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Contents

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A ppb Formaldehyde Gas Sensor for Fast Indoor Air Quality Measurements

Hélène PAOLACCI, Romain DAGNELIE, Dominique PORTERAT, François PIUZZI, Fabien LEPETIT, Thu-Hoa TRAN-THI

CEA-Saclay, DSM/DRECAM/SPAM and Laboratoire Francis Perrin URA 2453
91191 Gif-sur-Yvette Cedex, France
E-mail: thu-hoa.tran-thi@cea.fr

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Abstract: The development of a very sensitive and selective chemical sensor of formaldehyde is presented. We describe the strategies aimed at improving the trapping and detection of formaldehyde. These strategies are based on the use of nanoporous transparent matrices elaborated via the sol-gel process and doped with a colorimetric reagent, and on a fast detection of the absorption or fluorescence of the reaction product. The properties of the sensor are studied as a function of various parameters such as the concentration of the colorimetric agent, the formaldehyde content in the gas mixtures, the presence of other air contaminants and the mixture relative humidity (0-50%). From these studies, calibration curves have been established, which allow the determination of formaldehyde content in air with a fast response time and a sub-ppb sensitivity. We also show a home-made portable and miniaturized detection system developed for this purpose. *Copyright © 2007 IFSA.*

Keywords: Formaldehyde, Fluoral-P, Nanoporous matrices, Sol-gel, Fluorescence

1. Introduction

Formaldehyde (CH_2O) is one of the well-identified volatile chemical contaminants responsible for indoor pollution and "building sick" syndrome disease and was recently classified as carcinogenic [1]. Its most significant use in the home is as an adhesive resin in pressed wood products and urea-formol foams for isolation [2], the latter being regulated for its emission [3]. There is currently no regulation for air quality but only recommendations by the World Health Organization (WHO) and the Agency for Toxic Substance and Disease Registry (ATSDR) for a limit of 80 ppb over 30 minutes exposure [4] or 8 ppb for a chronic exposure [5], respectively.

During the last decade, the increase of the awareness of the importance of indoor air quality and its potential impact on human health has stimulated an interest in formaldehyde detection. Because of its low absorption coefficient in the UV, formaldehyde cannot be directly detected at ppb concentrations unless via techniques involving long distance probing such as differential optical absorption spectroscopy (DOAS) [6]. Other methods are now commercially available such as gas chromatography combined with a methanation process [7] or the Hantzsch method involving the bubling of the contaminated air in a liquid reactant [8]. However, these sensors have a few drawbacks in terms either of simplicity of the sampling, heavy maintenance, high cost and high cost of the consumables. More recently, new low cost systems have been proposed. Suzuki et al. [9] and Kawamura et al. [10] have developed a portable formaldehyde sensor based on colorimetric methods and reflectance measurements. In the first case, with the detection of a lutidine derivative, a reaction product of an enaminone with CH_2O, the authors obtained a detection of 50 ppb after a 5 minute test. With a new reagent, 4-amino hydrazine-5-mercapto-1,2,4-triazole, Kamamura et al. obtained a better detection limit of 40 ppb with a sampling time of 3 minutes [10].

In the present work, we will describe strategies aimed at improving the trapping and detection of formaldehyde which allow us to detect ppb concentrations. These strategies are based on the use of nanoporous transparent matrices doped with colorimetric reagents and optical methods of transduction, absorption and, in particular, fluorescence.

2. Experimental Section

2.1 Chemicals

Fluoral P or 4-amino-3-penten-2-one (98% pure) was purchased from TCI and used as such. Ethanol of Uvasol grade is from Merck and tetramethoxysilane from Aldrich. Water is purified with the Elix 3 and Milli-Q systems of Millipore to a resistivity of 18.2 $M\Omega.cm^{-1}$. Supelco cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) purchased from Aldrich were used to check the formaldehyde purity and concentration at various points of dilution in the dilution line. The DNPH cartridges were eluted with acetonitrile and analysed via HPLC coupled with MS. Nitrogen gas from Messer are of 6.0 purity grade.

