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Fiber optic sensors using novel substrates for hydrogen sulfide determination by solid surface fluorescence

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Abstract

Two different fiber optic sensors were developed for the determination of hydrogen sulfide at ppb concentration levels; a probe-type fiber optic sensor coated with polyethylene oxide containing 0.5 M $CdCl_2$ and a fiber optic sensor utilizing 0.5 M $CdCl_2$-pretreated filter paper as solid substrate. In the first type, $CdCl_2$–polyethyleneoxide (PEO) mixture was coated onto the tip of a fiber optic probe and the probe was exposed to H_2S. The methodology is based on the measurement of CdS fluorescence on the surface. Detection limit (3s) of the PEO-coated fiber optic system was 36.0 ppb for H_2S and precision at the 0.552 ppm level was 29% R.S.D. For the fiber optic system utilizing $CdCl_2$-pretreated filter paper, two different configurations were devised and evaluated; a bifurcated fiber optic sensor and a single fiber optic sensor. Similar figures were obtained with these two systems; the detection limit (3s) was 4.0 ppb for the bifurcated fiber optic sensor and 4.3 ppb for the single fiber optic sensor, and both sensors had linear responses in the range 0.032–1.0 ppm. Their precisions at 0.299 ppm level were also very similar, 10 and 11% R.S.D., respectively, for the bifurcated and single fiber systems. In addition to the fiber optic sensors developed, various surfactants (sodiumdodecylsulfate (SDS), Aerosol OT, Aerosol A102, Aerosol 501), some cellulosic substances (sodium carboxymethylcellulose (CMC), ethylcellulose, hydroxypropylmethylcellulose, ethylhydroxyethylcellulose, α-cellulose) and several water-soluble polymers (polyacrylicacid polyethleneoxide (PEO), polyvinylalcohol (PVA)) were dissolved in proper solvents and after mixing with 0.5 M $CdCl_2$, were spread over glass slides. These novel solid substrates were exposed to H_2S and fluorescence signal on the surfaces of the glass slides was measured with a luminescence spectrometer. The new substrates were shown to be good alternatives to filter paper for the determination of H_2S by room temperature solid surface fluorescence spectrometry.

Keywords: Hydrogen sulfide; Room temperature fluorescence; Solid surface fluorescence; Fiber optic sensor

1. Introduction

Hydrogen sulfide is a deadly substance and one of the main causes of sudden death for people working at certain occupational sites. Its charac-

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teristic odor of rotten eggs can be detected when its concentration is as low as 0.3 ppb (v/v). Permissible exposure limit value for H_2S, recommended by US National Institute for Occupational Safety and Health (NIOSH), is 10 ppm and the Immediately Dangerous to Life and Health (IDLH) level is 300 ppm [1]. It may be lethal in concentrations greater than 2000 ppm [2]; loss of olfactory sensation at 150–200 ppm may cause people to be unawaringly exposed to lethal concentrations. The amount of H_2S generated by industrial processes and other anthropogenic sources constitutes only 10% of the total H_2S in the atmosphere. The rest are produced by natural sources; through the decomposition of organic material by bacteria, from volcanic gases and sulfur springs. It is also a constituent of natural gas, petroleum and sulfur deposits.

In certain industrial locations, such as petroleum refineries, natural gas plants, petrochemical plants, iron smelters, food processing plants, tanneries and a variety of metal alloy manufacturing plants, it is necessary to monitor the concentration of H_2S continuously because the gas is released as a by-product. A variety of sampling and measurement techniques have been used for the determination of H_2S in occupational sites, of which the initial step is generally the collection of the gas in liquids or on impregnated solid substrates. A comparison of the classical techniques used in the determination of H_2S can be found in [3]. In liquid collection methods [4–6], the sample gas is bubbled through a solution containing a selective reagent for H_2S. The collected analyte is measured spectrophotometrically either directly or after conversion to a measurable form. In the solid substrate collection techniques [7–10], the resultant chemical species on the surface is either measured by reflectance techniques or spectrophotometrically.

The above-mentioned techniques can still be employed for the measurement of H_2S, but novel methods based on remote sensing principles can be considered as better alternatives because of the toxic nature of the gas. Conventional analytical techniques are based on the collection of samples, bringing them to laboratory and analyzing by a proper method. It is very important to bring the samples from sampling site to laboratory without causing any change in their properties. In some situations, it is not desirable to carry the sample to laboratory since this may induce some changes in the present form of analyte species; and, in some cases, it is rather impossible to perform sampling. In addition to these, it may be necessary to monitor the concentration of an analyte continuously. These situations can be approached mainly by two ways; either the analysis is achieved in situ with portable devices or the analyte signal is transported to the laboratory with electrochemical or optical ways. The ability to measure the concentration of chemical species both at a distance and in situ has been realized with the advent of optical fibers. The advantages of fiber optic sensors over other types of sensors can be summarized as follows; they are easily miniaturized, they enable simultaneous analyses with a single central instrument, they are more suitable for use in hazardous environment, they can carry much more information than another sensor and they can respond to many chemical analytes and physical parameters for which other sensors are not available [11–17]. As is the case for any measurement technique, fiber optic sensors are not exceptions regarding the negative aspects and they may have interference from ambient light unless the analysis is carried out in dark or the analyte signal is isolated. Sensors with indicator phases may have limited long-term stability because of photobleaching or wash-out; and for many indicator phase-sensors, a mass transfer is necessary since analyte and indicator are in different phases.

