Research Article

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pH-based colorimetric detection of monofunctional aldehydes in liquid and gas phases

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Abstract: An ammonium chloride–Congo red (NH_4Cl-CR) solution is presented as a potential sensing solution for aldehydes. Monofunctional aldehydes such as formaldehyde, acetaldehyde, benzaldehyde, and isobutyraldehyde caused changes in the pH of the sensing solution, producing a color transition from red-orange to violet to blue. This distinguished them from the other compounds, thereby acting as a qualitative test for the functional group. The NH_4Cl-CR solution was also employed in making filter paper-based and silica gel-based sensors for formaldehyde and acetaldehyde vapors. These sensors responded positively towards the aldehyde gases through a color transition from pink to blue. The NH_4Cl-CR mixture provides a simple and easy-to-handle reagent for the detection of both liquid and gaseous aldehydes which has potential applications in environmental monitoring.

Keywords: pH indicator, colorimetric, aldehydes, formaldehyde, paper strips, congo red

1 Introduction

Aldehydes constitute one of the most reactive classes of organic compounds. Most aldehydes occur widely in nature and are closely associated with numerous industrial applications [1,2]. However, some aldehydes are toxic and deleterious to human health and the environment. They are released into the air on a daily basis by residential wood burnings and the combustion of hydrocarbon fuels, fossil fuels, and biomass [3–6]. They are also spontaneously generated through photochemical oxidation of naturally occurring hydrocarbons [2,7]. They may also be present in rainwater or surface water [8], drinking water [9–11], fermented products [12–15], high-temperature frying oils [16,17], and cigarette smoke [18–20]. The minor exposure to aldehydes can manifest as nonspecific symptoms such as eye, nose, and throat irritation, headaches, and fatigue while exposure to high concentrations can lead to respiratory ailments, reproductive and neurological disturbances, and even cancer [21,22]. Thus, the detection of aldehydes in the environment to minimize risk of exposure is of vital importance.

Several colorimetric detections of aldehydes that have been developed relies mainly on chemical reactions that attack the –CHO functional group. Some of the approaches are based on well-known reactions such as the Tollen's test [23,24] and derivatization with 2,4-dinitrophenylhydrazine (DNPH) [9,25–27]. Recently, Liu et al. [28] reported the colorimetric detection of volatile aldehydes in edible oils based on the reaction of hydroxylamine sulfate. The release of sulfuric acid caused the color change of a pH indicator. While the sensor provided good sensitivity and selectivity, it required synthesis of the chitin films. Similar mechanisms incorporating pH indicators as sensing agents have also been employed [29–32]. However, simpler and more practical approaches toward colorimetric detection of aldehydes in the vapor or solution phase that incorporates pH indicators are few.

Here the naked-eye detection of aldehydes in aqueous solution and in the gas phase have been explored. The sensing reagent involves a mixture of ammonium chloride (NH_4Cl) and Congo red (CR) indicator dissolved in aqueous solution or absorbed into filter paper and silica gel.

2 Methods

Formalin was purchased from Ajax Finechem as 37% w/v formaldehyde in water. Acetaldehyde was purchased from

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Sigma-Aldrich. All other reagents in the study were obtained from TPC India and used without further purification. Saturated solution of NH_4Cl was prepared by adding NH_4Cl to 250 mL of distilled water with continuous stirring until no more salt dissolved. The excess salt was then removed via filtration. CR was prepared by dissolving 10 mg of the dye to 10 mL of distilled water to make a 0.1% w/v aqueous solution.

UV-vis spectral analysis was performed using a Shimadzu UV-1800 spectrophotometer.

2.1 Detection of aldehydes in aqueous solution

2.1.1 Reaction with CR

Two drops 0.1% CR, five drops of distilled water, and five drops of formaldehyde were placed in a 10 mL vial. The color of the resulting solution was then noted.

2.1.2 Reaction with NH_4Cl

One mL formaldehyde and 1 mL saturated solution of NH_4Cl were placed in a 10 mL vial. The pH of formaldehyde and NH_4Cl solution before mixing and 5 min after mixing were determined using a Whatman pH indicator paper. This procedure was done thrice.

2.1.3 Reaction with NH_4Cl and CR

In a 10 mL rubber-stoppered vial, five drops of a saturated solution of NH_4Cl and two drops of 0.1% CR solution were placed. The color of the resulting solution was noted. Afterwards, five drops of formaldehyde were added. The resulting solution was then observed for color changes.

