Colorimetric pad for low-concentration formaldehyde monitoring in indoor air

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Received 25 September 2020
Revised 27 October 2020
Accepted 4 December 2020

Abstract

Purpose – The purpose of this study was to develop an accurate, selective, low-cost and user-friendly colorimetric pad to detect formaldehyde at low concentration.

Design/methodology/approach – 1-phenyl-1,3-butanedione, a reactive chemical, was selected to develop the colorimetric pad for indoor air formaldehyde measurement. Silica nanoparticle impregnated with the reactive chemical was coated on the cellulose filter surface to increase the reactive site. A certified formaldehyde permeation tube was used to generate six varied concentrations between 0.01 and 0.10 ppm in a test chamber. The color intensity on the pads was measured using an image processing program to produce a formaldehyde concentration reading chart. The colorimetric pad was tested for optimum reaction time, accuracy, precision, stability, selectivity and shelf life.

Findings – The color of the pads changed from white to yellow and the color intensity varied with the concentrations and appeared to be stable after exposure to formaldehyde for 8 hours. At room temperature, the stability of the pad was 7 days, and shelf life was 120 days. The accuracy, precision and bias of the pad were 12.38%, 0.032 and 6.0%, respectively. Carbonyl compounds, benzene and toluene did not interfere with the reading of this developed colorimetric pad.

Originality/value – The developed colorimetric pad meets NIOSH's criteria for an overall accuracy of ±25%, bias = 10%. They were accurate at low concentrations, user-friendly and had low cost compared to an electronic direct reading instrument (cost of chemicals and materials was 21.50 Bath or 0.69 USD per piece) so that favorable for the use of general people for health protection.

Keywords Formaldehyde, Colorimetric, Silica nanoparticle, Digital image analysis, Paper-based analytical device

Paper type Research paper

Introduction

Formaldehyde has been classified as a carcinogen to humans by the International Agency for Research on Cancer in 2012 [1]. It has been used as raw materials for many products, e.g. urea-formaldehyde resin, that is used for adhesive in manufacturing of plywood, particleboard and fiberboard. Thus, several new construction and decoration materials could emit formaldehyde that accumulates in a poor ventilated occupancy space to harmful

Journal of Health Research
Vol. 36 No. 4, 2022
pp. 781-790
Emerald Publishing Limited
e-ISSN: 2586-940X
p-ISSN: 0857-4421
DOI 10.1108/JHR-09-2020-0428

concentrations. Young, elderly and ill people comprise the at-risk group [2] because chronic exposure has been associated with an increased risk of developing respiratory symptoms and cancer [3]. At high concentration from 0.5 to 2 ppm, formaldehyde causes severe adverse effects, e.g. discomfort, irritation of the eyes and upper airways, sneezing, coughing, nausea and death [4].

Indoor formaldehyde concentrations are likely to be higher than those outdoor due to several potential sources, e.g. insulation, particle board, plywood and limited ventilation [5]. Most people spend approximately 90% of their time indoor, meaning people could be exposed to formaldehyde from off-gassing of these indoor sources [6]. Knowing the formaldehyde concentration in a room could lead to appropriate actions to reduce the exposure, e.g. purging, bake-out or ventilating.

Several techniques are available to measure formaldehyde concentrations, e.g. taking air samples using sorbent tubes to analyze in a laboratory [7] or using electronic direct reading devices [8]. Although these methods are accurate and sensitive, they are also complicated, time consuming and expensive; thus, limiting their use in the home or office by general population, especially among those who are not specialized in air sampling and measurements. In such cases, a colorimetric method would be the most preferred option.

