



PAPER-BASED TEST STRIP FOR FORMALDEHYDE GAS ANALYSIS

WANNISA SROISARIKA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR MASTER DEGREE OF SCIENCE

IN CHEMISTRY

FACULTY OF SCIENCE

BURAPHA UNIVERSITY

2024

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วรรณิศา ศรีอัยสาริกา

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WANNISA SROISARIKA : PAPER-BASED TEST STRIP FOR FORMALDEHYDE GAS ANALYSIS . ADVISORY COMMITTEE: YUPAPORN SAMEENOI, Ph.D. 2024.

A novel and one-step analysis method for formaldehyde gas using a paper-based test strip has been developed. The analysis relied on the reaction between formaldehyde and acetylacetone in the presence of ammonium acetate (Nash's reagent), which yielded a yellow-colored product of 3,5-diacetyl-1,4-dihydropyridine (DDL). The paper-based test strip has a rectangular shape, measuring 6 cm long and 1 cm wide. The test zone, which is 1 cm long and 1 cm wide, is located at one end of the strip. To prepare the test zone, the paper is dipped into Nash's reagent dissolved in sodium carboxymethyl cellulose (Na-CMC) hydrogel and then dried at 40°C. The formaldehyde test is performed by exposing the test strip to formaldehyde gas. The intensity of the yellow color is directly proportional to the amount of formaldehyde in the sample. Under optimal conditions, the developed device was able to measure formaldehyde in the two-portion linear range of 0.25–1 ppmV and 3–40 ppmV, with a value of $R^2 = 0.9953$ and $R^2 = 0.9975$, respectively. The limit of detection was 12 ppbV, which is lower than the air quality threshold set by the Occupational Safety and Health Administration (OSHA). From the analysis of samples including house spray paint, paint for exterior wood, and wood glue, a high recovery in the range of 90–104% was obtained. Furthermore, this paper-based test strip was found to be stable for 2 months when stored at both ambient and low temperatures. These results demonstrated that the developed paper-based test strip is promising to be used for accurately measuring formaldehyde in air samples.

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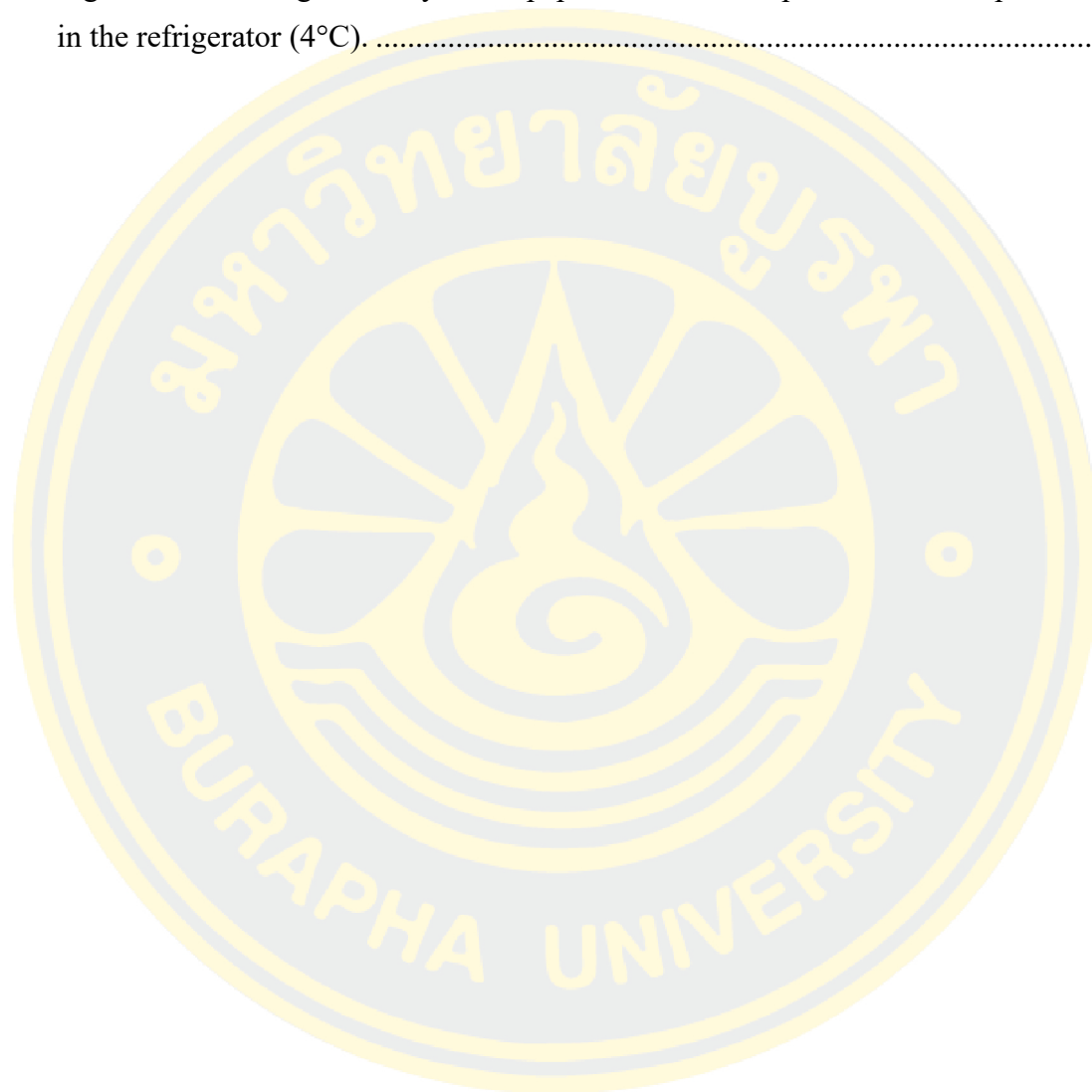
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CHAPTER 1

INTRODUCTION

1.1 Statement and significance of the problems

Formaldehyde (FA) is a colorless, flammable gas with a pungent odor and disinfecting properties. It is commonly used in formalin solutions containing approximately 37-40% formaldehyde gas by weight. Formalin solutions have become ubiquitous in various industries, including medicine, beauty, agriculture, and manufacturing. Despite its widespread use, formaldehyde is classified as a hazardous air pollutant and poses health risks upon prolonged exposure. Even low levels of formaldehyde exposure can result in headaches, fatigue, and respiratory and eye irritation. High levels of exposure can increase the risk of leukemia. Furthermore, formaldehyde has been classified as a carcinogen by the International Agency for Research on Cancer (IARC). The National Institute for Occupational Safety and Health (OSHA) has established a Permissible Exposure Limit (PEL) of 750 ppbV and an Immediately Harmful to Life or Health (IDLH) Limit of 20 ppmV ((OSHA), 2002). The Department of Industrial Control classifies formaldehyde as a type 2 hazardous substance, and the Hazardous Substance Act of 1992 mandates that officials be informed of any manufacturing, importation, exportation, or possession of hazardous substances and adhere to regulations for their manufacture or import (Changsap, 2015).

Formaldehyde analysis can be performed using a variety of methods such as spectrophotometry (Pedro F Brandão et al., 2017), gas chromatography (GC) (Lobo, Santos, Vieira, Osório, & Taylor, 2015), fluorescence spectrophotometry (Ai et al., 2019), and electrochemical (Menart, Jovanovski, & Hočevár, 2017). These methods offer high specificity, accuracy, precision, and sensitivity, enabling the detection of formaldehyde at low concentrations in parts per billion. However, they are associated with certain drawbacks such as the need for expensive instruments, trained personnel to operate them, and time-consuming analysis. Additionally, these methods may not be suitable for on-site analysis.

This study aims to develop a novel, one-step analysis method for formaldehyde gas using a paper-based test strip. The proposed method relies on the reaction between formaldehyde and acetylacetone in the presence of ammonium acetate (Nash's reagent), which yields a yellow-colored product of 3,5-diacetyl-1,4-dihydropyridine (DDL) (see Figure 1-1). The paper-based test strip has a rectangular shape, measuring 6 cm long and 1 cm wide. The test zone, which is 1 cm long and 1 cm wide, is located at one end of the strip. To prepare the test zone, the paper is dipped into Nash's reagent dissolved in sodium carboxymethyl cellulose (Na-CMC) hydrogel, and then dried at 40°C. The formaldehyde test is performed by exposing the test strip to formaldehyde gas. The paper test zone changes to yellow in the presence of formaldehyde gas (see Figure 1-2). The intensity of the yellow color is directly proportional to the amount of formaldehyde in the sample.

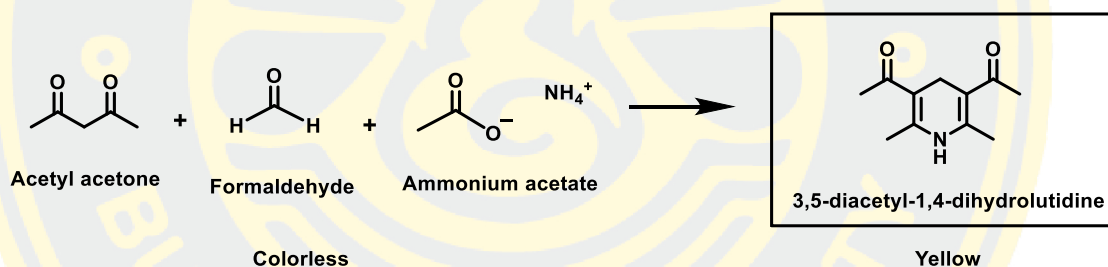


Figure 1-1 Reaction used for formaldehyde analysis.



Figure 1-2 Paper-based test strip for formaldehyde analysis.

1.2 Objectives

To develop a paper-based test strip for formaldehyde gas analysis using colorimetric measurement.

1.3 Scope of Study

1. Design the paper-based device that suit for analysis of formaldehyde gas.
2. Study the optimum conditions for formaldehyde gas analysis including types of paper, reaction time, and concentration of acetylacetone.
3. Study analytical features including linear range, the limit of detection, reproducibility, and stability for formaldehyde gas analysis using the optimal conditions.
4. Study accuracy of the developed method for formaldehyde gas analysis in terms of recovery and analysis of formaldehyde gas in the samples using the developed paper-based device compared to those obtained from the standard method.

1.4 Contribution to knowledge

The newly developed paper-based test strips are a highly effective means of analyzing formaldehyde gas, offering accurate results that are easy to obtain in a point-of-care setting. Moreover, this approach is rapid, user-friendly, and low-cost.

CHAPTER 2

LITERATURE REVIEWS

2.1 Formaldehyde

Formaldehyde is an aldehyde organic compound that occurs both synthetically and naturally. It can be found in various combustions, such as vehicle exhaust pipes, grass burning, wood burning, industrial boiler stoves, and cigarette smoke. Formaldehyde, at normal pressures, is a gaseous volatile chemical (volatile organic compounds, or VOCs). It is an unstable gaseous substance that is used for various purposes in the form of formaldehyde solution or formalin, which is a solution containing about 37–55% of formaldehyde gas weight. The properties of formaldehyde in the gaseous and liquid phases are different. Gaseous formaldehyde is flammable, colorless, has a pungent odor, is corrosive, is slightly heavier than air, is unstable, and is easy to polymerize. Formalin has different properties depending on the concentration of formaldehyde in water and the ratio of methanol in the solution (Changsap, 2015; Suradmanee, 2018).

Table 2-1 Specific properties (Works, 2010).

Molecular Formula	CH ₂ O
Structural Formula	$\begin{array}{c} \text{O} \\ \\ \text{H}-\text{C}-\text{H} \end{array}$
CAS Number	50-00-0
EC Number	200-001-8
UN Number	1198, 2209
Other names	<ul style="list-style-type: none"> - Formaldehyde solution - Formalin - Formic aldehyde - Fyde - Methanal, etc.

2.1.1 Physical and Chemical Properties

Formaldehyde in the gas phase and formalin in the liquid phase have physical and chemical properties as shown in Table 2-2.

Table 2-2 Physical and chemical properties of formaldehyde gas and formalin (Suradmanee, 2018).

Substance properties	Formaldehyde gas	Formalin
Molecular Weight	30.03	
Appearance	Colorless	
Smell	Strong pungent smell	
Autoignition Temperature	424 °C	
Boiling point	-19.5 °C at atmospheric pressure	96 °C at atmospheric pressure
Melting point/Freezing point	(none)	-92 °C
pH	-	2.8-4.0 at 20 °C
Reaction	<ul style="list-style-type: none"> - Polymerisation - Addition - Oxidation 	<ul style="list-style-type: none"> - Polymerisation - Oxidation - Decomposition - Condensation - Addition - Reduction
Hazardous decomposition products	When heated, the substance decomposes to form formic acid. When a fire decomposes into carbon monoxide, carbon dioxide, and hydrogen, toxic smog is formed.	

2.1.2 Benefits and Applications

Formaldehyde often has a gaseous nature. Prior to use in various fields, it must be made into a liquid by mixing with water to become a solution called "formalin". The highest concentration of formaldehyde that can be prepared is about 37–55% by weight. The use of formaldehyde in the medical field, industry, beauty, agriculture, and other fields is described as follows:

2.1.2.1 Industry

Formaldehyde is used in a number of industries. In particular, formaldehyde is used as a raw material in the production of urea-formaldehyde, phenol-formaldehyde, melamine-formaldehyde, polyoxymethylene, and other chemicals. In addition, it is used as a disinfectant and preservative and is also used as an ingredient in making particleboard, plywood, and furniture coatings (from urea formaldehyde), crockery (from melamine formaldehyde), car brake pads, insulation (from phenol-formaldehyde), automotive parts, electronic appliance parts (from polyacetal), etc. It is also used as an adhesive for wood furniture and as a precursor to the production of various chemicals. Formaldehyde applications in various industries in Thailand are mainly used in the production of urea formaldehyde, which accounts for 70% of the total production in the country, as shown in Figure 2-1 (Works, 2010).

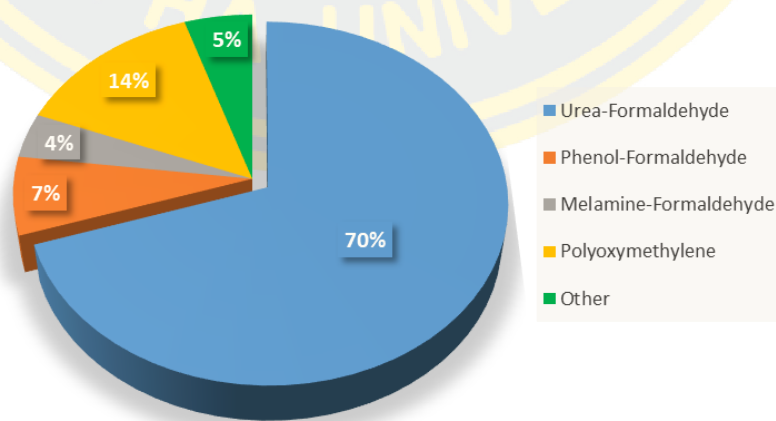


Figure 3-1 The use of formaldehyde in various industries in Thailand (Works, 2010).