The above procedures were repeated using acetaldehyde, benzaldehyde, isobutyraldehyde, vanillin, glucose, acetone, ethyl acetate, methanol, formamide, acetic anhydride, formic acid, and distilled water. All procedures were done thrice.

2.2 Detection of gaseous aldehydes

2.2.1 Preparation of solid-phase sensors

Gas sensors were prepared by impregnating the solid-phase medium with the sensing solution consisting of 3:2 mixture of saturated NH_4Cl solution and CR solution.

Filter Paper. A filter paper (Whatman) cut to a 0.5″ by 1.25″ strip was soaked in 5 mL of sensing solution. The resulting paper was allowed to dry in the fume hood for half an hour. A filter paper impregnated with CR only was also prepared using the same procedure.

Silica Gel. Five grams silica gel (Macherey-Nagel silica gel 60) was placed in a beaker and added with 3 mL of sensing solution. The silica gel was dried in the fume hood for 24 h. Approximately 50 mg of the resulting powder was then used for each sensing trial. For comparison, a sensor containing CR only was also made using the same procedure.

2.2.2 Aldehyde vapor sensing

Detection of gaseous aldehyde was done using two volatile aldehydes – formaldehyde and acetaldehyde. The aldehyde gases were obtained via evaporation of the liquid aldehydes. Three mL of the aldehyde were placed in a vial positioned inside a glass chamber (Figure 1). The chamber was then sealed and left for 10 min to allow evaporation prior to gas sensing. After saturation, the solid-phase sensor was placed inside the chamber. The set-up was monitored, and the resulting visible changes were noted. This was done in triplicates.

2.2.3 Simulation of formaldehyde detection

On the walls of an empty fume hood, paper-based sensors were placed. Starting from the base (work surface), the sensors were installed on the wall 5″ apart. Afterwards, a 50 mL beaker containing 25 mL of formalin solution (37% w/v formaldehyde in water) was placed on the other side of the hood (Figure 2). The hood was closed, and the set-up was left for 24 h. Afterwards, the resulting sensor response was noted.

Paper-based sensors were also installed in a biology laboratory during a dissection exercise where formalin was used. The sensor was left for an hour and the resulting response was noted.

3 Results and discussion

3.1 Detection of liquid aldehydes

The development of a sensor for liquid aldehydes was tested on representative aldehydes: formaldehyde, the simplest aldehyde; acetaldehyde, an aliphatic aldehyde;

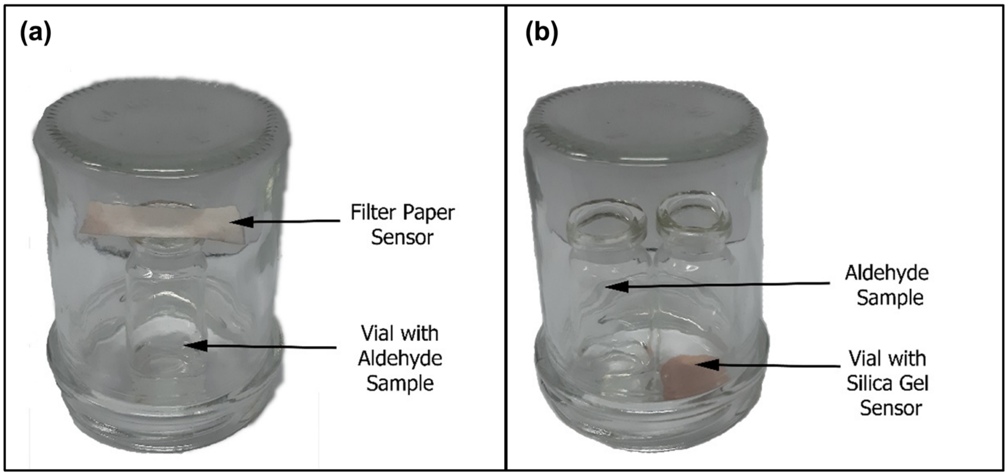


Figure 1: Experimental set-ups for detection of aldehyde vapors using (a) filter paper and (b) silica gel.

isobutyraldehyde, a branched-chain aldehyde; benzaldehyde, an aromatic aldehyde; and glucose and vanillin, polyfunctional compounds with aldehyde groups. Meanwhile, the ability of the detection method to distinguish aldehydes from other functional groups were tested against the following compounds: methanol (alcohol), acetone (ketone), ethyl acetate (ester), formamide (amide), acetic anhydride (anhydride), and formic acid (carboxylic acid). These compounds, apart from methanol, also possess a carbonyl center which is the reactive part of aldehydes.