Many studies have been conducted to develop colorimeters for formaldehyde measurement employing various reagents, i.e. chromotropic acid [9–11], pararosaniline [12, 13], 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) [14], 3-methyl-2-benzothiazolinone hydrazine (MBTH) [15], flouoral-p [16, 17] and 1-phenyl-1,3-butanedione [18]. In these studies, some drawbacks were encountered such as poor sensitivity and specificity, low stability, interferences and difficulty in the method, e.g. requires heat and chemicals to complete the reaction and needs to use a spectrophotometer to read the formaldehyde concentration. However, among these reagents, 1-phenyl-1,3-butanedione coated on porous glass indicated some beneficial properties, i.e. one-step reaction, dry process, no interferences, sensitive and a clearly visible color change [18]. Nevertheless, the reaction duration was quite long, 24 h after being exposed to formaldehyde.

The objective of this study was to develop an accurate, selective, low-cost and user-friendly colorimetric pad for general application in the measurement of indoor air formaldehyde. The World Health Organization's indoor air guidelines for formaldehyde have been set at 0.08 ppm to protect occupants from nasal cancer; however, NIOSH recommends a more rigorous occupational exposure standard of 0.016 ppm. Ideally, the developed colorimeter should be able to detect formaldehyde as low as 0.01 ppm within 8 h.

Materials and methods

Colorimetric pad

The colorimetric pad was composed of three components: substrate, media and reactive chemical. The reactive chemicals were prepared by mixing the following reagents at room temperature to obtain a homogeneous mixture according to Maruo *et al.* [18]: 0.1256 g 1-phenyl-1,3-butanedione and 0.6 g ammonium acetate (Sigma-Aldrich, St. Louis, MO, USA), 48 ml ethanol and 0.8 ml acetic acid (Merck, Darmstadt, Germany) and 8 ml de-ionized water (Milli-Q system, Millipore, Bedford, MA, USA).

The media comprised silica nanoparticles prepared by hydrolysis and condensation using the modified method reported by Rao *et al.* [19] Components included 1 ml tetraethyl orthosilicate (TEOS, 99%) (Fischer Scientific, Waltham, MA) in 22 ml ethanol (Merck, Darmstadt, Germany), 24 ml de-ionized water and 54 ml ammonium hydroxide (25% NH_3 in H_2O) (Merck, Darmstadt, Germany). The mixture was sonicated until the onset of turbidity that indicates the formation of silica nanoparticles. The nanoparticle was centrifuged and washed twice with ethanol and dried at 80 °C in an oven (Model LDO-100E, Labtech, Korea).

The average diameter of silica nanoparticle was 135.54 nm and the surface area measured by the BET (Brunauer–Emmett–Teller) method was 77.34 m^2/g.

The substrate, Whatman #1 cellulose filter (Merck, Darmstadt, Germany) was cut in 37 mm diameter circles and placed in a petri dish. Five millilitres of a solution of silica nanoparticles and the reactive chemicals were pipetted onto the substrate which was placed in a petri dish. After 1 h, the substrate was dried in an oven at 40 °C for 4 h, and then each of the pads was placed in a re-sealable plastic bag, sealed and stored in a desiccator until use.

Generation system for low formaldehyde concentrations

A certified permeation tube with the emission rate of 3 ng/min at 40 °C (Serial No. 62016, Part No. HRT-002.00-3024/40, Kin-Tek Laboratories, Inc., La Marque, Texas) was used for the continuous generation of formaldehyde at concentrations of 0.01, 0.02, 0.04, 0.06, 0.08 and 0.10 ppm. The permeation tube was submerged in a water bath controlled by PID-temperature controller (accuracy ± 0.5 °C) (Stuart, Model SWB15D). The calibrated mass flow controller (Bronkhorst, Mass Stream D-6311, Germany) was used to control flow rate of the dilution gas and nitrogen to obtain the expected formaldehyde concentrations in the test chamber (Figure 1).

Although this constitutes the gold standard of low concentration generation, the air in the test chamber was sampled and analyzed using the NIOSH method # 2016 to ensure the system worked well. The air in the test chamber was sampled for 8 h at a flow rate of 0.05 l/min.

