

Sol-gel based sensor for selective formaldehyde determination

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Abstract

We report the development of transparent sol-gels with entrapped sensitive and selective reagents for the detection of formaldehyde. The sampling method is based on the adsorption of formaldehyde from the air and reaction with β -diketones (for example acetylacetone) in a sol-gel matrix to produce a yellow product, lutidine, which was detected directly. The proposed method does not require preparation of samples prior to analysis and allows both screening by visual detection and quantitative measurement by simple spectrophotometry. The detection limit of 0.03 ppmv formaldehyde is reported which is lower than the maximum exposure concentrations recommended by both the World Health Organisation (WHO) and the Occupational Safety and Health Administration (OSHA). This sampling method was found to give good reproducibility, the relative standard deviation at 0.2 ppmv and 1 ppmv being 6.3 and 4.6 %, respectively. Other carbonyl compounds *i.e.* acetaldehyde, benzaldehyde, acetone and butanone do not interfere with this analytical approach. Results are provided for the determination of formaldehyde in indoor air.

Keyword: Formaldehyde; sol-gel; acetylacetone; spectrophotometry

Introduction

Formaldehyde is one of the most important air pollutants in residential and industrial occupational environments. Formaldehyde can cause irritation to the eyes and nose, central nervous system damage, immune system disorders, blindness and respiratory disease [1, 2]. Although, formaldehyde is toxic and allergenic, it is still widely used in industrial processes due to its high reactivity and relatively low cost. Formaldehyde is used mainly in the production of urea, phenolic and melamine resins [3, 4]. These resins are used widely as adhesives and binders in the manufacture of building materials such as particle-board, plywood, furniture and other wood products, as well as raw materials for surface coatings [5, 6]. All of these applications can lead to the release of formaldehyde within indoor environments [7].

The International Agency for Research on Cancer (IARC, 2006) has classified formaldehyde as a human carcinogen [3] and the US Environmental Protection Agency (EPA, 1999) has classified formaldehyde as a probable human carcinogen [8]. Due to formaldehyde toxicity, the World Health Organization (WHO) has furthermore established limits of exposure to formaldehyde at a maximum of 0.08 ppm averaged over 30 min. The Occupational Safety and Health Administration (OSHA) has also set a permissible exposure limit for formaldehyde of 0.75 ppm for an 8 hour workday.

For this reason, several analytical methods have been reported for formaldehyde determination including gas chromatography [9, 10], high-performance liquid chromatography [11], capillary electrophoresis [12], enzyme-based biosensors [13, 14, 15], gas sensors based on metal oxides [16, 17, 18] and piezoelectric sensors [19, 20, 21]. These methods all however require expensive and laboratory-based apparatus, cannot undertake real-time measurements and are able to only determine a single sample per test. Formaldehyde gas sensors and biosensors often furthermore lack the required selectivity [22].

Traditional methods to detect formaldehyde are based on either the collection of formaldehyde by active or passive sampling in cartridges impregnated with 2,4-dinitrophenylhydrazine [23, 24, 25] or are aqueous based [26] followed by the analysis of the formed hydrazones by HPLC. These methods however require post sample preparation steps and the acceptor solution can be subject to evaporation in high flow-rate air samples. These methods can moreover all be prone to interfering species leading to loss of performance of the sampling device. There is for these reasons a demand for a simple, inexpensive, and multi-sample detection method utilizing a solvent-free sorbent and sampling - without need of a pump.

