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Hongyan Yuan^a; Lianzhi Lin^a; Sheng-e Wang^a; Dan Xiao^a; Martin M. F. Choi^b; Wing Hong Chan^b

^a College of Chemical Engineering, Sichuan University, Chengdu, People's Republic of China ^b

Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong SAR, People's Republic of China

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A Simple Fluorophotometer for Airborne Formaldehyde Determination

Hongyan Yuan, Lianzhi Lin,[†] Sheng-e Wang,[†] and Dan Xiao

College of Chemical Engineering, Sichuan University, Chengdu,
People's Republic of China

Martin M. F. Choi and Wing Hong Chan

Department of Chemistry, Hong Kong Baptist University,
Kowloon Tong, Hong Kong SAR, People's Republic of China

Abstract: A novel, simple, and small synchronous fluorescence and absorbance device in conjunction with a homemade passive gas sampler for the determination of formaldehyde in ambient air is described. A purple-blue light LED is used as light source, and two perpendicular photoresistors are applied to measure absorbance and fluorescence, respectively. An absorbing reagent, which consisted of a 2,4-pentanedione, ammonium acetate, and acetic acid solution, is enclosed in the sampler and used to collect and react with airborne formaldehyde. The reaction product, yellow 3,5-diacetyl-1, 4-dihydropyridine, is then detected by the synchronous fluorescence and absorbance detectors. The light intensity is inversely proportional to the resistance of the photoresistor. The proposed device has been successfully applied to the determination of formaldehyde at various sites.

Keywords: Absorbance, Air, Fluorescence, Formaldehyde, Light-emitting diode, Photo resistor, Synchronous detector, Sampling

[†]On leave from Hunan University

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Address correspondence to Dan Xiao, College of Chemical Engineering, Sichuan University, Chengdu 610065, People's Republic of China. Tel.:86-28-85407958; E-mail: xiaodan99@sohu.com

INTRODUCTION

Formaldehyde is a main environmental pollutant that irritates the eyes and upper respiratory tract and causes headache, nausea, drowsiness, and allergic skin reactions.^[1] It is also suspected to be a human carcinogen.^[2] Formaldehyde as a ubiquitous airborne contaminant in the environment mainly originates from the manufacturing processes,^[3] of such products as particle-board, plywood, and urea-formaldehyde foam insulation. In addition, cigarette smoke, motor vehicles, and some other combustion sources^[4] generate formaldehyde. Although commercialized formaldehyde detectors have been sold, a device characterized by convenience, simplicity, and low-cost is still imperative.

To date, various sampling and analysis techniques have been developed for formaldehyde detection, and they are generally categorized as colorimetric, polarographic, gas and liquid chromatographic (GC and HPLC) methods. Airborne formaldehyde is usually collected by an active sampler^[5] using either a pump and bubbler or a passive sampler with impregnated filter or solid sorbent.^[6,7] The collected sample is then returned to the laboratory for further analysis. Chromatographic methods^[8–12] with a fluorescence detector or an absorbance detector are widely used because of their ability to separate the formaldehyde derivatives from other possible interferents and low detection limits. Chan et al.^[13,14] reported the application of Nafion-coated mercury film electrodes by differential-pulse voltammetry and differential-pulse polarography with Girard's Reagent T, which made available the direct quantification of formaldehyde in ambient air. The preparation and the lifetime of the mercury film electrode is time-consuming and cumbersome. Fluorometric^[15–17] and colorimetric methods have also been developed for formaldehyde detection. Fluorometric methods using the Hantzsch reaction, involving 2,4-pentanedione, have been much used for trace formaldehyde measurement. Colorimetric methods based on pararosaniline, enethylbenothia, zolinone hydrazone, chromotropic acid, and 2,4-pentanedione are also widely used. These colorimetric methods^[6] have been established as standard test methods for the measurement of formaldehyde in indoor air. In addition, Reche^[18] and Miksch et al.^[19] also reported the detection of formaldehyde by a spectrophotometer. Real-time measurement of formaldehyde is possible using some spectroscopic methods, but the required instrumentation is not readily portable; furthermore, detection based on either fluorometry or UV-absorptiometry is of relatively low sensitivity.

To our knowledge, fluorescence method has never been combined with the absorbance measurement for formaldehyde detection. This paper reports a homemade, portable, simple, low-cost photoelectric device for quantitative detection of formaldehyde. The detector can synchronously measure the fluorescence and absorbance value of a reaction product from formaldehyde and

Nash's reagent. A large-surface area passive sampler with 15-min sampling time is employed to collect the airborne formaldehyde. The proposed method is suitable for remote location measurements where a supply of electricity is not available. It has been applied to measure the concentration of airborne formaldehyde in various locations.