In a series of papers published before [18–21], it was shown that when H_2S reacts with a substrate treated with aqueous Cd^{2+} salts, a luminescent species is formed on the surface. As shown later, this luminescence originates from CdS species formed on the surface of filter paper in a well-defined size [20]. The fluorescence signal can be observed either by eye under UV light [18,21], or measured with a fluorimeter [19,20]. The formation of luminescent species on the surface can be explained in view of room temperature solid surface luminescence phenomenon. The basic difference between solution luminescence and solid

surface luminescence is that in solid surface luminescence, the luminescent species are usually adsorbed on a solid substrate. Since the molecules are isolated and collision-restricted, this technique enables very sensitive determinations for many organic and inorganic substances at room temperature without necessitating cryogenic conditions. [22–26].

In the present study, one goal was to develop novel substrates other than filter paper or silica gel for the determination of H_2S by solid surface fluorescence spectrometry. The final objective was to design a fiber optic sensor (or probe) working with remote sensing principles for H_2S determination in certain occupational sites.

2. Experimental

2.1. Apparatus and instrumentation

The experimental set-up used in the sample preparation is explained in the previous studies in detail [20,21]. To summarize, a constant flow of H_2S at standard concentrations was passed over impregnated solid substrates that were placed horizontally in the reaction chamber. The reaction chamber was manufactured from glass and had a cylindrical shape with a diameter of 10 cm and a length of 20 cm. Standard gas concentrations were prepared by a Vici Metronics Dynacalibrator Model 230-14-C gas dilution system using permeation tubes obtained from the same company. The calibrated permeation tubes were placed in the permeation chamber of the gas dilution system at a preset temperature of 30°C in order to obtain the required analyte concentration from these devices. The gas mixture formed here was transported to reaction chamber, which was at room temperature. All the experiments were carried out at room temperature. N_2 was used as the carrier and dilution gas. It was necessary to have a relative humidity of about 70% in the reaction chamber for the reaction to occur and this was realized by passing the diluent gas through a humidifier solution, saturated $Pb(NO_3)_2$, in an impinger. Relative humidity was measured by means of a Fisher Scientific humidity measuring device placed right after the reaction chamber. The gas was exhausted at the end. The solid substrates exposed to H_2S were examined under a Camag 29 000 UV lamp (254 and 366 nm) visually and the fluorescence signal on these substrates was, then, measured by a Perkin Elmer LS 50B luminescence spectrometer using the front surface accessory of the instrument. Excitation wavelength was 300 nm with 10 nm slit. Emission monochromator was scanned from 300 to 800 nm using 5 nm slit with a scan rate of 1000 nm min^{-1}. In all measurements with the luminescence spectrometer, a 350 nm cut-off filter was placed in front of the emission monochromator in order to prevent the higher order reflection or scattering of source radiation from the surface.

2.2. Preparation of impregnated solid substrates

2.2.1. Filter paper

Strips of papers, in 1.0×2.5 cm dimensions, were immersed in aqueous solution of 0.5 M $CdCl_2$. After an immersion period of 2 min, the papers were dried in a fume cupboard at room temperature.

2.2.2. Glass slides

Several surfactants, cellulosic materials and water-soluble polymers, after mixing with $CdCl_2$ solution, were used to coat the glass slides. Surfactants used were sodiumdodecylsulfate (SDS), N100S, Aerosol OT, Aerosol A 102 and aerosol 501 with respective concentrations of 0.50, 0.50, 1.25, 10 and 10% (v/v). Cellulosic substances were sodium carboxymethylcellulose (CMC), hydroxypropylmethyl cellulose, ethylhydroxyethyl cellulose, ethyl cellulose and α-cellulose with respective concentrations of 1.25, 0.25, 0.25, 1.25 and 1.25% (w/v). Water-soluble polymers used were melamine formaldehyde, polyacrylic acid (PAA), polyethylene adipate, polyvinyl alcohol (PVA) and polyethylene oxide (PEO) all of which had the same concentrations of 1.25% (w/v). Aliquots of 2.0 ml from the solutions thus prepared were taken and mixed with 0.5 ml of an aqueous solution of 2.5 M $CdCl_2$. The mixtures prepared this way were spread over the glass slides by means of a micropipette in volumes of

250 μl. The glass slides were dried in a fume cupboard at room temperature.

2.3. Fiber optic sensor studies

Three types of fiber optic probes were designed and evaluated; a polymer-coated fiber optic probe, a bare-ended bifurcated fiber optic probe and a bare-ended single fiber optic probe ('sensor' and 'probe' will be used interchangeably in the text). In the first design, several fiber optic probes having 1 cm lengths were prepared. Both ends of these fibers were polished and a PEO solution containing $CdCl_2$ was coated onto one end of each. Sodium CMC was also tried in a similar way. In the last two designs, the same filter paper substrates were used. The fiber optic cable used in these studies was supplied from Ensign and Bickford. Core and cladding parts are made of silica with respective diameters of 940 and 1000 μm and its numerical aperture is 0.22. The experimental set-ups for probe studies are shown in Fig. 1.

