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Microfluidic paper-based chip platform for formaldehyde concentration detection

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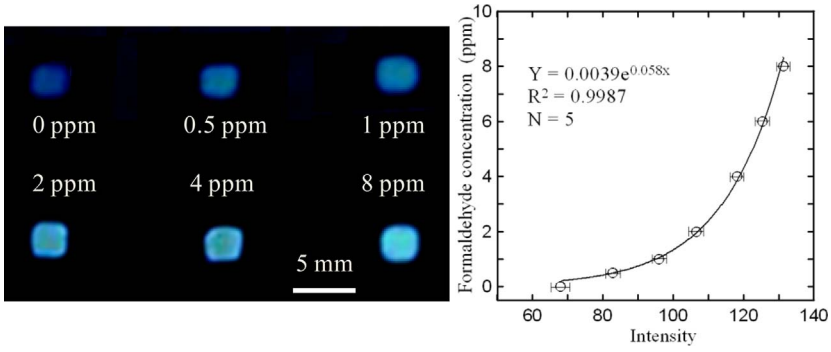
GRAPHICAL ABSTRACT



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ABSTRACT

An integrated platform consisting of a microfluidic paper-based chip and a mini-box detection system is proposed for the concentration detection of formaldehyde. In the proposed approach, the reaction region of the paper-based chip is implanted with Acetoacetanilide reagent, and the formaldehyde concentration is deduced from the UV light-induced fluorescence intensity of the formaldehyde-Acetoacetanilide complex (dihydropyridine) produced in a Hantzsch reaction process at room temperature for 2 min. The experimental results obtained using control samples with formaldehyde concentrations ranging from 0 to 8 ppm show that the formaldehyde concentration (Y) and fluorescence intensity (X) are related as $Y = 0.0039\ e^{0.058X}$. Moreover, the correlation coefficient (R^2) is equal to 0.9987. The real-world applicability of the proposed paper-based platform is demonstrated by measuring the formaldehyde concentration in eleven commercial food samples. It is found that the measurement results deviate from those obtained using a standard bench top method by no more than 4.7%. Overall, the results presented in this study show that the proposed system provides a rapid and reliable technique for formaldehyde concentration detection.

1. Introduction

Formaldehyde is a colorless, flammable, strong-smelling chemical, which readily transforms to polymerized gas at ambient temperature. Formaldehyde is one of the most common carbonyl compounds and occurs naturally in the environment and in a wide range of raw foods,

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including meat (5.7–20 ppm), vegetables/fruits (3.3–17.3 ppm), fish (1.0–98 ppm), and milk/dairy products (1.0–3.3 ppm) [1]. Formaldehyde is also commonly used in food processing for its preservative and bleaching effects However, while formaldehyde is harmless to human health in small quantities, it can have serious adverse effects if present in excessive amounts [2]. Accordingly, the US Environmental Protection Agency (EPA) has stipulated a maximum daily dose reference (RfD) of 0.2 mg/kg body weight.

Water solutions of formaldehyde are highly corrosive, and their ingestion can cause severe injury to the upper gastrointestinal tract. Furthermore, ingestion of even 30 mL (1 oz.) of a solution containing 37% formaldehyde can cause death in human adults. Early laboratory studies showed that exposure to formaldehyde can cause nasal cancer in rats. This finding raised the question as to whether formaldehyde exposure may also increase the risk of cancer in humans. As a precaution, the U.S. EPA classified formaldehyde as a probable human carcinogen under conditions of unusually high or prolonged exposure [3]. Since that time, many studies have confirmed that formaldehyde exposure is indeed strongly associated with certain types of cancer. Consequently, the International Agency for Research on Cancer (IARC) has formally classified formaldehyde as a human carcinogen [4]. Furthermore, in 2011, the National Toxicology Program, an interagency program of the Department of Health and Human Services in the USA, also named formaldehyde as a known human carcinogen in its 12th Report on Carcinogens [5].

In view of the potentially harmful effects of formaldehyde exposure/ingestion, the problem of developing reliable techniques for measuring the formaldehyde concentration in foods and beverages has attracted significant attention in the past few years. Many analytical methods for formaldehyde measurement have been reported, including Fourier transform infrared absorption (FTIR) [6], differential optical absorption spectroscopy (DOAS) [7], laser-induced fluorescence spectroscopy (LIFS) [8,9], tunable diode laser absorption spectroscopy (TDLAS) [10], fluorometric determination [11,12], gas chromatography or high-performance liquid chromatography (HPLC) [13–15], spectrophotometric detection [16,17], enzymatic reaction [18], colorimetric detection [19,20], kinetic measurement [21,22] and microfluidic sensing [9,23–28]. However, while all of these methods provide a useful approach for quantifying the formaldehyde concentration in different media, they suffer some major drawbacks. For example, the colorimetric method presented by Wang et al. [15] has the advantages of a low background level, high selectivity, and very little sample preparation, but suffers poor veracity (semi-quantitative determination).

