymer-based spectrofluorimetric sensor for H_2S determination as a polymeric membrane consisting of GMA, NVP, PEGDA, and HEMA. The surface properties of the prepared polymeric membrane were visualized by SEM, and a homogeneous membrane was obtained without any cracks or breaks. The changes in fluorescence intensity were investigated by measuring the membrane's response to H_2S, and the excitation and emission wavelengths were determined as 370 and 425 nm, respectively, in the presence of H_2S. Examining the effect of pH and time on fluorescence intensity, it was observed that the polymeric membrane material responded to H_2S in 15 s at pH 8.0. When the regeneration of the polymeric membrane was tested, it was determined that the membrane could return to its initial state by washing only with pure water and could be used at least 100 times.

Furthermore, it was observed that the polymeric membrane could operate in the concentration range of 2.19×10^{-8} M – 6.25×10^{-7} M, and the LOD value was calculated as 7.37×10^{-9} M. Examining the effect of foreign ions on the polymeric membrane, even in the presence of foreign ions of 800 times sulfide (SO_3^{2-}), 570 times sulfate (SO_4^{2-}), 440 times thiosulfate ($S_2O_3^{2-}$) and 650 times metabisulfite ($S_2O_5^{2-}$) as fold molar excess of H_2S, the method developed in the present study could be analyzed without any interference. To examine the applicability of the membrane to real samples, Seronorm Trace Elements Serum Level-1 and Seronorm Trace Elements Serum Level-2 certified reference solutions were used, and it was seen that the method could be successfully applied to real samples with relative errors of 4.20%, and 3.65%, respectively. In conclusion, the produced polymeric membrane was very sensitive to low H_2S concentrations, highly selective, exhibited fast response time, was easy to manufacture, and was reusable for repeatable tests. In this manner, it can be both an alternative to the existing methods in the literature and an example for future studies in the field of H_2S determination.

Author Contributions S.Ç.: Study design, Investigation, Preparation, Writing–original draft, Supervisor. A.Ş.Ü.: Photophysical measurements, Writing–original draft. A.B.Ç.: Photophysical measurements, Writing–original draft. M.V.K.: Study design, Investigation, Characterization. All authors reviewed the manuscript.

Data Availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Conflicts of Interest There are no conflicts to declare.

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