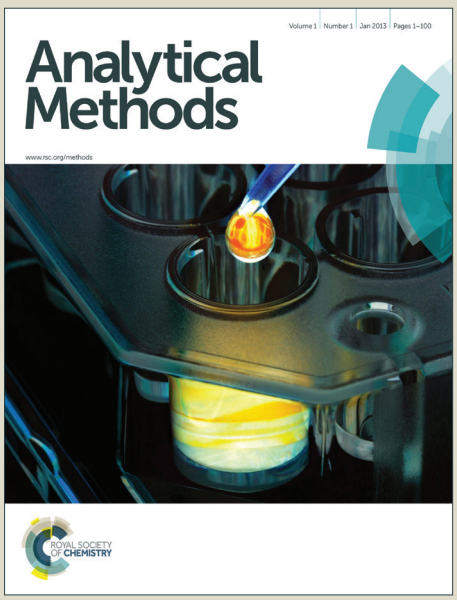
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

SENSITIVE LUMINESCENT PAPER-BASED SENSOR FOR DETERMINATION OF GASEOUS HYDROGEN SULFIDE

João Flávio da Silveira Petruci and Arnaldo Alves Cardoso

São Paulo State University, Department of Analytical Chemistry, UNESP,

CEP 14800-970, Araraquara, SP, Brazil

ABSTRACT

H_2S is extremely malodorous, toxic and corrosive gas. These properties make localized emissions of hydrogen sulfide an air pollution issue. Despite a relatively large number of papers dedicated to developing analytical methods to determine gaseous H_2S, it remains an analytical problem. In this paper, it is described a luminescent cellulose filter-based sensor for gaseous H_2S determination. The cellulose filter is impregnated with a palladium complex, containing a ligand with fluorescent properties. The measurements are made directly on the cellulose filter, not requiring an extraction step. The palladium complex - bis 2-aminobenzoic palladium (II) - impregnated on the surface of cellulose filter paper reacts with gaseous H_2S. The reaction results in the release of the fluorescent ligand, increasing the fluorescence intensity of the filter surface observed at 410 nm when excited at 338 nm. The linear calibration curve covers the range from 8 to 110 ppb with a limit of detection (LOD) of 2 ppb. The sampling time is approximately 15 min for this range of H_2S; however, longer sampling may decrease the detection limit. The factors affecting the collection characteristics, such as sampling flow, media moisture, cellulose filter paper type and amount of humectant (ethylene glycol) in the impregnating solution amount, were optimized.

INTRODUCTION

Hydrogen sulfide is an extremely malodorous (with low odor threshold), toxic and corrosive gas[1]. In the environment, H_2S is found in a range of low ppb (1.4 µg m^{-3}) to ppm levels (1.4 mg m^{-3})[2,3]. H_2S is largely produced from natural sources, such as volcanic activity, and through anaerobic bacterial reduction of sulfate and organic sulfur compounds[4]. Anthropogenic contributions to the global sulfur biogeochemical cycle are relatively negligible, but when localized it can result in an air pollution concerns. Typical emissions from industrial activities are related to petroleum extraction and fuel burning. Hydrogen sulfide can be generated in small quantities as undesired by-products from three-way catalysts. Processes such as production of detergents, and in the industrial processes of paper are sources of H_2S emissions[5,6,7]. H_2S is a common contaminant found in natural gas, being regulated not to surpass 13 ppb[8]. The human olfactory threshold for hydrogen sulfide detection is close to 10 ppb and varies depending on the individual and the exposure time, which can lead to olfactory fatigue resulting in the loss of the sense of the sulfide smell[9]. Atmospheric air containing concentrations higher than 70 ppb may cause serious harm to health after inhalation. At concentrations higher than 140 mg/m^3, olfactory paralysis occurs, making hydrogen sulfide very dangerous because a few breaths at 700 mg/m^3 can be fatal[8]. In humans, the emission of hydrogen sulfide may be indicative of a malfunctioning of the organism. Sulfide is endogenously synthetized via L-cysteine metabolism[10] and is produced in the human intestine by anaerobic bacteria and also in the mouth by microbial putrefaction. In the mouth, air levels between 1.4 and 140 µg/m^3 have been found[11].

