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Analytical Methods

A biodegradable colorimetric film for rapid low-cost field determination of formaldehyde contamination by digital image colorimetry

Worawit Wongniramaikul[a,b,c,*], Wadcharawadee Limsakul[a], Aree Choodum[a,b]

[a] Integrated Science and Technology (Applied Chemistry/Environmental Management and Software Engineering) Research Center, Faculty of Technology and Environment, Prince of Songkla University, Phuket Campus, Kathu, Phuket 83120, Thailand
[b] Trace Analysis and Biosensor Research Center, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[c] Center of Excellence on Hazardous Substance Management (HSM), Bangkok 10330, Thailand

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ABSTRACT

A biodegradable colorimetric film was fabricated on the lid of portable tube for in-tube formaldehyde detection. Based on the entrapment of colorimetric reagents within a thin film of tapioca starch, the yellow reaction product was observed with formaldehyde. Intensity of the blue channel from the digital image of yellow product showed a linear relationship in the range of 0–25 $mg\,L^{-1}$ with low detection limit of 0.7 ± 0.1 $mg\,L^{-1}$. Inter-day precision of 0.61–3.10%RSD were obtained with less than 4.2% relative error from control samples. The developed method was applied for various food samples in Phuket and formaldehyde concentration range was non-detectable to 1.413 $mg\,kg^{-1}$. The quantified concentrations of formaldehyde in fish and squid samples provided relative errors of −7.7% and +10.8% compared to spectrophotometry. This low cost sensor (~0.04 USD/test) with digital image colorimetry was thus an effective alternative for formaldehyde detection in food sample.

1. Introduction

Formaldehyde (HCHO) is a toxic substance, which can cause severe health issues (Bunkoed, Davis, Kanatharana, Thavarungkul, & Higson, 2010; International Agency for Research on Cancer, 2004; WHO Regional Office for Europe, 2001). It can irritate the eyes and nose, damage the central nervous system, and cause immune system disorders. Moreover, it has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) (International Agency for Research on Cancer, 2004). However, it is still widely used as a precursor in many industries (Halvarsson, Edlund, & Norgren, 2008; Kim, 2009), *e.g.* textile, plastics, and wood industries, due to its high reactivity and relatively low cost. It is also commonly used as a preservative in medical laboratories, mortuaries, and consumer products. Formaldehyde has been used also inappropriately to extend the shelf-life of food (Atahar, 2013; Riaz, Moin, Tasbira, Naz, & Kumar, 2011), as it was found in various foods at higher concentrations than deemed natural (*e.g.* 1.8 ppm in squid and 1.0–2.4 ppm in prawn) (Clary & Sullivan, 2001; World Health Organization, 2016). The liquid form of formaldehyde, namely formalin (35–40% aqueous solution stabilized in methanol), was commonly used for this purpose.

A wide range of analytical methods, *e.g.* gas chromatography-mass spectrometry (GC–MS), and high performance liquid chromatography (HPLC), have been reported for the determination of formaldehyde, or formalin, in food (Wahed, Razzaq, Dharmapuri, & Corrales, 2016; Wang et al., 2012; Yeh, Lin, Chen, & Wen, 2013; Zhu, Peng, Wang, Wang, & Rui, 2012). However, these are analytical laboratory methods with expensive and sensitive devices, not with robust portable field instruments. A colorimetric sensor would be an advantageous choice for rapid cost-effective on-site determinations of formaldehyde. This approach would provide a number of advantages such as field portability, visual qualitative feedback, rapid detection, and ease of handling (Maruo, Nakamura, Uchiyama, Higuchi, & Izumi, 2008b; Wang et al., 2014). It is typically based on entrapment or impregnation of a colorimetric reagent within various materials, such as a sol–gel matrix (Bunkoed et al., 2010), porous glass (Maruo et al., 2008b), or molecularly imprinted polymer (Feng, Liu, Zhou, & Hu, 2005). However, these types of substrate tend to be non-degradable and of themselves contribute to environmental problems. The use of a biodegradable natural polymer as the supporting material could eliminate this drawback and would be a further asset in a simple and rapid colorimetric sensor. In this work, a natural polymer that is inherently biodegradable (Chiellini & Solaro, 1996) has been used to fabricate the colorimetric sensor for formaldehyde detection. Starch was selected due to its natural availability,

* Corresponding author.
E-mail address: worawit.won@phuket.psu.ac.th (W. Wongniramaikul).