2.1.2.2 Medical Field

It is well known that formaldehyde is widely used in medicine. It is most commonly used for the preservation of anatomical specimens. Formaldehyde has also been used to preserve tissue. It is commonly used in pediatric root canal treatment or pulpotomy, which requires the right dosage and the shortest treatment time because formaldehyde is a toxic substance (Aslam, Kumarasinghe, & Lowe, 2021; Godhi, Sood, & Sharma, 2011).

2.1.2.3 Agriculture

Formaldehyde is used in a wide range of agricultural applications, whether it is for the production of substances that destroy or prevent microbial pathogens or for killing fungi in the soil. It is also used as a fertilizer to help increase agricultural productivity, mixed in animal feed to maintain quality and prevent spoilage in ruminant food, and used as a coating agent for vegetables and fruits to inhibit spoilage (Yamamoto, Pereira, Mattoso, Matsunaka, & Ribeiro, 2016).

2.1.2.4 Cosmetics

Formaldehyde is widely used as a cosmetic ingredient. Because of its properties as a preservative and disinfectant and prevents excessive sweating, it is used as an ingredient in toothpaste, mouthwash, soap, shaving cream, and nail polish. Formaldehyde is especially used in cosmetics that can be washed off, such as shampoo, lotion for washing skin, body wash, face wash, and other cleansing lotions (Pedro Francisco Brandão, Ramos, & Rodrigues, 2018; Wu, Chang, & Chou, 2003).

2.1.3 Hazards of Formaldehyde

Although formaldehyde is a substance that has a wide range of uses, inappropriate uses can cause a negative effect on humans, animals, and environment, either directly or indirectly. Exposures to formaldehyde have been reported most commonly from manufacturing processes and during use in the manufacture of end products in the industry, including exposure to formaldehyde in laboratories. Exposure to formaldehyde has been reported to have adverse effects on the respiratory

system and increase the risk of cancer (Mathur & Rastogi, 2007; Soltanpour, Mohammadian, & Fakhri, 2022). The International Agency for Research on Cancer (IARC) has classified formaldehyde as a carcinogen (Humans, 2006). The toxicity that has been exposed to formaldehyde will show more or less symptoms depending on the concentration of formaldehyde, as shown in Tables 2–3.

Table 2-3 Health effects of formaldehyde inhalation exposure at various doses in people and experimental animals (ATSDR, 2008).

Concentration in Air (ppm)	Health effects	
	Effects in Humans	Effects in Animals
0.008	Chronic MRL	
0.03	Intermediate MRL	
0.04	Acute MRL	
0.1 to 0.5	- Irritation of the nose and eyes	- Changes in lung function
	- Neurological effects	- Allergy
0.6 to 1.9	- Increase the risk of developing asthma	- Neurological effects
	- Allergy	- Alterations in lung function
2.0 to 5.9	- Skin dermatitis	- Alterations in lung function
	- Alterations in lung function	- Neurological effects
2.0 to 5.9	- Irritation of the nose and eyes	- Irritation of the nose, eyes, and throat
	- Irritation of the nose eyes and throat	- Skin dermatitis
2.0 to 5.9	- Skin dermatitis	- Alterations in lung function
	- Alterations in lung function	- Decreased body weight
2.0 to 5.9	- Irritation of the nose eyes and throat	- Allergy
	- Skin dermatitis	- Neurological effects, liver effects, testicular effects

Table 2-3 Health effects of formaldehyde inhalation exposure at various doses in people and experimental animals.(ATSDR, 2008)(cont.)

Concentration in Air (ppm)	Health effects	
	Effects in Humans	Effects in Animals
6.0 to 10.9	<ul style="list-style-type: none"> - Irritation of the nose, eyes, throat, and skin - Headache - Squeamishness - Difficulty breathing cough 	<ul style="list-style-type: none"> - Irritation of the nose, eyes - Alterations in lung function - liver effects, testicular effects - Nasopharyngeal cancer - Reduced survival
11 to 50	No studies	<ul style="list-style-type: none"> - Irritation of the nose, eyes - Nasal ulceration - Alterations in lung function - Decreased body weight - Liver effects, testicular effects - Nasopharyngeal cancer - Reduced survival
>50	No studies	<ul style="list-style-type: none"> - Pulmonary edema - Bloody nasal discharge

*Minimum risk exposure levels for humans (MRL)

Formaldehyde that enters the body through ingestion can cause gastrointestinal irritation. If high amount of formaldehyde was untaken into the body, about 30–60 ml, it can cause severe effects such as severe abdominal pain, vomiting, gastric ulcers, unconsciousness, and even death. The severity of the symptoms will depend on the concentration received, as shown in Tables 2-4, from animal studies at various concentrations, which affect the health of the experimental animals.

Table 2-4 Health effects on laboratory animals from ingestion of formaldehyde at various concentrations (ATSDR, 2008).

Dose (mg/kg/day)	Effects in Animals
0.2	Chronic MRL
0.3	Intermediate MRL
0 to 49	no effects
50 to 100	<ul style="list-style-type: none"> - Decreased food intake - Gastrointestinal effects - Kidney effects - Decreased body weight - Liver effects
101 to 150	<ul style="list-style-type: none"> - Decreased food and water intake - Gastrointestinal effects - Kidney effects - Decreased body weight - Liver effects
151 to 200	Testicular effects
201 to 250	No studies
251 to 300	<ul style="list-style-type: none"> - Decreased food and water intake - Gastrointestinal effects - Kidney effects - Decreased body weight - Liver effects - Decreased survival

*Minimum risk exposure levels for humans (MRL)

2.1.4 Formaldehyde Use Regulations

Formaldehyde can be applied in many applications as mentioned above. But the use of formaldehyde is subject to standard regulations to protect human health and the environment. These requirements facilitate the safe production, storage, handling, and use of chemicals.

2.1.4.1 Occupational Safety and Health Administration (OSHA)

The United States National Occupational Safety and Health Administration (OSHA) standards for the regulation and use of formaldehyde are intended to protect workers exposed to formaldehyde and apply to all occupational exposures to formaldehyde gas, its solutions, and items that release formaldehyde.

In the workplace, the permitted exposure limit (PEL) for formaldehyde is 0.75 parts formaldehyde per million parts air (0.75 ppm) assessed as an 8-hour time-weighted average (TWA). The standard includes a second PEL in the form of a short-term exposure limit (STEL) of 2 ppm which is the maximum exposure allowed during a 15-minute period. Concentrations of 100 ppm are immediately dangerous to life and health (IDLH). The National Institute for Occupational Safety and Health (NIOSH) considers 20 ppm of formaldehyde to be IDLH ((OSHA), 2002).

2.1.4.2 Department of Labor Protection and Welfare of Thailand

In Thailand, the Announcement of the Department of Labor Protection and Welfare on Limits of Hazardous Chemical Concentration 2017 has determined that the average concentration over an 8-hour working period for formaldehyde should not exceed 0.75 ppm. The maximum concentration in 15 minutes is not more than 2 ppm (DLPW, 2018).

2.2 Method for Formaldehyde Analysis

2.2.1 Spectrophotometry

By reacting between formaldehyde and specific chemicals, it can form a product with or without color and the concentration or change of the product at a wavelength suitable for that substance was measured which varies with the amount of formaldehyde in the samples.

One example for formaldehyde analysis using spectrophotometry is based on Hantzsch reaction. Formaldehyde in cork agglomerates, a common material used in various products such as flooring, insulation, and furniture was analyzed. The use of gas-diffusion microextraction (GDME) for the extraction of volatile formaldehyde directly from cork agglomerate samples with simultaneous derivatization with acetylacetone (Hantzsch reaction) was reported, as shown in figures 2–2. The absorbance of the colored solution was read in a spectrophotometer at 412 nm. Different extraction parameters were studied and optimized by means of asymmetric screening. The developed methodology was applied to the determination of formaldehyde in different cork agglomerate sample (Pedro F Brandão et al., 2017).

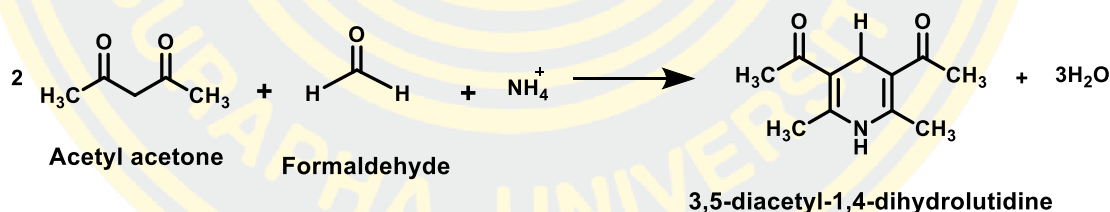


Figure 2-2 Hantzsch reaction between Formaldehyde and Acetylacetone (Pedro F Brandão et al., 2017).

2.2.2 Electrochemical

Another technique that has been reported for formaldehyde analysis is electrochemical technique. The sensor is made up of a three-electrode system that has been modified with hydrazinium polyacrylate, which serves a dual purpose of accumulating and derivatizing formaldehyde gas as well as enabling voltammetric measurements. The proposed mechanisms of the reaction between formaldehyde and hydrazine are shown in Figures 2-3a and 2-3b. Hydrazinium polyacrylate, which is

synthesized to serve a dual purpose, acts as a formaldehyde accumulation/derivatization medium and as a polyelectrolyte, enabling voltammetric measurements. In the polymer (Figure 2-3a), formaldehyde reacts with hydrazine to form a hydrazone derivative, which is electrochemically active and can be detected by the sensor. In the solution (Figure 2-3b), formaldehyde reacts with hydrazine to form a hydrazone derivative, which then reacts with the polymer to form a more stable product that can be detected by the sensor (Menart et al., 2017).

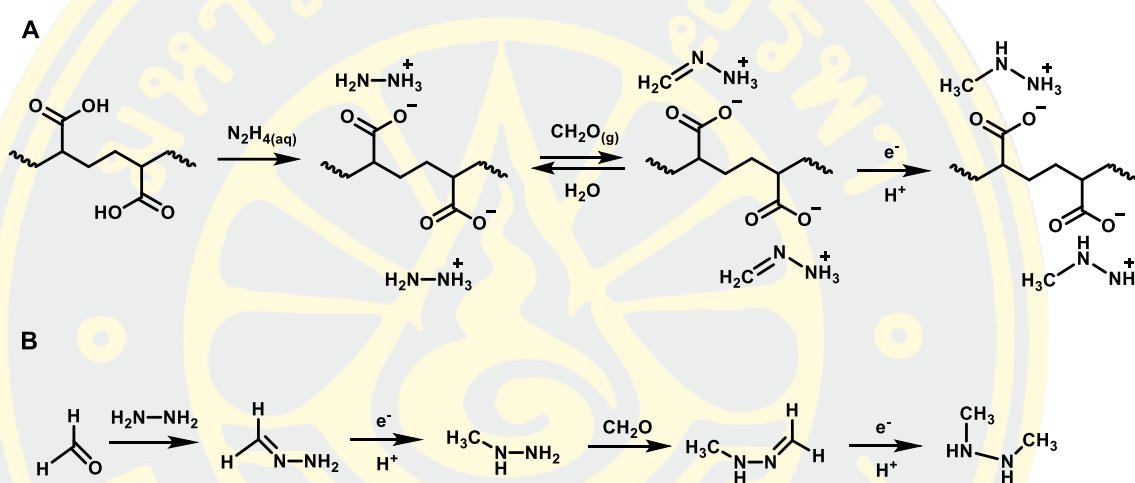


Figure 2-3 Mechanisms hypothesized for the reaction between formaldehyde and hydrazine in the polymer(A) and in solution (B) (Menart et al., 2017).

2.2.3 Gas Chromatography

Gas chromatography is one of techniques for formaldehyde analysis. Previous work demonstrated the use of GC to determine the presence of formaldehyde in hair creams. Gas chromatography-mass spectrometry (GC-MS) is a technique used to separate and identify different compounds in a sample. However, formaldehyde is a volatile and thermally unstable compound, which means that it cannot be directly injected into GC-MS for analysis. Therefore, a process called derivatization is used to convert formaldehyde into a more stable compound that can be analyzed by GC-MS. The reaction used in this work involves the derivatization of formaldehyde using 2,4-DNPH as a reagent to form formaldehyde-2,4 dinitrophenylhydrazone, as shown in

Figures 2–4. This derivative is then analyzed using gas chromatography-mass spectrometry (GC-MS) to quantify the amount of formaldehyde present in hair straightening cream (Lobo et al., 2015).

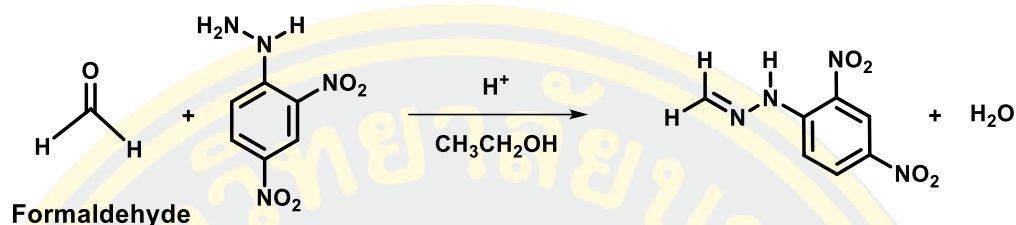


Figure 2-4 Reaction between 2,4-DNPH with Formaldehyde to form formaldehyde-2,4 dinitrophenylhydrazone (Lobo et al., 2015).

2.2.4 Fluorescence

Fluorescence spectrophotometric method has also been reported to detect formaldehyde in urine samples from patients with Alzheimer's disease. Formaldehyde-specific fluorescent probe called NaFA was employed for detection. The reaction used in this work is the chemical reaction between ampicillin and formaldehyde, as shown in Figures 2–5, which forms a derivative that can be detected by HPLC with a fluorescence detector (Ai et al., 2019).