Several analytical methods have been developed to determinate H_2S in gaseous samples[12–15]. There are numerous instruments available commercially for real time monitoring of H_2S, but they are limited to detect ppm levels. Semiconducting metal oxides[16,17] and electrochemical[18,19] based sensors have been employed to monitor H_2S with some advantages, such as rapid response, ease of preparation, direct measurements and low cost. The determination of H_2S at low ppb levels usually requires an efficient sample preconcentration step followed by off-line analysis in the laboratory[20]. One of the most commonly used preconcentration methods utilizes an absorption solution containing $Cd(OH)_2$, which has been subsequently replaced by Zn^{+2} due to the high toxicity of cadmium[21,22]. This methodology enables formation of highly insoluble sulfides, less susceptible to oxidation. Other sample enrichment techniques include metal-coated beads[23], reagent impregnated filters[24] and solids sorbents[25]. Many methods for the determination of H_2S involve gas chromatography coupled with flame ionization or flame photometric detection with remarkable sensitivity and precision[3]. However, the multi-stage protocol involving preconcentration sampling and desorption steps before the final determination makes this approach inconvenient for continuous monitoring analysis. Furthermore, the rather bulky dimensions and cost of the instrumentation renders *in situ* monitoring via GC techniques not field-usable.

Optical sensors are particularly advantageous because they can be sensitive, when properly designed, and adapted to small dedicated devices of low cost and easy to operate. Luminescent metal-based complexes have been used as sulfide recognition and determination probes. Mercury-

complexing agents, such as alkaline fluorescein mercuric acetate (FMA), have mainly been employed for sulfhydryl group determination[2,26]. Zinc[27], ruthenium[28] and copper[29] have also been used as luminescent metal-based probes.

Recently, efforts have been made to develop analytical approaches that can simultaneously sample and promote changes in the optical properties of reagents immobilized on a solid support. The changes in the optical signal on the solid surface can be converted directly into an analytical signal and recorded without any sample treatment[30].

Toda et al.[31] employed a membrane-based collection/analysis system using FMA to determine H_2S in a large concentration range (0.03 to 250 ppb). Tanaka et al.[32] developed a gas-detector-tube for H_2S and other organic sulfides combined with a portable sensor using a one-dimensional CCD image sensor. Narayanaswamy and Sevilla[33] developed a flow-through optosensor for hydrogen sulfide determination based on reflectance measurements on a paper surface impregnated with lead acetate. The sensor enables the determination of 50 ppb H_2S within 10 s.

Palladium (II) is a versatile transition metal and can coordinate with electron donor atoms, such as N and O. The low-spin d^8 Pd(II) ion has the highest formation constant with sulfur ligands, forming very well-defined compounds. In a previous paper, a new Pd chelate - bis 2-(aminobenzoate)palladium(II) or PdA_2 – was studied and used to determine aqueous sulfide[34]. The synthesis of the compound is simple and involves only one step. In an aqueous medium, the presence of the sulfide causes the formation of PdS and releases the ligand species with fluorescent properties

into the solution. The increase in the fluorescence intensity is proportional to the amount of sulfide present in the sample. Additionally, filter paper is a low cost material and is easy to handle as support for sensing materials.

In the present study, we describe a gaseous sensor for determination of H_2S through the change in fluorescence intensity of the Pd-complex impregnated onto the cellulose substrate. H_2S is trapped by bis 2-(aminobenzoate) palladium(II), leading to an increase of the fluorescence intensity on the cellulose filter. The method involves sampling and measurements without requiring of any sample treatment, thus providing an excellent alternative to the conventional analytical approaches for H_2S reported to date.

RESULTS AND DISCUSSION

Fluorescence behavior on H_2S exposure

Previous studies have shown that the 2-(aminobenzoate) (A) in solution has emission peak centered at 410 nm when excited at 245 or 338 nm. However, the reaction between A and $PdCl_4^-$ results in the formation of a stable complex, PdA_2, which present low fluorescence. The quenching effect might be explained by $S_1 \longrightarrow T_1$ intersystem crossing (CIS) transitions caused by Pd atom[35]. As a result of the high affinity between sulfide and Pd (II)), the PdA_2 complex releases its ligands A, canceling CIS effect and leading to an increase of the fluorescence intensity (Figure 1). To take advantage of this reaction to determine H_2S in air, the reagent was impregnated on cellulose filter paper.