Each compound was initially added with CR which possess a red color above pH 5 and a blue color below pH 3. The pH of each compound was also determined using a pH paper. As shown in Figure 3, the aldehyde samples have pH values ranging from 4 to 6 and thus, imparts a violet and red solution with the pH indicator. The other compounds, with pH ranging from 1 to 7, also caused color changes to CR which is consistent with their pH values.

The colors elicited by the aldehydes were not distinct from those of the other compounds. This suggests CR alone cannot differentiate aldehydes from other carbonyl compounds. However, when NH_4Cl was added to the sample compounds, the pH of the monofunctional aldehydes formaldehyde, acetaldehyde, benzaldehyde, and isobutyraldehyde changed while those of the other organic compounds remained unaffected, as shown in Table 1. This change in pH can be attributed to the reaction of NH_4Cl with aldehydes which promotes the release of hydrochloric acid [33]. The solution becomes acidic as the reaction progresses and triggers a shift in the color of CR. On the other hand, the polyfunctional compounds such as glucose and vanillin, though containing an aldehyde functional group, proved to be unresponsive. The lack of reactivity of vanillin could be attributed to the presence of a phenolic hydrogen which is slightly acidic [34]. This hinders the dissociation of ammonium ion to ammonia and hydrogen ion. Glucose, on the other hand, tend to exist in the cyclic form than in its linear form. The ring formation involves the aldehyde reacting with its alcohol group to form a hemiacetal [35]. This renders the aldehyde less susceptible to react with NH_4Cl.

The color transitions of CR with aldehydes in the presence of NH_4Cl can be monitored by UV-Vis spectroscopy. The absorption spectrum of CR is characterized by two

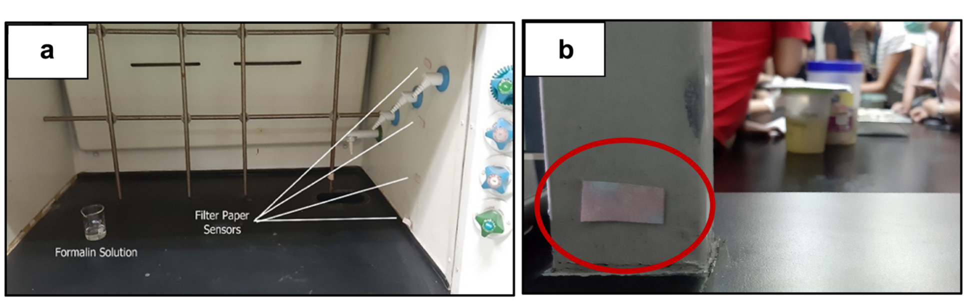


Figure 2: Experimental set-ups for detection of formaldehyde in a fume hood (a) and in a biology laboratory (b).

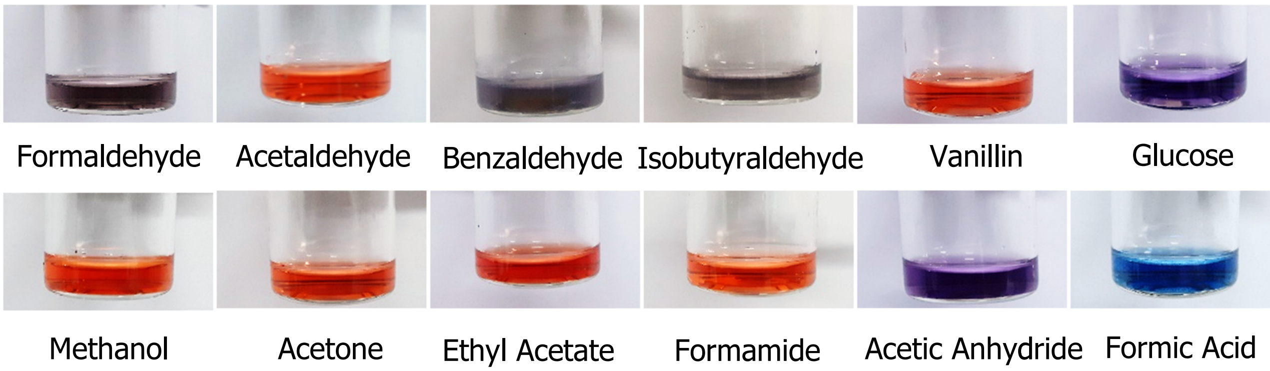


Figure 3: Colors of CR indicator in various organic compounds.

