

คลังเลอริเมทริกเซ็นเซอร์ของซีพีไอเจเนตส์สำหรับการตรวจวัดแก๊สฟอร์มัลดีไฮด์



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จุฬาลงกรณ์มหาวิทยาลัย

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บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)

เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

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ปีการศึกษา 2557

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

COLORIMETRIC SENSOR OF SCHIFF'S REAGENT FOR FORMALDEHYDE GAS DETECTION

Miss Pornpetcharat Kaewkingkao



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2014

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Thesis Title	COLORIMETRIC SENSOR OF SCHIFF'S REAGENT FOR FORMALDEHYDE GAS DETECTION
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พรเพชรรัตน์ แก้วกิ่งแก้ว : คัลเลอริเมตริกเซ็นเซอร์ของชิฟรีเอเจนต์สำหรับการตรวจวัดแก๊สฟอร์มัลดีไฮด์ (COLORIMETRIC SENSOR OF SCHIFF'S REAGENT FOR FORMALDEHYDE GAS DETECTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. เพ็ญฟ้า อุ๋นอบ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ลักษณ์า ดูปาส, 55 หน้า.

ทำการพัฒนาการตรวจวัดแก๊สฟอร์มัลดีไฮด์ด้วยตาเปล่าสองชนิด ได้แก่ แผ่นฟิล์มพอลิไวนิลแอลกอฮอล์และซิลิกาเจลที่โดปด้วยชิฟรีเอเจนต์ โดยทำการโดปที่ความเข้มข้นชิฟรีเอเจนต์ต่างกัน คือ 0.8 1.0 และ 1.3 มิลลิโมลาร์ โดยพิสูจน์เอกลักษณ์เซ็นเซอร์ด้วยการใช้ ATR-FTIR spectrometer, UV-Visible spectrophotometer และ DR-UV-Vis spectrophotometer ทั้งนี้เพื่อให้ง่ายต่อการใช้ ได้นำเซ็นเซอร์ชนิดฟิล์มขนาด 0.7x0.8 เซนติเมตร และมีความหนาเฉลี่ยเท่ากับ 0.162 ± 0.001 มิลลิเมตร ไปติดภายในหลอดแก้วซึ่งมีเส้นผ่านศูนย์กลางภายในหลอดเท่ากับ 4.5 มิลลิเมตร และบรรจุเซ็นเซอร์ชนิดของแข็งปริมาณ 0.01 กรัม ในหลอดแก้ว และได้มีการสร้างระบบสำหรับการผลิตแก๊สฟอร์มัลดีไฮด์ภายในห้องวิจัยและทำการทดสอบประสิทธิภาพ โดยทดสอบประสิทธิภาพของเซ็นเซอร์ชนิดฟิล์มและชนิดของแข็งกับแก๊สฟอร์มัลดีไฮด์ที่ความเข้มข้นประมาณ 6 ppb และ 62 ppb โดยใช้อัตราการไหลของแก๊สผสมคือ 100 มิลลิลิตรต่อนาที โดยเซ็นเซอร์ทั้งสองชนิดนี้มีการเปลี่ยนแปลงสีจากสีเหลืองเป็นสีแดงม่วงหรือสีม่วงเมื่อสัมผัสกับแก๊สฟอร์มัลดีไฮด์ ความเข้มของสีเซ็นเซอร์ขึ้นอยู่กับความเข้มข้นของชิฟรีเอเจนต์และความเข้มข้นของแก๊สฟอร์มัลดีไฮด์ ซึ่งเซ็นเซอร์ชนิดของแข็งที่โดปด้วยชิฟรีเอเจนต์เข้มข้น 0.8 และ 1.0 มิลลิโมลาร์ สามารถตรวจวัดแก๊สฟอร์มัลดีไฮด์แล้วให้ระดับสีที่เกิดขึ้นอย่างแตกต่างกัน และใช้เวลาของการตอบสนอง 2 และ 3 นาทีตามลำดับ สำหรับการใส่เซ็นเซอร์ชนิดฟิล์มที่มีความเข้มข้นของชิฟรีเอเจนต์ 1.3 มิลลิโมลาร์ สามารถตรวจวัดแก๊สฟอร์มัลดีไฮด์ได้ที่ความเข้มข้นประมาณ 62 ppb โดยใช้เวลาในการตอบสนอง 11 นาที ซึ่งประสิทธิภาพของเซ็นเซอร์ทั้งสองชนิดที่เตรียมขึ้นมานี้ได้รับการประเมินโดยการนำไปใช้ในการตรวจวัดกับตัวอย่างแก๊สที่สังเคราะห์ขึ้น

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต

ปีการศึกษา 2557

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5572057523 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: FORMALDEHYDE GAS / NAKED-EYES SENSORS / POLYVINYL ALCOHOL / SILICA / SCHIFF'S REAGENT

PORNPETCHARAT KAEWKINGKAO: COLORIMETRIC SENSOR OF SCHIFF'S REAGENT FOR FORMALDEHYDE GAS DETECTION. ADVISOR: ASST. PROF. FUANGFA UNOB, Ph.D., CO-ADVISOR: LUXSANA DUBAS, Ph.D., 55 pp.

Two gas sensing elements were developed for naked-eye detection of formaldehyde gas. Polyvinyl alcohol film and silica gel were doped with Schiff's reagent as sensing reagent of different concentrations (0.8, 1.0 and 1.3 mM). The sensors were characterized by ATR-FTIR spectrophotometer, UV-Visible spectrophotometer and DR-UV-Vis spectrophotometer. The film sensor (size 0.7x0.8 cm, thickness 0.162 ± 0.001 mm) was enclosed into a glass tube (4.5 mm i.d.) while the solid-phase sensor (0.01 g) was packed into a glass tube for easy usage. The formaldehyde generation system was developed in-house and their performance was tested. Formaldehyde gas with concentration of *ca.* 6 ppb and 62 ppb were used to test the performance of film and solid phase sensors. The gas mixture flow rate of 100 mL min^{-1} was used in this study. The both sensors showed color change from yellow to magenta or purple after exposure to formaldehyde gas and the intensity of the color depended on both Schiff's reagent concentration and formaldehyde concentration. The solid sensor doped with 0.8 and 1.0 mM Schiff's reagent could detect formaldehyde gas and gave different color tint with response time of 2 and 3 min, respectively. The film sensor doped with 1.3 mM could detect only *ca.* 62 ppb formaldehyde with response time of 11 min. The performance of the prepared sensors was evaluated by applying the sensors to detect a synthetic gas sample.

Field of Study: Petrochemistry and
Polymer Science

Academic Year: 2014

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ACKNOWLEDGEMENTS

This successful thesis can be accredited to my advisor, Asst. Prof. Dr. Fuangfa Unob and my thesis co-advisor, Dr. Luxsana Dubas, who have been giving useful advisement of solving many problems through my experiments. With their informal relationship, insightful discussions and suggestions make me pleasure and be joyous to my progress laboratory skill. I would like to express my sincere appreciation for them with my thankfulness.

In addition, my thesis committees, videlicet, Prof. Dr. Pattarapan Prasassarakich, Asst. Prof. Dr. Amarawan Intasiri and Asst. Prof. Dr. Jinda Yeunyongchaiwat, who give me any opinions and valuable suggestions for my work and devote their valuable time for my thesis defense examination. I would like to thank all of members in Environmental Analysis Research Unit (EARU), Miss Jarinya Sittiwong, Miss Viphavee Liangraksa, Miss Uma Pongkitdachoti, Mr. Natthaphon Ninpradubkaew, Mr. Kosin Kosem, Mr. Tana Suksawang and Mr. Eakkasit Punrat for their advice, encouragement, help, and lovely friendship. I would like to thank Dr. Aticha Chaisuwan and Mr. Sakchai Chunhong for good supports and suggestion concerning experimental techniques.

And not forgotten to utter mention, I would like to thank my beloved family, especially my lovely parents who have been giving me many supports and great willingness for further my lab until success comes. The usefulness of this work, I dedicated to my parents and all the teachers who have taught me since my childhood.

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LIST OF ABBREVIATIONS

cm^{-1}	wavenumber
$^{\circ}\text{C}$	degree celcius
g	gram
ID	inner diameter
L	litre
M	molar
mM	milimolar
ppm	part per million
ppb	part per billion
%w/w	percentage weight by weight
%w/v or %m/v	percentage weight by volume
PVA	polyvinyl alcohol
PVA-Schiff	doping polyvinyl alcohol with Schiff's reagent
Silica-Schiff	doping silica gel with Schiff's reagent

CHAPTER I

INTRODUCTION

1.1 Statement of purpose

Formaldehyde is widely used as a base chemical material to manufacture building materials and numerous household products in many industrial processes such as plastic products, adhesive and solvent. Formaldehyde is classified as a volatile organic compound (VOC) that became a gas at room temperature. Many new products could usually release high formaldehyde gas into the air. Formaldehyde can cause serious health effects, because of its potentially carcinogenic and mutagenic properties.

The World Health Organization (WHO) has set a standard of 0.08 ppm averaged over 30 minutes in residential indoor areas. The Occupational Safety and Health Administration (OSHA) reported that people must not be exposed to airborne concentration of formaldehyde that exceeds 0.75 ppm within an 8-h workday. The US National Institute for Occupational Safety and Health (NIOSH) has established a maximum long-time exposure limit of 0.016 ppm (TWA). In France, formaldehyde exposure limit is 0.01 ppm (~0.008 ppm) in indoor area for a long time exposure. Therefore, effective methods for formaldehyde detection have been demands for an air pollutant measurement and control. For this reason, several analytical methods have been reported for formaldehyde determination especially solid state colorimetric methods [1-4].

Colorimetric methods have been reported for formaldehyde detection using various sensing reagents such as hydroxylamine sulphate and 4-amino-4-phenylbut-3-en-2-one [5, 6], 4-amino-hydrazine-5-mercapto-1,2,4-triazole [7] and Schiff's reagent [8, 9]. However, using ordinary pH indicators in an amine-functionalized polymer film have been successfully designed to detect formaldehyde [10]. A lot of polymer prepared into nano-fiber/nets (NFN) structure as sensing materials loaded with sensing materials for ultrasensitive sensors. The developed NFN structure as

colorimetric sensor strip for formaldehyde detection was impregnated with reagents and indicator which would change color from pH value change after exposure to formaldehyde [11]. Adsorption of these reagents onto supporting materials has been utilized to provide a heterogeneous solid-state colorimetric sensor which could be observed by naked-eyes and analyzed spectroscopically. Moreover, silica based solid-state sensor could be prepared by adding colorimetric reagents during the sol-gel process [12]. However, those methods require long analysis time and could not detect continuously.

Therefore, the purpose of this work is to develop colorimetric sensors for formaldehyde detection that are able to analyze formaldehyde gas rapidly by observing visual color change, and color intensity. Two naked-eyes sensors i.e. polyvinyl alcohol film sensor and silica gel solid-phase sensor doped with Schiff's reagent as active reagent to react with formaldehyde were developed.

1.2 Objectives

1.2.1 Development of rapid formaldehyde sensors for naked-eyes detection.

1.2.2 Optimization of the formaldehyde detection parameters and determination of sensor efficiency.

1.3 Scopes of this research

Two formats of naked-eyes sensors in both polyvinyl alcohol film and silica particles using Schiff's reagent as sensing reagent to detect formaldehyde gas will be developed. The concentrations of Schiff's reagent will be varied in the range of 0.3-1.3 mM. The obtained sensors will be characterized by Attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) and UV-vis spectrophotometer. The formaldehyde gas was generated by heating formaldehyde solution and purging with nitrogen gas continuously through generating gas system, which was designed. Concentration of formaldehyde solutions used to generate formaldehyde gas will be varied and optimized. The generation gas conditions were controlled as well as formaldehyde concentration was determined by ASTM method. The efficiency of

formaldehyde sensors is studied in various formaldehyde concentrations by considering color change and using time in formaldehyde detection including life time and regeneration property.

1.4 The benefit of this research

This research aims to develop naked-eyes colorimetric sensors for formaldehyde gas detection rapidly and easy to prepare.



CHAPTER II

THEORY

2.1 Formaldehyde

2.1.1 Properties of formaldehyde

Formaldehyde, as a volatile organic compound (VOC), is the first member of aldehyde group that has the chemical formula of CH_2O or HCHO . Its molecular structure and dipolar resonance structure are shown in Figure 2.1, which makes the molecule a typical electrophile. Formaldehyde is commercially available as a 30-50%wt aqueous solution, referred to as formalin. To reduce intrinsic polymerization, stabilizers such as methanol and various amine derivatives are usually added to formaldehyde solution. In addition, solid form of formaldehyde as its cyclic trimer, trioxane and its polymer etc. is also promoted. Formaldehyde is colorless gas at ambient temperature with a pungent and irritating odor. It is flammable and soluble in water, ethanol and chloroform [1, 13, 14].

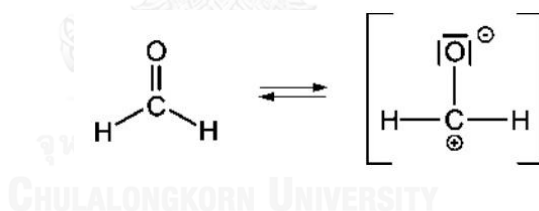


Figure 2.1 Resonance structure of formaldehyde and the molecular structure of formaldehyde (left).

2.1.2 Occurrence and health conditions

Formaldehyde is a gaseous pollutant from many outdoor and indoor sources and major sources include power plants, manufacturing facilities, incinerators, and automobile exhaust emissions. Formaldehyde gas is released from various building materials, consumer products, and may be present in food as a contaminant. Formaldehyde level is usually high in new construction, and increases with an increase in temperature and humidity but the levels will decrease over time. Airborne formaldehyde irritates the eyes, nose and throat in healthy humans and the

adverse effects to health associate with levels of formaldehyde exposure and time period of contact. Prolonged and repeated contact with this chemical can be dangerous. Formaldehyde has been classified as a carcinogenic for human (Group 1) in 2004 by the International Agency for Research on Cancer [2] and as a probable human carcinogen by the U.S. Environmental Protection Agency. Figure 2.2 concludes the adverse health effects as well as carcinogenic potential of formaldehyde in experimental rats and humans relative to formaldehyde levels in air [15]. The concentration of formaldehyde probably found in environment is presented in Figure 2.3.

