1. Introduction

Analysis of levels of volatile organic compounds (VOC) emitted to the environment has gained special attention within past few decades due to their potential impact on human health. Carbonyl compounds (CC) can be commonly associated with various processes produce adverse conditions to humans (Yu *et al*., 2011). Because of the potential impact on human health, it is important to monitor the levels of CC in enclosed areas used for human occupation. The most common CC that can be found in enclosed areas include formaldehyde, acetaldehyde, acrolein and acetone. Many man-made commonly found utilities and some human activities are responsible for the emission of CC to the environment. Out of the many man-made utilities, house hold furniture, electronic products, plastic-based products and recycled product are the main sources of CC (Weng *et al*., 2010). Formaldehyde is the most common CC found in residential indoor air. Even though the method reported can detect the total CC present in indoor air, only formaldehyde is used in the process of method development and validation in this study.

Most commonly used method for the collection of airborne CC is to use an adsorbing material with a derivatization agent to capture CC, followed by solvent (Soman *et al*., 2008) or thermal desorption (Ho, *et al*., 2004) and analysis using a chromatographic or spectroscopic methods (Szulejko, *et al*., 2015). Various derivatization materials are reported by many research groups (Szulejko *et al*., 2015). However 2,4-di-nitrophenyl hydrazine (2,4-DNPH) is the most commonly used derivatization agent (Szulejko *et al*., 2015). Even though there are few drawbacks (Pal *et al*., 2007), the 2,4-DNPH derivatization-based HPLC method can be considered as a cheaper and easier methods for the determination of CC. However, the use of advanced instruments such as HPLC-UV/VIS and GC/MS methods are not suitable to monitor the onsite CC levels under non-laboratory conditions. In addition to the chromatographic method (Ho *et al*., 2004), electrochemical sensors (Otson *et al*., 1988) are also available for the detection of some CC. However, the lack of sensitivity and selectivity limits the usability of these sensors.

Paper-based analytical tools are popular among scientists due to their simplicity, low cost, environmental friendly nature and portability. Development of paper-based tools for the detection of alcohol is previously reported (Gunawardhana *et al*., 2016). Objective of this study is to develop a simple and green paper-based tool that can be used as an onsite method to detect CC. A paper-based tool capable of detecting CC with minimum amount of organic solvents was successfully developed under this study.

2. Material and Methods

2.1. Chemicals and other materials

All chemicals were used as they were received unless specified. Conc. hydrochloric acid (37%), 2,4-DNPH and methanol were purchased from Sigma, Germany. Acetonitrile and formaldehyde were purchased from Merck Millipore.

2.2. *Reagents*

A 2,4-DNPH solution was prepared by mixing 0.01 g of 2,4-DNPH with 100 µL of

HCl and diluting up to 100.00 mL using distilled methanol. A series of formaldehyde standards with the concentrations of 1, 5, 10, 15, and 20 ppm was prepared using the 100.0 ppm standards of formaldehyde in methanol solution.

The calibration standard for HPLC analysis was prepared by mixing a solution of 2,4-DNPH (1.00 g of 2,4-DNPH + 2.00 mL of conc. HCl diluted up to 100.00 mL using distilled methanol) with excess acetone. The resultant precipitate was re-crystallized to obtain pure formaldehyde 2, 4-DNPH (HCHO-DNPH) derivatives. A series of standard solutions with the concentrations of 1, 5, 10, 15, 20 ppm were prepared using the purified HCHO-DNPH derivative using methanol as the solvent.

2.3. *Instruments*

An FTIR Spectrophotometer (Varian 660-IR) was used to measure the absorbance and percentage transmittance (%transmittance) of HCHO-DNPH complex. *High performance liquid chromatography (System Controller: Jasco 802-Sc with UV/VIS detector), was used for method validation. An* HP image scanner (HP Scan jet 2400) was used to obtain the high resolution image from the paper based devices, to determine the yellow color intensity (yellow number) developed region.

2.4. *Development of paper-based devices*

Disk shaped (diameter = 0.7 cm) devices were developed using Whatman No 1 filter papers. These disk shaped devices were soaked with 2,4-DNPH solution and dried to develop the paper-based tool. Blank response was recorded using devices soaked only with the 2,4-DNPH solution.