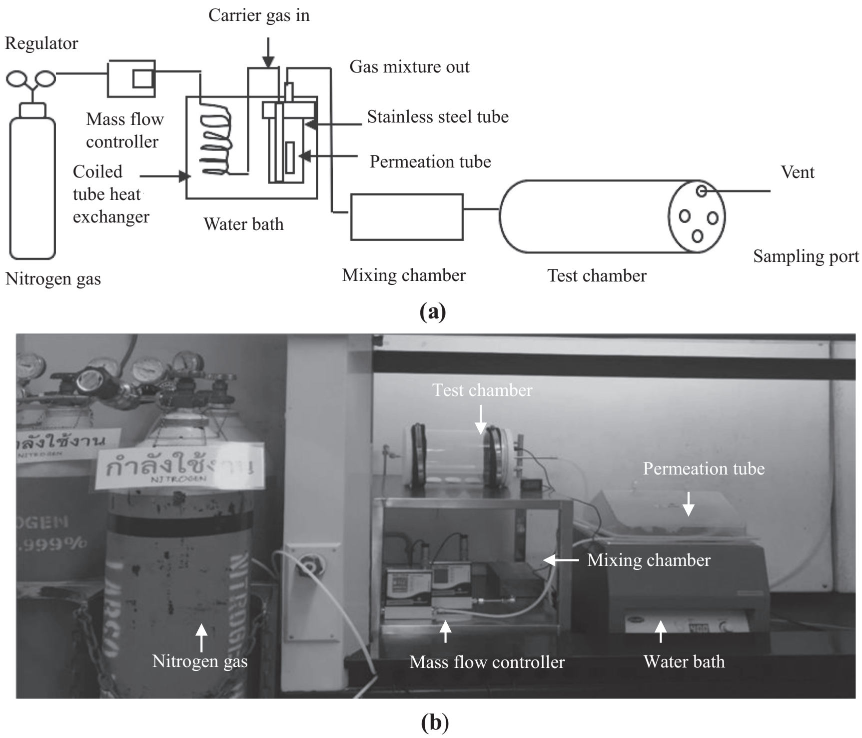


Figure 1. Schematic diagram (a) and picture (b) of the generation system for low formaldehyde concentrations and test chamber

Color intensity measurement

The color of the colorimetric pad changes from white to pale yellow when exposed to formaldehyde and the intensity of the yellow color increases as the concentration increase. Each exposed colorimetric pad was placed in the photography light-box to take a picture using a mobile phone (iPhone 6, Apple, USA model) and then analyzed by ImageJ [20]. The color intensity of a digital image presents as the average RGB (Red–Green–Blue) for which the values of each color vary from 0 to 255 (8 bits). To construct a concentration reading chart, RGB values were plotted against the formaldehyde concentrations generated in the chamber.

Colorimetric pad testing and evaluation

The colorimetric pad was tested in the test chamber at room temperature (24–26 °C) and humidity (61–69%RH) in a laboratory. The optimum reaction time (time required for the color to change from white to yellow and stabilize), accuracy, precision, bias, stability, selectivity and shelf life were evaluated. Six colorimetric pads were used for each test parameter at the specified concentrations.

Optimum reaction time

The six colorimetric pads were placed in the test chamber at each test concentration for 1, 2, 4, 6, 8, 12 and 24 h. At the end of each tested period, the color intensities of all six pads were measured using an image processing program. The color intensity values and the reaction time at each concentration were plotted. The optimum reaction time was the period for which the color intensity values were stable. This test period was used for the rest of the testing.

Accuracy, precision and bias

The accuracy, precision and bias were calculated using the equations: Accuracy ($\pm$%) = $(|Bi| + 2CV) \times 100$. The point of estimate and its 95% confidence limit should be within 25% [21].

Stability

The pads used for accuracy, precision and bias testing were sealed in a re-sealable plastic bag and stored at room temperature for the stability test. It was counted as Day 1 after color intensity measurement for the accuracy, precision and bias testing. They were analyzed for color intensity again on Day 7, 14 and 28. The color intensities were plotted against storage time to determine the stability of the pad.