EXPERIMENTAL

Apparatus and Procedures

A schematic diagram of the detection device is shown in Fig. 1. The detector consists of a homemade dark box to hold a 1-cm cuvette. A commercially available light-emitting diode (LED) as an excitation light source was seated in one side of the dark box as a light source for both excitation and

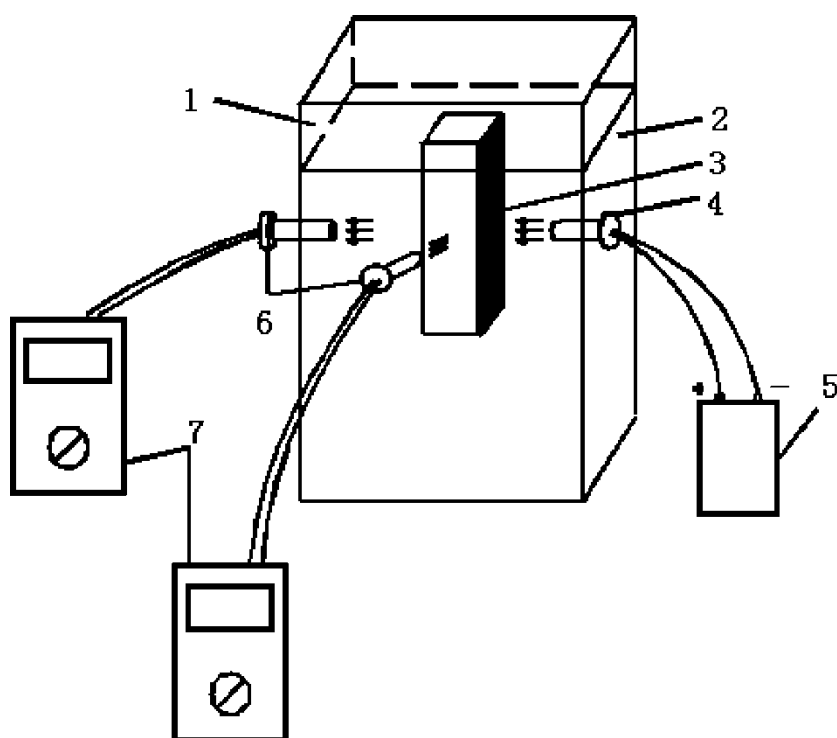


Figure 1. A schematic diagram of the synchronous device: (1) dark box cover, (2) dark box, (3) 1-cm quartz cell, (4) light-emitting diode (LED), (5) battery, (6) photoresistor, and (7) multimeter.

absorption. On the diametrically opposite side, the transmitted light is collected by one photoresistor (dark resistance 10 M Ω , commercially available) and converted to a digital signal by a digital multimeter. In the orthogonal position, fluorescence is collected by the other photoresistor and recorded by another multimeter. Three AA-size batteries were used as power source for the LED.

A homemade, handheld passive sampler^[20] was used to collect real formaldehyde samples at different sites. The sampler was fabricated with two porous polytetrafluoroethylene (PTFE) membranes to enclose a fixed volume of absorbing reagent for formaldehyde in a plastic body. Formaldehyde in ambient air is diffused through the porous PTFE membranes and reacts with the absorbing reagent. Hantzsch reaction was accelerated by heating 70–80°C, and the reaction time is 10 min. The special feature of this sampler is that its membrane has a very fast sampling rate and does not require external pump.

A TU-1901 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China) was used for the measurements of absorbance at 412 nm. Fluorescence was detected by a F-4500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) with excitation at 425 nm.

Reagent

2,4-Petanedione was obtained from Tianjin Reagent Plant (Tianjin Reagent Plant, Tianjin, China) and further purified by distillation before use. Ammonium acetate and acetic acid were from Kelong Reagent Plant (Chengdu, China). Nash reagent was prepared by dissolving 25 g of ammonium acetate in water, 3.0 mL of 70% acetic acid solution, and 0.2 mL of freshly distilled 2,4-pentanedione in water, and the resulting solution was made up to 100 mL with water. Formaldehyde solution (37.0–40.0%) was purchased from Chongqing Chemical Reagent Plant (Chongqing, China) and standardized by an iodometric method. All other chemicals were of analytical reagent grade. De-ionized water was used throughout the experiment.

RESULTS AND DISCUSSION

Sampler Performance

The proposed sampler with a surface-area of 39.25 cm² was used and compared with the performance of an active sampler,^[21] and their absorbance plots are shown respectively in Fig. 2. Within formaldehyde concentration range 0.1–2.0 μ g/mL, the results of the active sampler with flow rate of 400 mL/min had good linearity with the proposed sampler at room temperature and 1 atm. The sampling time of both samplers is only 15 min.