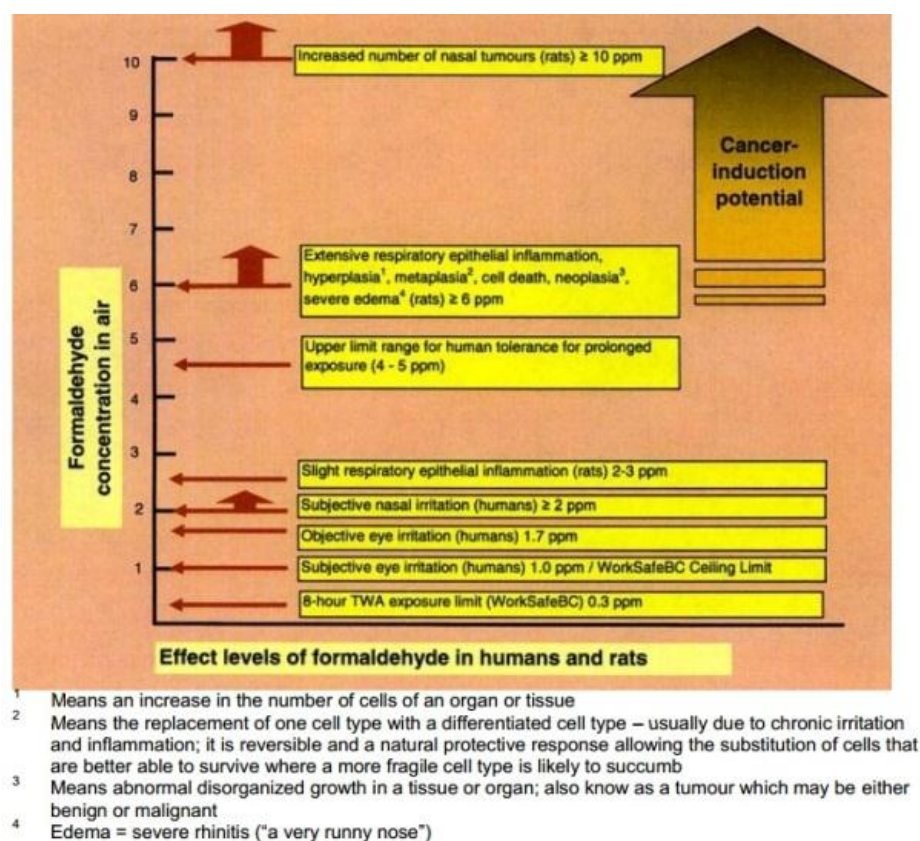


Figure 2.2 Summary of effect levels of formaldehyde in humans and experimental rats [15].

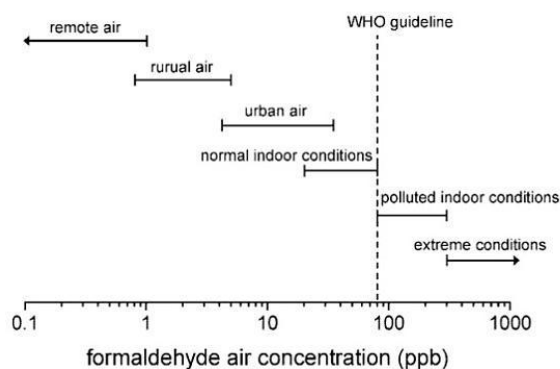


Figure 2.3 The range of formaldehyde concentration in air in different environments [2].

In addition, indoor formaldehyde concentration was found to be greater than those in outdoor environments and it is harmful to human health directly. Therefore, methods for formaldehyde measurements in indoor air are required and they should be simple, reliable and inexpensive [16].

2.2 Naked-eyes detection of formaldehyde

Naked-eyes technique is a simple method for formaldehyde detection based on color change or other physical properties change that could be observed by eyes. One of the attractive sensing applications is the observation of color change visually which can be performed and confirmed with other measurement techniques such as spectrophotometry and fluorescence. Examples of formaldehyde determination by naked-eye technique are reviewed in topic 2.6. This technique is applied for quantitative and qualitative analysis on site. However, the sensing element should have distinct colors and the method should be sensitive, rapid and inexpensive [17].

2.3 Schiff's reagent

Schiff's reagent is a solution for aldehyde test, first introduced by Feulgen and Rossenbeck in 1924 [18], and made from reaction of basic fuchsine and sulfur dioxide gas. The basic fuchsine is a mixture of four cationic red triphenylmethane dyes (pararosaniline, rosaniline, magenta II and new fuchsine). The addition of a sulphonic acid group to the central carbon is a cause of color change to pale yellow

or colorless. A positive test response to formaldehyde is a color change from pale yellow to deep red-violet upon addition of the aldehyde. The structure of Schiff's reagent and reactions with formaldehyde are shown in Figure 2.4. The pale yellow solution is stable only at low pH, but raising the pH or reducing the concentration of sulfurous acid increases the sensitivity of reagent for detecting aldehydes and leads to regeneration of the original dye as pink product [18]. The major component of Schiff's reagent is the zwitterionic form ($R-NH_2^+$) in which one of the amino groups is protonated.

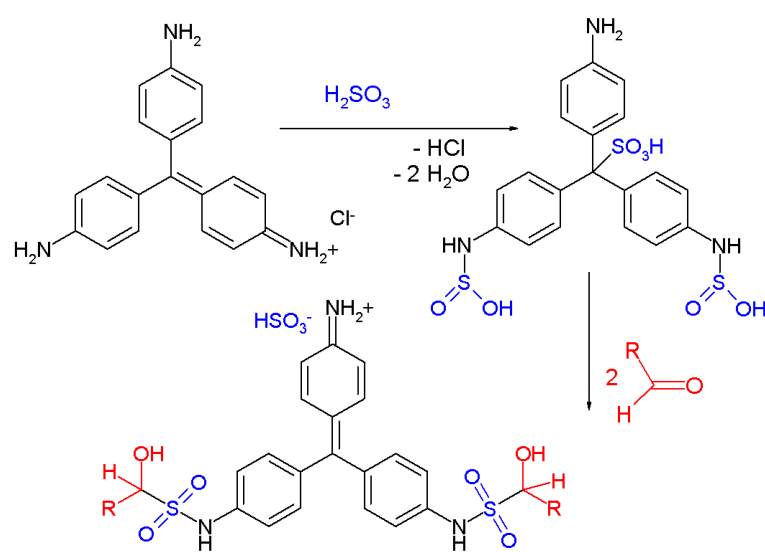


Figure 2.4 Mechanism of reaction between Schiff's reagent and formaldehyde [19].

2.4 Silica gel

2.4.1 Chemistry of silica gel

Silica is an inorganic polymer consisting of inter-linked SiO_4 in tetrahedral fashion. Silica gel is granular form of silica. The active sites on silica surface and its large specific surface area are of great important factors in adsorption and ion exchange. The structure on surface terminates is siloxane group ($Si-O-Si$), or one of the several forms of silanol groups ($Si-OH$) [20].

Silica gel surface can be modified chemically either by physical treatment or chemical treatment. Furthermore, the chemical treatment of surface can be performed by using several methods such as impregnation of the solutions of

modifiers or covalently grafting of molecule to silica matrix. Silica gel is used as solid support due to its good properties especially high surface area. In addition, it is a white solid which is suitable for the use as supporting materials for colorimetric sensors as the color change can be observed clearly without additional color from the support [21].

2.4.2 Modification of silica gel by impregnation

The modification for silica surface by impregnation may occur through physical interaction between the modifier and solid support by either inclusion in pores, adhesion process or electrostatic interaction. The modification of silica gel for detection of formaldehyde gas was reported as the impregnation of 2,4-Dinitrophenylhydrazine [21].

2.5 Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA; $[-\text{CH}_2-\text{CHOH}-]_n$), first synthesized by Hermann and Haehnel in 1924, is derived from poly(vinyl acetate) through partial or full hydroxylation. PVA is an odorless, translucent and white or cream colored granular powder. It has several good properties such as environmentally friendly product, flexibility, hydrophilicity, biocompatibility, fiber/film-forming ability, pH stability, chemical resistance and low cost [22]. The physical characteristic, chemical properties and mechanical properties of PVA polymer depend on the degree of the polymerization and degree of hydrolysis. PVA with high degree of hydroxylation and polymerization have low solubility in water and have higher glass transition temperature. However, PVA needs to be cross-linked to form hydrogel for a wide range of applications [23-25]. The structure of PVA containing hydroxyl group is shown in figure 2. 5.

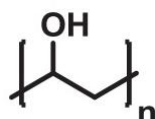


Figure 2.5 Structure of poly(vinyl alcohol) (PVA).

Moreover, PVA is thermoplastic and can be produced in form of thin and transparent films which soften when heated up to its glass transition temperature (T_g). The polymer with higher molecular weights has higher glass transition temperature whereas T_g of PVA (MW=146000-186000) is about 95°C. Furthermore, formaldehyde can react with hydroxyl groups of PVA as crosslinking agent [26].

2.5.1 Casting

The casting is a basic method in the production of polymer films from polymer melts or solution of polymer in solvent. The polymer solution is poured into a mold and allowed to dry. And then the product is removed after polymer solidification whereas film appearances depend on a designed mold, properties of polymer and temperature.

2.6 Literature reviews

Methods for formaldehyde gas detection both direct and indirect methods have been proposed. In this part, some sensors for formaldehyde gas are reviewed.

Nakano and Nagashima [5] prepared adsorbent from porous cellulose tape containing silica gel and impregnated it with hydroxylamine sulfate and methyl yellow. The response of sensor was observed as a color change resulted from pH change after being exposed to formaldehyde gas for 30 minutes. The reflectance value of the sensor was measured with a spectrophotometer. On the other hand, the impregnated cellulose tape without silica gel was not suitable for formaldehyde detection. The limit of detection was *ca.* 0.08 ppm with a sampling time of 30 minutes.

Lee *et al.* [27] prepared silica composites including silica/amine and silica/platinum composite via sol-gel reaction using a water-in-oil (W/O) emulsion and a self-hydrolysis in one-step process. The amine-functionalized silica sphere and silica/platinum composite would react with formaldehyde on amine sites and platinum nanoparticles, respectively. Schiff's reagent was used for monitoring formaldehyde concentration.

Wang *et al.* [11] developed colorimetric sensor based on methyl yellow-impregnated electro-spinning/netting nylon 6 nano-fiber/nets for formaldehyde detection. After exposure to formaldehyde, the sensor color changed from yellow to red with a detection limit of 50 ppb for 30 minutes and a good reproducibility.

Sadik and Joseph [28] prepared a conductive polymer film of poly(aniline)/poly(ethyleneimine) by spin casting method for formaldehyde vapor detection. The poly(ethyleneimine) (PEI) reacted with formaldehyde on primary amine functionalities of PEI resulting in a change of proton content on doped poly(aniline) and then a change in conductivity.

Maruo *et al.* [9] developed a formaldehyde sensing element using glass chip. A glass chip was impregnated with Schiff's reagent in phosphoric acid which further reacted with formaldehyde gas. The color of sensor element changed clearly from yellow to violet after exposure to formaldehyde in the concentration range of 10 ppb to 20 ppm for 1 hour. The sensing element can be regenerated.

Bunkoed *et al.* [29] developed a sensor for selective formaldehyde detection by entrapping acetylacetone into TEOS mixture solution. Formaldehyde gas was dissolved into the solution and reacted with acetylacetone directly to produce lutidine as a yellow product. This method required a visual detection accompanied with measurement by spectrophotometry. The detection limit was 0.03 ppmv with 3 hours of sampling time and the sampling time depended on formaldehyde concentration.

From these researches, it shows that Schiff's reagent and acetylacetone can be used as sensing reagent to react with formaldehyde gas directly, resulting in color change. Especially, the reaction between formaldehyde and Schiff's reagent gives a distinct products color. The silica material and some polymers were used as supporting materials for impregnation of colorimetric reagent. Therefore, this research aims to prepare Schiff's reagent doped sensors i.e. polyvinyl alcohol film sensor and silica gel sensor for formaldehyde detection by naked eyes.

CHAPTER III EXPERIMENTS

3.1 Apparatus

The apparatus used in this research are shown in Table 3.1

Table 3.1 List of apparatus and supplier

Apparatus	Suppliers
1. UV-visible spectrophotometer	Agilent, HP 8453
2. UV-visible spectrophotometer	SHIMADZU, UV-2550
3. Attenuated total reflectance fourier transform infrared spectrometer (ATR-FTIR)	Nicolet 6700
4. pH/ion meter	METTLER TOLEDO
5. Digimatic micrometer	Mitutoyo, IP 65
6. Hot plate stirrer	C-MAG HS 7 Digital IKAMAG®
7. Flow meter	Model RMA, Dwyer
8. 10 mL of screw thread head space vials and magnetic screw thread closures with ultra low bleed silicone liner	Vertical
9. Stainless steel ball valve 1/2 inch	J.S. Salakpan
10. T-way junction	J.S. Salakpan
11. Teflon tube and silicone tube	N.K. supply laboratory
12. 500 mL of triple necks round bottom flask, borosilicate glass grade	N.K. supply laboratory
13. Digital camera (α5100 mirrorless camera)	Sony
14. Temperature controller	IKA®, EST-D5
15. Heating block	Thermal TMD/1
16. Quartz slide	Electron Microscopy Sciences

3.2 Chemicals

All chemicals were analytical reagent grade and listed in Table 3.2

Table 3.2 Chemicals list and suppliers

Chemicals	Suppliers
1. Basic fuchsin	Acros Organics
2. Sodium sulphite	Ajex Finechem
3. Silica gel 60 (0.063-0.200 mm)	Merck KGaA
4. Hydrochloric acid	Fisher scientific
5. Ortho-phosphoric acid 85%	Merck KGaA
6. Formaldehyde solution 37-40% m/v	Carlo Erba Reagent
7. Acetylacetone	Carlo Erba Reagent
8. Poly (vinyl alcohol) (PVA, MW = 146,000-186,000, 99+% hydrolyzed)	Sigma-Aldrich
9. Ammonium acetate	Fisher scientific
10. Glacial acetic acid solution	Merck
11. Nitrogen gas	Praxair
12. Barium sulfate	Wako
13. Silane treated glass wool	Grace

3.3 Preparation

The reagents and sensors preparations were described below.

