POSTER

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Hydrogen sulfide determination by solid surface luminescence

Abstract In the analytical system suggested, atmospheric hydrogen sulfide reacts with the surface of a filter paper treated with aqueous cadmium chloride and yields a luminescent species whose intensity can be correlated with the analyte concentration in ambient air. It was shown that the luminescent species are CdS solid particles which were formed in a well defined size. The paper luminescence was also tried on polymeric surfaces; polyethyleneoxide, polyvinyl alcohol, ethylcellulose and carboxymethylcellulose were found to give a similar luminescence signal. The system can be used on the tip of an optical fiber for an irreversible, cumulative type of analytical device for hydrogen sulfide determination. The 3s detection limit for the paper luminescence detection system was 7.8 ppb H_2S.

Introduction

It is well known that hydrogen sulfide is a very toxic substance and thus exposition to it should be avoided. It enters atmosphere as a result of natural and anthropogenic processes. Natural sources include marshes, volcanic activities, sulfur springs, the decay of plant matter and others. A number of industrial processes have the potential to generate H_2S. Important sources include the petroleum refining industry, natural gas plants, petrochemical plants, coke oven plants, kraft pulp mills, tanneries. Harmful effects of H_2S have been well documented [1]. Its toxicity is due to paralysis of the respiratory system. Usually, the concentration of H_2S in ambient atmosphere is not so high to cause any health effects. However, it is necessary to measure its concentration continuously in certain locations since the presence of H_2S is one of the possible causes of casualties for people who work in sewers and similar environments.

Many methods exist for the determination of H_2S in ambient atmosphere. The most widely used techniques involve liquid collection and collection on impregnated solid substrates. In the liquid collection method, the sample gas is bubbled through an alkaline solution of a metal ion (e.g. $Cd(OH)_2$) and the dissolved gas produces a metal sulfide precipitate. Then, the precipitated sulfide is converted to methylene blue with N,N-dimethyl-p-phenylenediamine and ferric chloride for spectrophotometric measurements [2]. In addition, H_2S can also be collected on various solid substrates impregnated with metal salts like Pb^{2+}, Hg^{2+}, and Ag^{2+} [3]. The resultant metal sulfide stain is measured either by eye or by reflectance techniques. Other methods which are not as popular as the ones mentioned above involve determination by gas chromatography [4] and by infrared spectroscopy. Gas chromatography can be applied only if a series of columns are used to separate H_2S from other gases. IR spectroscopy is seldom used since all sulfides absorb at similar wavelengths.

In a previous study [5], a novel device for H_2S determination was reported where the sample gas stream was passed through a spiral channel which contained filter paper treated with $CdCl_2$; and the length of the visible yellow spot or bright pink luminescence under ultraviolet light was correlated with the analyte concentration. In a subsequent study, H_2S was passed over filter paper treated with $CdCl_2$ in the same manner; the fluorescence signal on the surface was measured on a fluorimeter and the filter paper was used as a dosimeter for H_2S [6].

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Solid surface room temperature luminescence (SSRTL) analysis involves the measurement of the fluorescence and/or phosphorescence of compounds adsorbed on solid substrates. Filter paper, silica gel, sodium acetate, some polymers and cyclodextrins are some examples of substrates used in SSRTL. The sample preparation in SSRTL analysis usually involves the application of several microliters of solution onto a solid material and drying the surface prior to the measurement. The principles of the technique have been reviewed in two monographs [7, 8]. The aim of this study is to develop a remote sensor for H_2S determination by solid surface luminescence. The necessity of remote sensing results from the toxicity of the gas. The advent of optical fibers has given rise to the ability to monitor analyte concentrations both at a distance and in in situ analyses. The use of a fiber optic probe may be employed in contaminated areas after optimization of the sampling procedures in solid surface luminescence determination of H_2S.

Experimental

Reagents. Analytical grade reagents and deionized water were used throughout the study.

Preparation of impregnated filter paper substrate. Various filter papers were employed to prepare chemically-treated solid sorbent. Strips of papers, 1.0×2.5 cm, were immersed in aqueous solution of Cd^{2+}. Different Cd^{2+} salts were tried. After 2 min immersion period, the papers were dried at room temperature.