2.2 Elaboration of the Doped Thin Films

Nanoporous thin films of inorganic polymers $(SiO_2)_n$, deposited on a quartz substrate, were prepared via the Sol-Gel method using as precursor tetramethoxysilane as described elsewhere [11]. Briefly, 0.1 g of Fluoral-P was dissolved in 1 mL of ethanol and the solution was sonicated during 5 minutes. 0.65 mL of TMOS and 0.32 mL of water are then added. The overall mixture is sonicated during 15 minutes and then kept in the dark for aging during 3 hours. The films are dip-coated at a constant rate (25 $mm.min^{-1}$). The temperature ranges from 19 to 25 °C and the relative humidity was kept between 20-30%.

The film thickness was measured via profilometry with a Sloan Dektat 3030ST.

Generation of Calibrated Mixtures of Nitrogen and CH_2O

The standard CH_2O gas was generated continuously by purging a diffusion tube containing the solid CH_2O trimmer, paraformaldehyde, with a constant flow of nitrogen (125 $mL.min^{-1}$). The diffusion tube

from Calibrage is maintained at 90±1°C, in a temperature regulated oven. The gas concentration was calculated from the flow rate and mass loss of paraformaldehyde. With the Supelco cartridges, we check the purity of the formaldehyde originated from the diffusion tube and found the presence of acetaldehyde (13±2), acetone (5.5±1.5) and propionaldehyde (5.8±1.2 weight %). With a two stage dilution system equipped with four flow meters, it is possible to vary the CH_2O concentration over a wide range of concentration from 150 ppt to 5 ppm. A diffusion tube containing liquid acetaldehyde from Calibrage was also used to generate gaseous mixtures with low content of acetaldehyde (80 and 900 ppb). Humidified CH_2O mixtures were prepared by injection of water vapor coming from a Bronkhorst controlled evaporator mixer, equipped with a temperature controlled oven. Values of the fluxes were currently checked with a flux meter Gilian calibrator and the humidity of the gas mixture with a Testo 605-H stick.

2.3 UV-Visible Spectroscopy

The samples were placed in a quartz flow cell equipped with gas entrance and exit. The housing of the flow cell displays three optical windows with optical fibre connections for excitation and detection purposes (see Fig. 1). The UV-visible absorption spectra and the fluorescence spectra of the doped films were recorded over the 190-600 nm wavelength range with an Ocean-Optics spectrometer QE65000. For fluorescence measurements, the excitation source is a light emitting diode LED405-02V from Roithner-Laser. The fluorescence signal was filtered with a high band pass filter GG 445 from MTO.

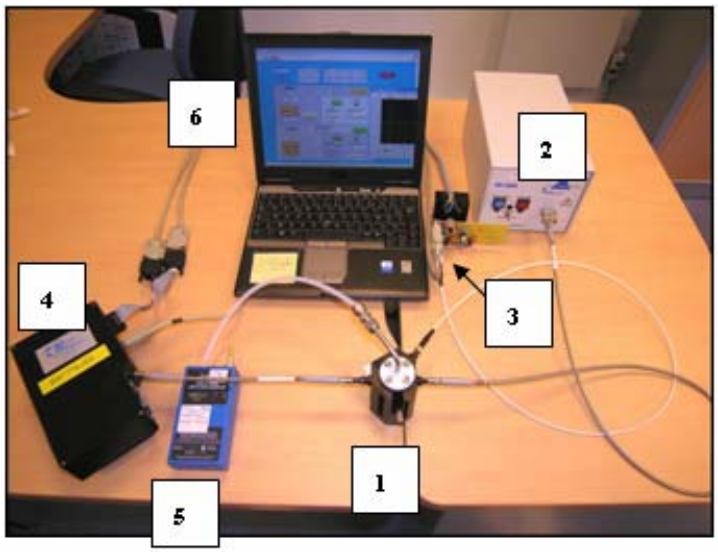

Fig. 1. Home-build detection system composed of: (1) a cuvette holder with a quartz flow cell, (2) UV-visible lamp, (3) LED 405 nm, (4) spectrometer QE65000, (5) micro pump, (6) laptop.