2.5. *Construction of calibration plot using FTIR measurement*

Disk shaped (diameter = 0.7 cm) devices were developed using Whatman No 1 filter papers and soaked with standard solutions of HCHO-DNPH derivative in methanol. These disks were dried and the % transmittance at 1648 cm^{-1} was recorded using the FTIR. The lowest %transmittance observed around 1648 cm^{-1} for each disk soaked with standard solutions of HCHO-DNPH derivative was used to construct the calibration plot.

2.6. *Construction of calibration plot using high resolution image scanner*

Disk shaped (diameter = 0.7 cm) devices were developed using Whatman No 1 filter papers and soaked with standard solutions of HCHO-DNPH derivative in methanol. Then the paper discs were scanned with an image scanner (HP Scan jet 2400) and then imported to Adobe Photoshop CS5®. Use of an image scanner to measure the colour intensity of paper-based devices is reported previously (Liana *et al.*, 2012). These images were converted to grayscale mode and the yellow color intensity was computed using the three primary colors. A graphical user interface (GUI) was developed to select individual paper-based device when multiple disks were scanned simultaneously. The averages of red, green and blue color intensities over a range of 50 pixels on the paper-based tool were taken for better accuracy. The center of the paper-based device was selected by using the GUI and the average yellow color intensity was calculated over a circular area with a diameter of 50 pixels. The calibration curve was then plotted between the mean color intensity versus the concentration.

2.7. *Construction of calibration plot using HPLC method*

A method reported by Soman *et. al*. (2008) was used for the quantification of HCHO-DNPH derivative. Double distilled acetonitrile and water 40:60 mixture was used as the mobile phase. A volume of 20 µL from each standard solutions of HCHO-DNPH derivative in methanol was analyzed. The peak area for each standard solution was used to construct the calibration plot.

2.8. *Method validation*

A gaseous phase formaldehyde series with concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L was prepared in a glass container of 5 L by introducing the standard formaldehyde solution. The air borne formaldehyde concentration in glass containers was estimated using the volume of glass container and the amount of formaldehyde introduced. Glass container was kept tightly closed for six hours after introducing the paper-based tool soaked with 2,4-DNPH. After six hours, paper-based devices were analyzed using FTIR and image scanner method. A second set of devices exposed to the standard formaldehyde air samples for a period of six hours were extracted in to a solution of methanol and the methanol extract was analyzed using HPLC (Pal *et al*., 2007).

2.9. *Analysis of real air samples*

An enclosed air tight room space contaminated with formaldehyde was tested using the paper-based devices and HPLC (Pal,*et al*., 2007) and FTIR methods were used to quantify the levels of CC in the air tight room. Two methods were compared statistically at 95% confidence limit using the method explained in Skoog *et al*.

3. Results

Paper-based devices soaked with the 2,4-DNPH solutions and treated with standard formaldehyde solutions were scanned with FTIR produced a characteristic transmittance pattern for the HCHO-DNPH derivative. The FTIR response for a 2,4-DNPH soaked paper-based device exposed to an air sample with formaldehyde is shown in Figure 1. The expected unique %transmittance for HCHO-DNPH was observed around 1648 cm^{-1} due to stretching vibrations of the double bond between C and N (C=N). The calibration plot constructed based on FTIR response is shown in Figure 2. The calibration plot developed based on HPLC study is shown in Figure 3.

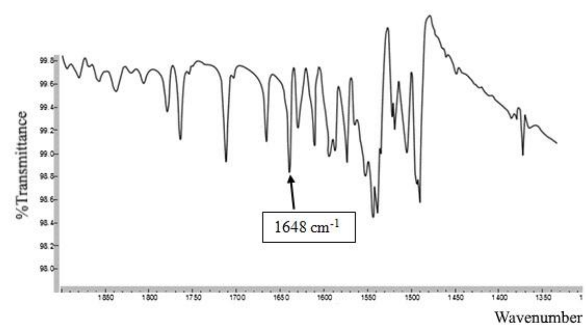

Figure 1. FTIR response for a 2,4-DNPH soaked paper-based device exposed to an air sample with formaldehyde.