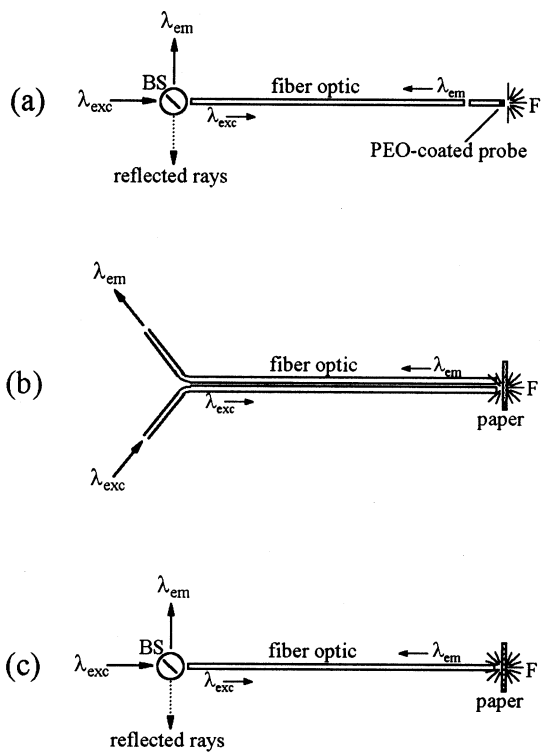

Fig. 1. Experimental set-ups employed in fiber optic sensor studies. (a) PEO-coated probe; (b) bare-ended bifurcated probe; (c) bare-ended single probe. (BS, beam splitter; F, fluorescence emission). Beam splitter in (a) and (c) was used to transfer the excitation beam of the luminescence spectrometer to the end of the fiber and to send the fluorescence emission signal formed to the emission monochromator and to the detector of the luminescence spectrometer.

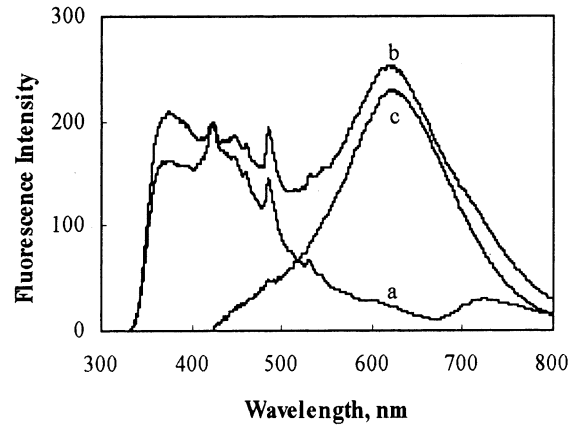

Fig. 2. Fluorescence spectra taken from (a) blank; (b) sample papers. Blank paper was treated with 0.5 M $CdCl_2$ but not exposed to H_2S. Sample paper is as blank but exposed to 0.870 ppm H_2S. (c) Difference spectrum.

3. Results and discussion

The typical fluorescence spectrum taken from the surface of filter paper that was pretreated with $CdCl_2$ and exposed to H_2S is shown in Fig. 2. This red fluorescence emission peak around 620 nm, the characteristic CdS fluorescence as demonstrated in the previous study [20], will be the subject of this study. The relatively high background signal from 350 to 550 nm originates from the reflection and/or scattering from the surface. The low wavelength section of the peak (<350 nm) is not observed because of the 350 nm cut-off filter placed in front of the emission monochromator. This background is on the hillside of the excitation wavelength and can be defined as stray radiation reaching to the detector. It is not the characteristic of filter paper itself and very similar background signals can be observed in different substrates [21]. After the measurements, this back-

ground signal was used as reference and all spectra were normalized to the same fluorescence intensity using 423 nm as the reference wavelength.

The first part of the study concentrates on the making of novel substrates for the determination of H_2S in ambient atmosphere by room temperature–solid surface luminescence (RT–SSL). In the second part, the applicability of a novel method, by means of fiber optic sensors, working with remote sensing principles is demonstrated for the same purpose.

3.1. Origin of fluorescence signal on the surface

As it has been stated before, filter paper is the most widely used solid surface in RT–SSL technique; other substrates are sodium acetate, a variety of silica gel plates, cyclodextrin–salt matrices and polymer–salt mixtures [22–26]. No generalization can be derived for the selection of a solid surface for RT–SSL, because the physicochemical interactions involved are not very clear. However, the main criterion has been the consideration of relative RTL of analyte compared with background signal of solid substrate. The primary interactions between the analyte species and the solid materials mentioned above can be summarized as follows [22–26]; in sodium acetate, the chief mechanisms are either the formation of sodium salt of the organic compound or hydrogen bonding between sodium acetate and the electron releasing group of the analyte organic molecule. Cyclodextrins, another large class of materials used in RTL works, have the ability of forming inclusion complexes with a large number of organic and inorganic compounds. In polymer–salt mixtures (especially PAA–NaCl or PAA–NaBr), the primary mechanism is the formation of hydrogen bonds between the analyte molecules and the carboxylate groups of PAA. In the case of silica gel, strong hydrogen bonding between the surface silanol hydroxyl groups and the π-electron system of the analyte organic molecules is responsible for RTL signal on the surface. Rather little is understood about the physicochemical interactions that are responsible for RTL on filter paper. Schulman and Parker [27] proposed that, hydrogen bonding of the ionic organic molecules to hydroxyl groups on the support is the primary mechanism of providing the rigid sample matrix for room temperature phosphorescence.