Spectrophotometric methods have been reported for formaldehyde detection using various sensing reagents such as chromotropic acid [28, 29, 30], pararosaniline [31], 3-methyl-2-benzothiazolone hydrazone (MBTH) [32], 4-amino hydrazine-5-mercapto-1, 2, 4-triazole (AHMT) [33] and bromate-Janus green [34], due to the ability to carry out simple colourimetric tests [35]. Chromotropic acid, pararosaniline and MBTH are, however, prone to interference by acetaldehyde [36] and provide poor limits of detection [37]. These reagents require moreover strongly acidic conditions which are not suitable for the development of a solvent free device. Sensitive colourimetric methods based on the Hantzsch reaction between formaldehyde, β -diketones and ammonium acetate under mild conditions have been reported [38, 39, 40, 41], although the reported methods are usually solution based and not suitable for personal sampling. Adsorption of these solutions into porous glass [40] has been utilized to provide a heterogeneous solid-state colourimetric sensor which could be analysed spectroscopically.

Sol-gels are suitable as a support matrix in that they are homogeneous, provide a chemically and physically stable environment with excellent optical transparency - and these have been used to entrap sensing reagents in aerogels [42, 43]. The sol-gel method is a room

temperature reaction in which a precursor alkoxide undergoes hydrolysis and condensation to form an optically transparent gel. During the gelling process, reagents can be entrapped within a polymeric network of the porous gel. This approach can therefore be applied to entrap sensitive reagents for formaldehyde determination while providing a transparent matrix as well as being suitable for preliminary visual detection. Since the sol-gel initially is liquid in form before gelling, it can easily be cast into whatever shape or thickness is required and the resultant gels were also soft and pliable enough to be cut to any required size.

In this paper we describe the development of a simple and cost effective method for monitoring of trace formaldehyde in air. The measurement was based on the diffusion of formaldehyde to react with acetylacetone entrapped within the sol-gel. The portable visual sampling device described here is solvent free and did not require post sample preparation steps such as preconcentration and extraction. This paper reports on this method being used for formaldehyde determination in air samples.

The sensor described measures cumulative dose of formaldehyde rather than a real time instantaneous reading of formaldehyde concentrations. In high level environments formaldehyde can be measured by utilizing short exposure times whereas in lower level environments, the cumulative dose over, for example, a working day can be assessed. Since the sensor response can be detected visually it can give a reasonably rapid response to high concentrations. Over a day the chemical reaction giving rise to the colour change is essentially irreversible and by using spectrographic methods allows quantification of the cumulative dose due to continuous exposure to low levels of formaldehyde.

2. Experiment

2.1. Reagents

Formaldehyde stock solution (1 mol L^{-1}) was prepared by diluting 37 % w/v solution (Sigma-Aldrich, St. Louis, USA). Standard working solutions were prepared daily by appropriate diluting of the stock solution in deionized water which was purified with a Milli-Q system (Millipore, USA).

Stock solutions of acetylacetone and methyl acetoacetate (Sigma-Aldrich, St. Louis, USA) was prepared by dissolving 0.75 g of ammonium acetate (Sigma-Aldrich, St. Louis, USA), 0.2 mL of acetic acid solution (BDH Laboratory Supplies, Poole, UK) and 0.02 mL acetylacetone/methyl acetoacetate in 10 mL deionized water. These reagents were stored at 4°C in the dark to avoid darkening of the solution. This was recommended to allow visual screening detection.

To evaluate the reaction of acetylacetone and methyl acetoacetate with formaldehyde, 300 μL of reagent solution was placed in disposable cuvettes; formaldehyde solution was then added to obtain a final concentration of 0.005, 0.01 or 0.02 mM of formaldehyde. The UV/Vis absorbance was measured versus reaction time at 376 nm and 410 nm for methyl acetoacetate and acetylacetone, respectively. UV-Vis spectra were recorded using a UV-2101PC Spectrophotometer (Shimadzu, Japan). Results of this work are discussed in section 3.1 and figure 2.

To investigate selectivity, 3 mmol L^{-1} solutions of formaldehyde, acetaldehyde, benzaldehyde (Sigma-Aldrich, St. Louis, USA), acetone and butanone (Fisher Scientific) were prepared in deionized water. 10 μL of each solution was added into separate 300 μL acetylacetone solutions in disposable cuvettes. After 3 h, the absorbance was measured by scanning wavelength between 300 nm-550 nm. Results of this work are discussed in section 3.5.