Paper-based devices exposed to air samples with known formaldehyde concentrations were analyzed using the

FTIR and HPLC methods and the results are given in Table 1.

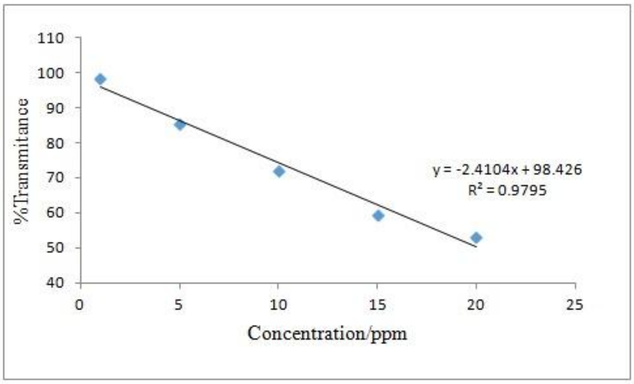

Figure 2. Calibration plot of FTIR %transmittance against formaldehyde 2,4-DNPH derivative concentration.

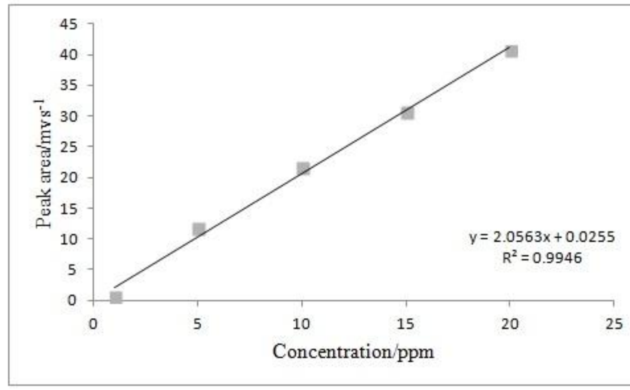

Figure 3. Calibration plot of peak area of HPLC response against standard formaldehyde 2,4-DNPH derivative concentration.

Table 1. Response of the paper-based tool exposed to air samples with the formaldehyde concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L were analyzed using the FTIR and HPLC methods.

Concentration / mg/L	Peak area/mvs^{-1}	%Transmittance
0.2	0.91	97.65
0.4	2.90	95.70
0.6	4.41	93.90
0.8	6.67	91.14
1.0	8.14	89.63

The RBC values, yellow value and the intensities of each paper-based device soaked with 2,4-DNPH exposed to the known formaldehyde air samples are given in the Table 2. The correlation between yellow values against formaldehyde concentration of air samples is shown in Figure 6.

Indoor air tested of enclosed areas contaminated with five various levels of formaldehyde (sample number 01, 02, 03, 04 and 05) using the developed paper-based device and HPLC methods. Results obtain for these samples are given in Table 3.

Indoor air tested of enclosed areas contaminated with five various levels of

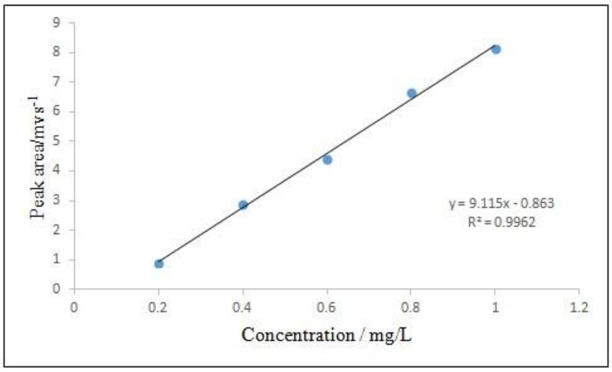

Figure 4. Correlation between the HPLC peak area and the formaldehyde concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L.