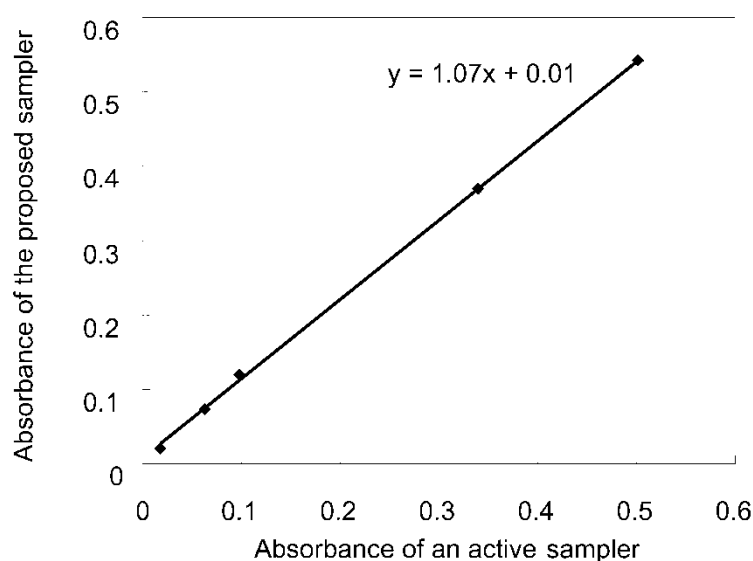


Figure 2. The plot of absorbance of the proposed sampler to absorbance of an active sampler.

The Characteristics of the LED

LED is a suitable light source for the device, and its emission band was obtained from a fluorescence spectrophotometer and is displayed in Fig. 3. The peak width at half peak height is only about 20 nm, and the maximum emission peak is at 412 nm, which agrees well with the peak absorption (412 nm) of the reaction product of formaldehyde and Nash reagent. Different working voltages at 3.0 V, 4.0 V, 4.5 V, and 5.0 V of the LED were tested. It was found that light source powered at 4.5 V had a better stability and low noise, which was used for both determination in fluorescence channel and absorption channel.

Calibration Characteristics

The relationship of resistances in the absorption channel and the fluorescence channel to formaldehyde concentration ($0.1\text{--}2.0\ \mu\text{g}\cdot\text{mL}^{-1}$) is shown in Fig. 4. Line b demonstrates that the absorbance response to formaldehyde concentration in the range $0.1\text{--}2.0\ \mu\text{g}/\text{mL}$ can be expressed by a linear fit equation $C = 7.5920 \log (R_t/R_0) - 0.0430$ with a square correlation

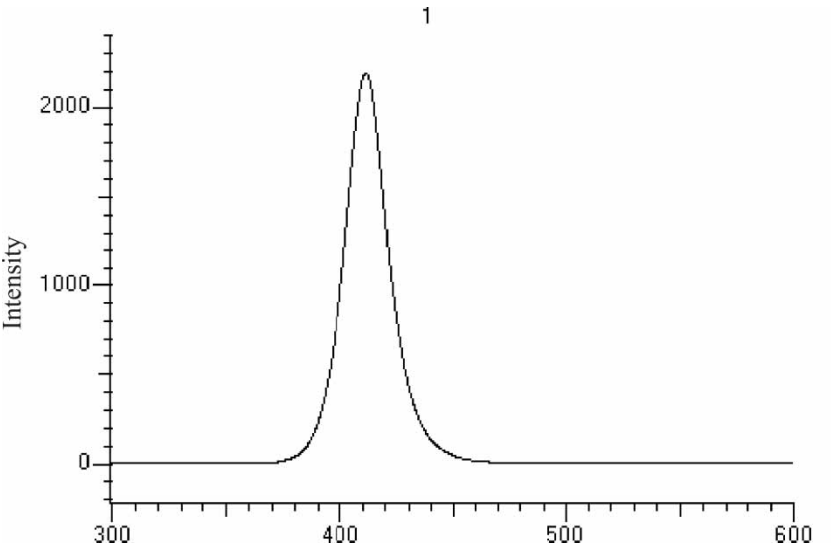


Figure 3. The emission spectrum of the LED: y-axis is intensity, and x-axis wavelength (nm).