The methods presented above utilize some form of bench top apparatus to perform formaldehyde detection. In contrast to such systems, microfluidic devices have many practical advantages, including a faster throughput time, a reduced sample/reagent consumption, a lower cost, and greater portability [29–31]. Accordingly, Weng et al. [23] presented a PDMS microfluidic chip in which the formaldehyde concentration in food samples was detected by illuminating the reaction region with UV light (410 nm) and measuring the absorption rate as the reaction proceeded. Similarly, Fu et al. [9] presented an integrated microfluidic chip with a three-layer PMMA structure for formaldehyde concentration detection in Chinese herbs using a laser-induced fluorescence (LIF) technique.

Microfluidic paper-based analytical devices (PADs) have emerged as a promising tool for the detection of analytes due to their low-cost, easy operation, high portability, and good disposability [32–40]. Moreover, the porous structure of cellulose paper provides a large surface-to-volume ratio, which allows reagent storage by simply drying the wetted area. Microfluidic paper-based assays have been widely applied in the medical, food industry, veterinary, agriculture/aquaculture, and environmental safety fields [41–45], and have proven a reliable technique for the detection of proteins in corporal fluids hormones, bacteria, viruses, and chemical contaminants [46–53]. However, although PADs are operationally straightforward and convenient, the final detection process still relies on the use of traditional macroscale techniques, such as electrochemistry [54], fluorescence detection [55], colorimetry [56], electroconductivity [57], electrochemiluminescence (ECL) [58], sensors [59], photoluminescence (PL) [60], chemiluminescence (CL) [61], and luminescence [62]. Consequently, the use of microfluidic PADS for point-of-care (POC) applications is still somewhat limited.

Accordingly, the present study proposes a microfluidic paper-based chip platform for rapid formaldehyde concentration detection consisting of a disposable microfluidic paper-based analytical device (micro-PAD) and a mini-box detection system incorporating a power source, a DC power supply, an LED UV source, a step-down module, a camera lens, a chip holder, and a digital camera. In the proposed detection process, an Acetoacetanilide indicator is implanted in the reaction region of the micro-PAD and the formaldehyde sample is then dripped on the reaction zone; prompting a Hantzsch reaction with the reagent. Following a predetermined reaction time (2 min), the disposable micro-PAD is inserted into the mini-box detection system, where it is illuminated by UV light. The formaldehyde concentration is then inversely derived from the measured intensity of the detected fluorescence signal using self-written image-processing software.

2. Fabrication and experimental details

2.1. Paper-based chip preparation

Fig. 1 presents a schematic illustration of the disposable micro-PAD fabrication process. The PAD (with diameter of 110 mm) was fabricated on Advantec qualitative filter paper (No. 1, Toyo Roshi Kaisha Ltd., Japan) with a pore size of 6 μm and a thickness of 0.2 mm. As shown in Fig. 1(a), the device consisted simply of a square reaction zone with a side-length of 3 mm bounded on all four sides by impermeable wax. The PAD was designed using AutoCAD 2012 software and was printed using a commercial wax printer (Fuji Xerox ColorQube 8750, Japan) (Fig. 1(b)). Following the printing process, the device was placed in a bench top furnace (Vulcan A-550, Taiwan) and baked at 180 °C for 60 s to ensure the full penetration of the wax through the paper thickness (Fig. 1(c)). The PADs were cut from their paper surround (Fig. 1(d)) and then reprinted with impermeable wax on the reverse side in order to prevent sample leakage (Fig. 1(e)).

Acetoacetanilide reagent solution was prepared consisting of 5 mg ammonium phosphate, 0.45 g Acetoacetanilide, and 30% 10 ml ethanol solution mixed in 20 ml de-ionized (DI) water. 10 μL of the Acetoacetanilide solution was dripped onto the reaction zone of the microfluidic paper-based chip and left to dry under room temperature conditions.

2.2. Mini-box detection system and chemical reaction

As shown in Fig. 2, the main components of the mini-box detection system included a power source, a DC power supply, an LED UV source, a step-down module, a camera lens, a chip holder, and a digital camera (D5200, Nikon, Japan). The LED UV source consisted of an LED with an emitting wavelength of 380 nm, a narrow-band filter (365 nm–375 nm), and a heat sink, as shown in Fig. 2(b).

In this mini-box detection system performing the formaldehyde concentration detection experiments, around 30 μL of the formaldehyde sample was dropped on the reaction zone of the micro-PAD using a digital micro-pipette. Following a reaction time of 2 min, the micro-PAD was transferred to the detection box (Fig. 2(d)) and the LED light source was activated. The resulting fluorescence images were captured by the digital camera and transferred to a computer, where the light intensity was analyzed using self-written software in order to determine the corresponding formaldehyde concentration. The accuracy of formaldehyde concentration measurement can be affected by the resolution of the digital camera.

The Hantzsch reaction has been widely used for spectrophotometric