Selectivity

Hydroxyl- and carbonyl- containing compounds, having similar chemical characteristics to formaldehyde, namely, ethanol, methanol, isoamyl alcohol, 2-butanol, 2-propanol and acetone, were tested for interferences in a static system. In addition, benzene and toluene, which are normally found in indoor atmosphere, were also tested. Interfering gases were individually generated by injecting 10 µl of the chemical in a 2-liter glass bottle. The concentration of ethanol, methanol, isoamyl alcohol, 2-butanol, 2-propanol, acetone, benzene and toluene was 2093, 3022, 1127, 1597, 1597, 1665, 1376 and 1150 ppm, respectively. The glass bottle was cleaned after each test. After placing three pads in the test unit, and allowing them stand for 8 h at room temperature, the color intensity on the pads was observed and measured using the same method as the ones exposed to formaldehyde.

Shelf life

A total of 180 fresh colorimetric pads were placed in sealed plastic bags, six pads in each bag and stored in a desiccator at room temperature. Six pads were exposed to formaldehyde at each concentration of 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 ppm in the test chamber after having been stored for 30, 60, 90, 120 and 150 days. The pads were considered to be expired when the average reading reached over ±25% true concentrations [21].

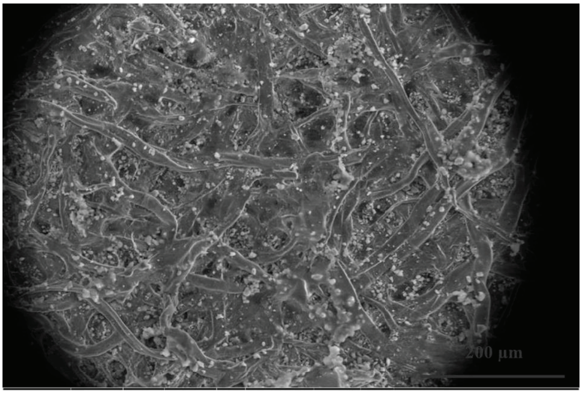
Results

The colorimetric pad

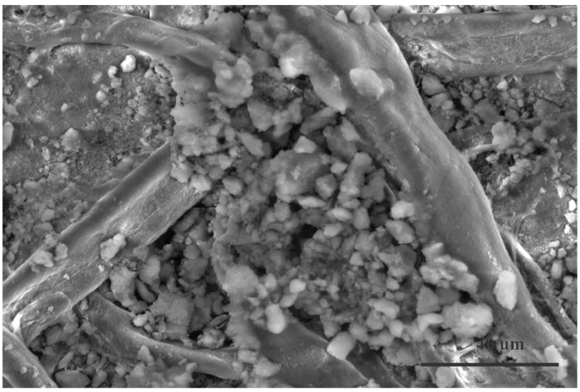
The dimensions of the colorimetric pad were 37 mm in diameter (surface area 0.001075 m^2) with a thickness of 0.011 mm. Approximately 0.02512 gm of nanoparticle was coated on it which comprised 1.942781 m^2 surface area of the reactive chemical impregnated on silica nanoparticle (Figure 2). Thus, reactive chemicals on the colorimetric pad could acquire about 2000 times larger surface area than that on the substrate itself.

Test chamber

The dilution gas flow rates were set at 22.4, 28.0, 37.3, 56, 111.9 and 223.8 ml/min to generate formaldehyde concentrations at 0.01, 0.02, 0.04, 0.06, 0.08 and 0.10 ppm respectively, according to the manufacturing equation. No significant difference was observed between the



500 x
(a)



2390 x
(b)

Figure 2.
(a) and (b) SEM images of silica nanoparticles on colorimetric pad at 500x and 2390x

above calculated concentrations and those obtained from air sampling using the NIOSH method #2016. Then, the calculated concentrations were used to plot against the color intensity for the concentration reading chart and for entire experiments.