To evaluate the feasibility as a solid substrate for the sensing material, cellulose filter papers were impregnated with 11.7 µg of PdA_2 and 100 µL of ethylene glycol. The filters were exposed to air contaminated with H_2S (66 ppb) for different sampling times. Cellulose filters were then placed in the instrument solid substrate apparatus to measure their fluorescence without any prior treatment. The excitation wavelength was set at 338 nm to minimize spectral interference from the cellulose. The effect of the exposition time to the H_2S contaminated gas flow on the fluorescence emission spectrum and on the fluorescence intensity (λ_{EX} = 338 nm; λ_{EM} = 410 nm) of the sensing material is shown in figure 2. The result shows a linear increase of the fluorescence intensity upon sampling time, indicating that the sensor breakthrough is not reached at 105 min of sampling. A suitable sampling time was established at 15 min, and a typical signal-to-noise ratio obtained for such measurement was 7.

Effect of sampling flow on sensor response

A gaseous sensor's performance might be measured in terms of its ability to trap the molecules passing through the sensor and allowing analyte-reagent contact. Sampling flow must be evaluated to obtain the optimum response for a sampling time. Thus, air with 33 ppb H_2S was passed through the cellulose filter paper containing PdA_2 and ethylene glycol for 15 min, and the gas flow rate was varied from 100 - 900 mL min^{-1}.

As evident in figure 3, the efficiency of the reaction between the H_2S and the complex PdA_2 is at its maximum with a sampling flow rate of 300 mL min^{-1}, and no improvement of the analytical signal was observed at flow

rates greater than 300 mL min^{-1}. For all further experiments, the sampling flow rate was established at 200 mL min^{-1}, providing a signal-to-noise ratio of 24.

Evaluation of the cellulose filter paper type on sensor response

There are a large number of commercially available cellulose filter papers for several quantitative and qualitative analytical purposes. Thus, the analytical signal response was evaluated in terms of the cellulose filter paper classification. Framex, Whatman 40 and Whatman 41 cellulose filter papers have porosities of 2, 8 and 20 µm, respectively and are classified as slow, medium and fast flow filter papers for quantitative analysis. Each filter paper was cut to rectangular dimensions of 230 (L) x 300 (H) mm and then impregnated with 100 µL of PdA_2 solution and ethylene glycol. These cellulose-impregnated filters were evaluated for their efficiency to collect H_2S. All filters were tested under the sampling conditions: 15 min of sampling of air with 33 ppb of H_2S. The effect of cellulose on the analytical signal is shown in figure 4. The best analytical signal was obtained using Framex filter paper. This fact may be explained by the lower porosity of this paper that might provide a more effective molecular interaction between H_2S and PdA_2 during sampling. The SEM images of a cellulose filter paper alone and of cellulose filter paper impregnated with PdA_2 before and after the interaction with H_2S are shown in figure 5. An increasing particle size can be seen, indicating the occurrence of the reaction on the cellulose surface.

Effect of ethylene glycol on the cellulose surface

Ethylene glycol is a humectant commonly used in cellulose filters impregnated with reagents and applied for gas sampling[36–38]. The humectant facilitates gas/solid reactions by increasing the amount of water molecules on the cellulose surface. Water molecules can mediate the reaction favoring the input of the gas molecules on the solid. Consequently, the effect of the amount of ethylene glycol on the cellulose surface, ranging of 0 – 200 µL, was evaluated. As evident in figure 6, an enhancement of the analytical signal was observed when the ethylene glycol amount was increased from 0 to 100 µL. After that, a decrease of the analytical signal occurred. We believe that an excess of humectant can block the reagent surface, inhibiting the reaction. Therefore, a volume of humectant of 100 µL was established as the optimum condition.

Interferences

Nitrogen dioxide is a classic interferent in the determination of H_2S. In industrial areas contaminated with H_2S, the presence of SO_2 is also common. In this study, the effect of NO_2 and SO_2 on the sensor was tested using standard gas mixtures of 33 ppb H_2S in air. Hydrogen sulfide standard mixtures were contaminated with NO_2 and SO_2 using permeation tubes and submitted to the analytical protocol. The results showed no significant interference, even when concentrations higher than 100 ppb of interferents were used, confirming the excellent selectivity of the sensor towards these species. Palladium is recognized for its ability to react with reduced sulfur (-2). As shown by the previous study, organic sulfides also produce reactions resulting in increasing fluorescence intensity. However, the formation rate of

fluorescent species is half that observed for H_2S. H_2S is usually the major component of reduced sulfur compounds found in polluted environments. In situations where other reduced sulfur compounds are equivalent in quantity to H_2S, the measurement of this method can serve as an indicator of the amount of the total sulfides measured as H_2S.