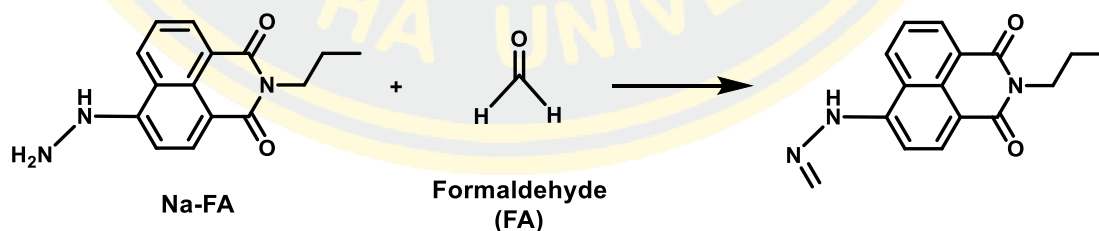


Figure 2-5 Reaction between Ampicillin and Formaldehyde (Ai et al., 2019).

2.3 Paper-based test strip

Paper-based device is currently a popular technology that use for chemical analysis. The devices can be constructed by patterning and impregnating hydrophobic materials on hydrophilic paper to create the analysis zones. The analyte can flow to the test area on the paper that is immobilized with the detection element to create the measuring signal. This technology has been applied in medical analysis, food quality control and environmental monitoring (Sameenoi, Nongkai, Nouanthavong, Henry, & Nacapricha, 2014). Several advantages of the device are that it can be produced easily, the cost of production is low. Moreover, the paper is a material that can be easily found in everyday life and the paper test strips are portable and can be discarded after analysis. The property of paper is that it is composed of cellulose fiber that can absorb water well (hydrophilic). It can also change the texture of the paper according to the needs of the users. Typical paper-based device are is shown in Figure 2-6 (Mahadeva, Walus, & Stoeber, 2015).

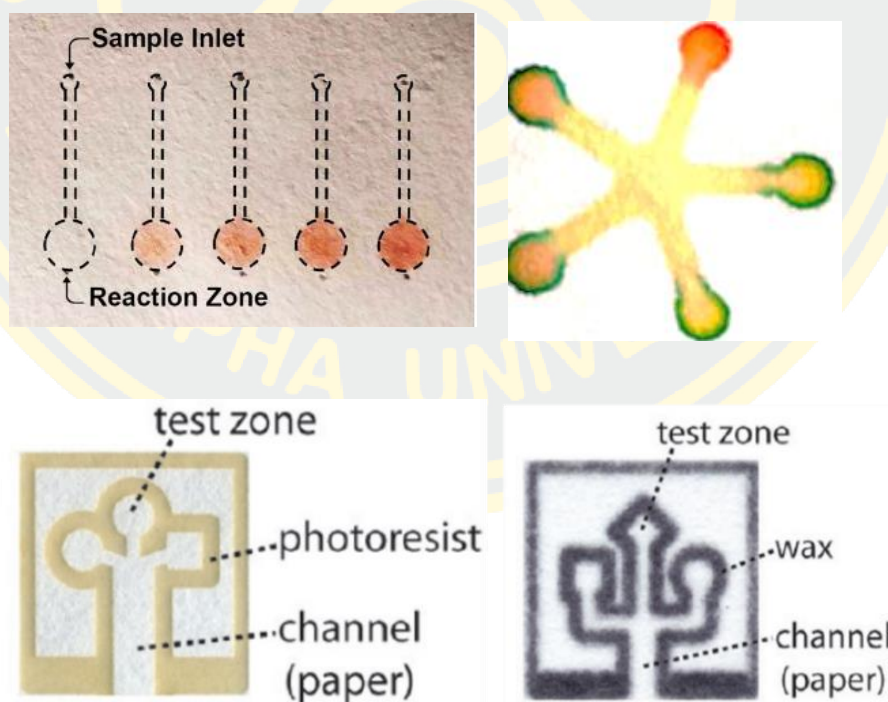


Figure 2-6 Patterns of paper-based devices used for analyzing the substance of interest (Lam, Devadhasan, Howse, & Kim, 2017; Martinez, Phillips, Whitesides, & Carrilho, 2010).

2.4 Related Literature Reviews

Bunkoed et al., (2010) have developed a transparent sol-gel-based sensor with an entrapped acetylacetone reagent for the determination of formaldehyde in the air. The developed sensing device can be used as a qualitative screening method for on-site analysis in the presence of formaldehyde. The proposed method is simple and requires no post-sample preparation. The chemical reaction mechanism used in the development of a new method for detecting formaldehyde in the air. The method involves using a sol-gel matrix that contains specific reagents, such as -diketones like acetylacetone, which react with formaldehyde to produce a yellow product called lutidine. The sol-gel matrix is transparent, allowing for easy visual detection of the yellow product. Additionally, the method allows for quantitative measurement of formaldehyde using simple spectrophotometry. The reaction mechanism involves the use of ammonium acetate and acetic acid in addition to the diketones. These chemicals help to facilitate the reaction between formaldehyde and the -diketones, resulting in the production of lutidine. All of the above-mentioned reactions are shown in Figure 2-7.

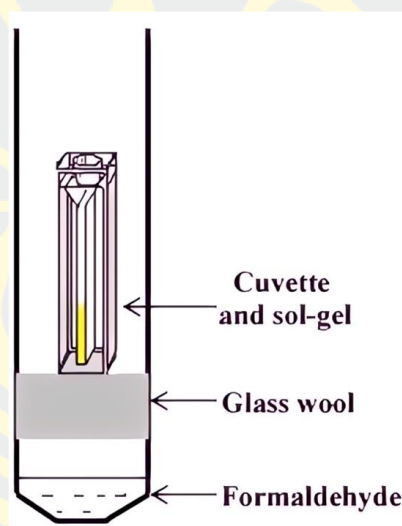
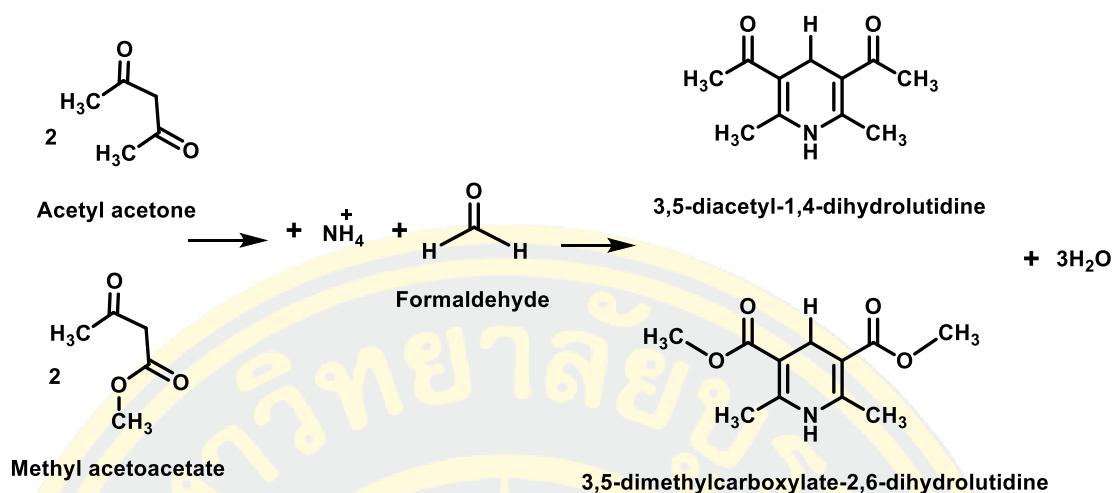


Figure 2-7 Reaction between formaldehyde with acetylacetone and methyl acetoacetate and the detection of formaldehyde gas using the sol-gel (Bunkoed, Davis, Kanatharana, Thavarungkul, & Higson, 2010).

The method has a detection limit of 0.03 ppmv formaldehyde, which is lower than the maximum exposure concentrations recommended by both the World Health Organization (WHO) and the Occupational Safety and Health Administration (OSHA). More importantly, other carbonyl compounds, such as acetaldehyde, benzaldehyde, acetone, and butanone, do not interfere with this analytical approach. Overall, the new method provides a simple and effective way to detect formaldehyde in indoor air without the need for sample preparation. The use of a sol-gel matrix with

entrapped reagents allows for both visual and quantitative detection of formaldehyde, making it a useful tool for monitoring air quality in various settings.

Fu et al., (2018) has reported a method for detecting gaseous formaldehyde at room temperature using a fluorescence spectroscopic test using Newton black film (NBF). Formaldehyde is a frequent indoor air contaminant that can cause health concerns. The researcher offers a method that is a detection for formaldehyde and does not respond to other prevalent indoor air pollutants based on the Hantzsch reaction of formaldehyde with ammonium citrate and acetylacetone, as shown in Figure 2-8.

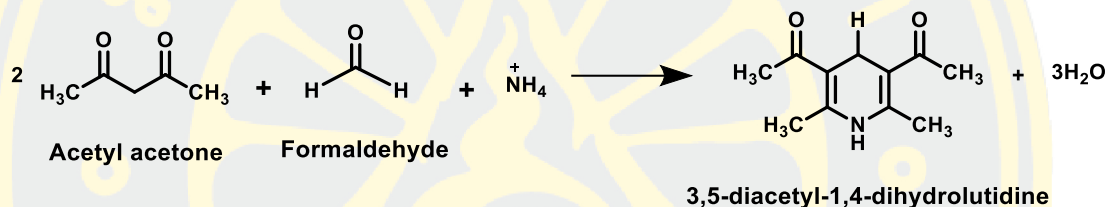


Figure 2-8-8 Hantzsch reaction of formaldehyde with ammonium citrate and acetylacetone yielded the product 3,5-diacetyl-1,4-dihydrolutidine (Fu & Zhang, 2018).

The use of NBF allows for efficient gas uptake and great sensitivity. This approach is also used in the study to detect formaldehyde outgassing from a plywood sample. This experiment made use of a cuvette, which is a tiny container used in spectroscopy investigations. The cuvette in this experiment includes Newton black film (NBF) and gaseous formaldehyde. Figure 2-9 depicts the use of NBF as a sensing material for the detection of formaldehyde gas.

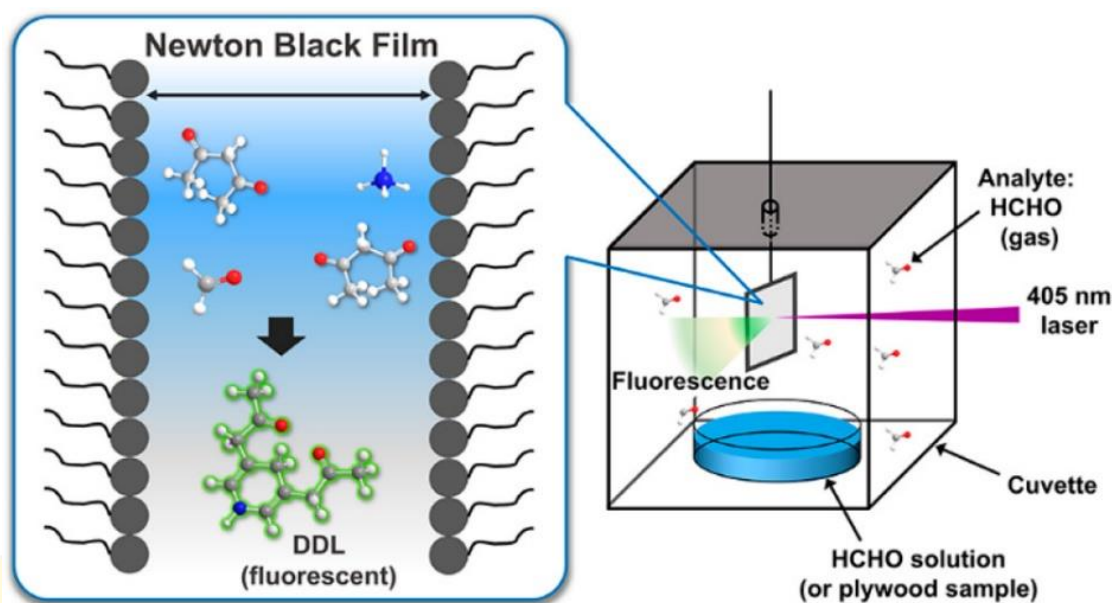


Figure 2-9 Patterns of devices for the detection of formaldehyde gas using NBF (Fu & Zhang, 2018).

The Hantzsch reaction of formaldehyde with ammonium citrate and acetylacetone is used in this experiment. This reaction results in the formation of a fluorescent chemical that can be detected via fluorescence spectroscopy. The NBF has a huge surface area-to-volume ratio of $5 \times 10^8 \text{ m}^{-1}$, allowing for efficient gas uptake by the NBF's nanometer-thick aqueous core. This improves the assay's sensitivity and selectivity, and it is unaffected by relevant analytes such as acetaldehyde, benzaldehyde, acetone, and propionaldehyde, indicating that it is specific to formaldehyde gas and does not produce false positive results in the presence of other gases, as shown in Figure 2-10.

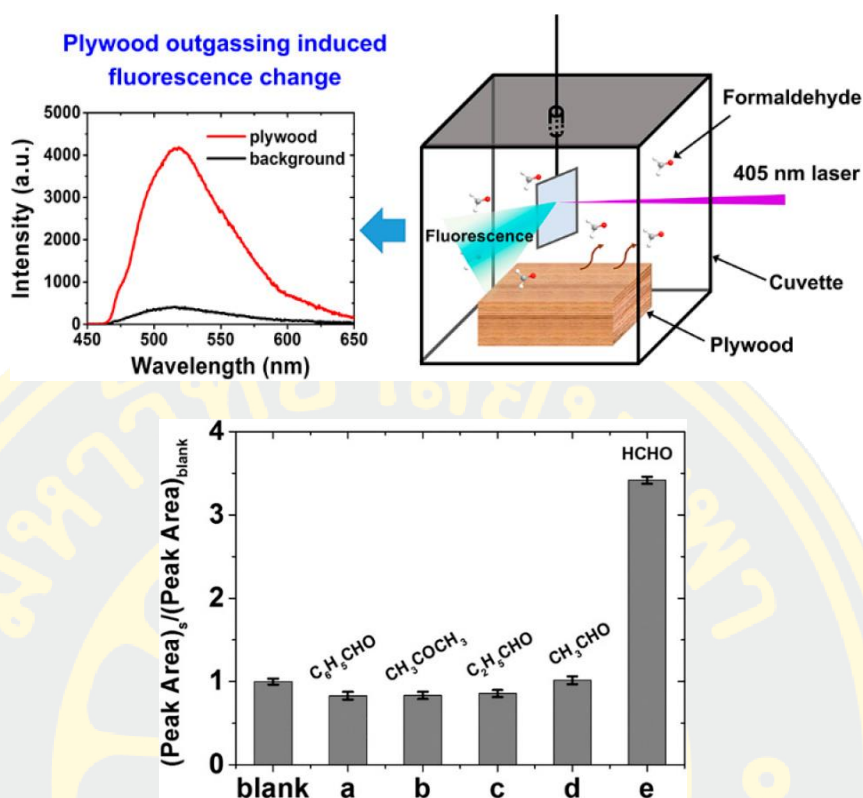


Figure 2-10 Formaldehyde gas detection in plywood samples is specific to formaldehyde gas and does not produce false positive results in the presence of other gases (Fu & Zhang, 2018).