Colorimetric pad testing and evaluation
The colorimetric pads were tested for optimum reaction time and evaluated for accuracy, precision and bias in the test chamber at six concentrations, namely 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1 ppm.

Optimum reaction time
The color of the pads changed from white to pale yellow at all studied concentrations and reached a constant intensity value after 8 h of exposure (Figure 3). Thus, 8 h was chosen as the optimum reaction time and used for further experiments.

The color intensities, in term of Red-Green-Blue (RGB) of the pad at six concentrations, were recorded and are shown in Figure 4.

The intensity of the blue color obviously decreased while those of the red and green color are slightly increase resulting in darker of yellow color on the colorimetric pad (Red + Green = Yellow). The decreasing of blue and increasing of yellow (Red + Green) are related to the formaldehyde concentrations; however, the decreasing of the blue has better correlation. Thus, the blue intensity was used to determine formaldehyde concentrations. The fitted linear regression model was: $y = -471.87x + 158.7$ with $R^2 = 0.9967$, when x represents the blue intensity and y represents formaldehyde concentrations (Figure 5).

Accuracy, precision and bias
The evaluation of the accuracy, precision and bias was presented in Table 1 and all met the NIOSH criterion [21].

Stability
The mean colorimetric pad reading after Day 7 of formaldehyde exposure was within 10% of the mean reading of Day 1, and the accuracy was out of the acceptable range after 7-day storage, and reached 20% after 28 days. Thus, the stability of the colorimetric pad was 7 days, which is considered to meet the stability requirement of NIOSH's recommendation [21].