Analytical figure of merit

An analytical curve showing the fluorescence intensity of the sensing material (at 410 nm) in function of the H_2S concentration was established for quantitative data evaluation. For each concentration, the mean value of three replicate measurements was calculated. The proposed method showed linear response over the concentration range of 8 to 110 ppb H_2S (R^2>0.993) selected for the present study. The obtained calibration equation was ΔFI = 2.78 (± 0.05) [H_2S] + 2.50 (± 2.17), where ΔFI represents the net fluorescence at 338 / 410 nm and *[H_2S]* is the hydrogen sulfide concentration in ppb. The calculated limit of detection (LOD) was considered as three times the standard deviation of the blank signal and was 2 ppb. Relative Standard Deviation (RSD) was evaluated by seven replicates of determination of H_2S at 100 ppb. The obtained results are summarized in table 2.

EXPERIMENTAL

Materials and solvents

Filter papers tested as solid support for the chemosensor were Framex (Schleicher and Schull, Germany), Whatman 41 and Whatman 40 (Whatman, Kent, England). A micropore (USA) gas sampler with diameter of 40 mm was

used as the holder for the filter paper. Ethylene glycol and methanol were provided by Synth (São Paulo, Brazil).

Generation of standard gaseous samples

A hydrogen sulfide permeation tube device (VICI Metronics, Santa Clara), certified to release H_2S at a rate of 45.83 ng min^{-1} (at 30ºC), was placed inside a permeation chamber (PC) and maintained at a constant temperature of 30.0 ± 0.1 ºC. Air was purified by passage through two sequential columns (20 mm × 400 mm) containing silica gel (A1) and activated carbon (A2). Gas flow controllers (FC) were positioned to prepare and deliver hydrogen sulfide in different concentrations at the sampling stream (S). The permeation chamber was kept on a fixed gas flow of 200 mL min^{-1}. The complete standard gas generator is schematically illustrated in figure S1 (supplementary material).

Reagent solution and preparation of sampling filters

The complex, bis 2-aminobenzoic palladium (II) or PdA_2, was synthetized by mixing 0.663 mmol of palladium chloride ($PdCl_2$), 1.543 mmol of sodium chloride (NaCl) and 1.350 mmol of aminobenzoic acid. This solution was stirred for 24 h, filtered and dried. The detailed synthesis and characterization of PdA_2 has been previous reported[34]. PdA_2 is sparingly soluble in methanol. A reagent solution was prepared by adding 25 ml of methanol to a flask containing 4.5 mg of PdA_2 and stirring vigorously.

Filter papers were cut to 230 (L) x 300 (H) mm and impregnated with 100 µL of PdA_2 solution. The relative concentration was 1.49 µg cm^{-2}. An

aliquot of 100 µL of ethylene glycol was added to each piece before H_2S exposure. The paper containing the reagent was placed into the holder and kept in contact with different concentrations of H_2S for 15 minutes with a gas flow of 200 mL min^{-1}

Instrumental

The fluorescence spectra and relative fluorescence intensities were measured using a spectrofluorimeter (Model RF-1501, Shimadzu, Japan) fitted with a solid holder positioned at 45º to the excitation/emission devices. The excitation and emission wavelength bandpasses were 10 nm and were set at 338 and 410 nm, respectively. The difference of the fluorescence intensity of the filter paper impregnated with the reagent before and after H_2S exposure was considered the analytical signal. SEM experiments were performed using a microscope (Model SM300, Topcon, United States).

CONCLUSIONS

In this study, we present a new method for the determination of H_2S in air. The principle of the method is based on the release of a luminescent species, which acted as a ligand to form a palladium complex. The luminescent palladium complex impregnated on a cellulose filter paper was used as the reaction surface. Whereas the majority of optical methods in the literature require sampling/extraction procedures, here, we performed the measurements directly on the paper surface without an extraction step. The contact of the gas and PdA_2 on the surface of the filter paper enables the H_2S determination with a limit of detection of 2 ppb with 15 minutes of sampling.