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complete biodegradability (Araújo, Cunha, & Mota, 2004), low cost and renewability (Zhang & Sun, 2004).

A colorimetric sensor is commonly used in conjunction with a spectrophotometric method for the quantitative analysis of formaldehyde (Bunkoed et al., 2010; Fagnani, Melios, Pezza, & Pezza, 2003; Maruo et al., 2008b). This requirement of a spectrophotometer could limit the field applications of an analytical method. However, in recent years digital image colorimetry (DIC) has gained attention due to its low cost in rapid real-time quantitative determinations (Choodum, Boonsamran, NicDaeid, & Wongniramaikul, 2015a; Choodum, Kanatharana, Wongniramaikul, & Nic Daeid, 2013; Choodum, Kanatharana, Wongniramaikul, & NicDaeid, 2012; Choodum & Nic Daeid, 2011; Choodum et al., 2014). The DIC is based on the analysis of RGB data (Red Green Blue basic color) from common digital images of the colorimetric product generated by a digital camera, such as a digital single-lens reflex camera (Choodum & Nic Daeid, 2011; Choodum et al., 2012), the built-in digital camera in a mobile phone (Choodum et al., 2013), or a web camera (Choodum et al., 2015a)). During imaging process, the reflected light from the object of colorimetric product is passed through RGB filters and separated into three spectral ranges. They were then detected and recorded as individual RGB values by the image sensor located behind the filter. The RGB data allows regenerating a subjectively faithful color digital image of the object. When the digital color image is analyzed by a color analysis program, *e.g.* Matlab (Lopez-Molinero, Liñan, Sipiera, & Falcon, 2010), Kylix (Gaiao et al., 2006), Visual basic (Maleki, Safavi, & Sedaghatpour, 2004), or Adobe Photoshop (Choodum & Nic Daeid, 2011; Choodum et al., 2012, 2013), the individual RGB image layers can be inspected. These RGB data can be used as analytical data to produce a calibration graph for quantitative analysis of the interested analyte. In this work, DIC was used for the rapid quantification of formaldehyde in foods, in conjunction with a biodegradable and portable sensor. Thus, the rapid and simple quantitative analysis of formaldehyde was achieved on-site, using an environmentally friendly colorimetric test kit and the digital camera of a mobile phone.

2. Materials and methods

2.1. Materials

A stock solution of 5000 mg L^{-1} formaldehyde was prepared from formaldehyde solution (37%*w/v*) (Supelco, Bellefonte, PA) in ultrapure water (Barnstead EasyPure II, Thermo fisher scientific, OH). Standard working solutions were prepared daily by diluting the stock solution to appropriate concentrations in ultrapure water. Acetylacetone and ammonium acetate were obtained from Sigma-Aldrich (St. Louis, USA), while acetic acid solution was purchased from BDH Laboratory Supplies (Poole, UK).

2.2. Preparation of the biodegradable colorimetric film

The biodegradable colorimetric film was prepared by mixing a starch solution with a formaldehyde specific reagent. Tapioca starch (0.5 g, from supermarket in Kathu, Phuket) was dispersed in ultrapure water (10 mL). It was then heated on a hot plate (~100 °C) under continuous stirring until a clear viscous solution was obtained. After the resultant solution was cooled down to room temperature, the colorimetric reagent was added. Acetylacetone (0.75 mL), ammonium acetate (1 g), and glacial acetic acid (0.1 mL) were added into 4 mL of the starch solution and stirred for 6–8 min to obtain a homogeneous solution. The mixture (100 µL) was then transferred into the flat cap of a centrifuge tube (1.5 mL) and heated at 120 °C for 30 min. This step produced the thin film on the lid of the tube (Fig. 1a). After cooled to room temperature, the lid was quickly closed onto the tube to avoid the contamination, and then stored in a desiccator until further use.