3.3.1 Schiff's reagent in phosphoric acid

A 100 mL of Schiff's reagent solution was prepared by mixing 0.1 g of basic fuchsin, 1 g of sodium sulfite and 1 mL of hydrochloric acid. The final volume was adjusted with deionized water. Then, 100 mL of Schiff's reagent was mixed with 20 mL of ortho-phosphoric acid and 100 mL of deionized water. The reagent solutions were stored at 4°C in brown bottle to avoid the degradation of reagents. The working concentrations of Schiff's reagent were 1.3 mM, 1.0 mM, 0.8 mM, 0.5 mM and 0.3

mM by diluting stock solution with deionized water before doping into supporting materials. The Schiff's reagent solutions were mixed with supporting materials, PVA solution or silica particles.

3.3.2 Acetylacetone reagent

The acetylacetone reagent was used for determination of formaldehyde concentration by UV-Visible spectrometer. Acetylacetone reagent was prepared by mixing 38.50-38.51 g of ammonium acetate, 500 μL of acetylacetone and 750 μL of glacial acetic acid and adjusting the final volume to 250 mL with deionized water.

3.3.3 Sodium carbonate solution

A 50 mL of 3.77×10^{-2} M sodium carbonate (MW = 105.99 g mol⁻¹) was prepared by dissolving 0.200 g with deionized water. The sodium carbonate solution was used in standardization of hydrochloric acid.

3.3.4 Sodium sulfite solutions

A 1.0 M of sodium sulfite solution was prepared by dissolving anhydrous sodium sulfite in 100 mL of deionized water. The sodium sulfite solution was used in standardization of formaldehyde stock solutions.

3.3.5 Formaldehyde solution for generating formaldehyde gas

In this study, the formaldehyde gas was generated from formalin solution that the different concentrations of formaldehyde solution affect concentration of generated formaldehyde gas (described in section 3.51). The concentrations of 45000 to 1000 ppm were prepared by diluting 37% m/v formaldehyde with deionized water which were prepared daily.

3.3.6 Formaldehyde standard solution for calibration curve

The various concentrations of formaldehyde were used as reagent in generating process of formaldehyde gas as well as standard solution for making calibration in range of 150 ppb to 500 ppb. The calibration was constructed from diluting 1000 ppm formaldehyde standard solution and then was prepared as 1 ppm for diluting concentration in calibration range (Table 3.3). Formaldehyde gas, which

was generated from various formaldehyde solution concentrations, would be able to find actual concentration from compare with calibration curve.

Table 3.3 Standard curve preparation

Concentration, ppm	mL of standard, 1 ppm	mL of water
0	0	0
0.3	0.6	1.4
0.4	0.8	1.2
0.5	1.0	1.0
0.6	1.2	0.8
0.7	1.4	0.6
0.8	1.6	0.4
0.9	1.8	0.2
1000	2	0

3.3.7 Standardization of formaldehyde standard solutions (1000 ppm) by ASTM method (D6303-98)

A 1000 ppm of formaldehyde solution was standardized by titration method. The pH value of sodium sulfite solution is measured before mixing with 50.00 mL of 1000 ppm formaldehyde solution. After that, HCl as titrant was added to mixture solution to bring pH value back to the initial pH value. The volumes of HCl added were recorded [30]. The concentration of the formaldehyde stock solution was calculated using equation 3.1. Finally, the formaldehyde standard solution must be standardized for at least every month (n=3).

$$\text{HCHO} \left(\frac{\text{mg}}{\text{mL}} \right) = \frac{(\text{HCl titrant, mL}) \times (\text{HCl, N}) \times (30.03)}{(\text{stock formaldehyde, mL})} \quad (3.1)$$

3.3.7.1 Standardization of hydrochloric acid solutions

Because HCl was used as titrant in the previous process, the exact concentration of a hydrochloric acid solution had to be determined using ASTM

standard method (E 200) [31]. A standard solution of sodium carbonate and methyl red as indicator were used.

3.3.8 Fabrication of sensors

Both sensors were prepared before testing performance formaldehyde detection. The sensors preparations were described below.

3.3.8.1 Polyvinyl alcohol film sensor

In our study, 10% w/w Schiff's reagent in PVA was prepared. A 3.11 ± 0.001 g of polyvinyl alcohol (PVA) granules was mixed with 18 mL of deionized water. The mass of this mixture was measured. Then, the mixture was slowly heated up to 95°C under stirring, until a clear and transparent PVA solution was obtained. The polymer solution was cooled down to room temperature and its weight was adjusted back to the initial weight. The Schiff's reagent was diluted concentration with DI water as describe in section 3.3.1. The working Schiff's reagents were added into the PVA solution under stirring until homogeneous for 1 hour.

Finally, 3.00 ± 0.05 g of Schiff's reagent/PVA solution was casted onto a 3.3 cm x 4.9 cm plastic box, dried at room temperature and kept in a desiccator for further use. The film sensor was cut (size 0.7x0.8 cm) and then the film was tapped onto a glass tube (ID of tube = 4.5 mm).

3.3.8.2 Solid-phase sensor

The solid-phase sensor was prepared by adding 25 mL of Schiff's reagent solution into 1 g of silica gel and the mixture was stirred for 3 hours. The solid was separated by nylon syringe filter, dried at room temperature and stored in a desiccator. Sensor performance were tested by packing 0.0100 ± 0.0002 g of modified silica into a tube (ID of tube = 4.5 mm) on top of glass wools and layer of raw silica gel (0.020 ± 0.005 g).

In order to confirm the relationship between the concentrations of Schiff solution with the doped amount on silica surface, the concentrations of Schiff's solution after adsorption on silica gel were measured absorbance at 463 nm.

3.4 Characterizations

3.4.1 UV-Vis spectrophotometer

UV-Visible spectrophotometer (Agilent, HP 8453) was used in the determination of formaldehyde concentration in gas phase, and stability study of film sensor (life time)

UV-Visible spectrophotometer (SHIMADZU, UV-2550) was used in the stability study of solid-phase sensor (life time).

3.4.2 Attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR)

Attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) was used to characterize the functional groups of Schiff's reagent on modified polymer and modified silica. The infrared spectra were recorded from 400 to 4000 cm^{-1} in transmittance mode.

3.5 Formaldehyde gas generation apparatus set-up

In this part, the system for generation and determination of formaldehyde gas was designed as describe below.

3.5.1 Formaldehyde gas generation system

The system for formaldehyde generation and detection was shown in figure 3.1.

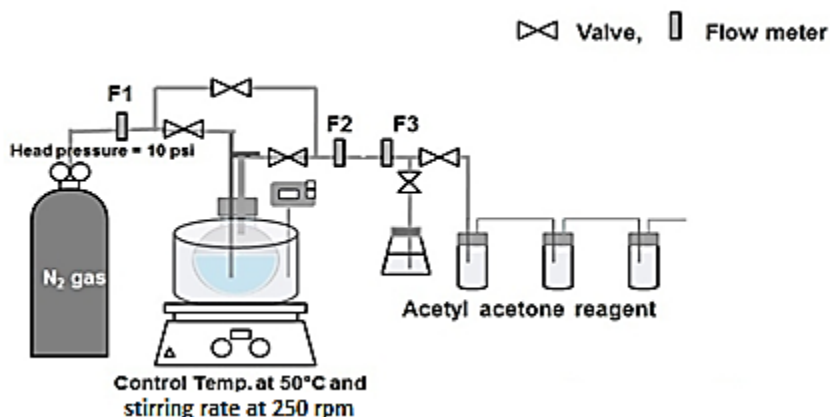


Figure 3.1 The formaldehyde generation system (F1: flow meter No.1 to monitor nitrogen flow rate, F2 and F3: flow meters No.2 and No.3).

The formaldehyde gas was generated by an artificial gas system by applying heat and bubbling nitrogen gas into solution. The generation system consists of two parts.

The first part is the gas generation part where nitrogen gas was bubbled into formaldehyde solution continuously. The formaldehyde gas, which was obtained from stirring and heating formaldehyde solution, was purged with nitrogen gas as carrier gas. Then, the concentration of formaldehyde in gas mixture must be studied to optimize the formaldehyde detection parameters before testing sensors.

The second part is the trapping system which will be described in section 3.5.2. In the study of sensor performance, formaldehyde gas would be flowed into sensor chamber to determine sensor efficiency.

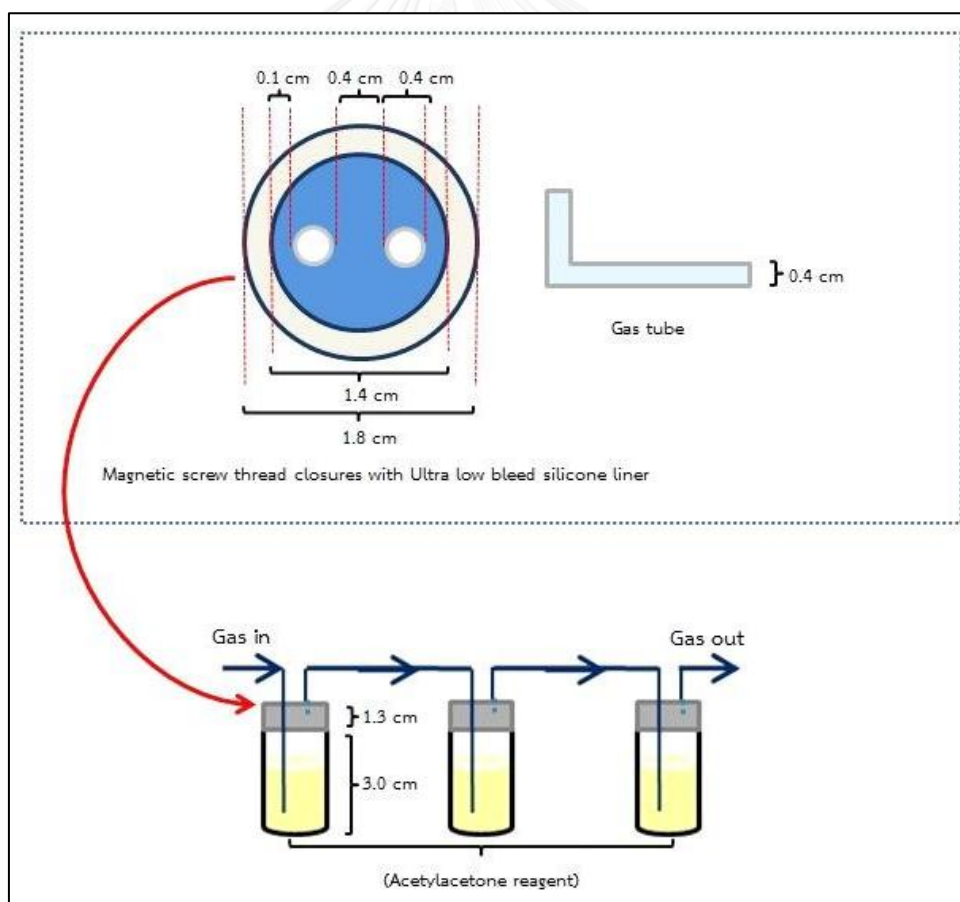
The controlled variables were pressure, temperature, volume of formaldehyde solution and distance between purge gas and trapping system. The condition of gas flow was controlled as in table 3.4.

Table 3. 4 Controlled variables for generation of formaldehyde gas

Parameters	Condition set
Volume of formaldehyde solution	200 mL
Heating temperature	50°C
Flow total of formaldehyde and nitrogen gas	100 cc/min
Head pressure of N ₂ gas	10 psi
Number of stirring rate	No. 1 (250 rpm)

3.5.2 Trapping system

The system of formaldehyde trapping was designed as shown in figure 3.2 for concentration determination.

**Figure 3.2** The designed system for formaldehyde trapping

The trapping system was constructed by each glass tubes (for gas in and gas out) were joined with silicone pipes. The triple vials contained acetylacetone reagent (trapping solution) to ensure the efficiency of our trapping gas system.

3.5.2.1 Optimized acetylacetone reagent volume

The volumes of acetylacetone reagent as trapping solution were studied. The studied volumes were 5, 6, 7, 8, 9 and 10 mL which were contained in vials and then gas was flowed into these vials. The result obtained from observing pressure system and overflow of solution in vials. The optimized volume was selected from maximum volume of reagent which wouldn't cause problems. Moreover, the suitable volume of trapping solution should be able to react with formaldehyde sufficiently in the first vial which was contained acetylacetone reagent.

3.6 Quantitative analysis of formaldehyde gas

After the formaldehyde gas was generated as described in section 3.5.1, the generated formaldehyde gas content was determined by passing the gas into acetylacetone solution in vial No.1 to 3. Then, the vials (figure 3.2) were capped tightly, shaken well before performing absorbance measurement at 412 nm. Finally, the content of generated formaldehyde gas was calculated from the calibration curve constructed as described in section 3.6.2.

In this part, effect of temperature in reaction rate between formaldehyde gas and acetylacetone reagent was also studied.