The synthesis of the PdA_2 complex has already been shown as a suitable probe for sensitive and selective reduced sulfur compounds determination.

The table 1 summarizes a comparison between the proposed method with others indirect optical methods for gaseous H_2S detection described in the literature. In terms of sensitivity and response time, this sensor has performance similar to the "gold-standards". However, easiness of handling, worldwide instrument's availability, low cost and use of non-toxic reagents are essential demands for gaseous compounds monitoring. These factors were demonstrated for this method.

In the future, the coupling of a fiber-optic to a portable fluorimeter might permit *in situ* measurements of H_2S in many environments requiring H_2S determination (e.g., clinical, environmental and industrial purposes).

ACKNOWLEDGMENTS

The authors thank FAPESP (2013/22995-4) for the financial support.

REFERENCES

1. Hendrickson, R. G., Chang, A., Hamilton, R. J. *Am. J. Ind. Med.*, 2004, **350,** 346–350.
2. Toda, K. *et al. Anal. Chem.,* 2001, **73,** 5716–5724.
3. Pandey, S. K., Kim, K.-H. *Environ. Sci. Technol.,* 2009, **43,** 3020–3029.
4. Pio, C. A. *et al. Atmos. Environ.,* 1996, **30,** 3115–3127.
5. Kim, K.-H. *Environ. Sci. Technol.,* 2005 **39,** 6765–6779.
6. Hemingway, M. A. *et al. J. Occup. Environ., Hyg.* 2012, **9,** 319–328.

7. Engler, B. et al. in Catalysis and Automotive Pollution Control II, Ed A. Crucq, Elsevier Science Publishers, Amsterdam, 1991.