This work also showed how to use this method to detect formaldehyde outgassing from a plywood sample. The results correspond with factory requirements. This means that the assay can be used to control quality in the production of plywood and other materials containing formaldehyde. This indicates that the Hantzsch reaction and NBF-based assay are reliable and accurate methods for evaluating formaldehyde outgassing from materials such as plywood.

Promphet et al., (2019) have developed a non-invasive textile-based colorimetric sensor. This sensor is designed to detect two different substances in sweat simultaneously: pH and lactate. The pH in sweat can be a sign of a variety of health issues, including dehydration, skin infections, and metabolic abnormalities. Sweat lactate levels can indicate physical activity, weariness, and muscle injury as shown in Figure 2-11.

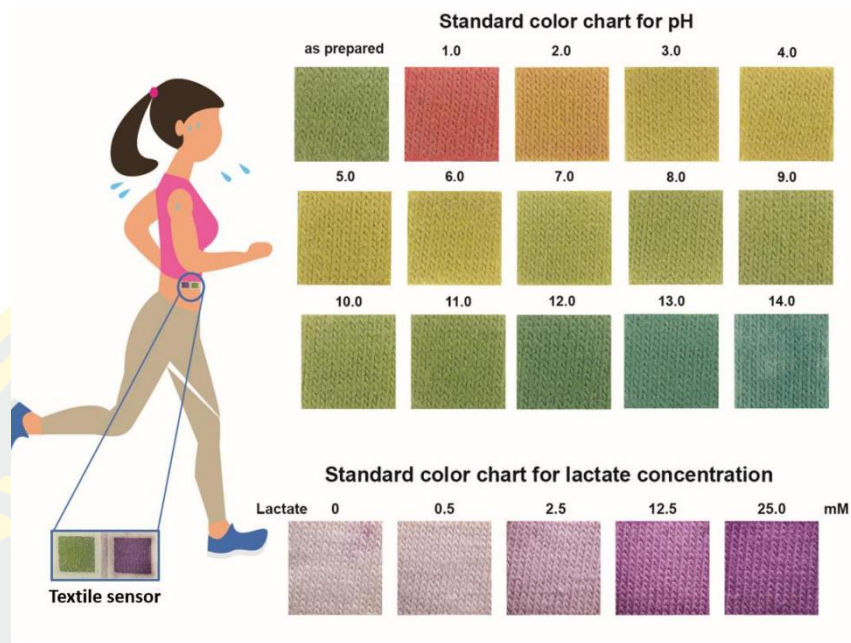


Figure 2-11 | The sensor detects two different chemicals in sweat at the same time: pH and lactate (Promphet et al., 2019).

Figure 2-12 shows the fabrication process of the sensor. This sensor comprised of a cotton substrate coated with a hydrogel layer of sodium carboxymethyl cellulose (NaCMC), cetyltrimethyl ammonium bromide (CTAB), chitosan, and a mixture of pH and lactate indicator colors. The sensor can distinguish between changes in sweat pH and lactate levels in human perspiration using both the naked eye and a spectrophotometer. The sensor has potential uses in non-intrusive real-time monitoring of human health and athletic performance.

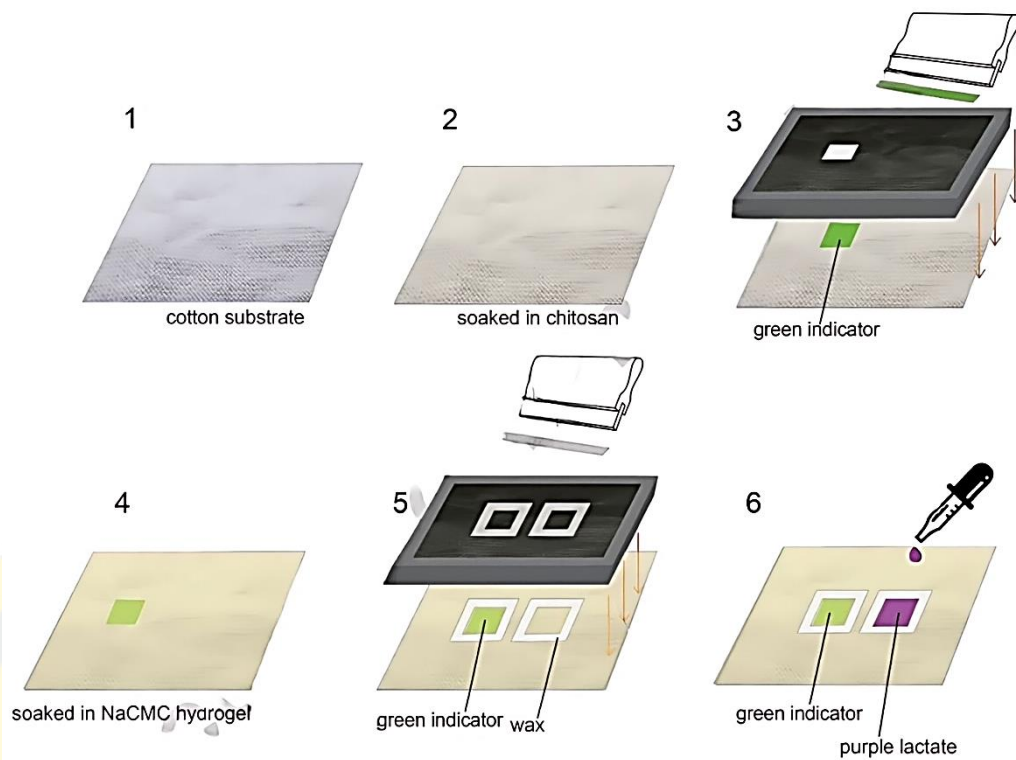


Figure 2-12 Fabrication procedure of a sensor for simultaneous monitoring of sweat and lactate pH using a hydrogel layer of sodium carboxymethyl cellulose (NaCMC), chitosan, and cetyltrimethylammonium ammonium bromide (CTAB) (Promphet et al., 2019).

CHAPTER 3

METHODOLOGY

3.1 Materials and chemicals

3.1.1 Materials

1. Oven (1375 FX, Delta Laboratory Company Ltd, Thailand)
2. 4-Digit Balance (MS, Mettler-Toledo Ltd., Thailand)
3. Filter papers Whatman No. 1 Sheet type 460 x 570 mm (GE Healthcare Company Ltd, China)
4. Clear tape Size 48 mm. x 40 m. (3M Scotch, 3M Thailand Ltd, Thailand)
5. Micropipettes size 1000 μ L, 100 μ L and 20 μ L (Eppendorf Research, Eppendorf Thailand Co., Ltd, Germany)
6. Magnetic stirrer (C-MAG HS 7, IKA Works Co., Ltd, Thailand)
7. Scanner (CanoScan LiDE 110, Cannon Marketing Company Ltd, Thailand)
8. Microcentrifuge tubes 50 mL
9. Laminated plastic A4, thickness 125 micron (ONE Essentials Ltd, Thailand)
10. Double-sided Tissue Tape 12 mm.x10 yards (3M Scotch, 3M Thailand Ltd, Thailand)
11. Attenuated Total Reflectance Fourier Transform Infrared Spectrometer (ATR- FTIR), model Frontier (PerkinElmer, USA)

3.1.2 Chemicals

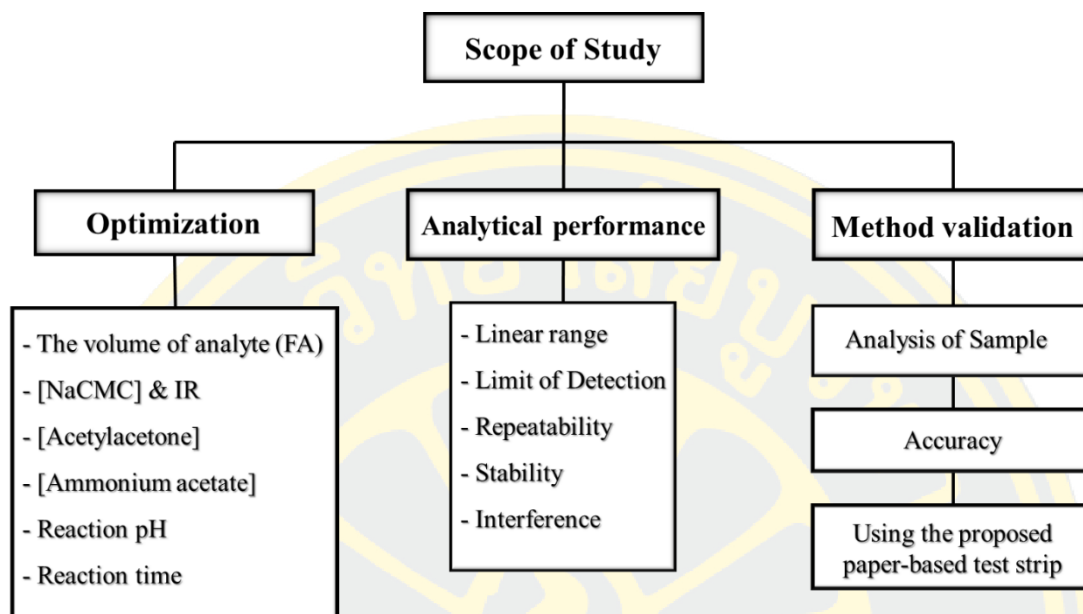
1. Ammonium acetate ($\text{CH}_3\text{COONH}_4$), 98% w/w, MW: 77.0825 g/mol, Density 1.073 g/mL, CAS: 631-61-8, (Loba Chemie Pvt.Ltd., India)
2. Acetic acid (CH_3COOH), 99.7% w/v, MW: 60.052 g/mol, CAS: 64-19-7, (RCI Labscan Thailand)
3. Acetyl acetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$), 99.5% w/w, MW: 100.13 g/mol, Density 0.975 g/mL, CAS: 123-54-6, (Loba Chemie Pvt.Ltd., India)

4. Formaldehyde (CH_2O), 37% w/w, MW: 30.031 g/mol, Density 1.09 g/mL, CAS: 50-00-0, (BDH Laboratory Suppliers, UK)
5. Sodium Carboxymethyl Cellulose ($\text{C}_8\text{H}_{15}\text{NaO}_8$), CAS: 9004-32-4, (Loba Chemie Pvt.Ltd., India)
6. Chloroform (CHCl_3), 99.5% w/w, MW: 119.37 g/mol, Density 1.479 g/mL, CAS: 67-66-3, (QRëC, New Zealand)
7. Ammonia solution (NH_4OH), 28% w/v, MW: 17.03 g/mol, CAS: 1336-21-6, (QRëC, New Zealand)
8. Ethyl Alcohol ($\text{C}_2\text{H}_6\text{O}$), 99.9% w/v, MW: 46.07 g/mol, CAS: 64-17-5, (QRëC, New Zealand)
9. Toluene ($\text{C}_6\text{H}_5\text{CH}_3$), 99.7% w/v, MW: 92.14 g/mol, CAS Number: 108-88-3, (RCI Labscan, Thailand)
10. Acetonitrile ($\text{C}_2\text{H}_3\text{N}$), 99.7% w/w, MW: 41.05 g/mol, Density 0.786 g/mL, CAS Number: 75-05-8, (RCI Labscan, Thailand)
11. Methanol (CH_3OH), 99.9% w/w, MW: 32.04 g/mol, Density 0.790 g/mL, CAS Number: 67-56-1, (RCI Labscan, Thailand)
12. Acetone ($\text{C}_3\text{H}_6\text{O}$), 99.5% w/w, MW: 58.08 g/mol, Density 0.790 g/mL, CAS: 67-64-1, (QRëC, New Zealand)
13. Dichloromethane (CH_2Cl_2), 99.5% w/v, MW: 84.93 g/mol, CAS: 75-09-2, (Ajax Finechem, Austria)

3.1.3 Samples

Samples of home spray paint, wood glue, and paint for exterior wood were employed for formaldehyde gas analysis for method validation purposes. The samples were purchased from a local store in Chonburi province, Thailand.

3.2 Research Plans



3.3 Experimental Procedures

3.3.1 Preparation of solutions

3.3.1.1 Preparation of Nash's reagent

Ten milliliter of Nash's reagent solution was prepared using the following procedure. A 1.5 g (2 M) of ammonium acetate was weighed and dissolved in deionized water. Next, 30 μ L of acetic acid was added followed by 3 mL (30 M) of acetylacetone. The total volume of 10 mL was adjusted using deionized water.

3.3.1.2 Preparation of sodium carboxymethyl cellulose solution

A 10 mL volume of 2% (w/v) sodium carboxymethyl cellulose was prepared by weighing 0.2 g of sodium carboxymethyl cellulose and dissolving it in 10 mL of Nash's reagent.

3.3.1.3 Preparation of formaldehyde gas

Various concentrations of formaldehyde gas were prepared as shown in Equation 3-1 (Dong & Dasgupta, 1986) from working standard formalin solution prepared by diluting stock formalin solution (13.79 M prepared from formalin 38% w/w, density 1.09 g/mL, analytical grade) using deionized water.

$$[\text{HCHO (aq)}] = 10^{[(4538/T) - 11.34]} [\text{HCHO (g)}]^{[(252.2/T) + 0.2088]} \quad (3-1)$$

3.3.1.4 Sample Preparation

Samples consisted of home spray paint, wood glue, and paint for exterior wood. Samples were poured into a 35 mL Petri dish and placed in a closed box (15 cm × 15 cm × 15 cm). The formaldehyde gas was allowed to generate for 1 hour until the analysis. For spiked samples, the formalin solution was added into the sample to generate formaldehyde gas at the concentration in the linear range to calculate the recovery of the method.