3.6.1 Effect of temperature on formaldehyde in trapping solutions

The temperature affecting reaction rate between formaldehyde gas and acetylacetone solution was studied. Based on the previous study [32] using the same quantitation method without heating, the reaction required 20 minutes reaction time. Therefore, in this study, the temperature effect on the rate of this reaction was studied. Thus, the formaldehyde in trapping solution was heated at 60°C for 10 minutes to compare with non-heated solution. The kinetic of this reaction was monitored by measuring the absorbance at 412 nm using UV-Vis spectrophotometer under kinetic mode for 3 hours (n=3).

3.6.2 Calibration curve of formaldehyde standard solution

In order to quantify the concentration of generated formaldehyde gas in trapping solution, the calibration curve of formaldehyde standard solution in the range of 0 to 0.5 ppm versus absorbance at 412 nm were constructed.

The calibration curve of formaldehyde standard solution was prepared by adding the specified aliquots of the standard solutions and water to the test tubes (2 mL). Then, 2 mL of 1 M acetylacetone reagent was added into various concentrations of formaldehyde standard solution, which were prepared as shown in table 3.3. Then, the standard solutions were heated at 60°C for 10±1 minute. The solution mixtures were cooled down to room temperature before performing absorbance measurement at 412 nm. The absorbance of mixture solution compared with water as blank following ASTM method (D6303-98) [30].

Finally, the concentrations of formaldehyde gas were calculated indirectly from 7 mL of acetylacetone reagent which gas mixture was purged, total flow rate of gas mixture and time of gas purge. The equation 3.2 was calculation of formaldehyde concentration in gas phase.

$$C_b(\text{ppb, gas}) = \frac{C_a(\text{ppb, liquid}) \times V_t(\text{mL, liquid}) \times 1000(\text{mL, gas})}{1000(\text{mL, liquid}) \times V_m(\text{mL, gas}) \times 1(\text{L, gas})} \quad (3.2)$$

Where:

C_b = concentration of formaldehyde gas (ppb)

C_a = concentration of formaldehyde gas in 7 mL of trapping solution (ppb)

V_t = volume of trapping solution (mL)

V_m = volume of gas mixture (whereas V_m = flow rate (mL min^{-1}) x purge time (min))

3.6.3 Determination of suitable formaldehyde solution concentration in the generation of formaldehyde gas and equilibrium time

Based on the NIOSH has set a maximum long-term exposure limit of 0.016 ppm (TWA) and the WHO has established exposure limit of 0.01 ppm (~0.008 ppm)

[4, 33], the suitable concentration of formaldehyde solution used in the generating as well as the equilibrium time were studied. The formaldehyde solution with various concentrations of 100, 250, 1000, 2500, 5000, 20000, 30000, 35000, 40000, 45000 ppm were used to generate formaldehyde gas.

After suitable concentrations of working formaldehyde solution were identified, the equilibrium time between liquid phase and gas phase of formaldehyde of each concentration was also studied. At 20, 30, 45, 60, 100, 120, 180 and 240 minutes, the concentration of generated formaldehyde gas in trapping solution was evaluated using calibration curve previously prepared in section 3.6.2.

3.7 Detection system

The formaldehyde gas detection system was shown in figure 3.3, which each part of flow was controlled with valve, flow meters and head pressure of N₂ gas tank. The performance of sensors toward various formaldehyde gas contents were studied. Both developed sensors, which were contained into glass tube, were connected to gas flow control system in the same distance with trapping solution, which was used in study of formaldehyde gas concentration. The detection system was observed with naked-eyes by considering color change. The photo of sensors was taken using a digital camera (α5100 Mirrorless Camera, Sony) to be an alternative for naked-eyes detection.

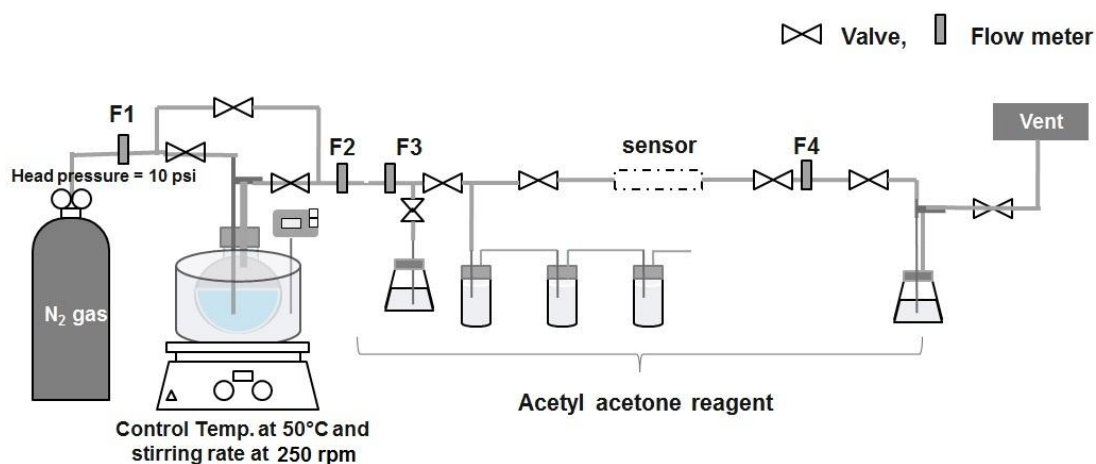


Figure 3.3 The detection system of formaldehyde gas by sensors.

3.7.1 Color response of sensors to formaldehyde gas

The polymer sensor and solid-phase sensor (figure 3.4) were tested with formaldehyde gas generated with the suitable formaldehyde solution found in section 3.6.3. The color of sensor was observed with naked-eyes after exposure to formaldehyde gas. All experiments were conducted in triplicate. The generated gas mixture was allowed to flow into sensor chamber or tube after the generation equilibrium time was reached. The color change of both sensors was recorded and applied in sensitivity study and color chart construction.

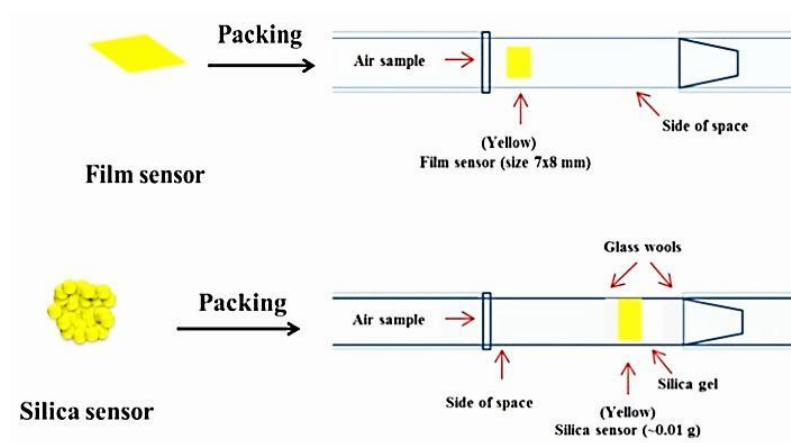


Figure 3.4 The film sensor and silica sensor.

3.7.2 Color response of sensors to nitrogen gas

Both polymer and silica sensors were tested with nitrogen gas for 3 hours. Nitrogen gas was flowed through the sensors to observe color change, which nitrogen was used as carried gas.

3.7.3 Testing performance sensors with synthetic gas sample

The performance of two sensors on sensing a synthetic gas sample was evaluated. The concentration of gas sample was determined (following in section 3.6) and compared with result from sensors testing.

3.8 Study the regeneration

The two sensors after exposure with formaldehyde gas were flowed through with nitrogen gas for 1 hour in order to test regeneration property by observing color change visually (n=3).

3.9 Study of sensor life times

The polymer sensor, which were enclosed on quartz slide and the silica sensors were kept in a desiccator. The absorbance of sensors was measured in two wavelength ranges: 400-500 and 550-600 nm. The change in the absorbance was monitored for 5 months (n=3).



CHAPTER IV

RESULTS AND DISCUSSION

A polymer film and solid-phase colorimetric sensors using Schiff's reagent as active reagent were developed for naked-eyes formaldehyde detection. This chapter is divided into 5 parts. In the first part, the results of preparation and characterization of the two colorimetric sensors using different concentration ratio of Schiff's reagent are reported. In the second part, the performance of in-house built formaldehyde gas generation system was evaluated. Several variables involved formaldehyde gas generation including the system of formaldehyde gas trapping, the temperature of the reaction between formaldehyde, the volume of trapping solution and the concentration of formaldehyde solution were studied. In the third part, two sensors were tested in the detection of formaldehyde gas at a concentration of *ca.* 6 ppb and 62 ppb. In the fourth part, the naked-eye detection using these sensors was validated by testing the sensors with a synthetic formaldehyde gas sample (*ca.* 11 ppb). Finally, the regeneration and stability of these two sensors were investigated.

4.1 Sensors fabrication

In this part, the results of fabrication and characterization of sensors are reported as follows.

4.1.1 The polymer sensor and solid-phase sensor

The both sensors were prepared by using varied concentrations of sensing reagent or Schiff's reagent in a range from 0.3 to 1.3 mM and the color of the obtained products is shown in figure 4.1. The sensing reagent, which was doped in sensors, would react with formaldehyde and generate product of distinct color. Silica gel and polyvinyl alcohol (PVA) film were white and colorless supporting materials, respectively while the Schiff's reagent in solution was yellow. The Schiff's reagent doped materials were expected to be yellow color sensors as reported in a previous work that proposed the preparation of Schiff's reagent doped PVA film [32]. Moreover, the sensing element for formaldehyde detection should give a color

change from yellow to purple after an exposure to formaldehyde gas. Figure 4.1 shows coloration of silica and polyvinyl alcohol film doped with various concentrations of sensing reagent. The Schiff's contents on silica were determined and the relationship between Schiff's content doped on surface and the initial Schiff's concentration added during the preparation is shown in figure 4.2. The results show that an increase in active reagent on the silica was directly related with an increase in Schiff's reagent concentration used in the preparation of the silica sensors.

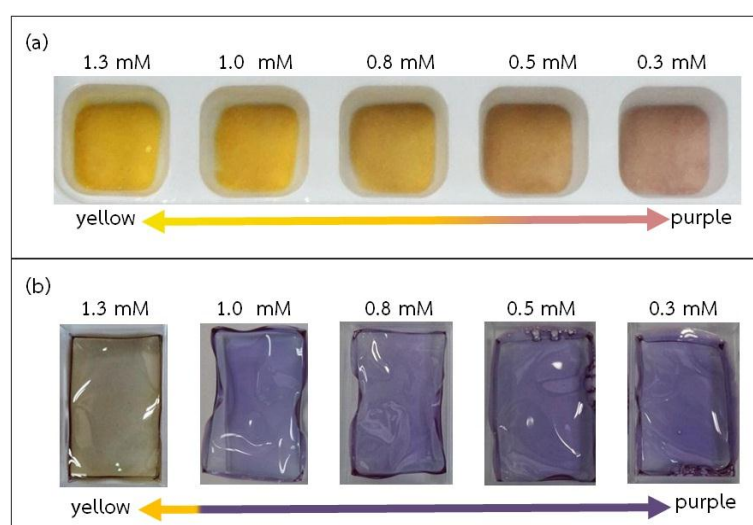


Figure 4.1 Photographs of naked-eyes (a) solid-phase sensors and (b) polymer sensors prepared with various Schiff's reagents concentrations.

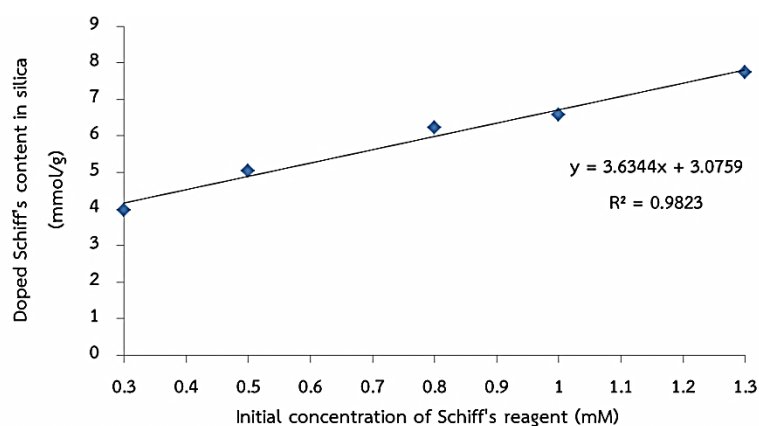


Figure 4.2 The doped Schiff's content in silica sensors when different concentrations of Schiff's reagent were used in the preparation.

For the solid-phase sensor (figure 4.1(a)), the color of silica changed from white to yellow in case of mixing the solid with 1.3, 1.0 and 0.8 mM of sensing reagent. When lower concentrations of Schiff's reagent i.e. 0.5 mM and 0.3 mM were used, the solid with pink-yellow and red-purple color were obtained, respectively. Thus, the silica sensors doped with 1.3, 1.0 and 0.8 mM Schiff's reagent were selected for formaldehyde gas detection. On the other hand, the PVA film doped with 1.3 mM Schiff's reagent was selected because it was the only condition giving yellow film (figure 4.1(b)). Using the other Schiff's reagent concentrations to mix with PVA gave purple films after preparation step.

In this study, the yellow sensors were preferable for visual formaldehyde detection as Schiff's reagent would react with formaldehyde to form purple product. Therefore, the starting color of Schiff's reagent doped sensors should not be in pink or purple color before reaction with target molecule, if not, it is difficult to observe the color change from pink to purple with naked-eyes.

In the case of sensor color that became pink, it was probably because it contained some regenerated basic fuchsin which might be obtained in decreasing sulfite level [18]. Finally, the prepared sensors were tested for their performance in formaldehyde detection in respect to color change and response time of color change. The desirable sensors should be able to give response at low level of formaldehyde quickly with obvious color change.

4.1.2 Characterizations

The colorimetric sensors were characterized by ATR-FTIR to confirm the presence of functional groups of Schiff's reagent as shown in Figure 4.4 and Figure 4.6. IR absorption band observed and the attributed functional groups are summarized in Table 4.1. The structure of Schiff's reagent, PVA and silica gel are shown below [18, 22].