Apparatus. The experimental set-up used in sample preparation is shown in Fig. 1. The reaction chamber was in the shape of a cylinder with a diameter of 10 cm and height of 20 cm made of glass. The chamber was positioned horizontally and the paper strips were placed on a horizontal polymer plate which is situated in the middle of the chamber. Standard gas concentrations were obtained by a Vici Metronics Dynacalibrator Model 230-14-C gas dilution system using permeation tubes obtained from the same company. For gas concentrations higher than 0.1 ppm, tubular type tubes having permeation rates between 4000 ng/min and 15000 ng/min were used, whereas wafer devices with permeation rates between 200 ng/min and 400 ng/min were used in the preparation of gas concentrations smaller than 0.1 ppm. The relative humidity in the reaction chamber was measured by a Fisher Scientific humidity measuring device. In fiber optic studies, a silica fiber from Ensign & Bickford Optic Company (diameters, core 940 μm, cladding 1000 μm) was used.

Cd^{2+}-treated papers placed in the reaction chamber were exposed to different concentrations of H_2S gas diluted with the carrier N_2 gas. The samples prepared by the above procedure were visually examined under a Camag 29000 UV lamp before studying them
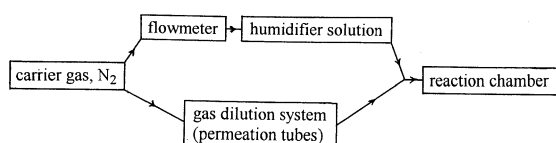

Fig. 1 Flowchart of the experimental set-up used in sample preparation

with the luminescence spectrometer Perkin Elmer LS 50B. During measurements, a yellow cut-off filter was used in front of the emission monochromator in order to eliminate the order peaks scattered from the solid surface. Unless stated otherwise, the wavelength chosen was 300 nm.

Results

Effect of various Cd^{2+} salts on the luminescence spectrum

Filter papers treated with aqueous solutions of $Cd(NO_3)_2$ and CdI_2 did not give any luminescence signal after exposure to H_2S. The possible reason for not getting any signal from $Cd(NO_3)_2$-treated paper may be the oxidation of the species on the surface of NO_3^- ions. For CdI_2, this should be the consequence of a heavy-ion effect. The excitation and emission spectra obtained from $CdCl_2$, $CdBr_2$ and $Cd(CH_3COO)_2$ treated papers exposed to H_2S are given in Figs. 2, 3, respectively. In most experiments $CdCl_2$ was used due to its availability and the formation of a more homogeneous signal with this salt.

Effect of relative humidity in the reaction chamber

In the previous study [6], it was reported that the relative humidity in the reaction chamber should be kept constant at 60%. The effect of different relative humidities on the formation of luminescent species on the filter paper surface was examined more closely. There is an increase of the signal linearly with percent humidity values and the highest luminescence signal is obtained when the relative humidity in the chamber is between 60 and 75%. A saturated solution of $Pb(NO_3)_2$ was used to keep the relative humidity constant at 70%
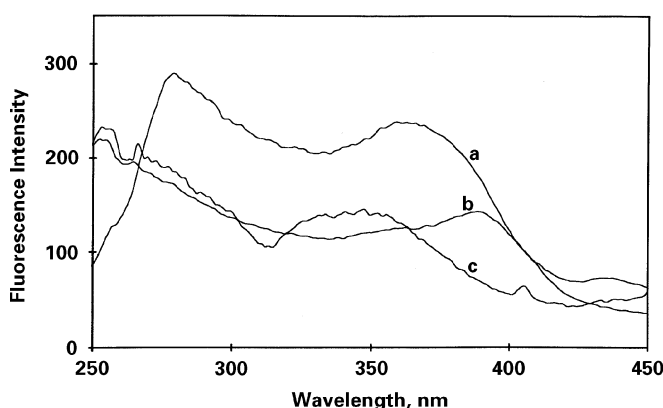

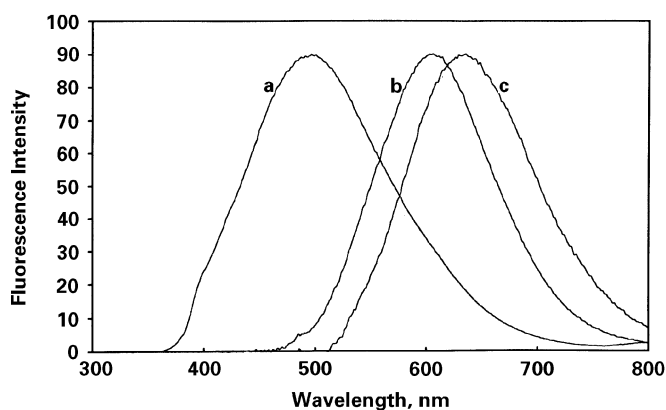**Fig. 2** Excitation spectra of surface species on filter paper treated with *a* 0.5 mol/l $CdCl_2$, *b* 0.5 mol/l $CdBr_2$, *c* 0.5 mol/l $Cd(CH_3COO)_2$ which were exposed to 2.86 ppm H_2S for 1 h. Emission wavelengths were 620 nm, 600 nm, and 495 nm for Cl^-, Br^-, and CH_3COO^- salts, respectively.