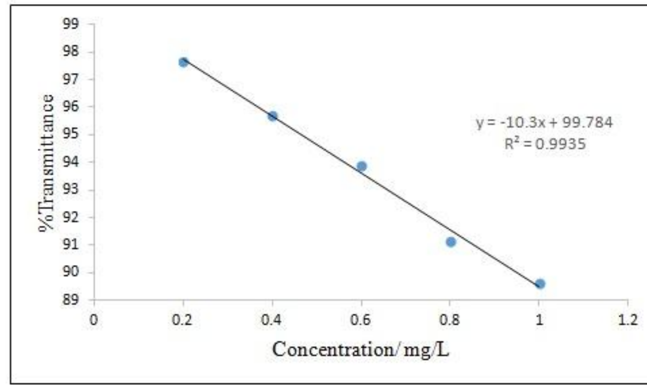

Figure 5. Correlation between the FTIR %transmittance and the formaldehyde concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L.

Table 2. The RGB values, yellow value and the intensities of each paper-based device exposed to 0.2, 0.4, 0.6, 0.8, 1 mg/L formaldehyde air samples 2,4-DNPH derivative concentrations

Concentration/ mg/L	Red	Green	Blue	Yellow	Intensity
0.2	245	242	42	211	244
0.4	241	238	40	213	240
0.6	245	241	37	216	243
0.8	246	245	37	217	246
1	217	206	31	219	212

Table 3. The concentration calculated based on the HPLC method is corrected using the response obtained for the blank sample.

Sample No	Calculated concentration using FTIR method / mg/L	Calculated concentration using standard HPLC method/ mg/L
1	0.05	0.09
2	0.08	0.09
3	0.25	0.35
4	0.26	0.30
5	0.27	0.30

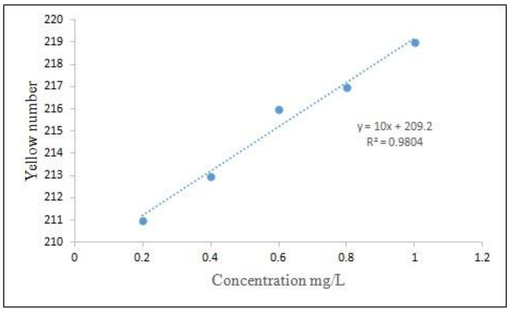

Figure 6. Correlation between the yellow value and formaldehyde concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L.

4. Discussion

The method described in this paper requires minute amounts of chemicals than that of other conventional methods used to quantify carbonyl compounds in indoor air. Hence, this novel method can be considered as a green technique for the determination of airborne total carbonyl compounds. Based on the repeatability and the correlation between %transmittance and formaldehyde concentration, disk shape was selected as the optimum shape for the paper-based device. Disk shape Whatman No 1 filter paper pieces soaked with 2,4-DNPH were used to trap CC. The chemical reaction between formaldehyde and 2,4-DNPH to from HCHO-DNPH derivatization is shown in Figure 7.

The resultant FTIR spectrum is shown in the Figure 01, and the peak generated due to the N-N=C can be seen around 1648 cm^{-1}. The level of HCHO-DNPH derivatization product or any carbonyl compound-DNPH derivatives on the paper-based device is proportional to the %transmittance at 1648 cm^{-1}. This correlation is used to produce a paper-based device that can be used to quantify the level of CC in air. Figure 2 shows the correlation between the %transmittance and the levels of HCHO-DNPH derivative in the range of 1 – 20 ppm on the paper-based device. The regression equation obtained for the paper-based FTIR detection was: $y = -2.4104x + 98.426$, where y is the %transmittance produced by the paper-based device and x is the level of HCHO-DNPH derivative on the paper in ppm. The correlation coefficient of 0.9795 (n = 5) provides satisfactory linearity between the %transmittance and the level of HCHO-DNPH derivative on the paper in the concentration range of 1 – 20 ppm. This study confirms the ability to use the proposed paper-based device for the detection of CC in air samples.

Paper-based devices soaked with 2,4-DNPH were kept under air tight conditions until used. Some paper-based devices soaked with the 2,4-DNPH solution are shown in Figure 8 .