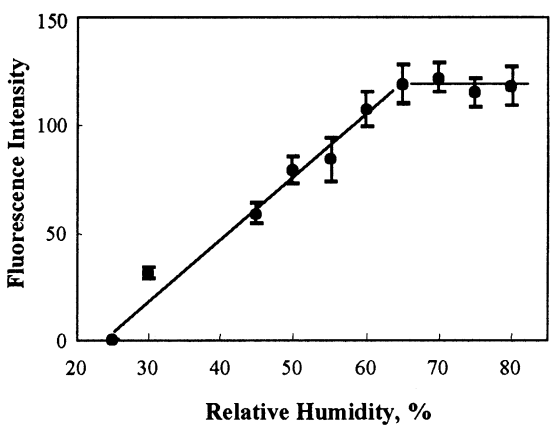

Fig. 3. Effect of relative humidity in the reaction chamber on fluorescence signal (substrate, filter paper treated with 0.5 M $CdCl_2$; H_2S concentration, 0.870 ppm).

As can be followed from the previous paragraph, almost all of the studies in this field concentrate on organic molecules. In this study, interactions between the analyte (H_2S) and the support ($CdCl_2$-treated substrate) might be including the mechanisms given above and possibly even more. All the necessary optimizations had been carried out in the previous studies [18–21] to obtain the best signal from the surface; such as, effect of relative humidity in the reaction chamber, effect of Cd^{2+} concentration, heavy-ion effect, decay features of luminescence signal and effect of possible interferences. Even more detailed investigations regarding humidity were carried out in this work. The most common way of supplying constant humidity in an atmosphere is the use of saturated salt solutions. The constant relative humidity in the reaction chamber was obtained by bubbling the carrier gas through various saturated salts. The change in the fluorescence signal with increasing relative humidity in the chamber is shown in Fig. 3. If the sample gas is not humidified, it is not possible to obtain the luminescent species on the surface; the fluorescence spectrum is not different than that of blank. When the relative humidity is at least 30%, a

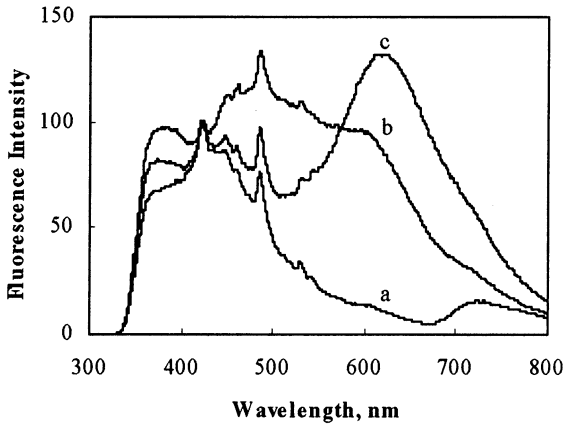

Fig. 4. Fluorescence spectra at various humidities, (a) 25%; (b) 50%; (c) 70% (the other conditions are as in Fig. 3).

small but observable signal is produced on the surface, but this signal can not be used in quantitative applications. The highest fluorescence signal is obtained when humidity reaches 60%; and beyond this value, very nice fluorescence spectra can be observed whose qualitative and quantitative features being independent of the relative humidity. The characteristic spectra obtained in different humidities are given in Fig. 4.

The humidity mentioned so far is the humidity in the reaction chamber and it is necessary for the formation of luminescent species on the surface of the filter paper; therefore, should not be confused with the humidity that is not desired during measurement with the luminescence spectrometer. Its function in the reaction chamber is believed to facilitate the reaction between H_2S and surface Cd^{2+} species by providing an aqueous medium on surface.

Moisture is one of the leading quenchers in luminescence studies. In solution work, an inert gas is generally passed through the sample solution in order to eliminate O_2 that is probably present as dissolved. In RTL study of organic molecules on filter paper, moisture acts as a dual quencher; firstly, it disrupts the hydrogen-bonding network with subsequent loss of sample matrix rigidity. Second effect of moisture is to help the transport of O_2 into the sample matrix [22–26]. Water molecules must be functional to compete with the luminophor molecules for hydrogen bonding to the hydroxyl groups on the support which are necessary to hold analyte molecules rigidly; i.e. water 'softens' the matrix, allowing collisional deactivation.

In our system, in order to test if the presence of O_2 is effective in the measurement of fluorescence signal, the sample filter papers were flushed with N_2; and the fluorescence signal on the surface was measured before and after the passage of N_2. Removal of O_2 from the surface caused a 25% increase in the fluorescence signal intensity whereas no change could be observed in background signal. The importance of O_2 removal can be observed from this experiment; but the elimination of moisture together with O_2 is more important in Room Temperature Phosphorescence (RTP) studies because of the relatively long lifetime of phosphorescence.

A simple experiment was designed to have a better understanding of the fundamental interaction occurring on the paper surface. For this purpose, a standard chromatography paper (Whatman 1 Chr) and a cation exchange paper (Whatman cation exchange) were compared after treating with the aqueous solution of $CdCl_2$ and exposed to H_2S in the usual manner. The characteristic fluorescence signal is obtained on the standard chromatography paper whereas no signal is observable on the surface of cation exchange paper. This finding suggests that Cd^{2+} should not be bound to the surface by forming strong ionic bonds. In fact, there are no available ionic sites in standard chromatography papers unless pretreated with the necessary chemicals to add specific functional groups. But, in the case of cation exchange paper, immersion of this special paper into the aqueous solution of $CdCl_2$ causes the ionic groups to change from Na^+ form to Cd^{2+} form; Cd^{2+} ions to be bound in the paper network; and thus, prohibition of Cd^{2+} ions from catching H_2S. Therefore, it was concluded that, Cd^{2+} ions should be adsorbed on, rather than ionically bound to the surface. The surface adsorption of the luminescent species, then, provides the rigidity necessary to prevent collisions between the analyte molecules.