3. Results and Discussion

3.1 Properties of the Films

The sol containing TMOS, ethanol, water and Fluoral-P was left to maturation over 3 hours during which the viscosity of the sol increases. The quartz substrates (15*8*1 mm), dipped into the sol at various intervals of time, were coated with a thin film of inorganic polymer doped with Fluoral-P. For

each sample, the absorption spectrum was collected and the thickness of the film determined. The variation of Fluoral-P absorbance as a function of the maturation time of the sol, is shown in Fig. 2, witnesses the fast increase of the sol viscosity within a short period (65 minutes) after 180 minutes of maturation. This short period precludes the transition of the sol to a gel. As the substrates were dip-coated at the same speed, the film thickness increased with the increasing viscosity of the sol. A linear correlation was found between the Fluoral-P absorbance and the film thickness.

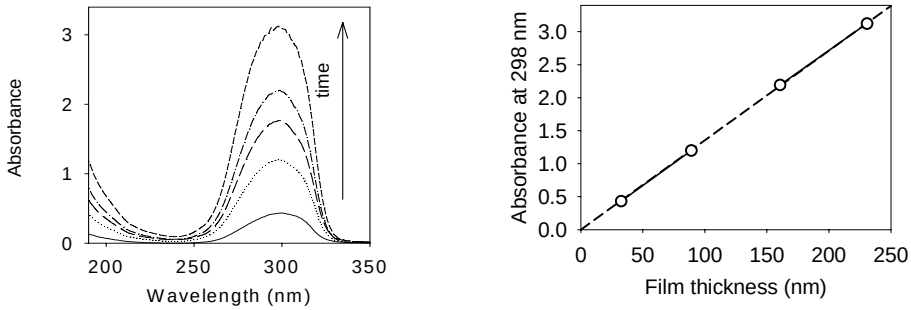

Fig. 2. Variation of the absorbance of the thin film doped with Fluoral-P as a function of the maturation time of the sol, respectively 180, 220, 230, 240 and 245 minutes (left) and thickness of the thin film (right). The absorption coefficient of Fluoral-P at 298 nm is 16800±900 $mol.^{-1}.L.cm^{-1}$.

3.2 Detection of Formaldehyde: Principle

The detection of formaldehyde is based on the well-known reaction of Fluoral-P which condenses in aqueous solution with formaldehyde to give 3,5-diacetyl-1,4-dihydrolutidine (DDL) [8] (see Fig. 3).

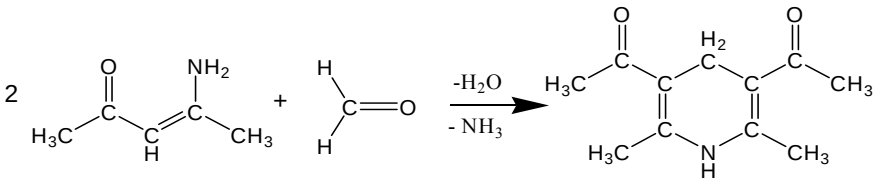

Fig. 3. Schematic representation of the reaction of Fluoral-P with formaldehyde, which leads to the formation of 3,5-diacetyl-1,4-dihydrolutidine.

DDL displays two absorption bands over 200-480 nm peaking at 255 and 416 nm. Although the extinction coefficient of DDL (ε(412 nm) = 8000±500 and ε(405 nm) = 6900 $M^{-1}cm^{-1}$ in water and methanol [12], respectively) is low compared to that of Fluoral-P (16800±900 $M^{-1}cm^{-1}$ in ethanol), the position of DDL lowest transition is far shifted to the red (see Fig. 4) over a wavelength domain where the reactants do not absorb. Moreover, DDL fluoresces while the reactants do not.

In the porous matrix, the absorption and fluorescence spectra of DDL are comparable to those of DDL in ethanol.

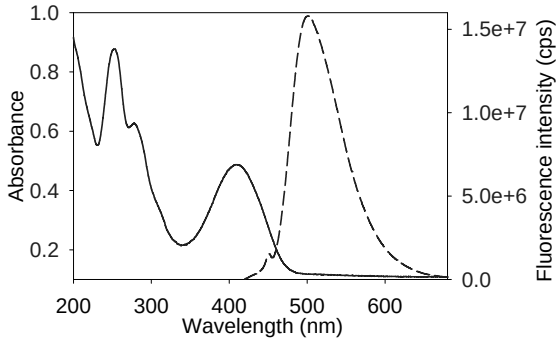

Fig. 4. Absorption and fluorescence spectra of 3,5-diacetyl-1,4-dihydrolutidine in the porous matrix.