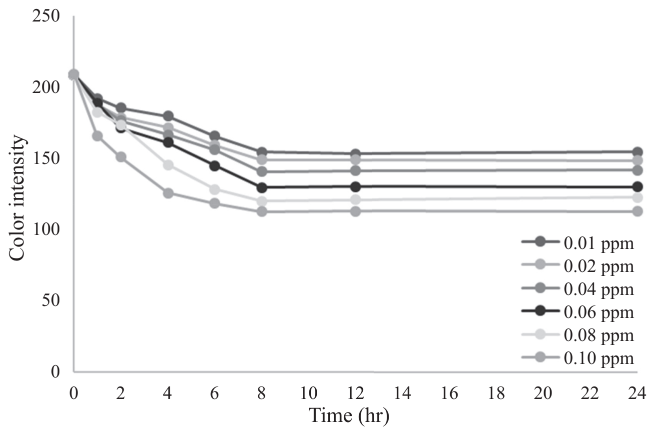


Figure 3.
Color intensity and test duration obtained from each concentration

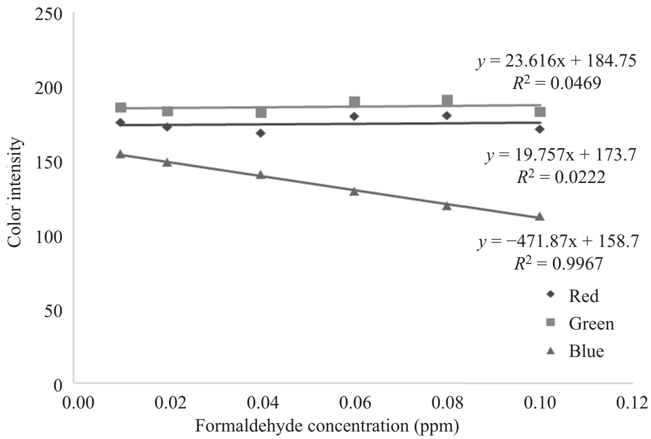


Figure 4. Color intensity and test duration obtained from each concentration

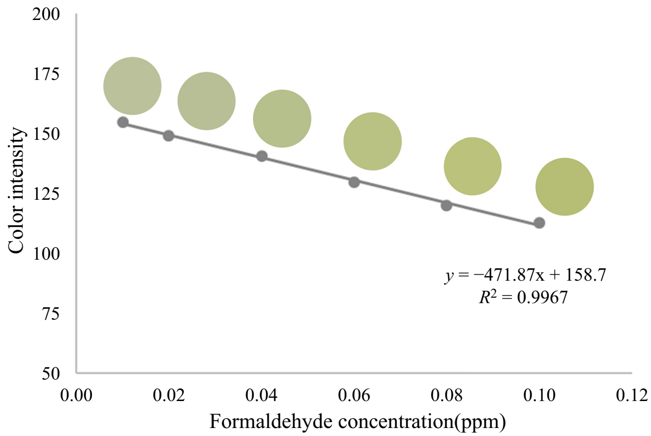


Figure 5. Formaldehyde concentration reading or color chart

Mean concentration in test chamber (ppm)	Mean concentration obtained from the color chart (ppm)	Bias	Sd	Precision	% Overall accuracy
0.011	0.010 (0.0004)	0.103	0.034	0.038	17.918
0.021	0.021 (0.0004)	0.029	0.019	0.020	6.929
0.045	0.042 (0.0015)	0.077	0.033	0.036	14.938
0.068	0.064 (0.0022)	0.068	0.033	0.035	13.812
0.091	0.086 (0.0028)	0.052	0.031	0.032	11.612
0.106	0.105 (0.0033)	0.028	0.031	0.031	9.057
		0.060		0.032	12.378

Table 1. Accuracy precision and bias of colorimetric pad

Selectivity

After being exposed to the suspected interference chemicals for 8 h, the colorimetric pads still maintained the same color. Therefore, it was clearly demonstrated that the pad has good selectivity.

Shelf life

The overall accuracy of the colorimetric pads, which were stored for 30, 60, 90, 120 and 150 days before use, was 14.78%, 18.94%, 22.29%, 23.95% and 31.03%, respectively. The shelf life of the colorimetric pads was determined to be 120 days based on the decrease in accuracy below acceptable levels beyond this time frame.

Discussion

The application of developed colorimetric pads met our expectation and achieved the purpose of this study. They were accurate at low concentrations, user-friendly and had low cost based on materials and method used.

The use of silica nanoparticles increased the surface area of reactive chemicals significantly and allowed gas molecules to be adsorbed on the surface and trapped in the porous layer. This shortened the reaction time from 24 h to 8 h [18]. Although this remains a long optimum reaction time, the benefits of ease-of-use and accuracy at low concentrations outweigh this drawback. Furthermore, the stability of one week ensures the 8-hour reaction time is sufficient for everyday use.

Another good point to address here is that a mobile phone was used to record the color and an image processing program was applied to analyze the color intensity in order to obtain the concentration accurately. Thus, complicated apparatus such as a spectrophotometer is unnecessary for the analysis.

Limitations of the study

One limitation of this pad is on its fairly short shelf life. In the case of commercial production, 120-days shelf life is considered too short. Thus, further research and development to extend its shelf life may be needed. Furthermore, the RH and temperature in the test chamber varied within very narrow range (temp = 25 ± 3 ℃; RH = 65 ± 5%) even though these are in the normal or suggested indoor conditions. Because the pads may be used in extreme condition out of this range, further testing of the pad is recommended in varied conditions of differing temperature and humidity such as temperature <15 ℃ and >35 ℃, and <40%RH and >80%RH.

Conclusion

An accurate, selective, low-cost and user-friendly colorimetric pad was developed for monitoring of formaldehyde at very low concentrations. The pad was produced by coating a cellulose filter with silica nanoparticles impregnated with reactive chemicals. Combining digital image-based colorimetry with a mobile phone allowed for highly accurate and precise measurement. The colorimetric pad has been tested to detect formaldehyde at as low as 0.01 ppm with ±25% accuracy and bias of ≤10%.

Conflict of Interest: None

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