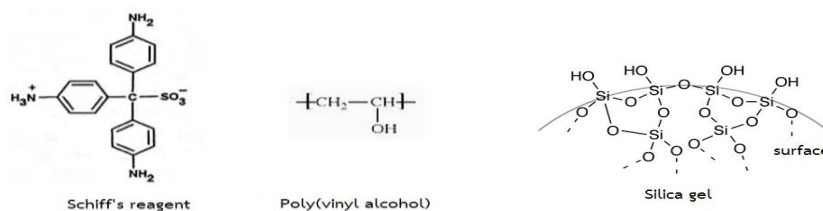


Figure 4.3 The structure of Schiff's reagent, poly(vinyl alcohol) and silica gel.

Table 4.1 Results of IR absorption band [34].

Functional group	Major functional group	Absorption frequency region (cm ⁻¹)
Polyvinyl alcohol (PVA)		
Alcohols	O-H stretching	~3270
	C-O stretching	~1087
Alkanes	C-H stretching	~2909
PVA-Schiff film sensor (additional bands)		
amines	N-H stretching	~3241
	C-N stretching (aryl)	~1323
aromatics	C=C stretching	~1635 and ~1420
sulfonates	S=O stretching, S-O stretching	~981, ~1084 and ~1142
Silica gel		
	Si-O-H stretching and O-H bending	~3403
	(Si-O-Si) stretching	~1057, ~794
	Si-OH stretching	~960
Silica-Schiff solid sensor (additional bands)		
amine	N-H stretching	~3359
sulfonate	S-O stretching	~1042
aromatic	C=C stretching	~1634

4.1.2.1 Film sensor

The average thickness of obtained polymer films was 0.162 ± 0.001 mm. The PVA film sensors were characterized with ATR-FTIR to confirm the doping of Schiff's reagent on PVA (figure 4.4). The IR spectrum of pure PVA film showed band at $\sim 3270 \text{ cm}^{-1}$ (O-H), at $\sim 2909 \text{ cm}^{-1}$ (aliphatic C-H) and at $\sim 1087 \text{ cm}^{-1}$ (C-O). When PVA was doped with Schiff's reagent, additional bands appeared at $\sim 3241 \text{ cm}^{-1}$ (N-H), $\sim 1323 \text{ cm}^{-1}$ (C-N), ~ 1635 and $\sim 1420 \text{ cm}^{-1}$ (aromatics). The characteristic infrared bands for the sulfonate group (HSO_3^-) at ~ 981 , ~ 1084 and $\sim 1142 \text{ cm}^{-1}$ were also observed in spectra of PVA-Schiff film sensor. Moreover, the characteristic absorptions of amine (N-H stretch) in range of 3500 to 3300 cm^{-1} (m) may overlap with band of PVA hydroxyl group. These results confirm the presence of Schiff's reagent in PVA films.

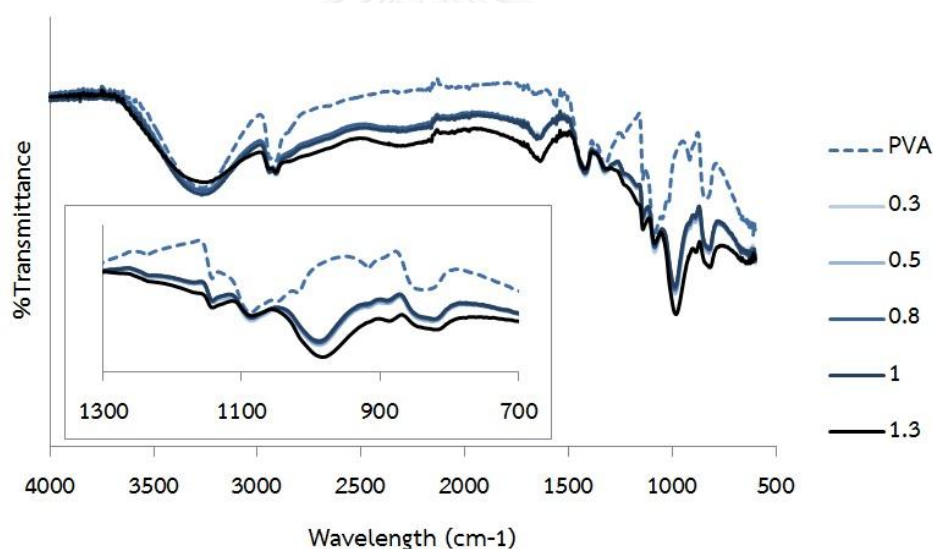


Figure 4.4 ATR-IR spectra of PVA film and PVA film doped with Schiff's reagent of different concentrations.

Furthermore, the presence of Schiff's reagent in the yellow film sensor was observed by DR-UV spectrophotometer (figure 4.5). The results show that the maximum absorption peak appeared in range of 400 to 500 nm and small peak in range of 550 to 600 nm. The absorption spectra of Schiff's reagent consisted of two peaks in range of visible light that increasing absorbance value in range of 550 to 600 was presented decreasing stability [35].

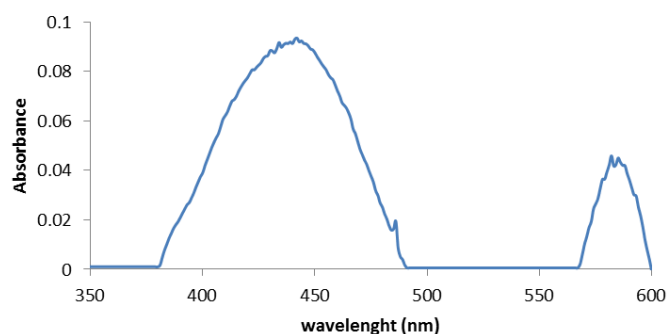


Figure 4.5 The DR-UV spectra of polymer sensor before exposure with formaldehyde.

4.1.2.2 Solid-phase sensor

The IR spectra of silica gel displayed the vibration bands of at $\sim 3403\text{ cm}^{-1}$ (O-H), $\sim 1057\text{ cm}^{-1}$ and $\sim 794\text{ cm}^{-1}$ (Si-O-Si) and $\sim 960\text{ cm}^{-1}$ (Si-OH) (figure 4.3). In case of Schiff's reagent doped solid-phase sensor, the additional characteristic infrared band of Schiff's reagent appeared at 3359 cm^{-1} (N-H), 1042 cm^{-1} (S-O) and 1634 cm^{-1} (aromatic). From the results, signal of silanol group on the surface of silica gel may overlap with the characteristic signal of 1°amine and sulfonate groups of Schiff's reagent. Therefore, DR-UV spectrophotometer was used to confirm the presence of Schiff's reagent on the doped sensors.

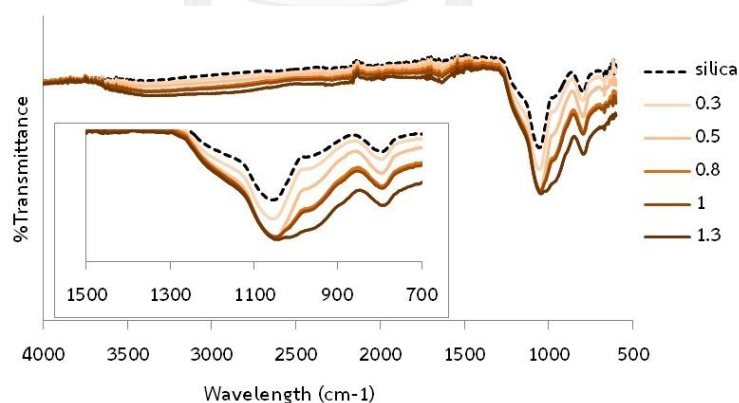


Figure 4.6 ATR-IR spectra of silica and silica doped with Schiff's reagent of different concentrations.

The DR-UV absorption spectra of silica sensor and native silica were recorded and shown in figure 4.7. The two adsorption bands in the wavelength range of 400 to 500 nm and 550 to 600 nm were observed. On the other hand, the spectra of

native silica gel did not show the absorption band in these wavelength ranges. Therefore, the two bands in the absorption spectra of the doped silica gel were attributed to the absorption of Schiff's reagent on the silica. The absorption band at 550 – 600 nm was probably the absorption of the regenerated basic fuchsine. The high absorbance value in range of 400 to 500 nm was required for the effective application in formaldehyde detection. However, the increasing absorbance value in range of 550 to 600 nm revealed a decrease in sensor stability and the sensor became purple.

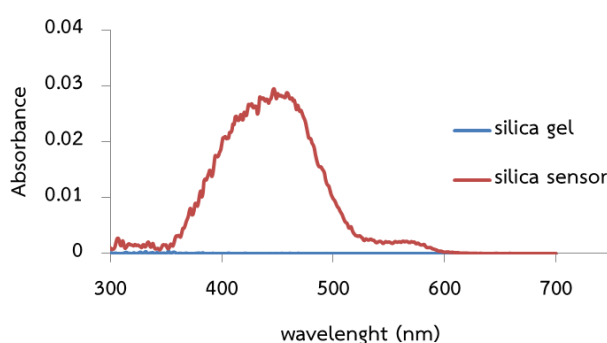


Figure 4.7 The spectra of silica sensor before exposure with formaldehyde.

These results indicate the successful doping of Schiff's reagent in these two sensors. The response to formaldehyde gas of both sensors was further investigated by following the color change of sensing reagent. In order to evaluate the performance of the sensors, a system for formaldehyde gas generation was required. An in-house designed system was built and tested.

4.2 Formaldehyde gas generation

The apparatus set-up for formaldehyde generation is shown in figure 4.8. The formaldehyde gas was generated by heating formaldehyde solution. Nitrogen gas was bubbled continuously into the formaldehyde gas to purge the generated formaldehyde gas to the detection part where the sensor located.

Firstly, to determine the concentration of formaldehyde gas in the gas mixture, the generated formaldehyde was purged to the trapping system consisting of a series of bottles containing acetylacetone reagent (trapping solution). The

reaction between formaldehyde and acetylacetone in solutions produce a yellow product that could be detected by a UV-Vis spectrophotometer and the formaldehyde concentration could be obtained. After that a suitable condition of formaldehyde gas generation was obtained, the formaldehyde gas at concentration of interest was generated and passed through the sensor chamber to test the response of the sensor.

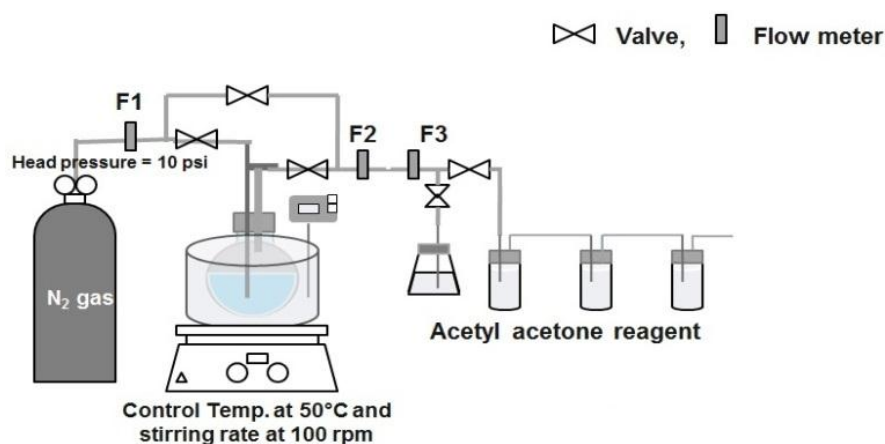


Figure 4.8 Formaldehyde generation system.

4.2.1 Volume of acetylacetone reagent for formaldehyde gas trapping

The volume of acetylacetone reagent (as trapping solution) in a vial with a capacity of 10 mL was varied to find a suitable condition which formaldehyde in gas mixture could be trapped completely when the flow rate of system was controlled at 100 mL min⁻¹. The results showed that 7 mL of trapping solution was the most suitable in this system. Using a lower volume of trapping solution resulted in incomplete trapping, while using a higher volume of solution, the solution in vial No.1 would move to another vial and it caused swings in gas flow rate. Thus, 7 mL of reagent was chosen for this set-up and used to evaluate formaldehyde concentration in the next part.

4.2.2 Performance of the trapping system

The trapping system was designed for monitoring the formaldehyde gas concentration. To determine formaldehyde concentration in gas mixture, the

generated gas mixture was passed directly into the acetylacetone trapping solutions. The dissolved formaldehyde reacted with acetylacetone to yield yellow products after heating. The product solution was further analyzed by UV-Vis spectrophotometer and the absorbance at 412 nm was recorded as described in section 3.5. In order to obtain a system that could completely trap formaldehyde gas, the trapping system consisted of 3 joined vials containing 7 mL of trapping solution each was connected to the generation system and their performance in formaldehyde trapping was evaluated. Formaldehyde gas generated from low and high concentration of formaldehyde solution (100 and 5000 ppm) was subjected to test the trapping system. The absorbance values of trapping solution observed by UV-Vis spectrophotometer in 3 vials after gas flow were compared with that of acetylacetone reagent without formaldehyde as shown in figure 4.9.