3.3 Exposure of the Doped Films to Calibrated Mixtures of CH_2O in Nitrogen

Typical spectral variations observed upon exposure of a nanoporous thin film doped with Fluoral-P to formaldehyde are shown in Fig. 5. The pollutant is trapped in the pores of the matrix, a confined medium which favours the reactivity between the two reactants. The intensity of the absorption band of Fluoral-P decreases on behalf of the appearance of two new bands peaking at 255 and 410 nm, which can be attributed to the 3,5-diacetyl-1,4-dihydrolutidine electronic transitions. The fluorescence intensity of DDL, excited at 405 nm, was collected in parallel with one minute delay.

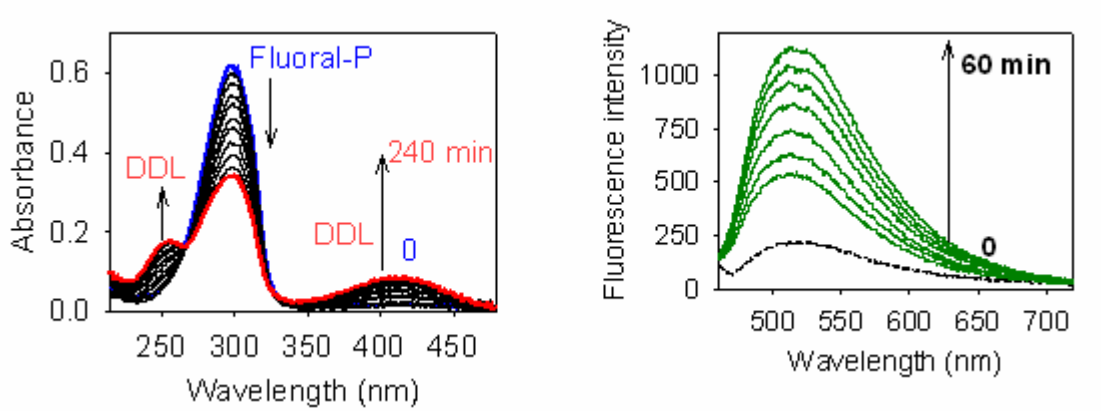

Fig.5: Left: Spectral evolution observed upon exposure of a thin film doped with Fluoral-P to a mixture of N_2 containing CH_2O (15 ppb). Flux: 220 mL.min^{-1}, relative humidity: 0%. Right: Evolution of the fluorescence band of DDL excited at 405 nm with the LED. The fluorescence intensity is expressed in number of counts collected after 5 minutes of irradiation.

All the experimental curves of the kinetics of appearance of 3,5-diacetyl-1,4-dihydrolutidine (DDL), recorded for the films, could be fitted with an exponential rise with a plateau. Because of the high concentration of Fluoral-P in the films as compared to that of CH_2O in the gas stream which continuously flushes the film, the reaction of CH_2O with Fluoral-P should obey to a pseudo-first order kinetics. DDL concentration varies with time as:

$$[DDL] = a\left(1-\exp^{-bt}\right), \tag{1}$$

where *a* is a constant which corresponds to the concentration of DDL at the plateau when the Fluoral-P is totally consumed, and *b*, is proportional to the rate constant of the reaction between Fluoral-P and CH_2O.

With the detection of DDL via fluorescence measurements, it is possible to detect sub-ppb concentrations of formaldehyde as shown in Fig. 6. In this case, the integrated fluorescence area is plotted as a function of time and "a" corresponds to its value at the plateau.