3.4 Design and fabrication of paper-based device

The paper-based test strip was designed to have a rectangular shape similar to pH strip with the size of 6 cm long and 1 cm wide, with a test area at one end measuring 1 cm long and 1 cm wide, as shown in Figure 3-1. A test strip was made from Whatman No. 1 filter paper by attaching 3M tape to the back of the filter paper. NaCMC-Nash's solution was immobilized on a paper-based test strip by immersing the filter paper in the solution to form hydrogel on the filter paper. After that, the immobilized paper was dried at approximately 40 °C for 1 hour. Next, the reagent-immobilized filter paper was attached with double-sided membrane tape and cut into pieces measuring 1 cm long and 1 cm wide. Then, the paper was attached to a clear plastic sheet with a length of 6 cm and a width of 1 cm to give a ready-to-use paper-based test strip for formaldehyde gas analysis as shown in Figure 3-2.

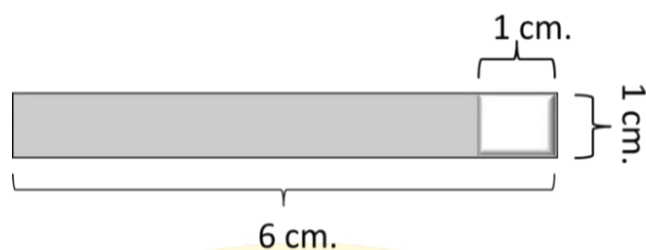


Figure 3-1 Paper-based test strip for formaldehyde gas analysis.

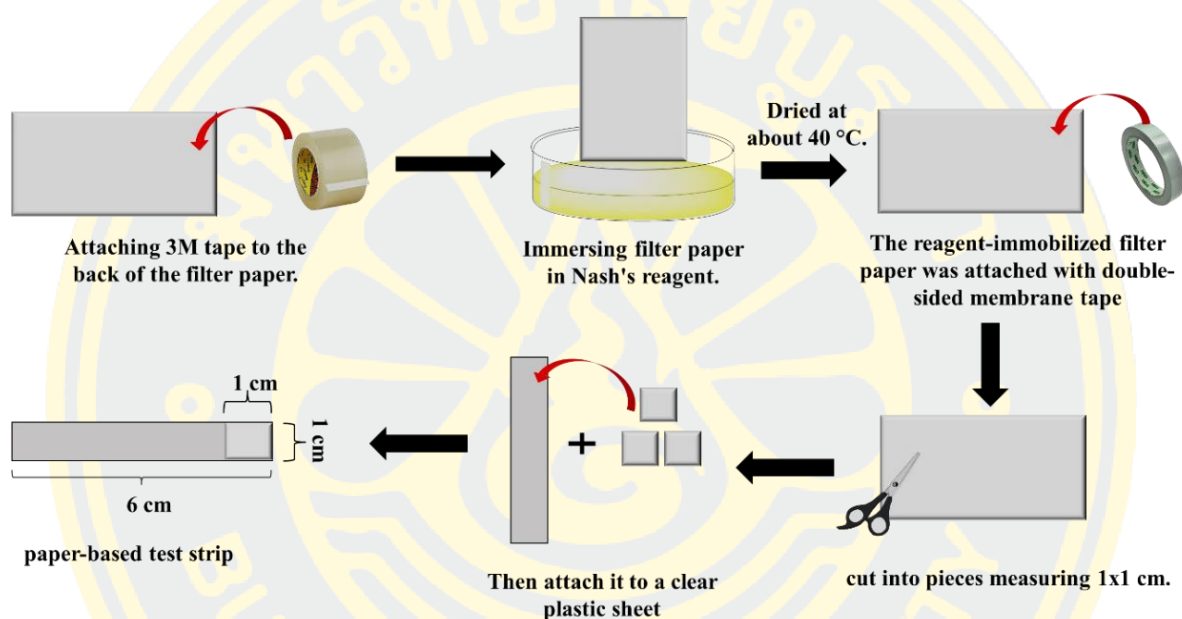


Figure 3-2 Fabrication process of paper-based test strip for formaldehyde gas detection

3.5 Formaldehyde gas detection using the developed paper-based test strip

Formaldehyde gas detection with the developed test strip can be easily performed in one step by attaching a paper-based test strip to the inside of the box cover and allowed to expose to formaldehyde gas. After 20 min, the paper-based test strip produced yellow color of 3,5-diacetyl-1,4-dihydropyridine (DDL) as a result of the reaction between acetylacetone and formaldehyde in the presence of ammonium acetate, as shown in Figure 3-3. The test strip was scanned, and the image was analyzed for color intensity using ImageJ software for quantitative analysis of formaldehyde gas.



Figure 3-3 The color that appears after using the strip test to measure formaldehyde gas

3.6 Study the optimization conditions for analysis.

3.6.1 The volume of analyte (FA)

The appropriate volume of formalin solution in the range of 1–60 mL for use in generating formaldehyde gas was evaluated (preparation steps are described in Section 3.3.1.3). The 0.064 M formalin concentration at the investigated volume was placed in the Petri dish in the cap box and allowed to generate 15 ppmV formaldehyde gas. The plot of intensity as a function of the volume of the formalin solution is generated to determine the volume that provides the highest color intensity and is used as the optimal volume.

3.6.2 Acetylacetone concentration

Acetylacetone in the concentration of 2.2–3.6 M prepared in similar procedure as described above was investigated for optimal concentration for formaldehyde gas analysis. The fabricated paper-based test strip at different concentration of acetylacetone was employed for detection of formaldehyde gas at the concentration of 15 ppmV. The plot of intensity as a function of acetylacetone concentration was constructed to determine the concentration that give the highest color intensity and used as optimal concentration.

3.6.3 Concentration of NaCMC and Characterization by FTIR

NaCMC in the concentration range of 0-5% (w/v) was investigated for its impact on analytical sensitivity. Other experiment conditions are similar to Section

3.6.2. The paper-based test strip containing the most appropriate NaCMC concentration underwent characterization using the FTIR technique.

3.6.4 Concentration of Ammonium acetate

Ammonium acetate in the concentration range of 0-7 M was investigated for its impact on analytical sensitivity. Other experiment conditions are similar to Section 3.6.2.

3.6.5 Reaction pH

The effect of pH on the Hantzsch reaction in the range 2-8 was investigated for its impact on analytical sensitivity. Other experiment conditions are similar to Section 3.6.2.

3.6.6 Reaction time

The reaction time between formaldehyde and Nash'reagent was studied in the range of 1–60 min ($n = 3$) to determine optimal reaction time. Other experimental procedure is similar to the one describe above.

3.7 Analytical features for the amount of formaldehyde gas

3.7.1 Linear range

A paper-based test strip prepared under suitable conditions was employed to measure formaldehyde gas at a concentration in the range of 1–60 ppmV. Color intensity was then analysed using the ImageJ program and plotted against formaldehyde gas concentration to determine the linearity range of the formaldehyde gas analysis using the developed paper-based test strip.

3.7.2 Repeatability

The repeatability for the formaldehyde gas analysis was studied. The formaldehyde gas was studied at the concentration specified in section 3.7.1 ($n = 3$). The percentage of relative standard deviation (%RSD) of the analysis will be calculated as shown in Equation 3-2.

$$\%RSD = \frac{SD}{\bar{x}} \times 100 \quad (3-2)$$

3.7.3 Limit of detection: LOD

Replicate analysis (n=10) of blank gas prepared by gas generation from 0 M formalin solution was carried out using the developed paper-based test strip. The color intensity appeared on the paper-based test strip was measured. The mean standard deviation was calculated and used for determining LOD using the formula in Equation 3-3.

$$LOD = \frac{3SD}{Slope} \quad (3-3)$$

3.7.4 Interference

The effect of potential interferences such as volatile organic compounds (VOC) and other common chemicals found in the air on developed assay for formaldehyde analysis was studied. The experiment was carried out in a similar manner as the method described in (section 3.3.1.4). The VOC and other common chemicals include acetic acid, toluene, acetonitrile, acetone, methanol, chloroform, ammonia solution, dichloromethane, and ethyl alcohol.

3.7.5 Stability study

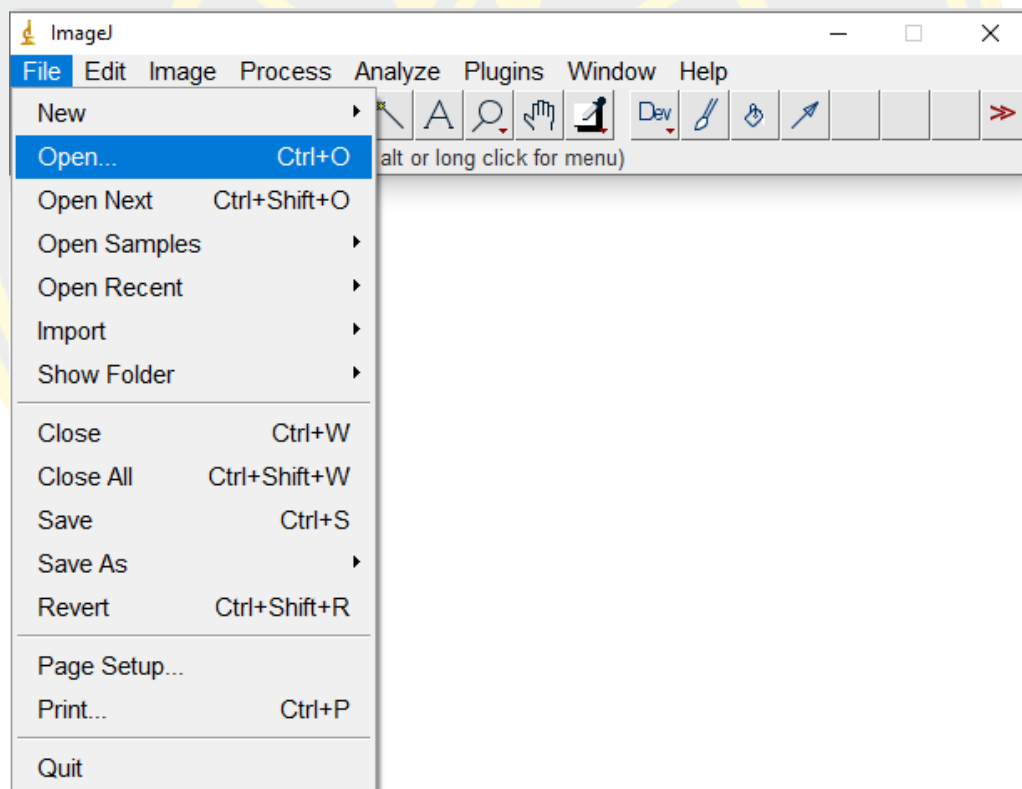
A stability study of test strips was carried to assess the shelf life under different storage conditions. The test strips were stored in two different conditions: first at ambient temperature (25–36 °C) and second at approximately 4 °C (refrigerator). All test strips are prepared at the same time and stored in a zip-close foil bag that also has a moisture-proof envelope. Stability was tested with formaldehyde gas at a concentration of 15 ppmV every 5 days for two months and the results were compared to that obtained from the freshly prepared devices.

3.8 Sample analysis

Samples from (section 3.3.1.4), each with a volume of 35 mL, were poured into a petri dish and placed into a box. A petri dish containing 35 mL formalin solution was then added to the box to generate the formaldehyde gas with the concentration of 1, 15, and 25 ppmV mixed with the gas from the samples. The gas mixture was then detected using the developed test strip for formaldehyde gas measurement to evaluate the recovery.

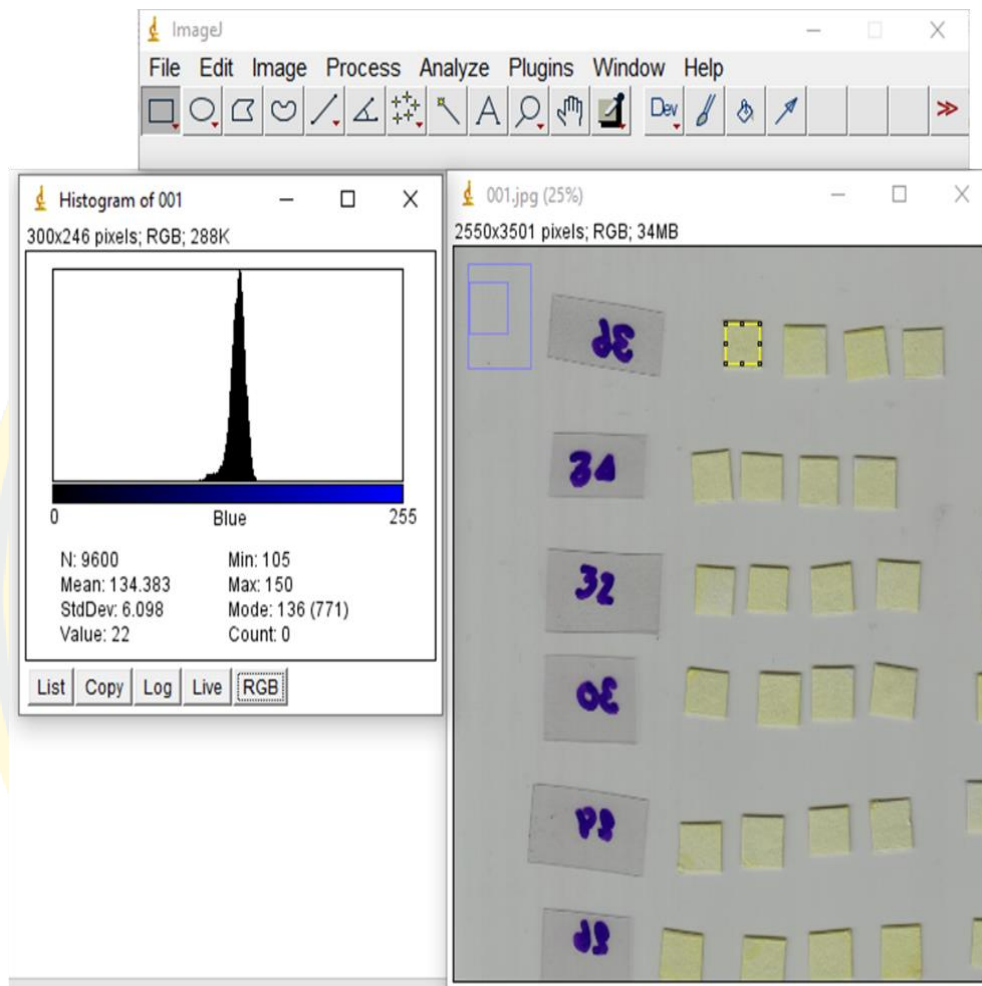
3.9 Color intensity analysis by ImageJ

1. Open the ImageJ program, press the File menu, "Open," and select the image to be analysed



2. Select the area to measure the intensity. The mode selected for analysis is RGB (red, green, and blue). Start by selecting Rectangle and then dragging over the area to be measured. When the desired area was obtained, go to Analyze, "Select

Histogram," or press Ctrl + H. The displayed mean value is the mean RGB intensity obtained from image processing in the selected area.