2.2. Preparation of sol-gel formaldehyde sensors

Sol-gel solution was prepared by mixing tetraethoxysilane (TEOS) (Merck, Darmstadt, Germany), 0.04 mol L⁻¹ HCl solution and ethanol (HPLC grade; Fisher Scientific) in the ratio 2:1:2 (v/v). The mixture was then magnetically stirred for 2 h at room temperature. This solution was used as the stock sol-gel solution throughout.

In the present work, sol-gel formaldehyde sensors were prepared by mixing the sol-gel solution and acetylacetone solution in a 1:1 ratio. 300 µL of the resultant formaldehyde sensing solution was pipeted into 1.5 mL disposable cuvette with care being taken that the solution did not adhere at the cuvette walls which would otherwise lead to variable responses. The sol-gel mixture was left at room temperature for 30 min to give a colourless gel containing entrapped acetylacetone. The sol-gel was stored in the freezer to avoid the evaporation of any components. A reference sol-gel was prepared in the same time and stored under the same conditions for use as a blank sample for UV-visible determination.

2.3. Standard gaseous formaldehyde

To obtain a calibration curve for formaldehyde vapour, standard gaseous formaldehyde was generated according to the reaction described given by Dong and Dasgupta at 20°C [44], where aqueous formaldehyde is used to generate equilibrium concentrations of gaseous formaldehyde Eqn 1.

$$\text{Eqn 1: } [\text{HCHO}(\text{aq})] = 16650 [\text{HCHO}(\text{g})]^{1.0798}$$

A range of diluted formaldehyde solutions were placed in 50 mL polypropylene exposure tubes to give the specified equilibrium concentrations of gaseous formaldehyde. The relationship between the concentration of diluted formaldehyde aqueous solution and gas

phase formaldehyde concentrations is shown in **Table 1**. For exposure of sol-gel to formaldehyde, the sol-gel was cast into the UV cuvette, allowed to set and then placed inside the polypropylene tube (Fig. 1).

3 Results and discussion

3.1 Evaluation of the Reaction of acetylacetone and methyl acetoacetate with formaldehyde

The reactions of acetylacetone and methyl acetoacetate with formaldehyde were investigated to evaluate sensitivity. The reaction mechanisms are shown in **Fig. 1**. The reactions rate were investigated by adding three different concentrations of formaldehyde solutions into 300 μL of acetylacetone or methyl acetoacetate solution to obtain 0.005, 0.01 or 0.02 mmol L^{-1} formaldehyde concentrations. Both reactions were monitored with time and the results show that acetylacetone reacts with formaldehyde faster than methyl acetoacetate under the same conditions, the reaction being completed within 2 h and 6 h, respectively (**Fig. 2**). The UV spectrum (**Fig. 2c**) demonstrated the maximum adsorptions observed for the products of methyl acetoacetate and acetylacetone were found to occur at wavelengths of 376 nm and 410 nm, respectively. A strong yellow colour was obtained when formaldehyde reacted with acetylacetone, whereas the product of reaction of formaldehyde with methyl acetoacetate provides a weaker yellow at the same concentration. This means that the presence of the ester groups cause a decrease in both reaction rate and yellow colouration. Due to the faster reaction and stronger colour with acetylacetone, this approach was chosen for development of the visual approach for formaldehyde determination.

It has been previously noted [40] that the product of the acetylacetone formaldehyde reaction is not indefinitely stable but decomposes to a non-coloured product, albeit with a rate constant some 100000 times less than that of the formation of coloured product. The stability of 3, 5-diacetyl-2, 6-dihydrolutidine (i.e the reaction product of acetyl acetone with

formaldehyde) in the sol-gel was investigated to evaluate and select a suitable sampling time. **Fig. 3** indicates that the product was stable for 6 h in daylight and exposed to the laboratory atmosphere, with the absorbance decreasing after longer time. The decomposition was quicker when the product was exposed to light and conversely was slower in the dark. This is approximately what we would expect; the colour develops rapidly due to the reaction with formaldehyde and then a slow decrease caused by decomposition of the coloured product. These results indicate that measurement should be made within a 6 h period to minimise the decomposition of the product. Previous workers [40] gave longer stability times but their samples were stored in sealed bags and it is not stated whether they were in daylight.