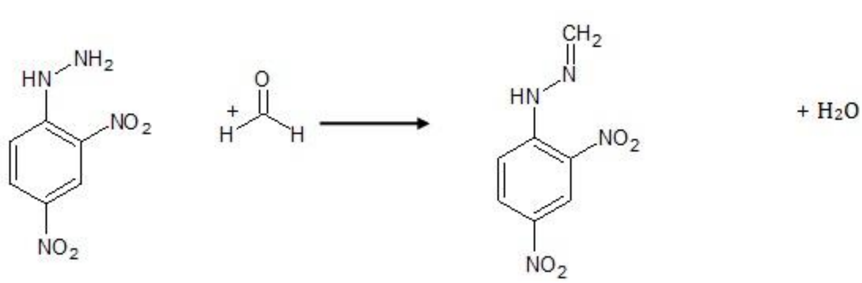

Figure 7. The chemical reaction between formaldehyde and 2,4-DNPH.

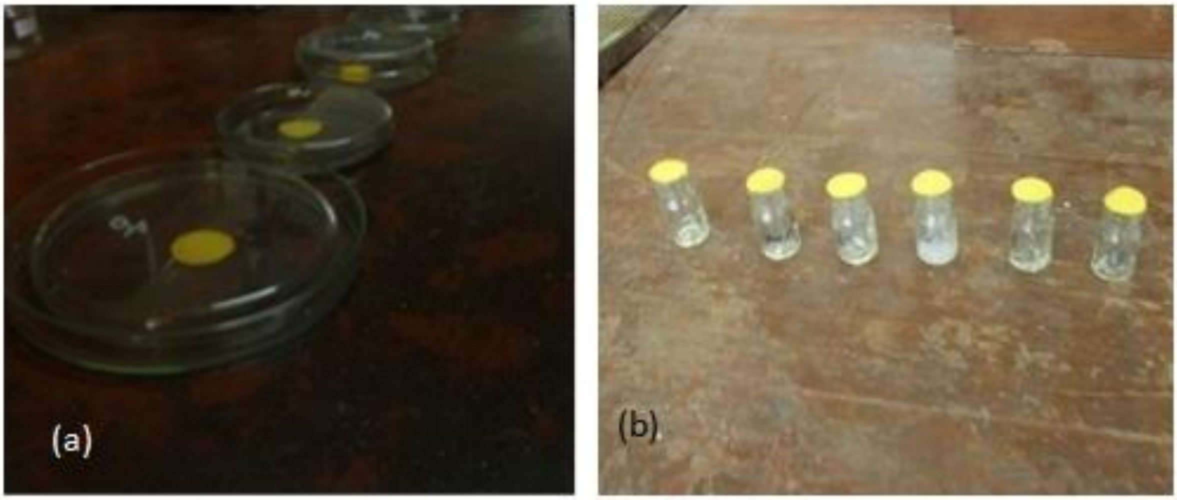

Figure 8. Paper based devices soaked with 2,4-DNPH solution (a): kept inside the Petri dishes and (b): kept on a small vial opening.

Previously reported HPLC based method was used to validate the novel method proposed based on a paper-based device to quantify the levels of CC in air. Figure 03 shows correlation between the area of the HPLC peak for the HCHO-DNPH derivative and the concentration in the range of 1 -20 ppm. The regression equation obtained for the HPLC detection was: $y = 2.056\,3x + 0.0255$, where y is the peak area and x is the concentration of HCHO-DNPH in ppm.

The proposed paper-based method was tested using laboratory prepared air samples with the concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L. These samples were prepared using 5 L glass bottles spiked with the standard formaldehyde volumes to build the required levels of formaldehyde. The paper-based devices were inserted in to the glass bottles and allowed to stand for a period of six hours.

The FTIR response produced for each paper-based device exposed to these laboratory prepared air samples are shown in Figure 5. The regression equation obtained for the paper-based FTIR detection for standard formaldehyde air samples was: $y = -10.3\,x + 99.784$, where y is the %transmittance produce by the paper-based device and x is the level of formaldehyde in mg/L. The correlation coefficient of 0.9935 (n = 5) provides satisfactory linearity between the %transmittance and the level of formaldehyde in air samples in the concentration range of 0.2 - 1 mg/L. Figure 04 shows the correlation between the area of the HPLC peak for the HCHO-DNPH derivative and with the concentrations of 0.2, 0.4, 0.6, 0.8, 1 mg/L.