Another experiment to enlighten the nature of the chemical reaction between H_2S and $CdCl_2$-

treated paper was about the reaction (exposure-to-H_2S) time. Almost equal fluorescence signals were obtained when the pretreated papers were exposed to H_2S for durations between 45 and 120 min, as shown in Fig. 5. An exposure time of 60 min was used in all studies since relatively more homogeneous signals were obtained in this duration. Relatively high signals on the surface of the substrates were observed under UV lamp even in 2 min while the reaction was taking place. This very short reaction period makes the chemical system ideal for sensor applications. It must be noted that the $CdCl_2$-treated paper is not behaving as a time-basis integrator for analyte; and possibly an equilibrium is established between the surface analyte species and free analyte molecules, where the former is proportional to the latter.

3.2. Interferences

Interference from sulfur dioxide (SO_2), nitrogen dioxide (NO_2), mercaptans, sulfides and disulfides has been reported in many of the methods used in the determination of H_2S [3–10]. In most of these previous studies, workers eliminate the interferences from these gases by using pretreated filters for selective adsorption, by adding some reagents into the absorbing solution in liquid collection techniques, or by changing the sampling conditions in the presence of a particular gas.

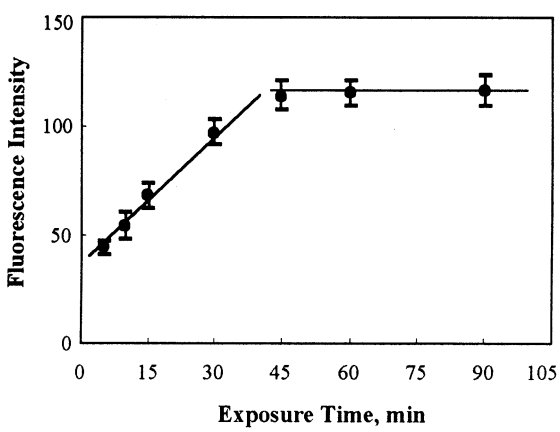

Fig. 5. Change in fluorescence intensity as a function of exposure time (conditions are as in Fig. 3).

In the present study, interference effects of SO_2 (0.302–0.460 ppm), methyl mercaptan (CH_3SH, 0.055–0.119 ppm), ethyl mercaptan (CH_3CH_2SH, 0.161 ppm), dimethyl sulfide ($(CH_3)_2S$, 0.140 ppm) and NO_2 (1.95 ppm) on H_2S (0.018–0.679 ppm) signal were investigated. These gases were chosen because, except NO_2, they are the expected gases that can be found in the environments where H_2S is present. The effects of SO_2 and CH_3SH were explored in more detail since these gases have been reported as the major interferants in H_2S determination; therefore, different concentrations of these two gases were prepared while changing the concentration of H_2S too. No signal was observed when the pretreated solid substrates were exposed to the gases mentioned above separately (without H_2S). A different strategy was also followed; H_2S and the tested gas were sent to the reaction chamber together and the pretreated filter paper substrates were exposed to this gas mixture. The fluorescence signals on these filter papers were compared with the fluorescence signals on the standard filter papers that were exposed to known concentrations of H_2S. As in the first case, no statistical difference was seen between these samples.

In addition to the above studies, the total interference effect of a gas mixture containing CH_3SH (0.114 ppm), CH_3CH_2SH (0.289 ppm) and $CH_3CH_2CH_2SH$ (0.090 ppm) was investigated on 0.654 ppm H_2S and no interference was found in any of the cases. No signal was obtained on pretreated filter papers when this mixture of mercaptans was sent to reaction chamber alone (no H_2S), and no change in the fluorescence intensity on filter paper surface caused by H_2S when total mercaptans and H_2S were sent to reaction chamber together. It can be concluded from these results that the sampling procedure is free from interference regarding the most likely interferants.

3.3. Novel substrates for the determination of H_2S by RT–SSL

It can be felt from the previous discussions that the solid surface will affect the analysis from the beginning to the end. There have been various efforts by many workers in the search of new

Table 1
Substances used in coating glass slides and the fluorescence signals taken from their surfaces[a]

Substance	(%, w/v) in H_2O	Fluorescence intensity[b]
Filter paper (Whatman 1 Chr)	[c]	100
Surfactants		
Sodiumdodecylsulfate (SDS)	0.50	24
A nonionic surfactant (N100S)	0.50	47
Aerosol OT	1.25[d]	57
Aerosol A 102	[e]	140
Aerosol 501	[e]	84
Cellulosic substances		
Sodium carboxymethylcellulose (CMC)	1.25	69
Hydroxypropylmethylcellulose (HPMC)	0.25	28
Ethylhydroxyethylcellulose (EHEC)	0.25	41
Ethylcellulose (EC)	1.25[f]	18
α-Cellulose (α-C)	1.25[f]	54
Water-soluble polymers		
Melamineformaldehyde (F10)	1.25	22
Polyacrylicacid (PAA)	1.25	NS[g]
Polyethyleneadipate (PEA)	1.25	NS[g]
Polyvinylalcohol (PVA)	1.25	7
Polyethyleneoxide (PEO)	1.25	74

[a] H_2S concentration, 0.970 ppm.
[b] Relative maximum intensities at 620 nm compared with the signal on filter paper surface.
[c] Strips of filter paper were immersed in aqueous solution of 0.5 M $CdCl_2$.
[d] Dissolved in 1:1 EtOH:H_2O mixture.
[e] The commercial solution (1.0 ml) was mixed with 10.0 ml of H_2O.
[f] The suspension was dispersed on glass slides.
[g] NS, no signal.

solid surfaces instead of the most widely used ones. A variety of solid substrates, in addition to filter paper, were tried in this study too as described under Section 2.