Fig. 3 Emission spectra of surface species on filter paper treated with *a* 0.5 mol/l CdCl$_2$, *b* 0.5 mol/l CdBr$_2$, *c* 0.5 mol/l Cd(CH$_3$COO)$_2$ which were exposed to 2.86 ppm H$_2$S for 1 h. Excitation wavelengths were 300 nm for Cl$^-$ and Br$^-$ salts, and 350 nm for CH$_3$COO$^-$ salt. Spectra were background corrected

throughout the study. This humidity is essential in the reaction chamber only during sample preparation and should not be confused with the humidity that quenches the luminescence during measurement with the luminescence spectrometer.

Choice of filter paper

Filter paper is the most widely used substrate in SSRTL studies. The important parameters that should be taken into consideration in the selection of a substrate are the homogeneity of the surface and the level of the background signal. Among the various brands of filter papers examined, Whatman 1 Chr (reel) has provided the most sensitive result with the best surface homogeneity for signal.

Heavy-ion effect

The presence of heavy ions is known to quench the fluorescence and to increase the phosphorescence. In this study, the fluorescence signal was quenched with increasing concentration of NaI without appearance of any phosphorescence emission. The mentioned effect appears for NaI concentrations higher than 1.0×10^{-3} mol/l, and increases with increasing concentration values almost linearly. The signal disappears when 0.5 mol/l NaI was used in treating the aqueous solution of CdCl$_2$.

Effect of CdCl$_2$ concentration

The concentration of CdCl$_2$ solution into which filter papers are immersed has a direct effect on the lumines-

cence signal formed on the surface. The signal increases linearly with higher CdCl$_2$ molarities and beyond 0.5 mol/l the signal is independent of the CdCl$_2$ concentration and does not change much. In subsequent experiments 0.5 mol/l CdCl$_2$ was used unless stated otherwise.

Effect of exposure time

Almost equal signals are obtained when the exposure time is between 45 and 120 min, illustrating the saturation of surface. However, about 50% of the signal is obtained in the first 5 min. An exposure time of 60 min was chosen throughout the study since more homogeneous surfaces had been obtained for this duration. Longer exposure times were avoided because of the possibility of self-quenching.

Interferences from other gases

The interference effect of various gases were investigated in a way that both H$_2$S and the interferent gas permeation tubes were placed in the permeation chamber of the gas dilution system. When the H$_2$S concentration was 1.89 ppm, 0.123 ppm dimethylsulfide and 0.111 ppm ethylmercaptan had no significant interference effect. Sulfur dioxide had a positive effect (approximately 30%) when its concentration was 0.49 ppm. It is not certain that the interference of SO$_2$ is due to a gas–gas interaction. Methylmercaptan (0.340 ppm) had also a positive effect (app. 20%).

Calibration plots

The hydrogen sulfide concentration was varied from 0.030 ppm to 10 ppm and it was found that a direct correlation between the luminescence intensity on the surface and H$_2$S concentration exists upto 3.0 ppm; the equation for the calibration line was $y = 13.6 + 29.2x$ with a correlation coefficient of R = 0.967. Beyond 3.0 ppm, the luminescence signal starts to decrease. Five paper strips were used for each point on the calibration plot and the relative standard deviation varied between 5 and 23%. The detection limit (3s) was found to be 7.8 ppb.

Decay features of the luminescence signals

The instrument used for the measurement of the luminescence signals, Perkin Elmer LS 50B Luminescence Spectrometer, has the property of measuring both fluorescence and phosphorescence. The phosphorescence spectra of CdCl$_2$, CdBr$_2$ and Cd(CH$_3$COO)$_2$-treated papers which were exposed to 2.50 ppm H$_2$S

were taken at different delay times (t_d). The luminescence lifetimes of Cd(CH₃COO)₂-treated paper (exposed to H₂S) and blank papers (Cd²⁺-treated but not exposed to H₂S) are very close to each other and after a delay time of 0.05 ms, the emission signal on their surfaces becomes undetectable. On the other hand, the luminescence signal on CdCl₂ and CdBr₂-treated papers (exposed to H₂S) can be observed at longer delay times. Therefore, in case of CdCl₂ and CdBr₂, adjusting a proper delay time may be chosen to eliminate the background.