CHAPTER 4

RESULTS AND DISCUSSION

4.1 Principle of the proposed assay

This work presents a simple, rapid, portable, and inexpensive paper-based test for gas formaldehyde analysis. The analysis is based on the Hantzsch reaction involving the condensation of acetylacetone in ammonium acetate (Nash's reagent), and formaldehyde, which yields a yellow-colored product of 3,5-diacetyl-1,4-dihydrolutidine (DDL) (Belman, 1963; Nash, 1953; Saini, Kumar, & Sandhu, 2008). The paper-based test strip was designed to have a rectangular shape similar to a pH strip consisting of a transparent plastic sheet support and a paper test zone at one end. To prepare the test zone, the paper is dipped into Nash's reagent dissolved in sodium carboxymethyl cellulose (Na-CMC) hydrogel and then dried at 40°C for 1 hour. The formaldehyde test is performed by exposing the test strip to formaldehyde gas (see Figure 4-1). The yellow color that appeared on the test zone was measured for intensity using a scanner and ImageJ software under appropriate conditions. The intensity of the yellow color is directly proportional to the amount of formaldehyde in the sample.

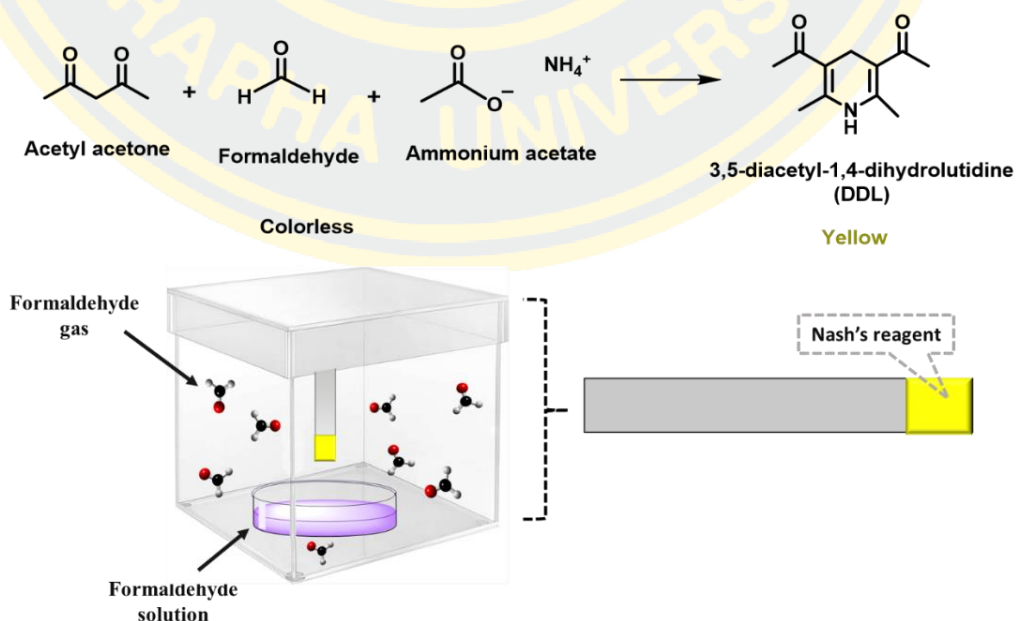


Figure 4-1 Detection of formaldehyde gas using the developed paper-based test strip.

4.2 Study the optimal conditions for formaldehyde gas analysis

The assay for formaldehyde gas detection using the developed paper-based test strip was first optimized to obtain highly sensitive analysis with a user-friendly detection procedure. The optimized parameters included formalin volume, amount of NaCMC, acetylacetone concentration, ammonium acetate concentration, reaction pH and reaction time.

4.2.1 The volume of analyte (FA)

The formalin volume was optimized as it affects amount of formaldehyde gas formation at equilibrium (Hackling & Garnett, 2007; Halperin & Howard, 2011; Yıldırım, Küçük, & Ayas, 2012). The study was carried out using 0.064 M formalin solution to generate formaldehyde gas inside the cap box where a varied volume of this solution was placed in the petri dish and allowed to generate an equilibrium concentration of 15 ppmV formaldehyde gas. After detection using the developed paper-based test strip, the color intensity increased as the volume of formalin solution increased and started to saturate at 25 mL (Figure 4-2). Therefore, 35 mL of formalin solution was selected as the optimal volume to ensure the complete generation of formaldehyde gas and used for further experiments.

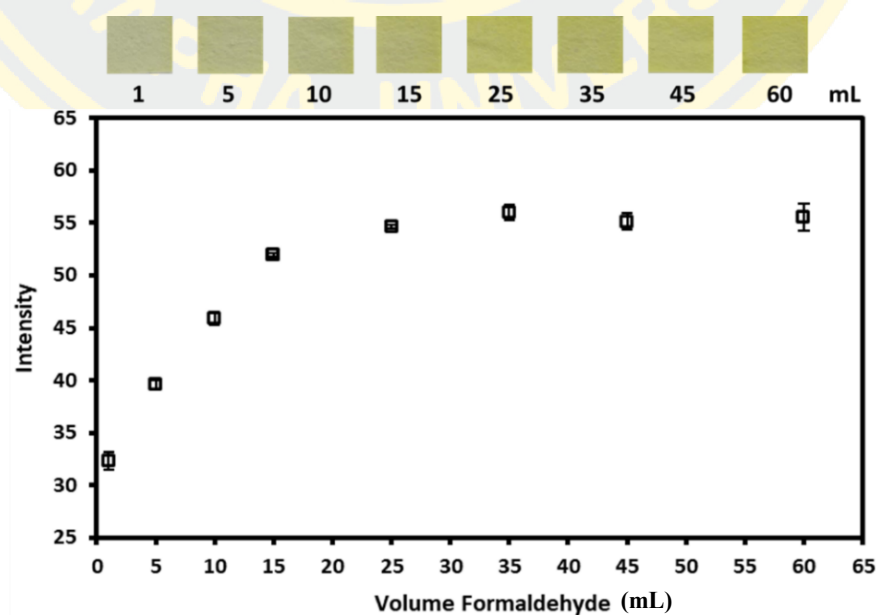


Figure 4-2 Study of formalin solution volume used to generate formaldehyde gas (n=3).

4.2.2 Sodium carboxymethyl cellulose (NaCMC) concentration

NaCMC plays an important role in stabilizing the reagents immobilized on paper-based test strips, allowing the paper-based test strip to be stored for longer periods (Feddersen & Thorp, 1993; Yang & Zhu, 2007). However, an excess of NaCMC can obstruct the reaction between formaldehyde gas and the immobilized reagent, resulting in a lower observed signal. Therefore, the concentration of NaCMC in Nash's reagent was optimized to obtain a concentration that can stabilize the reagent on the paper-based test strip and still provide a sensitive assay for formaldehyde gas detection. From the analysis of 15 ppmV formaldehyde gas, the color intensity increased as the NaCMC concentration in Nash's reagent increased between 1-2% w/v and became saturated in the range of 2-3% w/v (Figure 4-3A). At concentrations greater than 3% w/v NaCMC, the color intensity decreased because formaldehyde gas could not diffuse to react with reagents on the paper due to the excessive amount of NaCMC obstructing the reaction. Hence, the 2% w/v NaCMC was selected as the optimal concentration and used for further experiments.

Furthermore, characterization of NaCMC immobilized on the paper-based test strip was carried out. The FTIR spectra of cellulose, Nash's reagent, and NaCMC are shown in Figure 4-3B. The transmittance bands at 3336 cm^{-1} and 2902 cm^{-1} belong to the stretching vibrations of O-H and C-H groups, respectively, which are related to the functional groups present in cellulose and NaCMC (Vitamin, 2015). While 1730 cm^{-1} corresponds to the C=O stretching of carboxylic acid and ketone related to the functional groups present in NaCMC and Nash's reagent, respectively (George et al., 2015) confirming that there is indeed NaCMC as a component coated on the test strip.

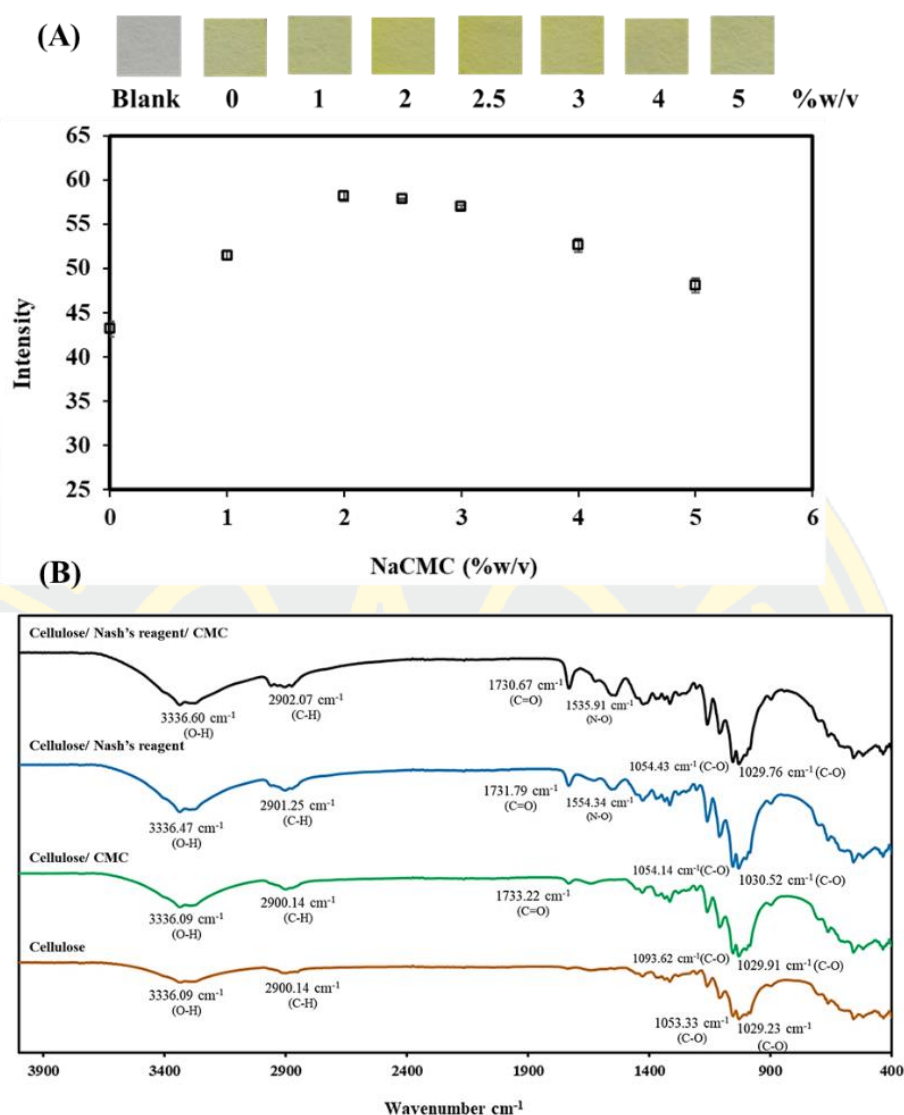


Figure 4-3 (A) Optimization of NaCMC used to immobilize Nash's reagent on the paper-based test strip ($n=3$) and (B) FTIR spectra for characterization of NaCMC on the paper-based test strip.

4.2.3 Acetylacetone concentration

The acetylacetone concentration in Nash's reagent was also optimized as it plays an important role in reacting with formaldehyde which generating a yellow color product. The color intensity from the measurement of 15 ppmV formaldehyde increased when the concentration of acetylacetone in Nash's reagent increased between 2–3 M and became saturated above 3 M (Figure 4-4). As a result, a 3M

acetylacetone was selected as the optimal concentration and this concentration was used for further experiments.

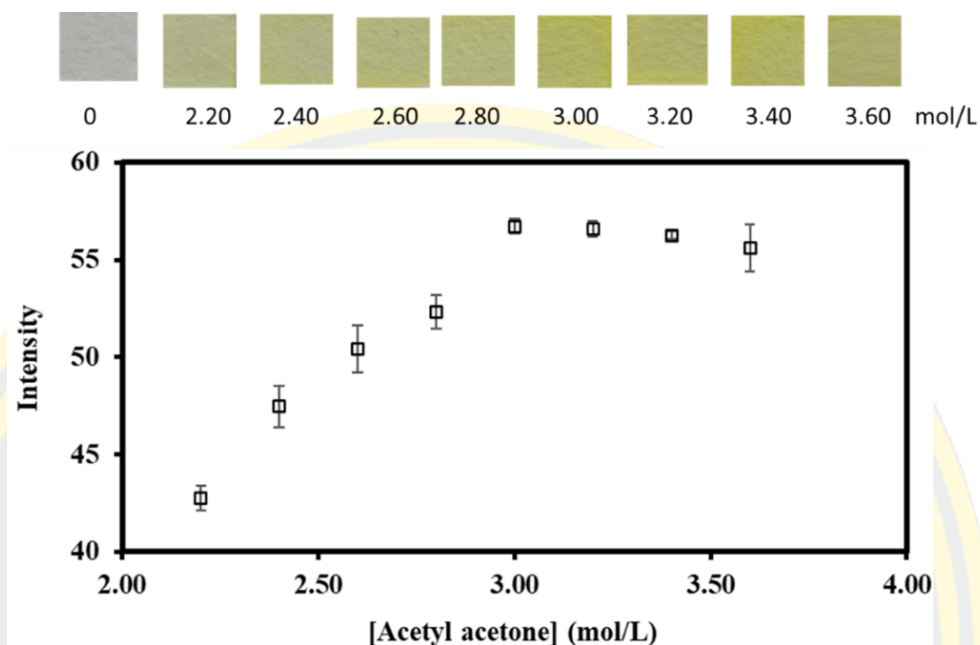


Figure 4-4 The optimization of acetylacetone concentration for formaldehyde detection using a paper-based test strip (n= 3).

4.2.4 Ammonium acetate concentration

Concentration of ammonium acetate in Nash's reagent was next optimized as it involved in the reagent to react with formaldehyde gas. As shown in Figure 4-5, the color intensity from measuring 15 ppmV formaldehyde increased as the concentration of ammonium acetate increased in the range of 0.05-2 M and became saturated above 2 M. Therefore, ammonium acetate at the concentration of 2 M was selected and used for further experiments as it was the lowest concentration that provided high detection signal.