The first set was including some surface-active agents (surfactants) namely SDS, a nonionic surfactant (N100S), Aerosol A 102, Aerosol 501 and Aerosol OT. Surfactants dissolve in many solutions when they are in very small amounts; but when their concentration exceeds a typical minimum value called 'critical micelle concentration', they form aggregates or clusters in a very organized environment. The physicochemical interactions in micellar systems can be found elsewhere [22–25]. After some trial-and-error experiments, the above-mentioned surfactant solutions were prepared in the concentrations given in Table 1. Glass slides used in microscopic applications were coated with these surfactants as explained in Section 2 and after exposure to H_2S, the expected CdS signal was produced on each of them. By using surfactant, it was planned to have a more homogeneous distribution of Cd^{2+} species on the surface. The relative maximum fluorescence intensities at 620 nm using these surfaces are given in Table 1. These surfaces were sticky and some of them had inhomogeneous luminescing centers, as revealed in Fig. 6a. The scanning electron microscope (SEM) photograph of filter paper is also shown in Fig. 6 for comparison. Although, apparently the best conditions have not been obtained here, some values showing the superior but erratic performance (e.g. Aerosol A 102) indicate that a better coating procedure may result in successful use of these novel surfaces.

As a second set of compounds, several cellulosic substances were applied in a way that they were either dissolved or dispersed in water and mixed with $CdCl_2$ solution (Section 2.2.2). The glass slides were coated in the same manner and air-dried. The fluorescence spectra on these surfaces after being exposed to H_2S were obtained; the relative maximum intensities at 620 nm are given in Table 1. The relatively high and very homogeneous fluorescence signals are in accordance with the reproducible signals on the surface of filter paper. Among the cellulosic substances investigated, CMC gave the most sensitive and the most homogeneous signal on the surface; so that, it was taken as the first candidate for the application of the system, worked on so far, onto the tip of the fiber optic cable. The SEM photograph of CMC-coated glass slide can be seen in Fig. 6b.

Some water-soluble polymers were investigated as another class of materials. The fluorescence spectra on the glass slides prepared as explained in Section 2.2.2 were obtained; the relative maximum intensities are given in Table 1. The fluorescence signal from the surfaces coated with PVA was too low; therefore it was not used in subsequent studies. The other water-soluble polymers, PAA and polyethyleneadipate provided no fluorescence in a similar experiment. The relatively high and homogeneous signals on the surfaces of glass slides coated with different molecular weight PEOs made them as the second candidate for fiber optic applications. The SEM photograph of PEO-coated glass slide is given in Fig. 6c. The glass slides coated with PEO were exposed to different concentrations of H_2S in order to test whether a linear relationship could be obtained between the fluorescence intensity and H_2S concentration, and it was found that, they exhibited a linear relationship up to 1.0 ppm with a correlation coefficient of 0.975.

The results demonstrated the possibility of using these novel substrates in quantitative applications. In addition to their properties listed above, the signal-to-background ratio obtained with these surfaces was often better than that obtained from filter paper surfaces.

3.4. Fiber optic probe studies

As explained in Section 1, the final objective of this study was to design a fiber optic sensor working with remote sensing principles. For this purpose, experiments on both glass slides and filter paper were taken as intermediate steps in