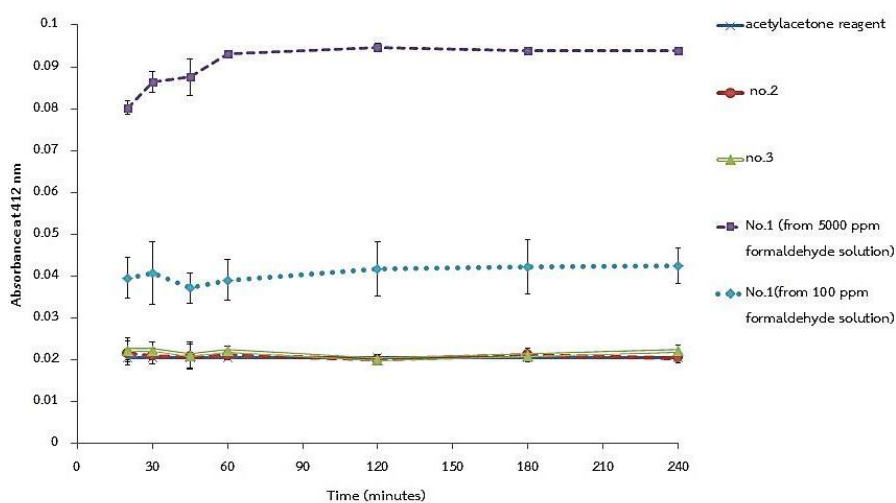


Figure 4.9 The absorbance values of acetylacetone reagent compared with trapping reagent solution in vial no.1, no.2 and no.3 after passing formaldehyde gas generated from formaldehyde solution of different concentrations (100 and 5000 ppm).

The absorption at 412 nm which was attributed to the absorption of products of the reaction of formaldehyde with acetylacetone was monitored when analyzed the solution in the first vial (no.1), the second vial (no.2) and the third vial (no.3) and compared with just acetylacetone reagent. The absorbance values were observed from solutions in the first vial, while the signal observed from solutions in vial no.2

and vial no.3 were not different from the signal of acetylacetone reagent blank. The results indicate that this trapping system with this volume was sufficient to trap formaldehyde gas in gas mixture. Furthermore, the results also showed that the trapping efficiency was relatively constant. Whenever the trapping system was used to trap formaldehyde gas (at different time of generation), the results were also the same. Thus, the system was employed for formaldehyde gas trapping for the determination of formaldehyde concentration in gas mixture.

4.2.3 Quantitative analysis of formaldehyde gas

The concentration of formaldehyde gas were determined by trapping formaldehyde in gas mixture with acetylacetone reagent and then the product of reaction was measured spectroscopically compared with calibration curve. However, the effect of heating the mixture solution between formaldehyde and acetylacetone reagent was studied before measurement with spectrophotometer in order to find suitable conditions for determination of formaldehyde concentration in the trapping solutions.

4.2.4 Effect of temperature on reaction of formaldehyde and acetylacetone

The temperature at 60°C was adopted in this study [30, 32]. The formaldehyde in gas mixture was trapped in acetylacetone reagent and the mixture was heated at 60°C for 10 minutes before measurement with spectrophotometer. The results were compared to the signal of acetylacetone reagent after trapping formaldehyde gas of the same concentration but kept at room temperature before measurement. The absorbance of these mixtures was monitored for 3 hours as shown figure 4.10.

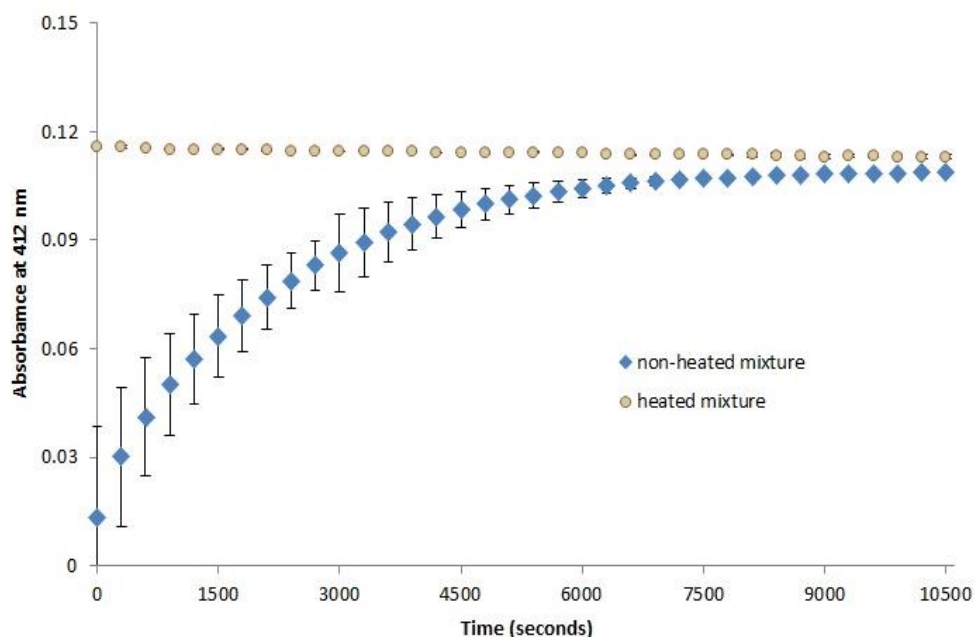


Figure 4.10 The absorbance value at 412 nm of heated and non-heated acetylacetone reagent mixed with formaldehyde in gas mixture generated from 4000 ppm of formaldehyde solution.

The results show that the reaction between formaldehyde and acetylacetone reagent without heating occurred slowly. Therefore, the mixtures solution of formaldehyde and trapping solution should be heated immediately in order to complete the reaction and save time before measurement by UV-Vis spectrophotometer.

4.2.5 Determination of formaldehyde concentration in solution by UV-Vis spectrophotometer using acetylacetone reagent

After trapping the formaldehyde gas in trapping solution, the concentration of formaldehyde dissolved in trapping solution was determined by measuring the absorbance of the solution at 412 nm and comparing these absorbance values to a standard calibration curve constructed by using standard formaldehyde solution and acetylacetone reagent by following ASTM method (D6303-98). Moreover, as formaldehyde is volatile, formaldehyde solution used as standards and solution for formaldehyde gas generation was standardized. The formaldehyde standard solution (1000 ppm) was standardized with a standard solution of hydrochloric acid (following

ASTM method (E 200)) and a sodium sulfite solution in observing pH value as described in 3.3.2.

The formaldehyde standard solution (1000 ppm) was diluted with deionized water to obtain standard solutions for calibration curve construction in a range of 150 to 500 ppb. Acetylacetone reagent was added into formaldehyde standard solutions and heated. The absorbance of the product obtained from the reaction between formaldehyde and acetylacetone was measured, whereas the blank signal (0 ppb) was that of pure acetylacetone reagent (figure 4.11).

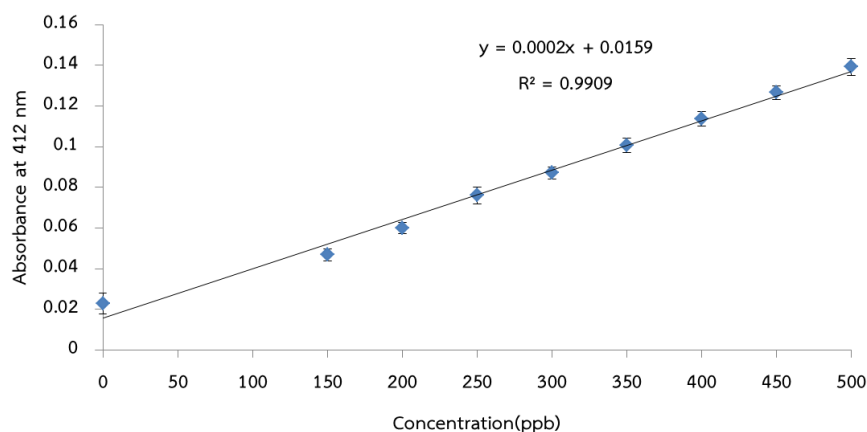


Figure 4.11 The calibration curve for determination of formaldehyde concentration in solutions (n=5).

The linear range for formaldehyde determination was obtained in a range of 0 to 500 ppb. This method was applied for the determination of formaldehyde concentration in gas mixture and unknown samples.

4.3 Formaldehyde gas generation

Formaldehyde gas of different concentrations could be generated by using a formaldehyde solution diluted to different concentrations. In this work, the purpose of formaldehyde solution dilution was to find the starting concentration of formaldehyde solution that can generate formaldehyde gas with an average concentration of interest. The controlled variables in the set up included nitrogen carrier gas pressure and flow rate, temperature in heating of formaldehyde solution and gas flow distance. The results are shown in table 4.2 and the concentration of

formaldehyde dissolved in trapping solution was determined by comparing with calibration curve prepared daily.

Table 4.2 Formaldehyde gas concentration generated from various formaldehyde solutions

Concentration of formaldehyde solution	Concentration of generated formaldehyde gas
100 ppm	ca. 6 ppb
250 ppm	ca. 11 ppb
1000 ppm	27 ppb
2500 ppm	30 ppb
5000 ppm	ca. 62 ppb
20000 ppm	287 ppb
30000 ppm	320 ppb
35000 ppm	340 ppb
40000 ppm	387 ppb
45000 ppm	510 ppb

The concentration of formaldehyde gas of ca. 6 ppb and 62 ppb were selected to further test the sensors performance.

4.4.1 Equilibrium of formaldehyde gas generation

Using the proposed gas generation set-up and condition, formaldehyde gas in concentration range of 57 to 67 ppb (n=3) was generated from a 5000 ppm formaldehyde solution. The equilibrium of formaldehyde gas generation or equilibrium between liquid phase and gas phase was reached within 30 minutes and under the system proposed, after 30 min, the equilibrium concentration of formaldehyde was maintained relatively constant for another 4 hours. When started with a 100 ppm formaldehyde solution, formaldehyde gas in a concentration range of 5 to 7 ppb (n=3) could be generated. The equilibrium between liquid phase and

gas phase was reached within 20 minutes and also lasted for 4 hours as shown in figure 4.12.

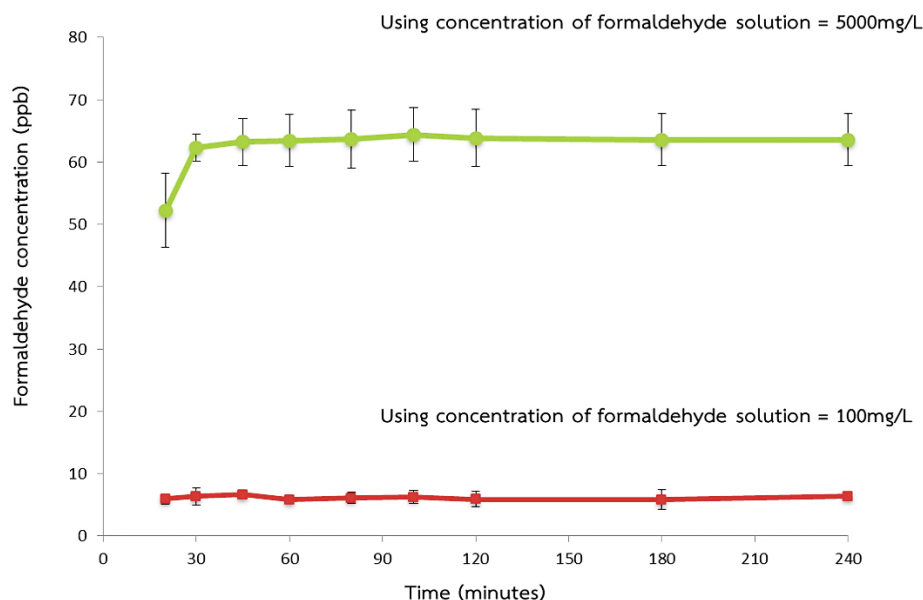


Figure 4.12 The formaldehyde gas concentration obtained in the generation at different times.

The initial concentration of formaldehyde solution may affect the gas evaporation equilibrium and also equilibrium gas concentration. In this study, the generated formaldehyde gas was passed through the sensor chamber after 30 minutes of generation to assure that the equilibrium was attained. The sensor testing was performed after that and finished before 4 hours; thus, formaldehyde concentration was relatively constant during the testing period.









4.4 Sensors performance testing

In this study, the polyvinyl alcohol film sensor and silica sensor were tested in formaldehyde gas detection by observing the color change with naked eyes. The condition in formaldehyde generation was controlled as described in table 3.4. The system was purged with nitrogen gas all the time to avoid contamination problem from exposure to interferences such as others aldehydes, ketones and alcohols that cause false-positive test results. After 30 minutes of generation time, the mixture of

formaldehyde and nitrogen gases was then passed through a chamber containing sensor.

In order to ensure that the observed color changes of sensors was caused by formaldehyde gas, the sensors were exposed to pure nitrogen gas for 3 hours and the results are observed as shown in Table 4.3.

Table 4.3 Color of the sensors after exposure to pure nitrogen gas.

Flow of nitrogen gas	Concentration of Schiff's reagent			
	0.841 mM	1.093 mM	1.345 mM	
Before				
After				

The results show that the color of the both sensors did not change after being exposed to nitrogen gas for 3 hours. Thus, nitrogen gas was suitable to be used as carrier gas as it did not induce the color change of sensor.

4.4.1 Color response of solid-phase sensor

A weight of solid gas sensor contained in glass tube was controlled to be 0.0100 ± 0.0002 g. Three different concentrations of Schiff's reagent doped solid sensors were selected regarding the starting color of obtained sensors after preparation (as described in section 4.1). The silica doped with 0.8, 1.0 and 1.3 mM of Schiff's reagents were used to detect 6 and 62 ppb formaldehyde gas and the response of sensors as color change as a function of exposure time was observed with naked eyes.

Response to 62 ppb of formaldehyde gas

The color of each solid-phase sensors became purple after exposure to approximately 62 ppb formaldehyde gas in gas mixture as shown in figure 4.13.