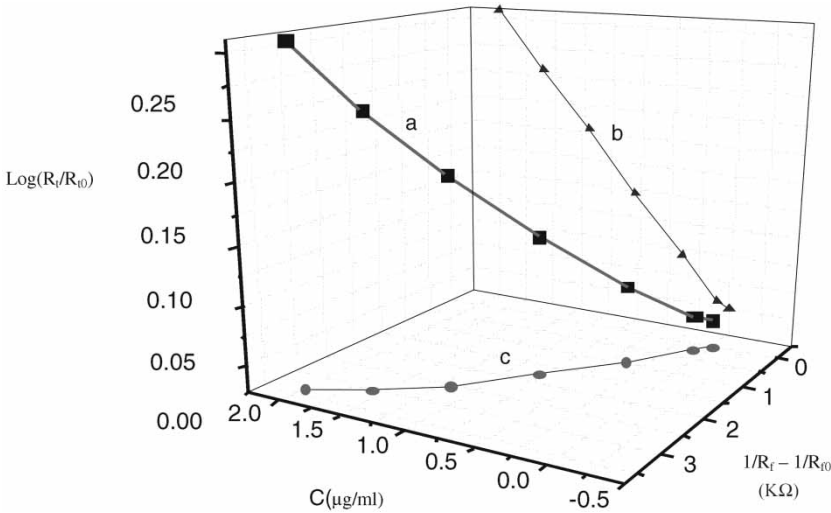


Figure 4. The response obtained at the absorption channel (line b) and fluorescence b channel (line c) against formaldehyde concentration. The linear fit curve for the synchronous method is line a.

coefficient (r^2) of 0.996, where C is the concentration of sample solution, R_t is the resistance of the photoresistor when a sample solution is put in the cuvette, and R_{t0} is the resistance of photoresistor when the blank solution used. The $\log(R_t/R_{t0})$ value increases with the increase in formaldehyde, which can be explained by the Lambert–Beer law as $A = \log I_0/I$, where I_0 and I are the intensity of transmitted light when blank and sample solutions are measured, respectively, and A is the absorbance value, which is proportional to the concentration of sample solution. Because the resistance of the photoresistor is inversely proportional to the intensity of transmitted light, the concentration of the sample solution is proportional to $\log(R_t/R_{t0})$. The results from the fluorescence channel for formaldehyde measurement is depicted as line c in Fig. 4. In the concentration range 0.1–2.0 $\mu\text{g/mL}$, the intensity of fluorescence is proportional to the concentration of formaldehyde. The resistance of photoresistor increases with decrease in the fluorescence intensity. Thus, the reciprocal of resistance of the photoresistor at fluorescence channel to formaldehyde showed good linearity in linear fit equation of $C = 0.5710(1/R_f - 1/R_{f0}) + 0.0920$, $r^2 = 0.983$, where R_f and R_{f0} are the resistance of the photoresistor when the sample solution and blank solution are measured, respectively. So the regression equation of the proposed synchronous method can be obtained according to the resistance of fluorescence and absorption channel. It describes as $C = 0.02245 + 5.7260 \log(R_t/R_{t0}) + 0.1260 (1/R_f - 1/R_{f0})$ ($r^2 = 0.999$) in line a. Some parameters of the synchronous methods were compared with those of the fluorometric and absorptiometric methods used individually, as shown in Table 1. Table 1 shows that the square of correlation coefficient ($r^2 = 0.999$) and the standard deviation (SD) (0.02) of the synchronous method are larger and much lower, respectively, than those for the fluorometric method ($r^2 = 0.983$, and $\text{SD} = 0.09$) and the absorptiometric method ($r^2 = 0.996$, and $\text{SD} = 0.04$). The results clearly indicate that a better correlation relationship was obtained in the synchronous method, and the SD was reduced to 0.02.

Table 1. Calibration characteristics of the three measuring systems

Method	Calibration equation	r^2	Standard deviation (SD)
Fluorometric method	$C = 0.5710(1/R_f - 1/R_{f0}) + 0.0920$	0.983	0.09
Absorptiometric method	$C = 7.5920 \log(R_t/R_{t0}) - 0.0430$	0.996	0.04
Synchronous method	$C = 0.0225 + 5.7260 \log(R_t/R_{t0}) + 0.1260 (1/R_f - 1/R_{f0})$	0.999	0.02

Table 2. Comparison of formaldehyde determination at various sampling sites when fluorometer, spectrometer, and the synchronous method were employed

Sampling sites	Method			$ S - F /F$ (%)	$ S - A /A$ (%)
	Fluorometric method (F) (mg/m ³)	Absorptio-metric method (A) (mg/m ³)	Synchronous method (S) (mg/m ³)		
1	0.2389	0.2486	0.2476	3.64	0.40
2	0.1046	0.1109	0.1080	3.25	2.62

Field Measurements

Table 2 displays the results from measurement at different sites by using UV-Vis spectrophotometer, fluorescence spectrophotometer, and synchronous device, respectively. The % error of the synchronous method compared with the results obtained with fluorescence spectrometer and spectrophotometer was less than 4%.

CONCLUSIONS

The current synchronous detector is a simple and effective method to obtain a reliable and fast analysis, and it is especially suitable for field analysis. The performance of synchronous detection may improve the selectivity of the detection, as the determination is done by both fluorescence and absorbance measurements.

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