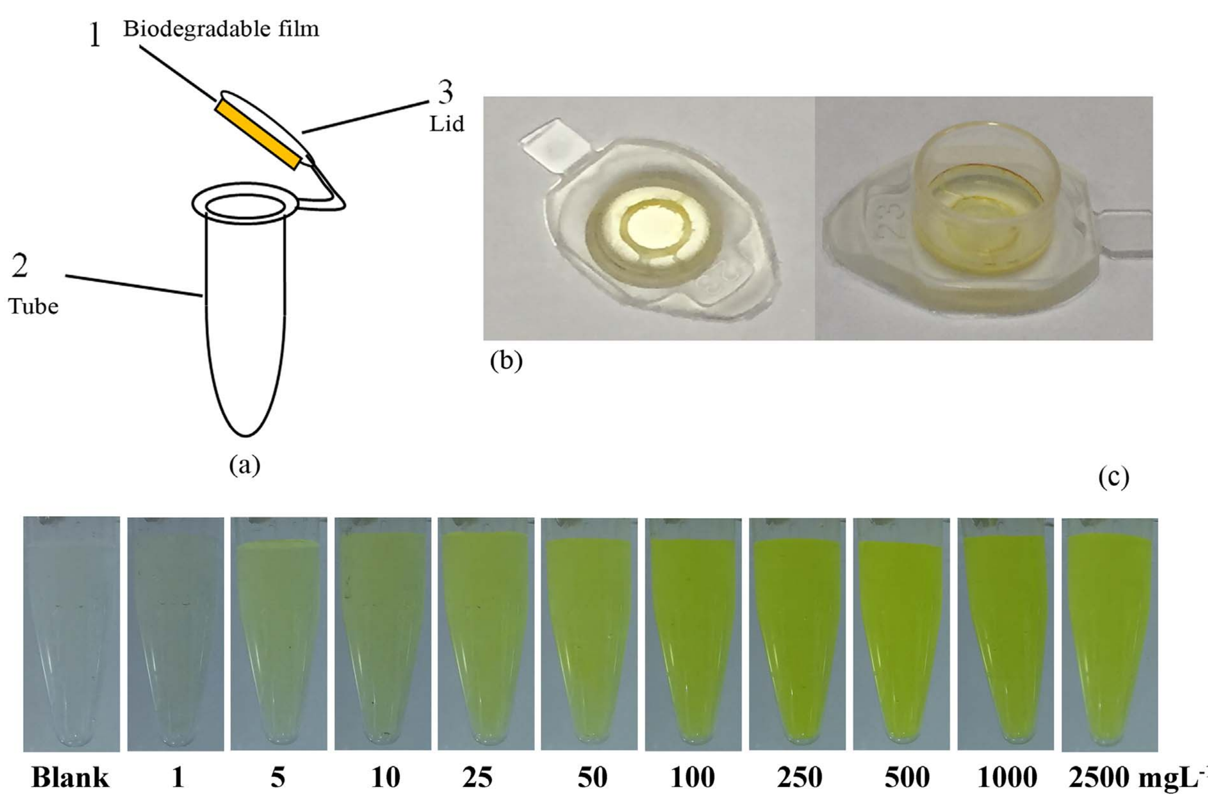

Fig. 1. A biodegradable colorimetric film on the lid of a centrifuge tube: (a) schematic, (b) the film, and (c) colorimetric reaction products from various formaldehyde concentrations (0–2500 mg L^{-1}).