Table 1: pH values of organic compounds with NH_4Cl

Sample	pH without NH_4Cl	pH with NH_4Cl	
		Immediately after addition	5 min after addition
Formaldehyde	4	3.5	1
Acetaldehyde	5	3.5	2.5
Benzaldehyde	4	4	2*
Isobutyraldehyde	4	4	2.5*
Vanillin	6	5	5
Glucose	4.5	4.5	4.5
Water	6	5.5	5.5
Methanol	6.5	5.5	5.5
Acetone	5.5	5.5	5.5
Ethyl acetate	5	5	5
Formamide	7	5.5	5.5
Acetic anhydride	3	3	3
Formic acid	1	1	1

*Measurement of the pH was done 15 min after addition of NH_4Cl solution.

peaks. The first peak at 345 nm is due to the $\pi \rightarrow \pi^*$ transition of the C═C bonds present in the aromatic moiety of the dye while the prominent peak at 498 nm is due to the $\pi \rightarrow \pi^*$ of the azo linkage of the molecule [36]. In the presence of NH_4Cl, the peak at 498 nm shifted to 476 nm, as shown in Figure 4. Upon addition of the monofunctional aldehydes, the red-orange NH_4Cl-CR solution immediately turned violet which then gradually turned blue, as shown in Figure 5. In the case of formaldehyde, the absorption spectra of CR displayed an abrupt shift of the peak at 476 to 500 nm upon addition of formaldehyde. This was followed by a gradual bathochromic shift to 600 nm within 5 min (Figure 6). These results suggest an equilibrium shift from the CR azo form to the quinone form which is triggered by the reaction of the aldehyde with the ammonium ion (Scheme 1). Similar mechanisms have been proposed in previous works [28,31,33].

On the other hand, other organic compounds methanol, acetone, ethyl acetate, and formamide did not show obvious color differences from the original NH_4Cl-CR solution.

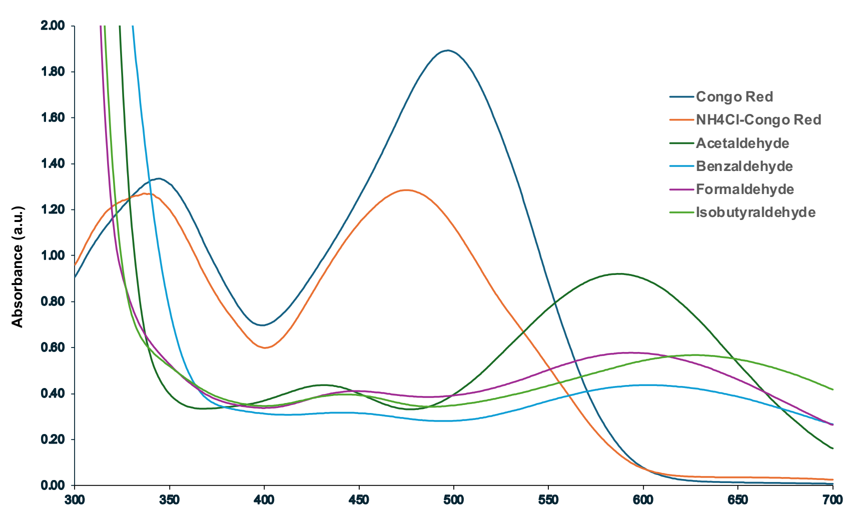


Figure 4: Absorption spectra of NH_4Cl-CR with aldehydes.