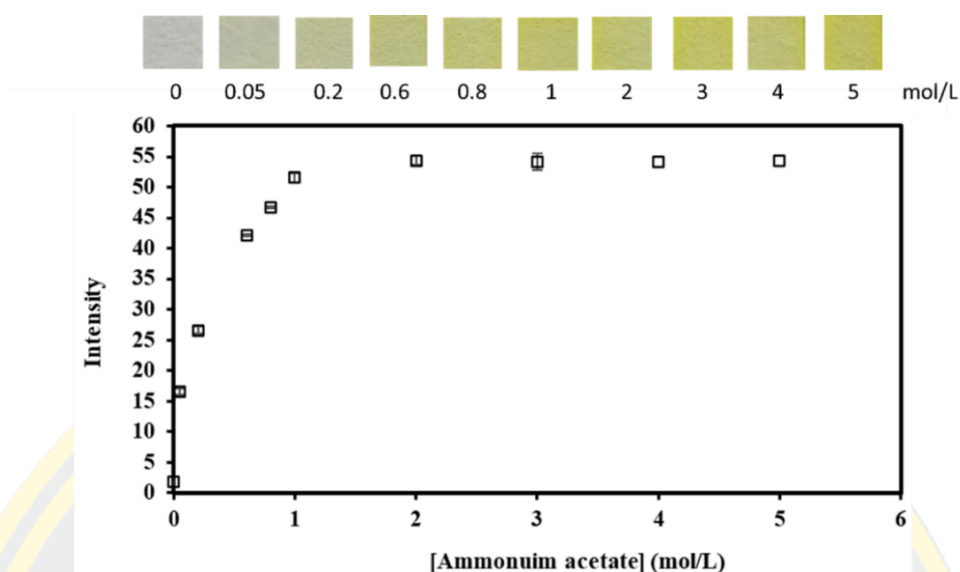


Figure 4-5 The optimization of ammonium acetate for formaldehyde detection using a paper-based test strip (n= 3).

4.2.5 Reaction pH

The reaction pH was also evaluated by adjusting the Nash's reagent coated onto the paper-based test strip using acetic acid and NaOH. From the analysis of 15 ppmV formaldehyde gas, highest color intensity was obtained at the pH of 5.5 and hence this reaction pH was considered as optimum pH for formaldehyde gas detection using the developed paper-based test strip and used for further experiments (Figure 4-6).

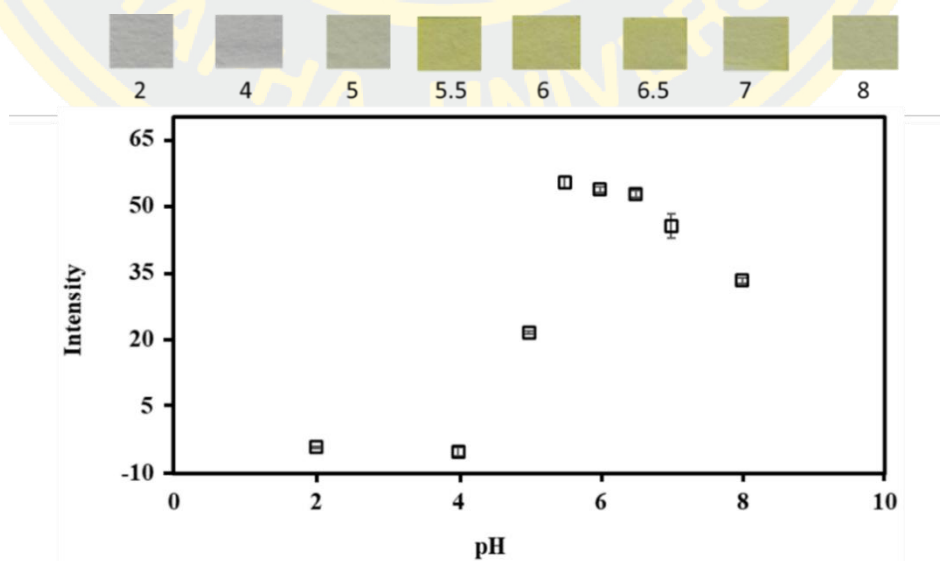


Figure 4-6 The optimization of Nash's reagent pH for formaldehyde detection using a paper-based test strip (n= 3)

4.2.6 Reaction time

Reaction time of the formaldehyde detection was next optimized in the range of 1-60 min. From measuring 15 ppmV formaldehyde gas, the color intensity increased reached saturation in 20 min (Figure 4-7). Consequently, a reaction time of 20 min was used as the optimum reaction time to measure formaldehyde gas using the developed paper-based test strip to obtain sensitive analysis.

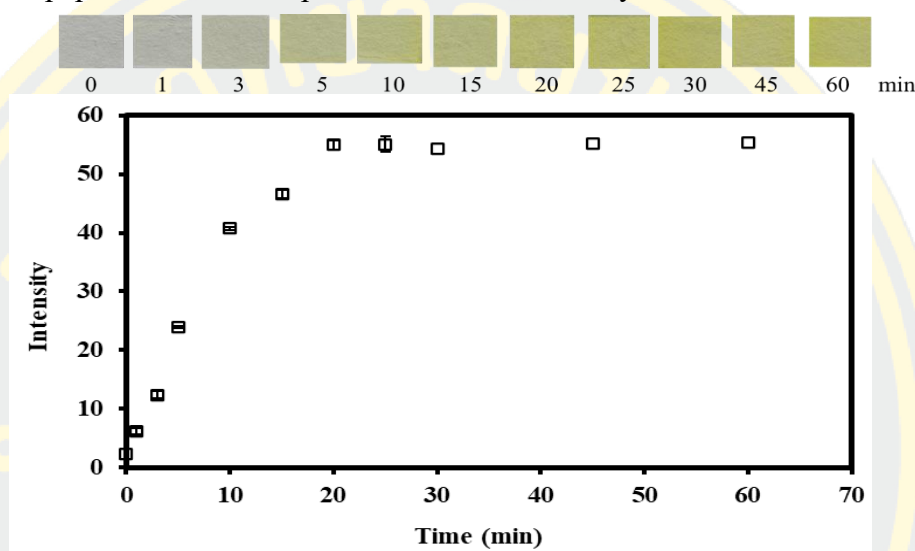


Figure 4-7 Study of reaction time for formaldehyde gas analysis (n=3).

4.3 Formaldehyde gas analysis

Once optimal conditions were obtained, the performance of the developed paper-based test strip was investigated for the analysis of formaldehyde gas in terms of linearity, reproducibility, and limit of detection.

4.3.1 Linearity

Under optimal conditions, paper-based test strips were used to analyze formaldehyde gas. Using different concentrations of formalin solution, formaldehyde gas at different level was generated in the cap box and detected using the developed assay. As the concentration of formaldehyde gas increased, the yellow color intensity increased. A plot of color intensity as a function of formaldehyde gas concentration was generated with two linear ranges: 0.25–1 ppmV and 3–40 ppmV (n = 3), as shown in Figure 4-8. The limit of detection was determined to be 12 ppbV, calculated

as three times the standard deviation of the 10 replicate blank signals divided by the slope of the calibration curve (3sd (blank)/slope). This value is lower than the air quality threshold set by the Occupational Safety and Health Administration (OSHA), indicating that the developed assay is suitable for on-site detection of formaldehyde gas.

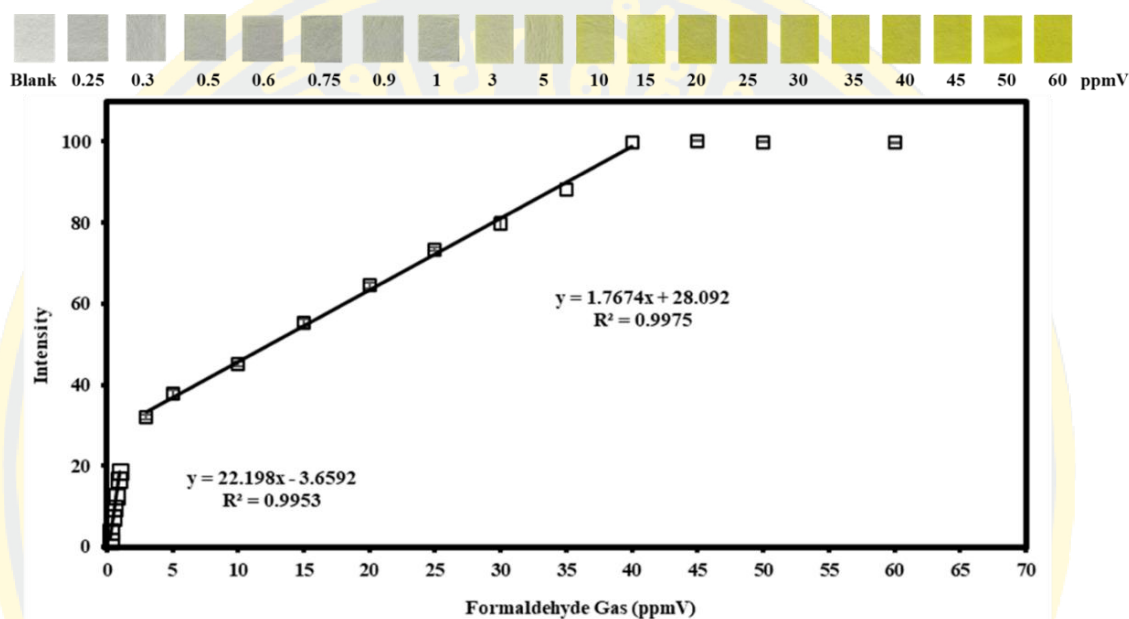


Figure 4-8 The relationship between the color intensity and the concentration of formaldehyde gas (n=3).

4.3.2 Reproducibility

The repeatability of the proposed paper-based test strip was investigated by replicate analysis of formaldehyde gas at concentrations in the range of 0.25–40 ppmV (n = 3). For all concentration tested, the relative standard deviation (%RSD) was found in the range of 0.55–6.50, as shown in Table 4-1. This result indicated that the proposed method has high repeatability for the quantification of formaldehyde gas as the values were in acceptable range according to AOAC standards (%RSD not exceed 3.7–7.3%) (International, 2016).

Table 4-1 Analytical performance for the detection of formaldehyde gas using the developed paper-based test strip.

Linear range (ppmV)	R ²	LOD (ppbV)	%RSD (n=3)
0.25-1 and 3-40	0.9953 and 0.9975	12	0.55-6.50

4.3.3 Limit of detection (LOD)

The experimental limit of detection was investigated on the developed paper-based test strip by performing formaldehyde gas analysis at a concentration of 0–60 ppmV. It was found that the concentration of formaldehyde at 0.25 ppmV is the initial concentration that makes the color visible to the naked eye, as shown in Figure 4-9. Therefore, the developed paper-based test strip has an experimental detection limit of 0.25 ppmV for the naked eye and a calculated detection limit of 12 ppbV as described above.

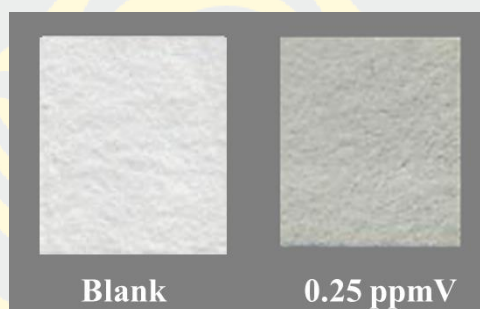


Figure 4-9 The color formed on the paper-based test strip was obtained by analysis of formaldehyde gas at a concentration of 0.25 ppmV.

4.4 Interference

The impact of potential interferences commonly found in gas samples including toluene, ethanol, acetone, ammonia, methanol, dichloromethane, chloroform, and acetonitrile was investigated to assess their effect on the developed formaldehyde gas assay. To conduct the measurements, 35 mL of each of these solutions (100% w/w) were placed into a petri dish, allowing them to evaporate into the gas inside the cap box. The measurements were then carried out using the

developed paper-based test strip. As shown in Figure 4-10, even at much higher concentration, all investigated compounds gave much less signal on the paper-based test strips than that of 15 ppmV formaldehyde gas. These results confirmed that the test strip specifically responded to formaldehyde even at low concentrations and was not influenced by the presence of other substances.

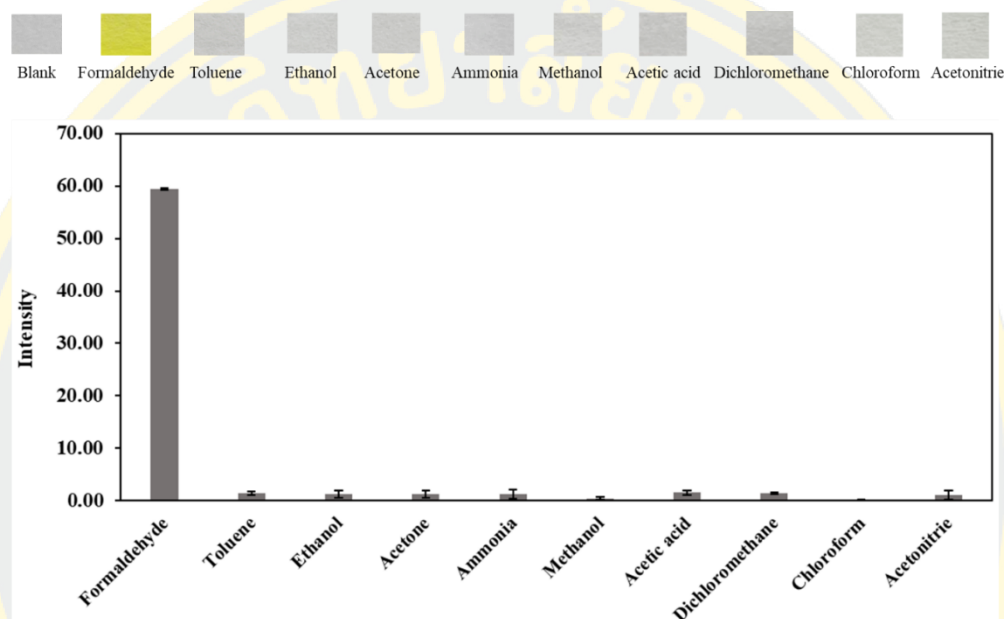


Figure 4-10 The interference study of the paper-based test strip upon exposure to 15 ppmV formaldehyde, in comparison to volatile organic compounds and gas chemicals (n=3).