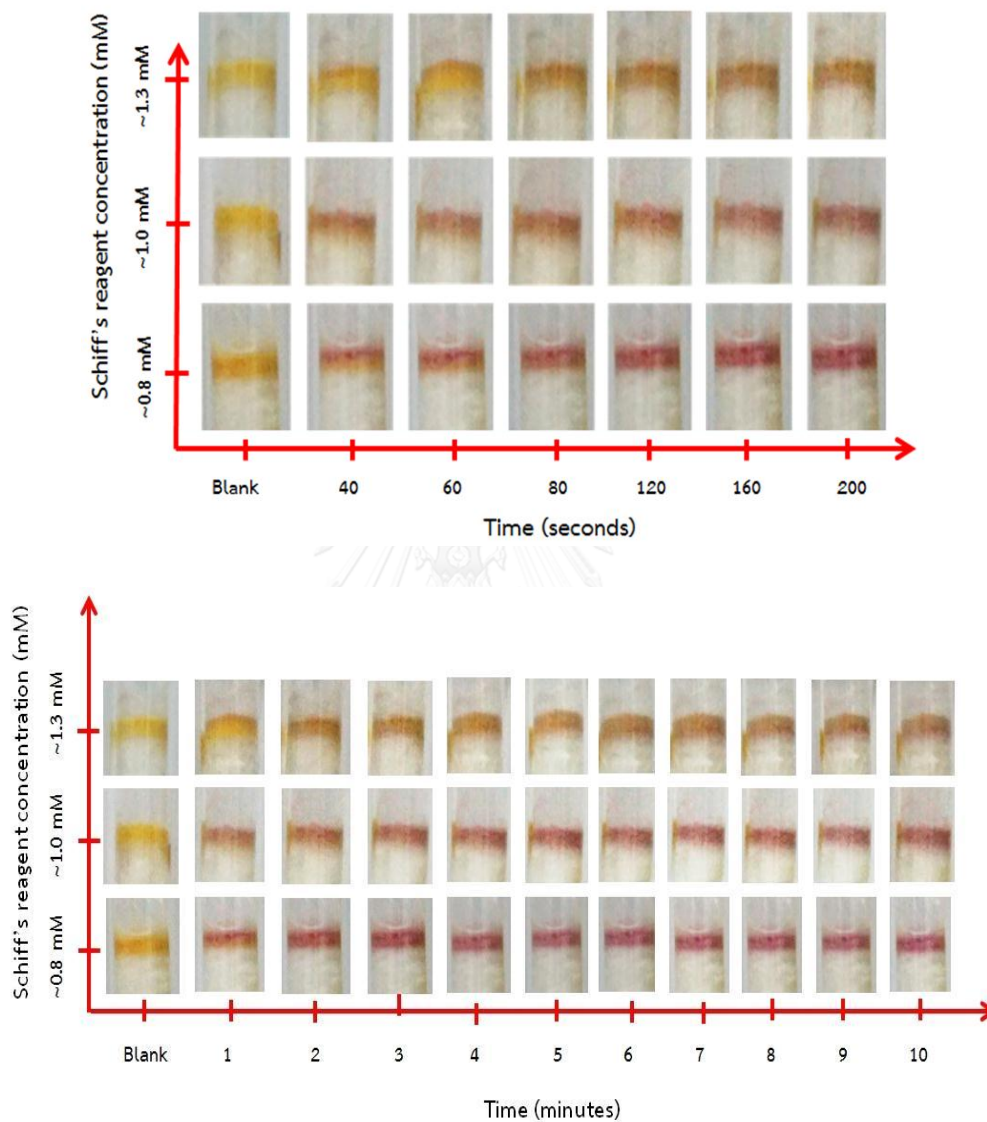


Figure 4.13 The color chart of solid-phase sensors after exposure to formaldehyde gas with concentration of 62 ± 5 ppb.

Figure 4.13 shows that the increasing of exposure time of the sensors to formaldehyde gas resulted in a change of color from yellow to magenta and purple for all sensors. The tone of color change was different in each sensors; particularly the sensor doped with 1.3 mM of Schiff's reagent, color change could

not be observed clearly due to high content of Schiff's reagent on sensors compared to formaldehyde gas concentration.

If the color change occurred rapidly when exposed to low formaldehyde concentration, then the sensors were sensitive. The time for the sensor color to change thoroughly all surface was selected as response time in formaldehyde detection. At 2 minutes, solid-phase sensors doped with 0.8 mM of Schiff's reagent were purple and the color change occurred faster than that observed in solid-phase sensor doped with 1.0 mM (3minutes). The doping with 1.3 mM of Schiff's reagent could not be observed clearly.

Response to 6 ppb of formaldehyde gas

The response and color change of Schiff-silica sensor was expected to be rapid and to change from yellow to magenta after formaldehyde exposure. In this experiment, low formaldehyde gas concentration was subjected to the test of sensor sensitivity and the results are shown in figure 4.14.

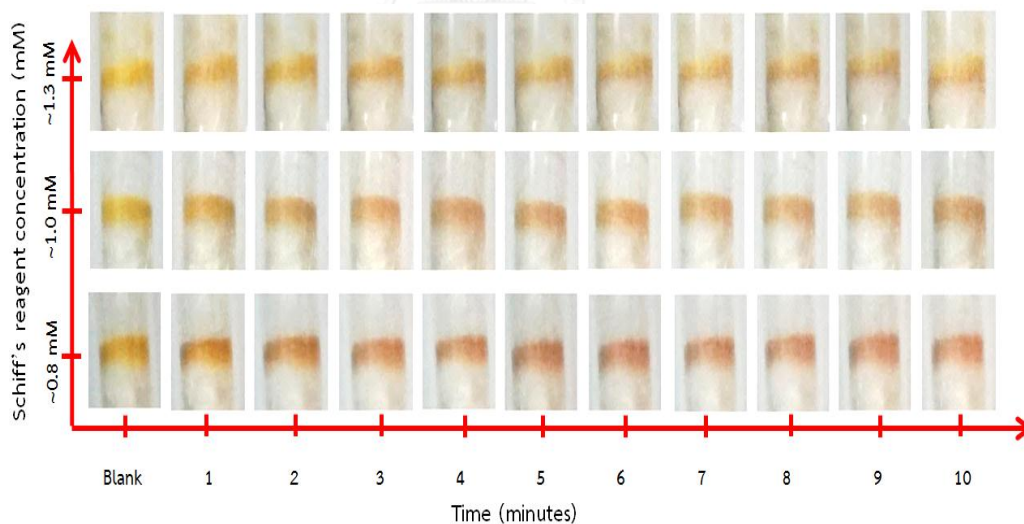


Figure 4.14 The color chart of solid-phase sensors after exposure to formaldehyde gas in concentration range of 6 ± 1 ppb.

The sensor color changed rapidly which indicated a high sensitivity of sensor in low level formaldehyde gas detection. The color tint of each sensor was different in particular sensor doped with 0.8 mM Schiff's reagent, its complete color

change from yellow to reddish-purple was observed within 2 minutes. On the other hand, sensor doped with 1.0 mM of Schiff's reagent appeared deep reddish-yellow which indicated partial reaction of formaldehyde with Schiff's reagent on the surface at 3 minutes. The color change of sensor doped with 1.3 mM of sensing reagent could not be seen clearly after exposure with formaldehyde gas at this low concentration for 10 minutes. The complete color change of sensors doped with 1.0 mM and 1.3 mM of Schiff's reagent could not be achieved within 10 minutes of gas flow. The color response of each sensor depends strongly on Schiff's reagent content. However, each of these solid phases showed different color tint when exposed to low and high concentration of formaldehyde, which indicated a good sensitivity in detection of different concentration of formaldehyde gas.

From the testing, Schiff's reagent in sensors would change color from yellow to reddish-yellow, magenta and purple, respectively after the exposure to formaldehyde gas. The red color intensity increased as the product of the reaction between Schiff's reagent and formaldehyde increased. Therefore, the sensor exposed to formaldehyde with a high concentration (62 ± 5 ppb) could have more intense color than that exposed to lower formaldehyde gas concentration (6 ± 1 ppb).

Furthermore, response time or the time used in formaldehyde detection also depended strongly on Schiff's content and formaldehyde concentration. The color of sensor doped with low Schiff's content changed faster when exposed to formaldehyde gas. From the results of each sensor, response time of sensor doped with 0.8 mM of Schiff's reagent was 2 minutes while the sensor doped with 1.0 mM of sensing reagent responded at 3 minutes of gas flow. Considering the color response, the both sensors could distinguish between two formaldehyde concentrations studied (figure 4.15). However, sensor doped with 1.3 mM of sensing reagent could not give the clear color change. The response time for sensor doped with 0.8 mM of sensing reagent was faster than other sensor. However, for applying the sensor to detect formaldehyde at concentration of *ca.* 62 ppb, sensor doped with 0.8 mM was not suitable because the color change occurred too quickly. The silica doped with 1.0 mM of Schiff's reagent was a good choice for this study because

it gave distinct color when exposed to formaldehyde concentration of *ca.* 6 ppb and 62 ppb for 3 minutes of gas flow. Therefore, this sensor was further tested with synthetic gas sample.

From the results obtained, the response time depended strongly on Schiff's reagent concentration. Considering the exposure of the sensors to the same formaldehyde gas concentration and flow time, when higher concentration of Schiff's reagent was doped onto sensor, there was a higher number of the unreacted Schiff's reagent left on the sensor. Therefore, the mixed color of the sensor would be observed. On the other hand, using very low concentration of Schiff's reagent, the sensor color would change rapidly or the sensor would respond to formaldehyde gas quickly due to low amount of Schiff's reagent. However, when this sensor was exposed to formaldehyde gas at high concentration, it would respond too quickly and it was difficult to detect at specific time. Therefore, the response time and color change of the sensor should be detected accurately and clearly.

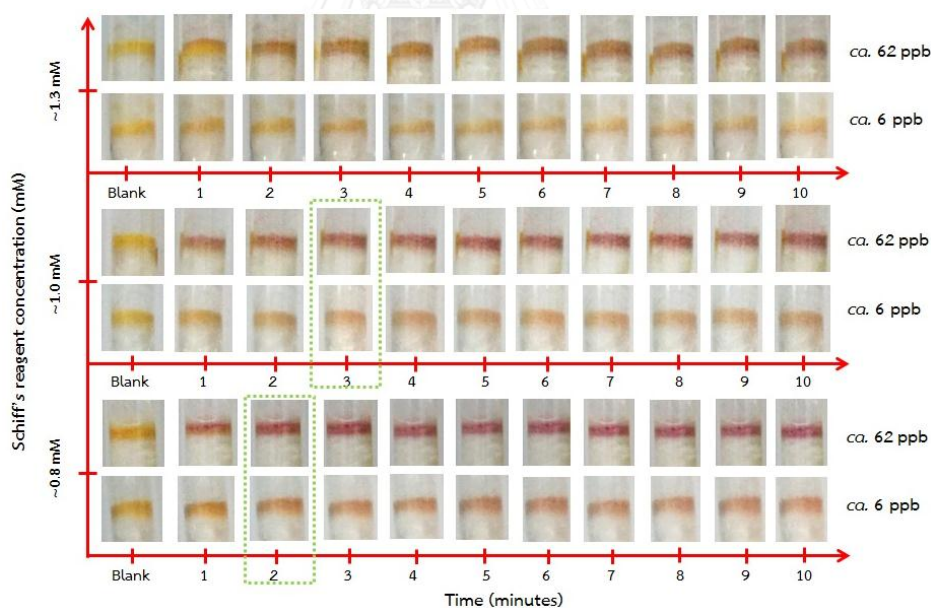


Figure 4.15 The color chart of solid-phase sensors after exposure to formaldehyde *ca.* 6 and *ca.* 62 ppb.

4.4.2 Color response of film sensor

Film sensor was prepared with 10% w/w Schiff's reagent-PVA solution. Based on the result in section 4.1, only the polymer sensor doped with 1.3 mM of Schiff's

reagent could be used for the testing. The film sensor was exposed to formaldehyde in gas mixture after 30 minutes of formaldehyde generation to ensure that formaldehyde gas concentration reach its equilibrium concentration. The sensors response was observed via colorimetric detection by naked eyes.

Response to 62 ppb of formaldehyde gas

The change of sensor color was monitored at different exposure time. The film sensor was cut into a size of 0.7x0.8 cm and put in an open ended glass tube. The color of the film sensor would change from yellow to purple slowly while its surface was exposed to formaldehyde gas as shown in figure 4.16.

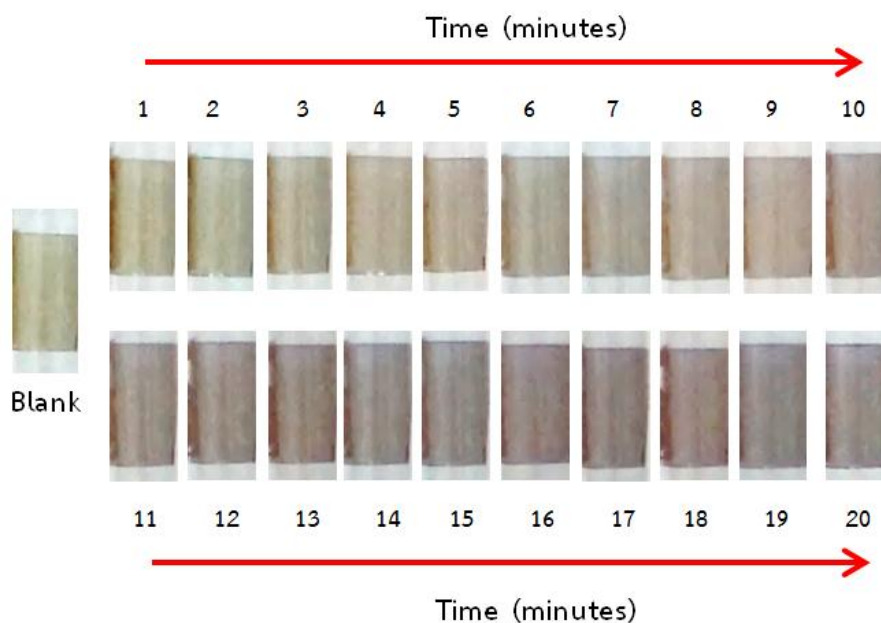


Figure 4.16 Film sensor before and after exposure to formaldehyde gas in concentration range of 62 ± 5 ppb.