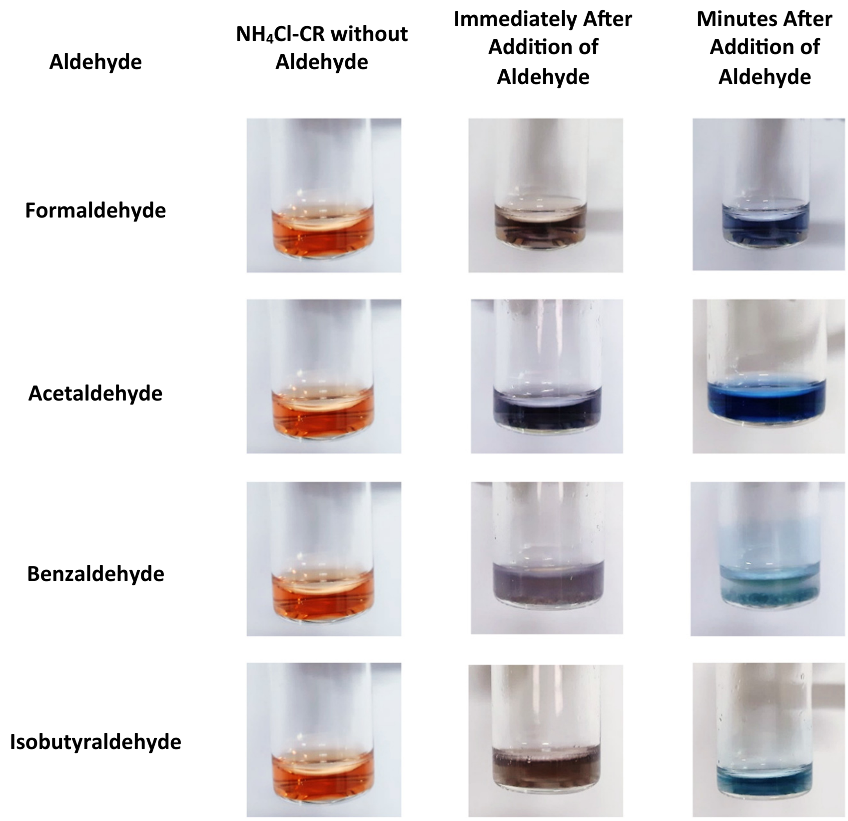


Figure 5: NH_4Cl-CR solution with aldehyde samples.

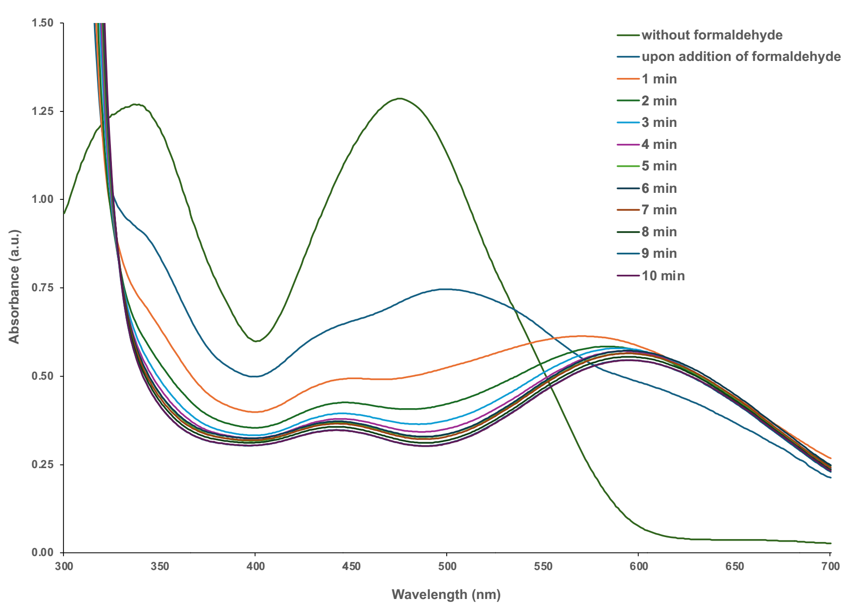
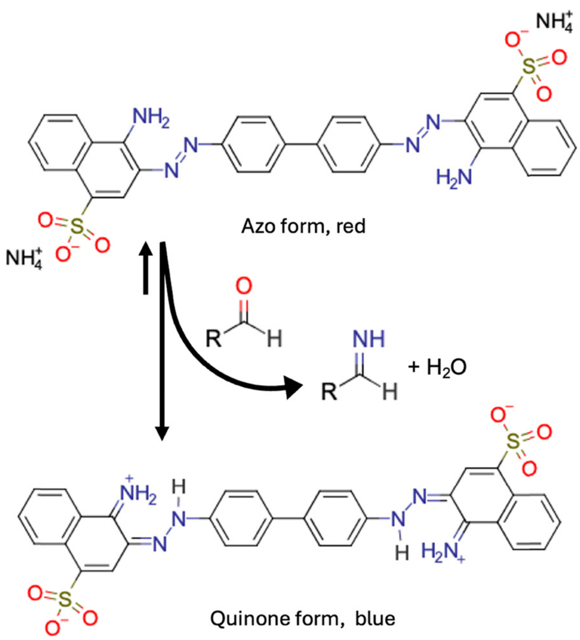


Figure 6: Absorption spectra of NH_4Cl-CR with formaldehyde at different time intervals.