This proposed paper-based method does not require any mechanical method to collect air samples and the sample collection can be performed within six hours. The FTIR %transmittance around

1648 cm^{-1} can be directly used for the quantification of CC. Based on Figure 5, the limit of detection(LOD) and the limit of quantification(LOQ) were calculated. Using the calibration plot shown in Figure 05, standard deviation of the slope (Sy) and the slope (S) were calculated. The LOD, which was calculated using the relationship LOD = 3.3(Sy/S), is 0.19 mg/L. The LOQ, which was calculated using the relationship, LOD = 10(Sy/S), is 0.29 mg/L. The reported LOD and LOQ for the HPLC based detection of formaldehyde is 0.1 and 0.33 ppm, respectively (Soman *et. al*., 2008). Even though the proposed method is not capable of detecting lower concentrations as HPLC method, the proposed method is cheap, easy and uses less chemicals. LOD and LOQ of the proposed method can be improved by increasing the exposure time.

The method validation was done by testing an enclosed area contained with formaldehyde by using the new paper-based device and the standard HPLC methods. Five different concentrations (sample 1, 2, 3, 4 and 5) were set in the enclosed area and the CC levels were separately measured. The levels of CC obtained by both methods are given in Table 03. The two sets of experimental concentrations obtained using the new paper-based and HPLC methods were tested using the t-statistic according to the method given in Skoog *et al*. Based on the statistical evaluation, there is no significant difference at 95% confidence level between the two methods.

The proposed paper-based method is based on the FTIR detection and this hinders the ability to use this method without laboratory facilities. To overcome this drawback, the possibility of using a high resolution image scanner instead of FTIR detection was tested.

Paper-based devices exposed to laboratory prepared air samples were examined using a high resolution image scanner as explained in the Methodology section. Adobe Photoshop CS5 ® software was used to measure the yellow color intensity (yellow number) of the test zones of the paper-based microfluidic devices. All images were converted to grayscale mode in order to avoid unnecessary color detection by the software. Image scanner responses produced for each paper-based device exposed to laboratory prepared formaldehyde air samples are shown in Table 2 and Figure 6. The regression equation obtained for the paper-based image scanner detection for the standard formaldehyde air samples was: $y = 10x + 209.2$, where y is the yellow number generated for the paper-based device and x is the level of formaldehyde in ppm. The correlation coefficient of 0.9804 (n = 5) provides satisfactory linearity between the yellow number and the level of formaldehyde in the air samples in the concentration range of 0.2 – 1 mg/L. The LOD, which was calculated using the relationship, LOD = 3.3(Sy/S) is 0.07 mg/L. The image scanner-based method allows this proposed paper-based method to be used as a portable and user-friendly method. Also, this proposed method can be performed with laboratory facilities under industrial or domestic conditions to monitor the level of CC in any given situation.

Only limitation of this proposed method is that the paper based-device should be stored in an air tight container until use. Also, paper disks and 2,4-DNPH solution can be separately stored and the devices can be prepared when required. When an image scanner is used, the image can be digitally sent to a laboratory, so that the data can be analyzed by a specialist and the results can be sent real time, to the field. Recently, some research groups have managed to use smart phones to capture the color intensity of the paper-based device to quantify the level of analyte (Lee *et al*., 2011).The same approach can be used to improve this proposed paper-based device to detect CC. The amount of solvent and other chemicals used in both paper-based devices coupled FTIR and image scanner detection are lesser than the conventional HPLC method, hence these proposed methods can be considered as green methods.

5. Conclusion

This report presents the development and validation of a paper-based tool for the quantification of CC in indoor air. This method is an inexpensive, green, sensitive and reliable method for the detection of trace levels of CC. Circular shaped paper-based tools soaked with 2,4-DNPH successfully managed to capture airborne CC. The %transmittance was measured using FTIR and the yellow color intensity was calculated using an image scanner. Percentage of transmittance around 1648 cm^{-1} and the yellow color intensity measured produced a linier correlation with the airborne formaldehyde concentration. An airtight region contaminated with formaldehyde was tested using the newly developed method and the standard HPLC method. Newly developed FTIR-based method is agreeable with the standards HPLC method at 95% confidence limit.

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