8. Tuan, H. P. *et al. J. High Resolut. Chromatogr.*, 1994, **17,** 373–389.

9. Guidotti, T. L. *Int. J. Toxicol.*, 2010, **29,** 569–581.

10. Li, T. *et al. Exp. Biol. Med.,* 2008, **233,** 1081–1087.

11. Rosenberg, M. *et al. J. Period.,* 1991, **62**, 487–489.

12. Choi, M. M. F., Hawkins, P. *Sensors Actuators B Chem.*, 2003, **90,** 211–215.

13. Rodr, J., Pereiro, R., Sanz-medel, A. *Anal. Chim. Acta.*, 2002, **471,** 13–23.

14. Pandey, S. K., Kim, K.-H., Tang, K.-T. *TrAC Trends Anal. Chem.*, 2012, **32,** 87–99.

15. Petruci, J. F. S. *et al. Analyst*, 2014, **139,** 198–203.

16. Asefa, T., Duncan, C. T., Sharma, K. K. *Analyst*, 2009, **134,** 1980–1990.

17. Yu, C. *et al. Sensors Actuators B Chem.*, 2002, **86,** 259–265.

18. Wang, Y., Yan, H., Wang, E. *Sensors Actuators B Chem.*, 2002, **87,** 115–121.

19. Costello, B. P. J. D. L., Ewen, R. J., Ratcliffe, N. M. *J. Breath Res.*, 2008, **2,** 037011.

20. Lawrence, N. S., Davis, J., Compton, R. G. *Talanta,* 2000, **52,** 771–784.

21. Shahriari, M. R., Ding, J. *Opt. Lett.*, 1994, **19,** 1085–1087.

22. Natusch, D. F. S. *et al. Anal. Chem.*, 1972, **209,** 2067–2070.

23. Braman, R. S., Ammons, J. M., Bricker, J. L. *Anal. Chem.,* 1978, **50**, 992–996.

24. Kumura, M. O. *et al. Anal. Sci.*, 1999, **15**, 427–431

25. Nelson, F. *et al. Anal. Chem.,* 1978*,* **50***,* 1976–1979.

26. Hunt, A. L., Alder, J. F. *Anal. Chim. Acta.*, 1999, **387,** 207-215.

27. Galardon, E. *et al. Dalton Trans.* 2009, **48**, 9126–9130.

28. Ye, Z. *et al. Dalton Trans.*, 2014, **43,** 13055–13060.

29. Sarfraz, J. *et al. Sensors Actuators B Chem.*, 2012, **173,** 868–873.

30. Sun, K. *et al RSC Adv.* 2013, **3,** 14543.

31. Toda, K. *et al. Environ. Sci. Technol.,* 2004, **38,** 1529–1536.

32. Tanaka, Y., Nakamoto, T., Moriizumi, T. *Sensors Actuators B Chem.*, 2006, **119,** 84–88.

33. Narayanaswamy, R., Sevilla, F. *Analyst***,** 1986, **111**, 1085–1088.

34. Petruci, J. F. S., Cardoso, A. A. *Microchem. J.*, 2013, **106,** 368–372.

35. Valeur, B. in *Molecular Fluorescence*, ed. wiley-vch, Darmstadt, Germany, 1st ed., 2002, pp 41.

36. Felix, E. P., Cardoso, A. A. *J. Braz. Chem. Soc.*, 2012, **23,** 142–147.

37. Felix, E. P. *et al. Microchem. J.*, 2011, **99,** 530–534.

38. Garcia, G., Allen, A. G., Cardoso, A. A. *Water, Air, Soil Pollut.*, 2014, **225,** 1836-1841.

39. Sen, A., et al. *Sensors Actuators B Chem.,* 2008, **134,** 234–237.

40. Ninh, H. P. et al. *Sensors Actuators B Chem., 2007,* **125,** 138–143

Table 1. Comparison between the proposed method with other sensors for H_2S determination.

Sensor device	Response time	LOD (ppb)	Matrix	Chemosensor	Ref
Gas detector tube + A4 size optical scanner	60 min	19	Wind tunnel	Commercial dyes	[32]
Microchannel scrubber + microfluorescence detector	30 min	1	Standard gas	FMA	[31]
Membrane-based diffusion scrubber	2 min	0.1	Standard gas	FMA	[2]
Colorimetric sensor		50	Standard gas	Commercial dyes	[39]
Gas detector tube	30 min		Standard gas	Commercial dyes	[40]
Filter paper based sensor	15 min	2	Standard gas	bis (2-aminobenzoic) palladium (II)	This work

Table 2. Analytical-figures-of-merit obtained for the hydrogen sulfide gas sensing system.

Value	Value
Analytical curve	$\Delta FI = 2.78 (\pm 0.05) [H_2S] + 2.50 (\pm 2.17)$
Linear range	8 – 110 ppb
LOD	2 ppb
LOQ	8 ppb
RSD	7,4 %
Sampling time	15 min
Sampling flow	200 mL min^{-1}

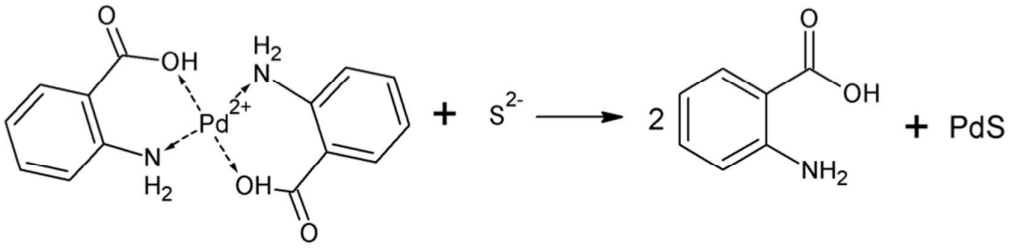


Figure 1. Reaction of sulfide with the palladium complex.