4.5 Stability study

A stability study of the developed test strips was carried out over a period of 2 months. All test strips were prepared simultaneously, stored in a zip-close foil bag containing a 1-gram silica gel bag, and kept at ambient temperature (25–36°C) and in a refrigerator (4°C). Stability was tested using 15 ppmV formaldehyde gas every 3-5 days. Figure 4-11 shows a plot of measured signal obtained at the two storage conditions expressed as %color intensity when compared with those from freshly prepared devices. The results showed that the test strip has excellent storage stability at both ambient temperature and in the refrigerator for over two months as the %intensity did not significantly differ from 100% over time. These results indicate

that the test strip was stable for long periods and is suitable for development as a commercially ready-to-use sensor for on-site formaldehyde gas detection.

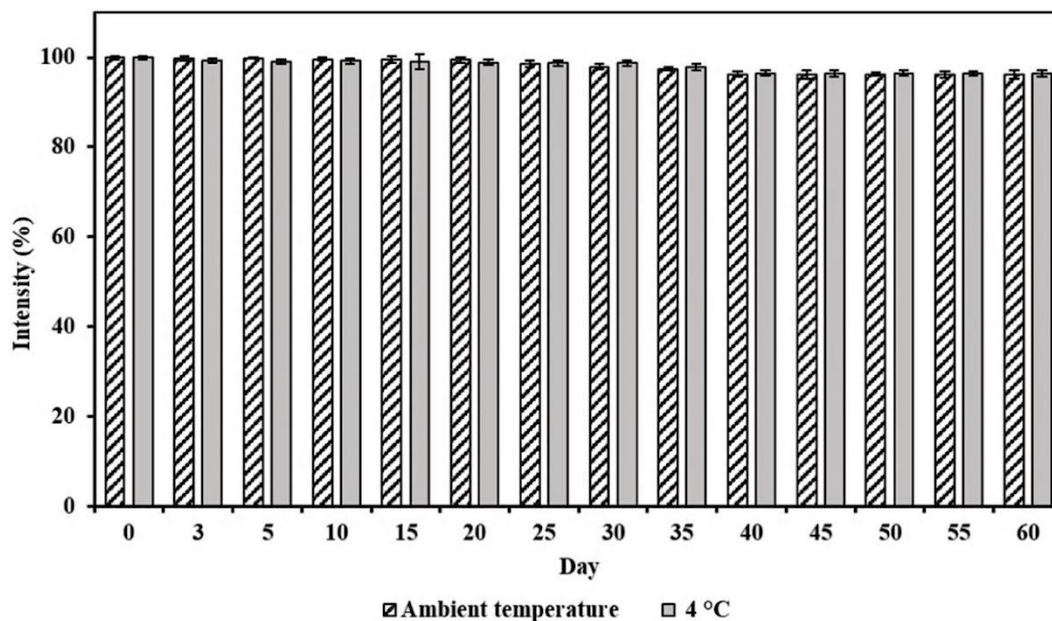


Figure 4-11 Storage stability of the paper-based test strip at ambient temperature and in the refrigerator (4°C).

4.6 Real sample analysis

To verify the usability of the developed test strip, samples of formaldehyde-containing products commonly found in households, such as house spray paint, paint for exterior wood, and wood glue (Crump, Squire, & Yu, 1997; Wieslander, Norbäck, Björnsson, Janson, & Boman, 1996) were analyzed using the developed paper-based test strip. These products have been verified to contain either no volatile organic compounds or only low levels. Sample gas containing different formaldehyde gas concentration (1, 15, and 25 ppmV) was evaluated to determine recovery. As shown in Table 1, both home spray paint and wood glue were found to contain formaldehyde gas. However, it was at levels below the air quality threshold set by OSHA, which has established a Permissible Exposure Limit (PEL) of 750 ppbV and an Immediately Harmful to Life or Health (IDLH) limit of 20 ppmV (Halperin & Howard, 2011). Tested recovery of spiked samples in the range of 90–104% was observed for all samples indicating that the method has acceptable accuracy when applied with these samples (International, 2016).

Table 4-2 Analysis of Formaldehyde gas in samples by the developed method.

Sample	Spiked Formaldehyde (ppmV)	Found (ppmV) \pm SD (n=3)	Recovery (%)	Figure
Home spray paint 1	0	0.51	-	
	1	1.43 \pm 0.01	92	
	15	16.04 \pm 0.15	104	
	25	24.19 \pm 0.22	95	
Home spray paint 2	0	0.48	-	
	1	1.40 \pm 0.01	92	
	15	15.07 \pm 0.44	97	
	25	25.82 \pm 0.30	101	
Wood glue 1	0	0.19	-	
	1	1.09 \pm 0.00	90	
	15	14.92 \pm 0.22	98	
	25	24.83 \pm 0.07	99	
Wood glue 2	0	0.24	-	
	1	1.15 \pm 0.00	90.6	
	15	15.49 \pm 0.04	101.7	
	25	25.22 \pm 0.85	99.9	
Paint for Exterior Wood	0	0.16	-	
	1	1.07 \pm 0.01	91	
	15	15.68 \pm 0.13	104	
	25	24.53 \pm 0.25	98	

CHAPTER 5

CONCLUSION AND FUTURE PERSPECTIVES

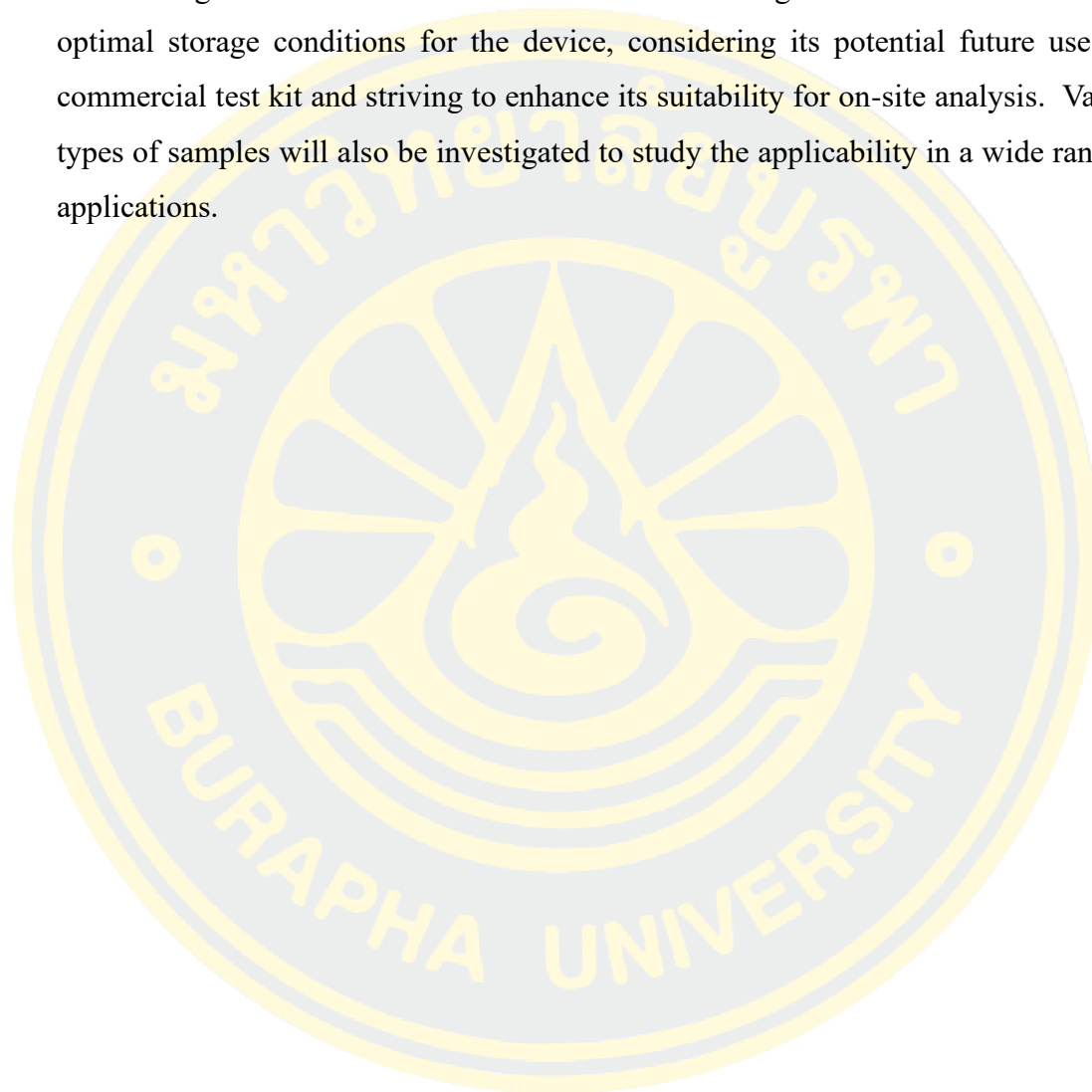
5.1 Conclusions

A novel, one-step analysis method for formaldehyde gas using a paper-based test strip was successfully developed. The analysis relied on the reaction between formaldehyde and acetylacetone in the presence of ammonium acetate (Nash's reagent), which yielded a yellow-colored product of 3,5-diacetyl-1,4-dihydropyridine (DDL). The paper-based test strips have a rectangular shape similar to a pH strip consisting of a transparent plastic sheet support and a paper test zone that was coated with the reagents. Formaldehyde gas detection with the developed test strip can be easily performed in one step by placing samples with a volume of 35 mL into a box, and attaching a paper-based test strip to the inside of the box cover and allowing it to be exposed to formaldehyde gas. After 20 min, if formaldehyde is present in the sample, the paper-based test strip produced a yellow color of 3,5-diacetyl-1,4-dihydropyridine (DDL) as a result of the reaction between acetylacetone and formaldehyde in the presence of ammonium acetate. The intensity of the yellow color is directly proportional to the amount of formaldehyde being tested. The test strip was scanned, and the image was analyzed for color intensity using ImageJ software for quantitative analysis of formaldehyde gas.

Under optimal conditions, the developed device was able to measure formaldehyde in the two-portion linear range of 0.25–1 ppmV and 3–40 ppmV, with a limit of detection of 12 ppbV, which is lower than the air quality threshold set by the Occupational Safety and Health Administration (OSHA). The paper-based test strip exhibits high selectivity for formaldehyde gas and remains stable for over 2 months when stored at ambient temperature and around 4 °C. The developed paper-based test strip requires low-cost materials, low analysis time and cost, and can be used for formaldehyde gas detection in one step. These preliminary results indicated that the developed paper-based test strip holds promise for measuring formaldehyde in air samples and is suitable for use in on-site formaldehyde gas measurement.

5.2 Future perspective

In future studies, we will explore the storage stability period of the paper-based test strip, aiming for an extended duration beyond what has been examined under refrigerated and ambient conditions. This investigation seeks to determine the optimal storage conditions for the device, considering its potential future use as a commercial test kit and striving to enhance its suitability for on-site analysis. Various types of samples will also be investigated to study the applicability in a wide range of applications.

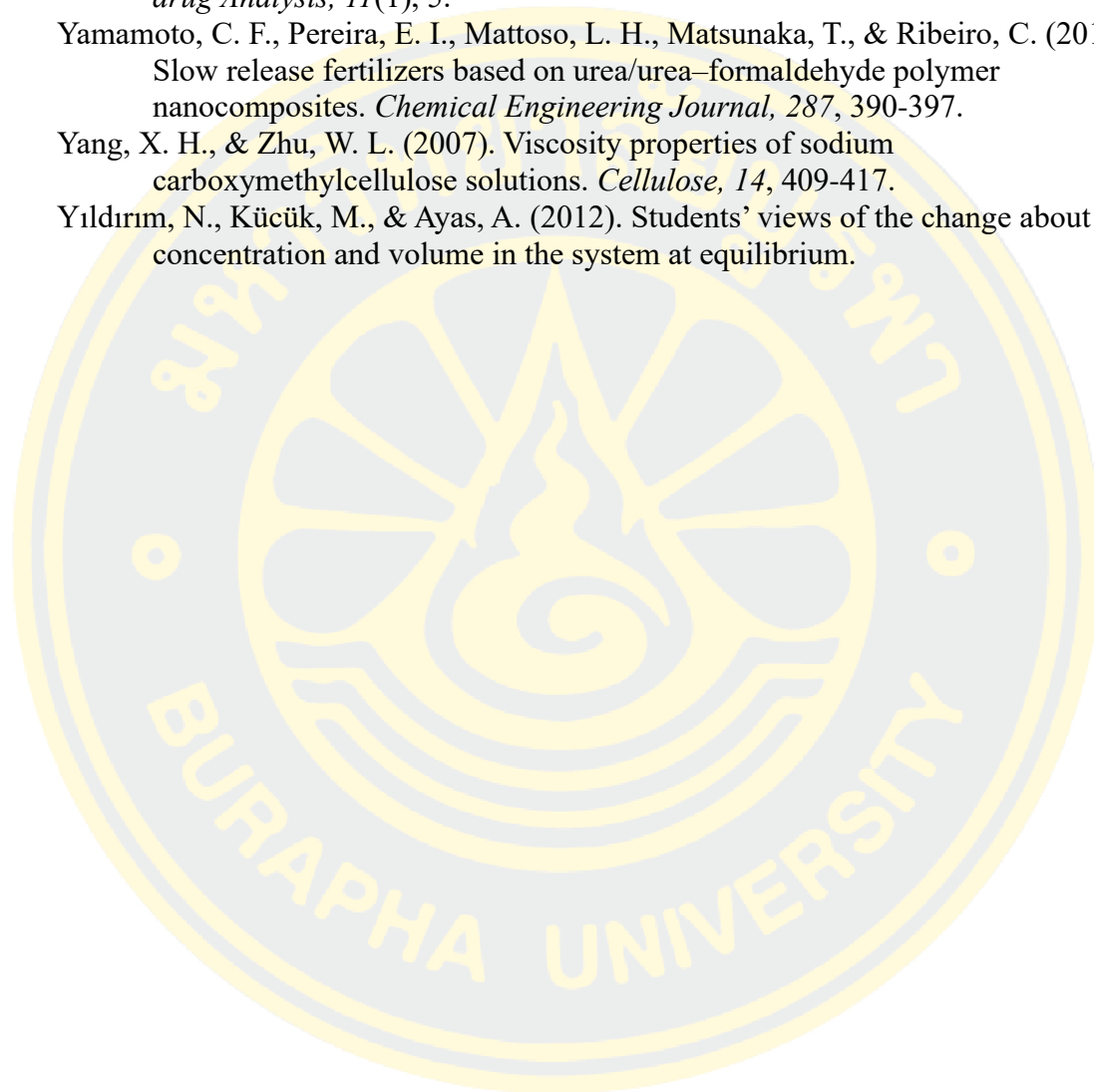


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