Scheme 1: Proposed mechanism for sensing aldehydes with NH_4Cl-CR.

Consequently, the pH and absorption spectra of the solutions did not change significantly. Acidic compounds acetic anhydride and formic acid turned violet and blue, respectively (Figure 7). However, the color formed after addition of these samples to the sensing solution did not change even after a few minutes. These are in contrast with the characteristic color transitions exhibited by the aldehyde samples. The two other aldehyde samples which showed no significant pH change in response to the NH_4Cl solution did not proceed to the formation of a blue color. Vanillin merely induced a lighter red-orange solution while glucose elicited a violet color which persisted even after several minutes. This is consistent with the initial finding that the pH of vanillin and glucose did not change in the presence of NH_4Cl.

3.2 Detection of gaseous aldehydes

The detection of gaseous aldehydes was also investigated using strips of filter paper and silica gel soaked in NH_4Cl-CR solution. Exposure of the filter paper sensor to formaldehyde or acetaldehyde vapors resulted in a shift from pink to blue within 15 min (Figure 8). This is consistent with the observed change with liquid aldehydes. A similar result is observed for silica gel-based sensor for formaldehyde or acetaldehyde. The pink silica powder also turned blue after exposure to formaldehyde within 15 min. These observations suggest that the same reaction between aldehydes and NH_4Cl can occur even in the solid medium such as paper and silica gel.

Sensing of formaldehyde in an enclosed fume hood was also performed to demonstrate the potential application of the solid-based sensors for environmental monitoring. As shown in Figure 9, the sensor placed at the lower part of the fume hood (A and B) turned blue. This indicates that formaldehyde vapors were detected. On the other hand, sensors placed on the upper portion of the fume hood only elicited a slight color change. This suggests that formaldehyde vapors tend to settle at the floor of the fume hood perhaps due to its relative vapor density of 1.03 vs 1.07 of air

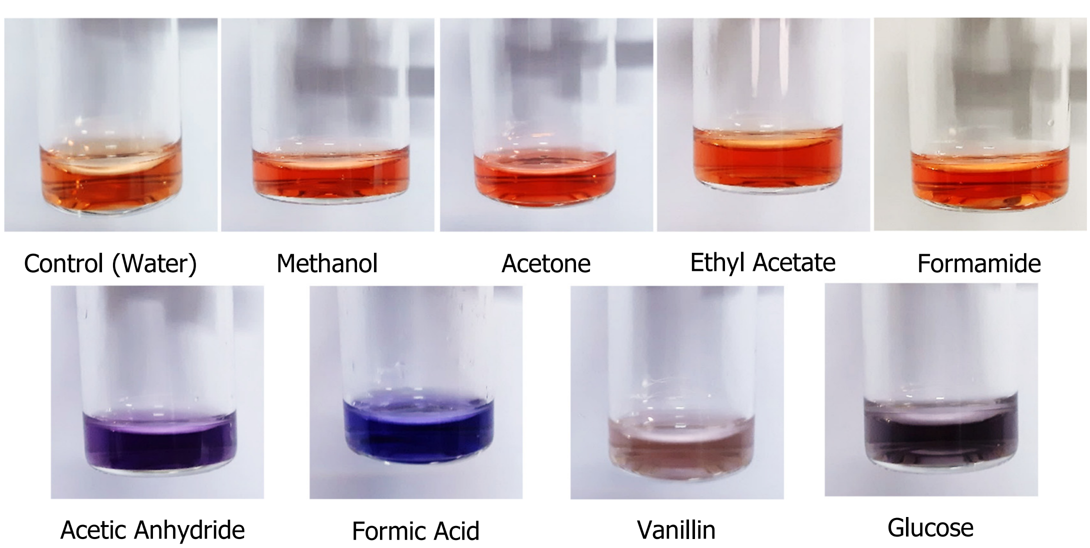


Figure 7: NH_4Cl-CR solution with other organic compounds.