The results show a slow color change of film sensor and the complete change of color was obtained within 11 minutes. The Schiff's reagent and formaldehyde could react in the polymer matrix and/or on film surface and generate purple product in film sensor later. Thus, the response time of film sensor for detection of 62 ppb formaldehyde gas was 11 minutes. The response time of film sensor was much slower than solid sensor because surface area of polymer film was

much less than silica gel and hence formaldehyde gas might slowly diffuse in film matrix to react with sensing reagent.

Response to 6 ppb of formaldehyde gas

The polymer sensor was tested for formaldehyde detection at concentration of 6 ppb. The color was observed every 1 minute until 30 minutes (figure 4.17).

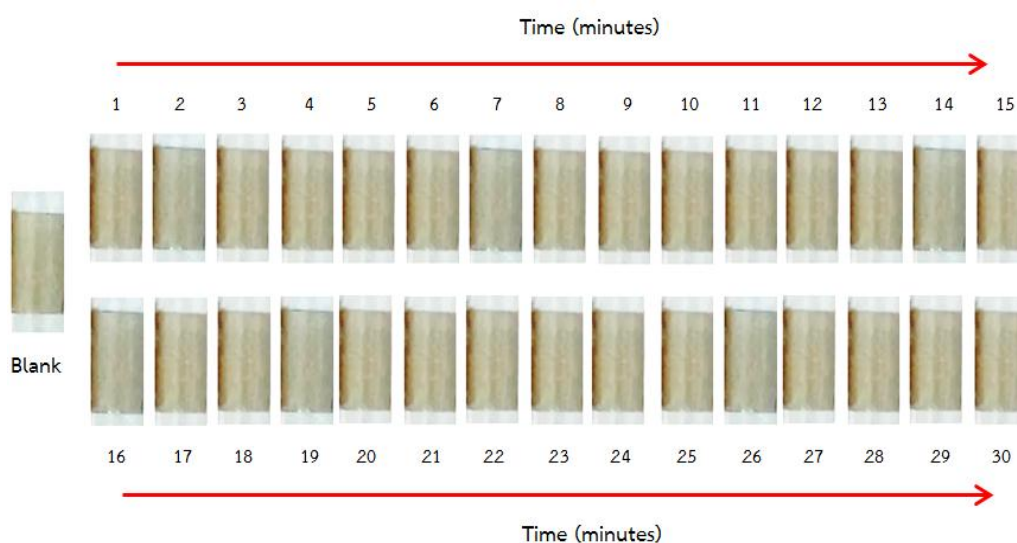


Figure 4.17 Film sensor before and after exposure to formaldehyde gas in concentration range of 5-7 ppb.

From figure 4.17, there was no color change on sensor observed within 30 minutes. It might be because Schiff's reagent content was high which gave color as deep yellow and the purple product from reaction of Schiff's reagent and formaldehyde at low concentration was in a small content. Thus, the color of product could not be well distinguished on this film sensor and therefore, the film sensor did not give clear response for visual detection of formaldehyde at low concentration within 30 minutes.

Regarding all results of film sensor, the film sensor was able to detect only 62 ± 5 ppb of formaldehyde gas within reasonable time. Moreover, to detect low amount of formaldehyde, exposure time of longer than 30 minutes was required. To

achieve rapid response to formaldehyde gas, the film sensor was suitable for formaldehyde gas detection in the concentration range of 57-67 ppb or higher.

4.5 Application of the sensors to detect formaldehyde in synthetic gas sample

The both sensors were tested with formaldehyde gas in a synthetic gas sample containing *ca.* 11 ppb of formaldehyde gas. The silica sensor and film sensor were used to detect formaldehyde gas in sample within 3 minutes and 11 minutes respectively. The results are shown in figure 4.18.

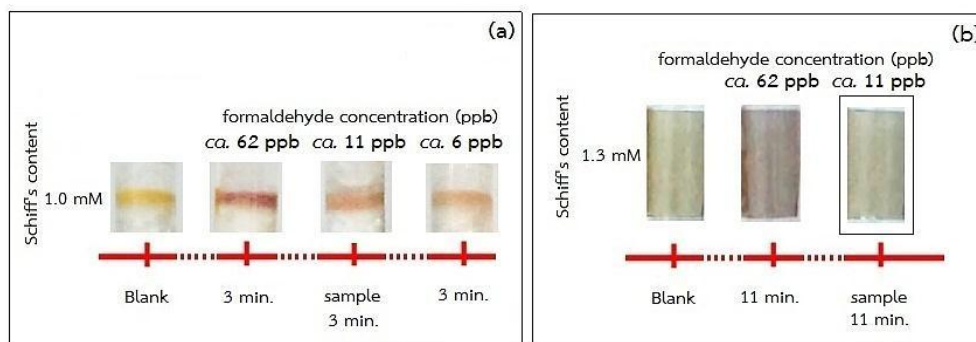


Figure 4.18 Testing the performance of silica sensor (a) and film sensor (b) in the detection of formaldehyde in a synthetic gas sample containing *ca.* 11 ppb formaldehyde gas.

To test performance of film sensor, the formaldehyde gas sample was passed through film sensor for 11 minutes. The color of the film sensor did not change, indicating that the formaldehyde concentration was lower than 62 ppb, which is in agreement to the concentration of gas sample. Moreover, the testing of solid-phase sensor after exposure with *ca.* 11 ppb formaldehyde for 3 minutes of gas flow, the sensor was red-yellow, which could be the response of the sensor when exposed to formaldehyde at concentration higher than 6 ppb but less than *ca.* 62 ppb. The result was in agreement with the concentration of formaldehyde gas in the synthetic gas mixture.

In the application, the color chart of the both sensors could be created in order to use in comparison with the color of the sensors after exposure to a gas sample (figure 4.19).

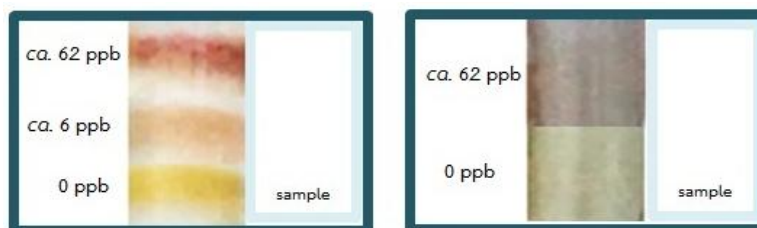


Figure 4.19 The color chart of the both sensors for use to compare with sample color.

4.6 Lifetime and regeneration property of gas sensors

The stability of Schiff's reagent on sensors which indicates the lifetime of sensors was evaluated by using diffuse reflectance UV-vis spectrophotometer (DR-UV-vis spectrophotometer) and color observation. The stability of gas sensor was observed by monitoring the maximum absorbance values in the two range of wavelength which are from 400 to 500 nm (absorption band of yellow Schiff's reagent) and from 550 to 600 nm (absorption band of blue and violet product and/or basic fuchsine). The both sensors were kept in a desiccator at room temperature for different period of time. The results are shown in figure 4.20 and figure 4.21.

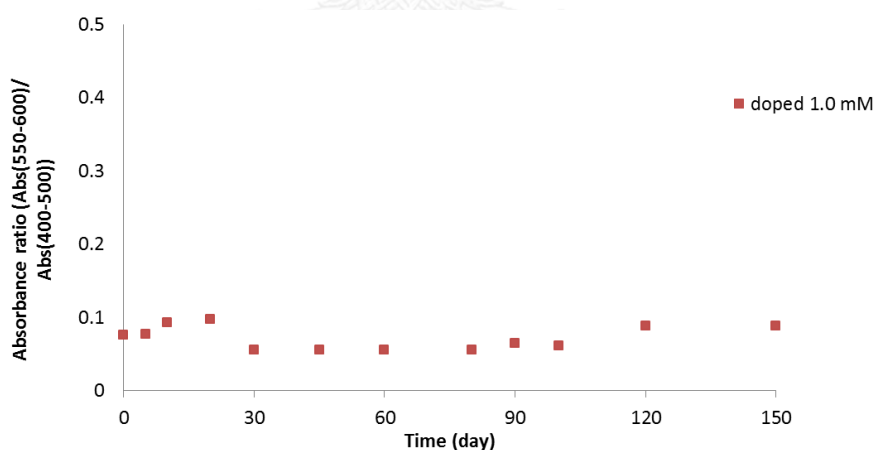


Figure 4.20 The absorbance ratio ($\text{Abs.}(\lambda=550-600)/\text{Abs.}(\lambda=400-500)$) in wavelength range of 400-600 nm of silica sensors doped with 1.0 mM Schiff's reagent observed at different time period.

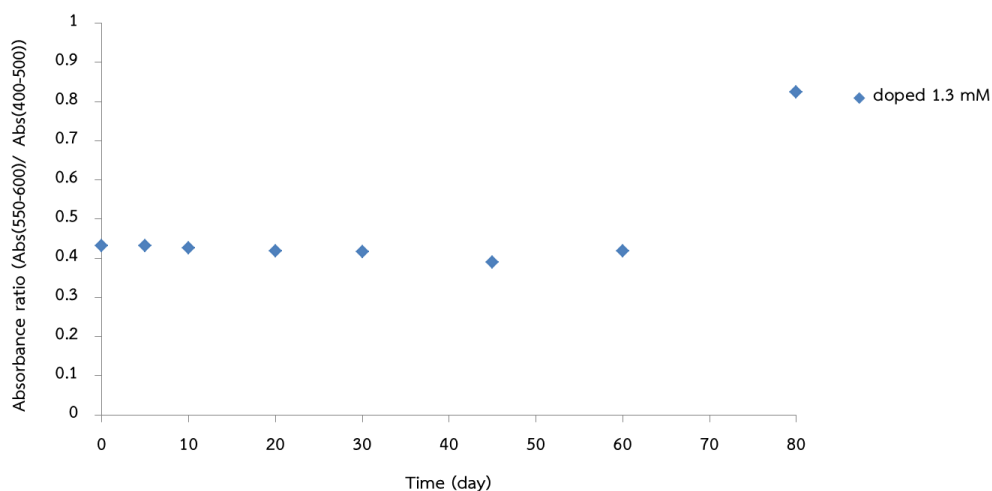


Figure 4.21 The absorbance ratio ($\text{Abs. } (\lambda=550-600) / \text{Abs. } (\lambda=400-500)$) in wavelength range of 400-600 nm of film sensor doped with 1.3 mM Schiff's reagent observed at different time period.

The life time of silica sensor was at least 5 months. As the results of film sensor, its lifetime was 60 days that film remained in yellow color. Then, the film sensor became pink-violet afterward because it contained some converted basic fuchsine from releasing sulfur dioxide [18] and it was not suitable for use.

Finally, the regeneration of both sensors was investigated by purging the used sensors with nitrogen gas and the color of used sensor was not reversible. Therefore, these sensors could not be reused.

CHAPTER V

CONCLUSION

5.1 Conclusion

The silica sensor and film sensor were prepared by doping Schiff's reagent on silica gel and polyvinyl alcohol, respectively. The fabricated sensors were characterized with ATR-FTIR spectrometer and UV-Visible spectrophotometer accompanied with considering coloration of sensor in preparation step.

The performance of both sensors in formaldehyde detection was evaluated. The system of formaldehyde gas generation was developed in-house. Formaldehyde gas was produced by heating formaldehyde solution and purged with nitrogen gas into the detection or trapping system. With this system, formaldehyde gas having concentration in a range from *ca.* 150 to 500 ppb could be generated.

The silica sensors, doped with 0.8, 1.0 and 1.3 mM of Schiff's reagent, could detect formaldehyde gas rapidly. The solid sensor doped with 0.8 and 1.0 mM Schiff's reagent could detect formaldehyde gas in concentration range of 57-67 ppb and 5-7 ppb and gave different color tint with response time of 2 and 3 min, respectively. Under the same condition, the film sensor, which was doped with 1.3 mM of Schiff's reagent, could detect only formaldehyde gas in concentration range of 57-67 ppb with response time of 11 minutes.

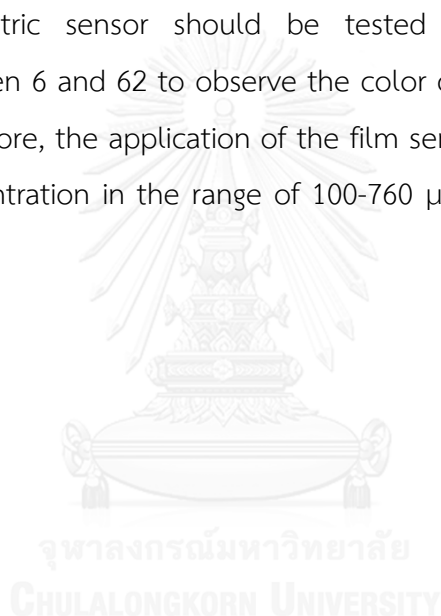
The coloration of sensors after exposure with formaldehyde gas was the result from reaction between formaldehyde molecules and active reagent in sensor. The sensors contained less Schiff's content were more sensitive to formaldehyde at low concentration than the sensors doped with higher Schiff's concentration. The sensitivity of solid-phase sensor was better than film sensor by considering response time or the time for color change all over sensor surface. The surface area of solid-phase sensor was much higher than film sensor and Schiff's content could be doped onto silica gel in much higher amount than in film. When exposed to formaldehyde gas, formaldehyde would react with Schiff's reagent on silica sensor rapidly by

diffusing into pores, while formaldehyde gas would probably be absorbed slowly on film surface before the reaction with Schiff's reagent.

Moreover, the performance of the sensors was tested by using them to detect *ca.* 11 ppb of formaldehyde gas. By comparing the obtained sensor color to the standard color chart (6 ppb and 62 ppb formaldehyde), the results obtained was in agreement with the real formaldehyde concentration. Finally, the both sensors could not be regenerated by purging with nitrogen gas.

5.2 Suggestion of future work

The colorimetric sensor should be tested with formaldehyde gas at concentration between 6 and 62 to observe the color change and produce standard color chart. Furthermore, the application of the film sensors toward the detection of formaldehyde concentration in the range of 100-760 $\mu\text{g/L}$ should be investigated in the future.



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