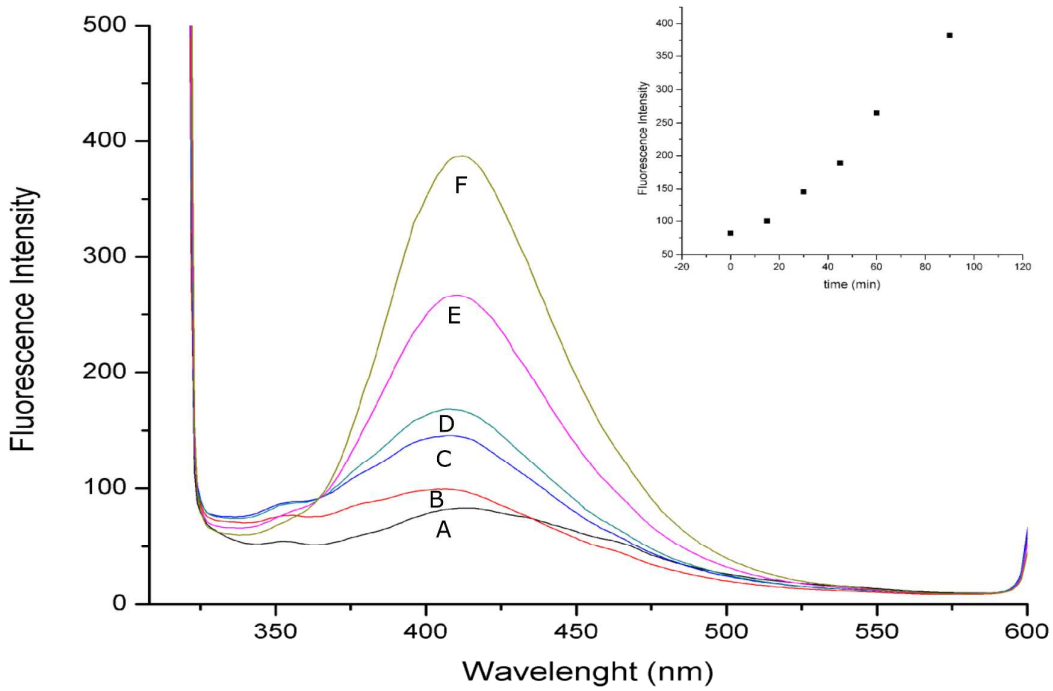


Figure 2. Emission spectra of bis-(2-aminobenzoate) palladium (II) after exposure to 33 ppb H_2S for different sampling times. Inset: The fluorescence intensity at 410 nm as a function of the sampling time. Gas flow rate: 500 mL min^{-1}. (A) Blank; (B) 15 min; (C) 30 min; (D) 45 min; (E) 75 min; (F) 105 min

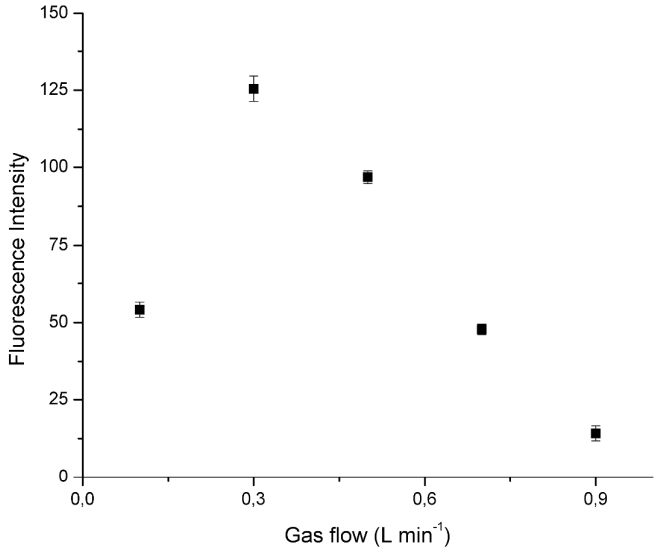


Figure 3. Effect of the sampling gas flow rate (air contaminated with 33 ppb H_2S) on the fluorescence (338/410) of the sensor.