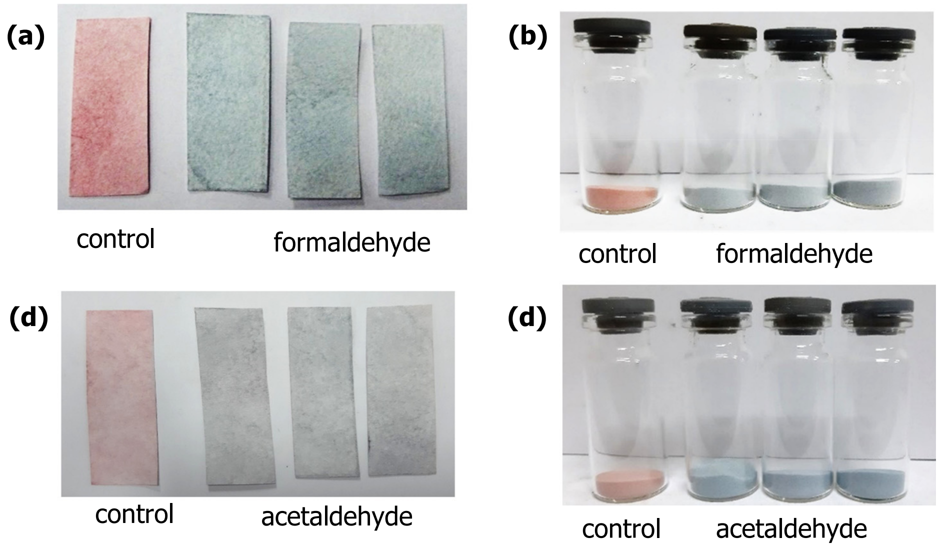


Figure 8: Formaldehyde detection using filter paper sensor (a) and silica gel sensor, (b) acetaldehyde detection using filter paper sensor (c) and silica gel sensor (d).

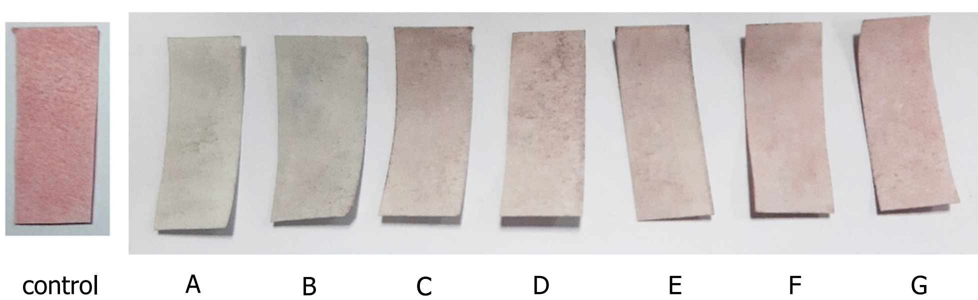


Figure 9: Filter paper sensor exposed to formaldehyde vapors in a fume hood. The sensors (A to G) were aligned vertically on the wall 5” apart from the work surface of the fume hood.

[37]. This result provides information on the suitable location where the sensor should be installed for practical purposes. Similar results were observed when paper-based sensors were attached on the pillars of a biology laboratory workbench during a dissection exercise. Blue spots were observed on the sensor after an hour of exposure (Figure 10). This indicates the presence of formaldehyde vapors in the room which comes from the formalin solution being used.

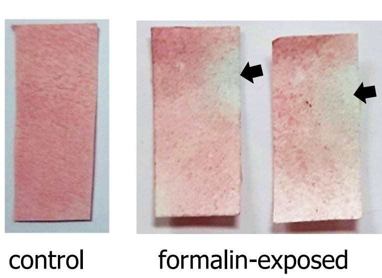


Figure 10: Filter paper sensor exposed to formaldehyde vapors from formalin in a biology laboratory room. Arrows show the formation of blue spots on the filter paper.

4 Conclusion

NH_4Cl-CR solution was able to distinguish monofunctional aldehydes from polyfunctional aldehydes and other compounds such as ketones, esters, amides, alcohols, anhydrides, and carboxylic acids. The characteristic color transition from red-orange to violet to blue provides a unique approach towards sensing simple aldehydes in the solution phase. The NH_4Cl-CR solution absorbed in filter paper and silica gel was also found to detect formaldehyde and acetaldehyde vapors. This allows for further development towards a solid-based sensing of simple aldehydes for environmental monitoring.

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Conflict of interest: The authors declare no conflict of interest.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: All data generated or analyzed during this study are included in this published article.

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