Studies to elucidate the nature of the luminescent species on the surface

One of the expected species to be formed on the surface of the filter paper is CdS due to the reaction

$$Cd^{2+}(aq) + H_2S(aq) \rightarrow CdS(s) + 2H^+(aq)$$
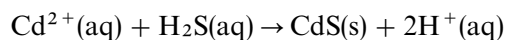
Although the most probable species on the surface is CdS, this could not been confirmed by some surface techniques such as EDAX and ESCA. The answer to this question has been obtained by the luminescence spectrum that was produced from the colloidal suspension formed when CdCl₂ solution in isopropanol was mixed very rapidly with Na₂S solution in methanol. It is known that crystalline CdS particles do not give any fluorescence whereas CdS colloids formed in micrometer size luminesce at different wavelengths depending on their particle sizes [9]. Cadmium sulfide formed with the above procedure had colloidal dimensions and gave exactly the same fluorescence spectrum as that from the CdCl₂-treated filter paper exposed to H₂S (Fig. 4). Therefore, it has been concluded that the luminescent species are CdS solid particles which were formed in a certain size.

Bifurcated fiber optic probe

After optimization of the sampling parameters for the SSRTL determination of H₂S, a bifurcated fiber optic probe was constructed (Fig. 5). The excitation wavelength of 300 nm from the Xe-lamp of LS 50B was passed onto the surface of filter paper sample by means of a silica fiber optic cable and the luminescence on the surface was carried to the detector of the instrument with another fiber. This system worked well and comparable results were obtained, which are very similar to the results obtained with SSRTL. In addition, some polymers and surfactants were tested on glass slides, which might be alternative to the bifurcated probe utilizing filter paper substrate. The glass slides were prepared in such a way that the polymer solutions were mixed with CdCl₂ solution and the resultant mixture was spread over the glass slide by means of a micropipette. Then, the coated glass slides which were

exposed to H₂S were placed in the sample compartment unit of the luminescence spectrometer. The fluorescence spectra taken in this way are shown in Fig. 6. These high luminescence signals on the glass surface seem to be promising to accomplish a bifurcated probe coated with the substances mentioned in the figure instead of using a paper substrate.
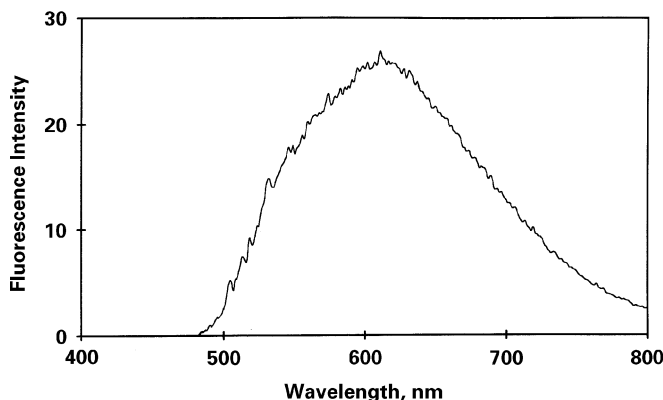

Fig. 4 Fluorescence spectrum of colloidal CdS particles

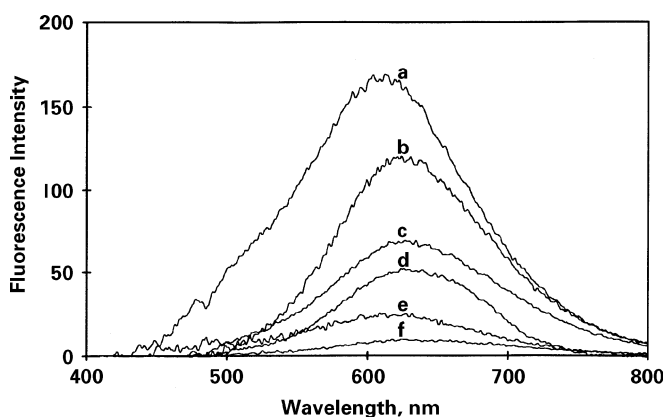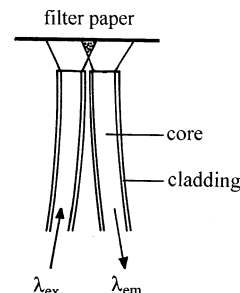**Fig. 5** Scheme of bifurcated fiber optic probe using paper substrate

Fig. 6 Fluorescence spectra taken from glass slides coated with 0.5 mol/l CdCl₂ in various polymers and in a surfactant solution and then exposed to 2.50 ppm H₂S for 1 h. (λ_{ex} = 300 nm). *a* poly(ethylene oxide); *b* carboxy methyl cellulose; *c* sephadex gel; *d* ethyl cellulose; *e* poly(vinyl alcohol); *f* aerosol 501 (surfactant)

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