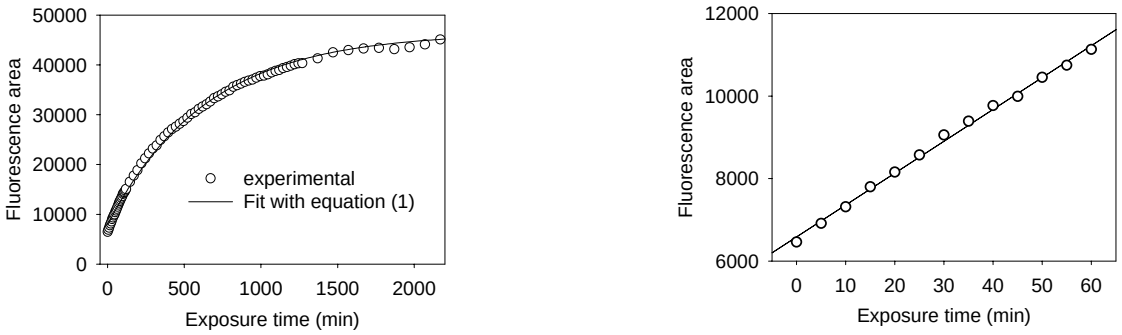

Fig.6. Left: Kinetics of formation of DDL obtained from fluorescence measurements.The film doped with Fluoral-P (absorbance at 298 nm = 2.0±0.1) was exposed to a gas mixture containing 400 ppt of formaldehyde (Flux= 220 mL.min^{-1}) until the complete consumption of Fluoral-P. Right: Zoom on the kinetics at early time and determination of the corresponding rate of reaction (slope).

The rate of formation of DDL, equal to *a*b*, can also be determined from the slope of the curve. As both *a* and *b* depend on the concentration of Fluoral-P in the film and on the concentration of formaldehyde in the gas mixture, the calibration curves were established with thin films doped with various amount of Fluoral-P (absorbance at 298 nm = 0.9-2.0) (see Fig. 7). These calibration curves correspond to the plot of the rate of formation of DDL as a function of the CH_2O content in the gas mixture. They are shown for two given relative humidity of the gas mixture.

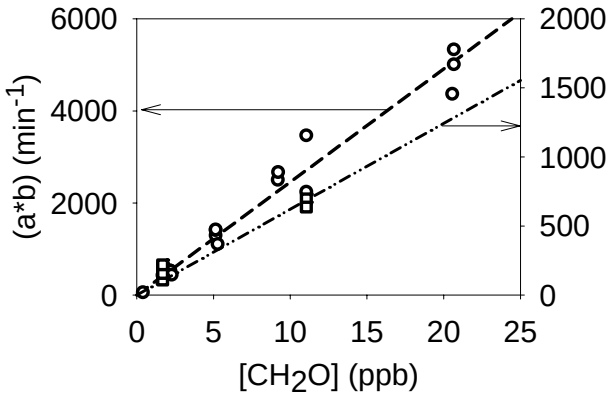

Fig. 7. Calibration curves for the quantitative determination of formaldehyde.
Relative humidity: left = 0, right= 45%.

Preliminary studies on the potential interference of the indoor air pollutants have shown that other aldehydes (acetaldehyde, benzaldehyde) and carbonylated compounds (acetone), present at few tens of

ppb, do not interfere and that the main interference only comes from water. Fig. 8 displays the variation of (a*b) as a function of the relative humidity. It can be noted that, even when the content of formaldehyde in the humidified gas mixtures is very low (2 ppb), DDL remains detectable up to 50% of relative humidity.

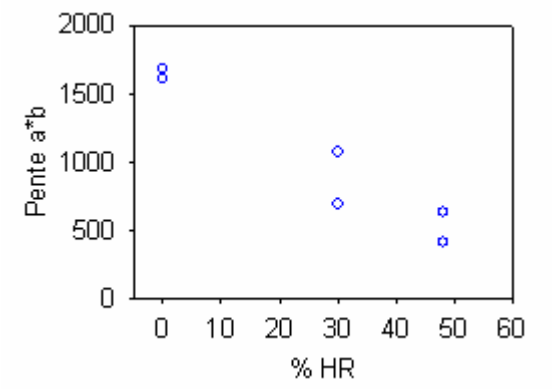

Fig.8: Variation of 'a*b' with the relative humidity of the gas mixtures. The content of formaldehyde was kept equal to 2 ppb and the flux was 220 mL.min^{-1}.

4. Conclusion

With the present work, we have shown the high potentiality of chemical sensors composed of inorganic porous matrices doped with a colorimetric agent, Fluoral-P, for the detection of low level of formaldehyde concentration in the ppb range. The response time of the sensor is fast: 400ppt and 10 ppb of formaldehyde can be detected within 30 and 10 minutes, respectively, in dry atmosphere. There is still a need to improve the response of the sensor to formaldehyde at high humidity (> 50%). Work is in progress to achieve these goals.

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