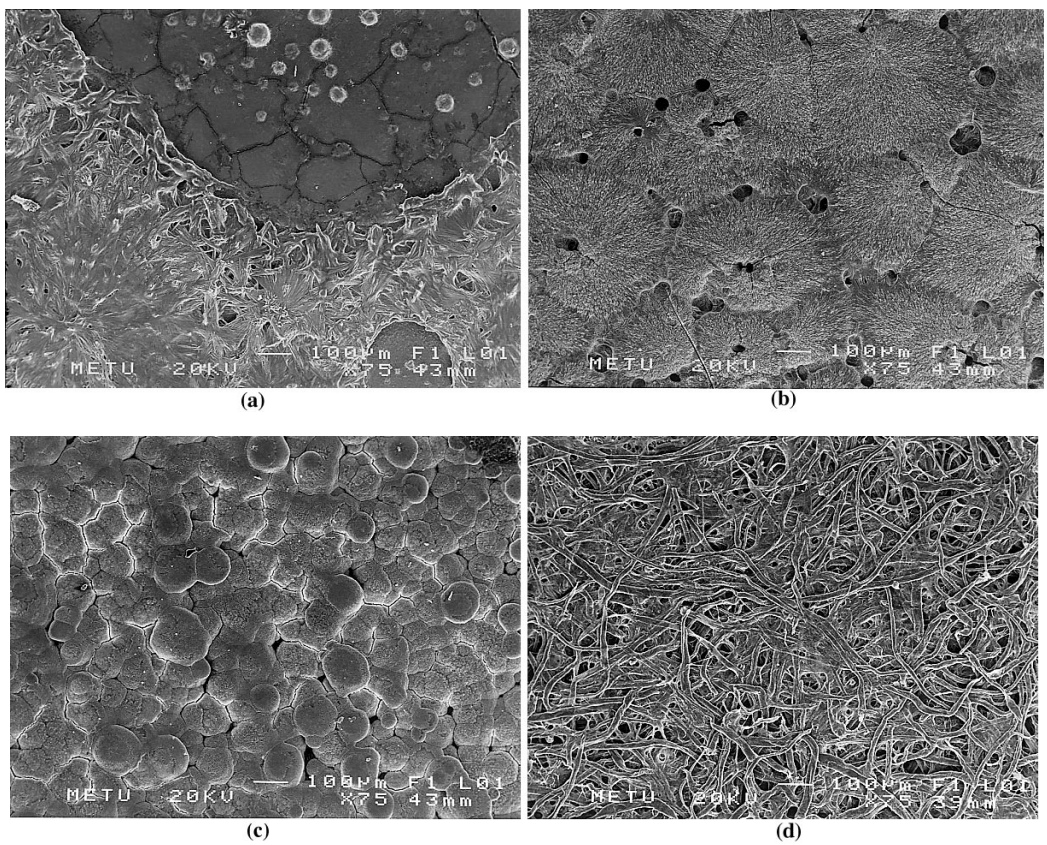

Fig. 6. SEM photographs (× 75) of the surfaces of glass slides coated with (a) surfactant aerosol 501; (b) CMC; (c) PEO; (d) filter paper.

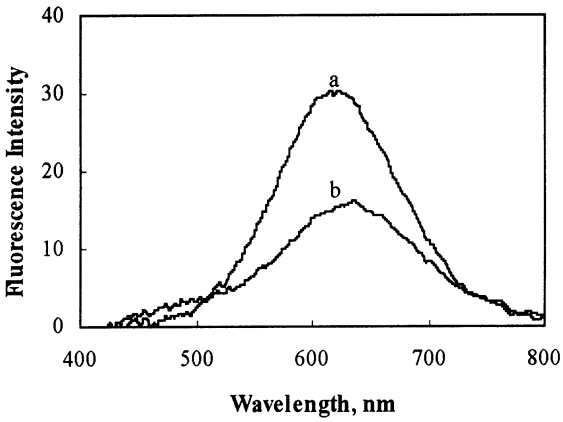

Fig. 7. Fluorescence spectra taken from the tip of fiber optic probes coated with 0.5 M $CdCl_2$ dissolved in (a) CMC; (b) PEO (H_2S concentration, 2.50 ppm).

going from the surfaces to the tip of the fiber optic cable. Three types of fiber optic probes were designed and their performance characteristics were evaluated in the subsequent sections.

3.4.1. CMC- and PEO-coated fiber optic probes

As explained in previous sections, CMC- and PEO-coated glass slides gave very sensitive and homogeneous fluorescence signals. For this reason, 0.5 M $CdCl_2$ aliquots were prepared in 1.0% (w/v) solutions of CMC and PEO separately. By using a micropipette, 1 μl of these solutions was applied onto the well-polished tips of the respective fiber optic probes. The wetted tip of the probe was dried at room temperature. The probes were then placed in the reaction chamber and exposed to 2.50 ppm H_2S. After 1-h exposure, they were taken out of the reaction chamber and the luminescence on these tips was excited from the other side of the fiber and measured by the luminescence spectrometer (Fig. 1a). The spectra obtained are shown in Fig. 7. Both compounds gave very sensitive results in this spot experiment. However, in subsequent experiments, fiber optic probes prepared with CMC did not show a linear relationship between the fluorescence intensity and H_2S concentration although its sensitivity was higher than that of PEO. Therefore, in subsequent studies, fiber optic probes were prepared using PEO. Tips of the prepared probes were examined under a microscope and the probes with inhomogeneous coatings were not used. The selected probes were placed in the reaction chamber and exposed to different concentrations of H_2S in 0.098–0.837 ppm range. Similarly, after 1-h exposure, the probes were taken out of the reaction chamber and the fluorescence spectra of the sample probes were taken by using the experimental set-up described in Fig. 1a. The calibration plot for this system had a line equation of $y = 6.85 + 16.94x$ and was linear up to 1.0 ppm; beyond this concentration the line curved down. Although a straight line with a correlation coefficient of $r = 0.954$ was obtained, the inhomogeneous coating on the fiber tips causes a relatively high intercept and the scattering of fluorescence values among triplicate measurements. The 3s detection limit of this system was 36.0 ppb. If these are regarded as initial studies based on fiber optics, some improvements can be expected together with the realization of more homogeneous coatings.

3.4.2. Bare-ended bifurcated fiber optic probe

In this configuration (Fig. 1b), the fiber optic cables were used only for the transportation of the excitation and emission beams. The excitation beam of wavelength 300 nm was carried onto the surface of a sample filter paper by means of the fiber optic cable and the luminescence on the surface was excited. The fluorescence emission scattered from the surface was collected in the other fiber and sent to the emission monochromator of the luminescence spectrometer. Various sample papers which had previously been exposed to different H_2S concentrations were measured with this system and a calibration line ($y = 9.10 + 134.64x$) with a correlation coefficient of $r = 0.992$ was obtained. The linear region was ending at around 1.0 ppm as in the case of PEO-coated fiber optic probe. In the detection limit calculation, the sample paper exposed to 32 ppb H_2S was used and 20 measurements were taken from its surface. The detection limit based on 3s was found as 4.0 ppb.