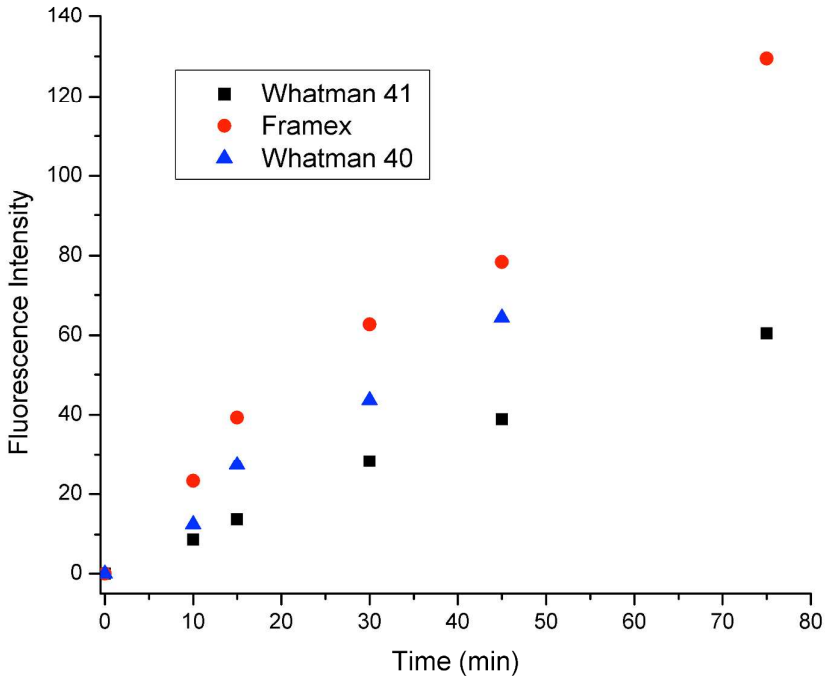
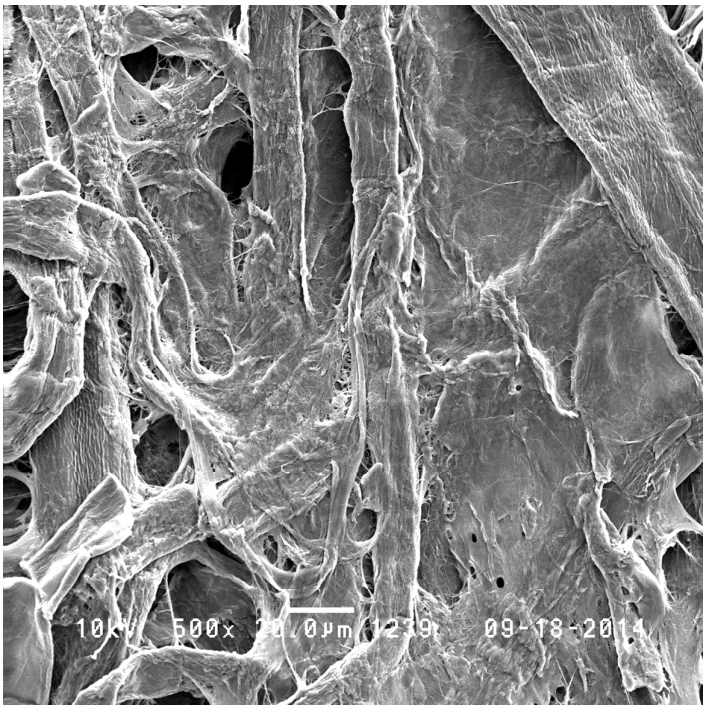


Figure 4. Evaluation of the filter paper type on H_2S sampling.

5a



5b

5c

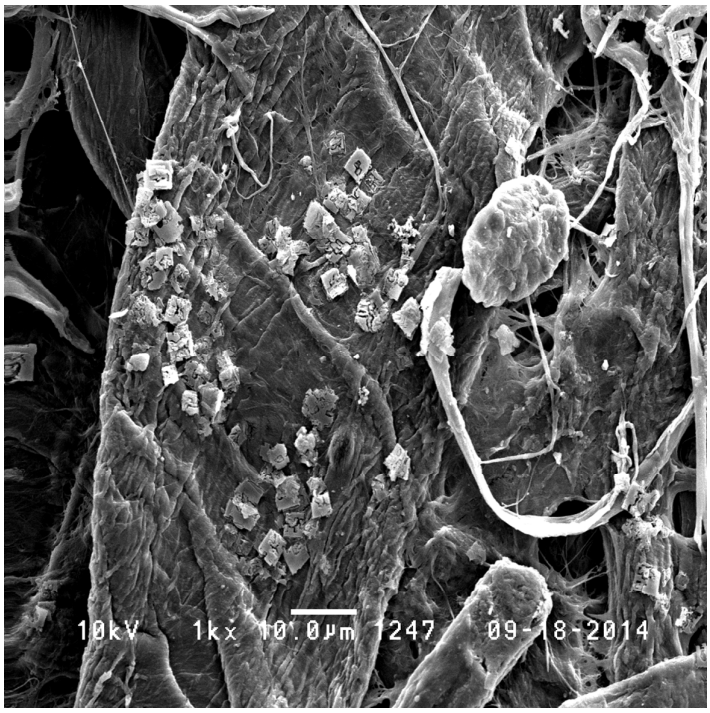


Figure 5. SEM images of the filter paper (5a), filter paper impregnated with PdA_2 (5b) and filter paper after reaction with H_2S (5c).