The performance data for the three fiber optic probes are documented in Table 2 for comparison.

Table 2
Performance data for the fiber optic probes

Probe type	Equation[a]	Correlation coefficient	R.S.D. (%)	DL_{3s} (ppb)
PEO-coated	$y = 6.85 + 16.94x$	0.954	29[b]	36.0[c]
Bifurcated	$y = 9.10 + 134.64x$	0.992	10[d]	4.0[e]
Single	$y = 5.75 + 74.55x$	0.996	11[d]	4.3[e]

[a] Equation for the linear portion of the calibration plot (0.032–1.0 ppm).
[b] Percent R.S.D. among the measurements taken from three fiber optic tips which were exposed to 0.552 ppm H_2S.
[c] Based on the 20 measurements of the same fiber optic tip which were exposed to 0.098 ppm H_2S.
[d] Percent R.S.D. among the measurements taken from three filter papers which were exposed to 0.299 ppm H_2S.
[e] Based on the 20 measurements of the same filter paper which were exposed to 0.032 ppm H_2S.

3.4.3. Bare-ended single fiber optic probe

As it is seen in Fig. 1c, the same fiber optic cable was used to carry both the excitation and emission wavelengths with an additional optical component, a beam splitter, in place of the sample compartment. This configuration is more flexible than the previous system in a way that it removes the necessity of using two separate fiber optic cables for excitation and emission separately. A similar calibration plot ($y = 5.75 + 74.55x$) with a correlation coefficient of $r = 0.996$ and detection limit ($DL_{3s} = 4.3$ ppb) were obtained with this system. The plot was linear up to 1.0 ppm and the fluorescence signal started to decrease beyond this concentration (Fig. 8). These types of response curves are very typical for solid surface luminescence measurements where the plot starts to curve down when the threshold concentration is exceeded. The reason for this is the saturation of the surface with the analyte molecules. The molecules approach to each other and are now able to collide (self-quenching effect). The dynamic range of the system is short when compared with the calibration plots usually encountered in solution luminescence measurements; but still very efficient relative to the other determination techniques for H_2S.

As an initial test for the applicability of the new method to real situations, three papers pretreated in the usual way were placed in a fume cupboard of one of the laboratories in the Chemistry Department and the ambient air inside the fume cupboard was sampled with the same sampling flowrate as explained in Section 2. The papers were taken out of the hood and fluorescence on the papers was measured using the bare-ended single fiber optic system (Fig. 1c). Although no signal was expected on the papers, very surprisingly, a H_2S concentration of 0.34 ± 0.09 ppm (26% R.S.D.) was found inside the hood. The H_2S was thought to have come from the students' Analytical Chemistry laboratory where H_2S was being produced in the experiment of the day. The reason for observing H_2S in a place relatively far away from the Analytical Chemistry laboratory could be due to a momentary failure of the ventilation system. This experiment demonstrated the applicability of the newly developed technique for monitoring purposes.

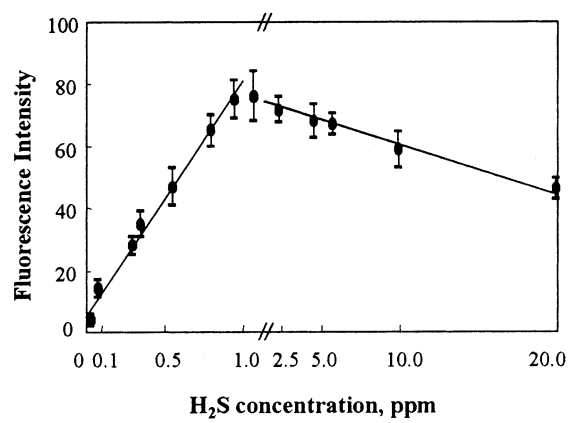

Fig. 8. Change in fluorescence intensity as a function of H_2S concentration. Papers exposed to different concentrations of H_2S were measured using bare-ended single fiber optic probe. In the calculation of H_2S concentrations, the linear portion of the plot (0.032–1.0 ppm) was used (note the change in concentration scale beyond 1.0 ppm).

4. Conclusion

It has been demonstrated that the glass slides coated with aqueous Cd^{2+} which is dissolved in some surfactants, cellulosic substances and water-soluble polymers may be good alternatives to filter paper in the determination of H_2S by RT–SSL spectrometry. They give enhanced fluorescence signals and better S/N ratios compared with filter paper and may be used in H_2S determination if the efficiency of coating procedure is improved and more homogeneous surfaces are realized.

It has also been shown that newly developed fiber optic sensors can find many applications in the remote sensor field. This is especially true in the determination of H_2S since many people may be exposed to very high levels of H_2S in some occupational sites and may even die due to H_2S poisoning. With the fiber optic sensors developed in this study, it can now be possible to measure the concentration of H_2S with a portable fluorimeter utilizing fiber optic sensors.

These novel fiber optic sensors can also be used in such cases where it is necessary to monitor the concentration of H_2S. It should be remembered that all of the probes developed in this study are irreversible devices. However, by means of an automatic sampling device that will be used to introduce a new filter surface can eliminate this disadvantage and enable sequential determinations. When the previously kept unexposed new surface is introduced to the viewing zone of fiber optic, the measurement (or the reaction) time can be adjusted knowing that the CdS starts to be formed on the surface even in 2 min.

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