3.2. Effect of reagent compositions

Effects caused by the variation of the concentration of individual reagents *i.e.* acetylacetone, ammonium acetate and acetic acid concentration on sol-gel formaldehyde sensing was investigated. The studies were carried out by varying one parameter while keeping other parameters constant. Acetylacetone solutions in the concentration range 1-80 mmol L⁻¹ were firstly prepared and mixed with sol-gel solution 1:1 (v/v) to obtain clear sol-gels. These were pipetted into UV cuvettes whilst liquid and allowed to set. The cuvettes were placed into 50 ml vials as described (section 2.3) along with aqueous solutions of formaldehyde. By choosing the correct concentration of solution, an equilibrium concentration of 1 ppmv formaldehyde vapour was generated within the tube. The absorbance was then measured after the exposure of the sol-gel to 1 ppmv gaseous formaldehyde for 6 h. The cuvettes were then from the tubes removed and measured using UV spectroscopy. The results demonstrated that the absorbance increased with increasing concentration of acetylacetone up to 10 mmol L⁻¹, after which time a greater concentration of acetylacetone did not lead to an increase in the observed absorbance. For these reasons 10

mmol L⁻¹ of acetylacetone was selected for determination of formaldehyde up to a concentration of 1 ppmv since concentrations of formaldehyde in the environment air are typically lower than 1 ppmv.

The effects of ammonium acetate and acetic acid concentrations are shown in **Fig. 4**. It was found that the absorbance increased with increasing ammonium acetate up to 1 mol L⁻¹ and that the absorbance decreased for concentrations of ammonium acetate in excess of 2 mol L⁻¹. Formation of the sol-gel also depends on the concentration of ammonium acetate; the sol-gel was found to form more quickly with increased concentration of ammonium acetate (30 min at 1 mol L⁻¹ of ammonium acetate). Higher concentration of ammonium acetate also caused the sol-gel to become cloudy. The effect of concentration of the acetic acid shows that the absorbance of exposed sol-gels increased with increasing the concentration up to 2 % and that no further increase in absorbance was observed for higher concentration. Concentrations of 10 mmol L⁻¹ acetylacetone, 1 mmol L⁻¹ ammonium acetate and 2 % (v/v) acetic acid were therefore chosen for preparing sol-gel sensors for detection of formaldehyde up to 1 ppmv.

3.3. Effect of the ratio of sol-gel solution to sensing reagent

In order to obtain the best formaldehyde sensing material, the ratios of sol-gel matrix materials and sensing reagents were optimized. Sol-gels are porous materials with porosity depending on the ratio of solvent to precursor. The characteristics of sol-gel formaldehyde sensors prepared with different ratios of sol-gel solution to acetylacetone were therefore investigated. The sol-gel and 10 mmol⁻¹ acetylacetone solution were mixed in ratios of 3:1, 2:1, 1:1, 1:2 and 1:3 (v/v) – nitrogen gas was then passed through the mixed solution for 1 min to remove any bubbles that can form in the sol-gel. The sol-gel sensing solution was placed in a 1.5 mL disposable cuvette and allowed to set to give a clear sol-gel. The sol-gels were exposed to saturated formaldehyde vapour under the conditions described earlier. After

exposure to formaldehyde the sol-gels became yellow, allowing direct detection with UV/Vis spectroscopy without any post exposure preparation. The spectral absorption plot (**Fig. 5.**) demonstrated that lowering the ratio of acetylactone to sol-gel below 1:1 led to a decrease in response - probably due to lack of reagents diminishing the extent of reaction with formaldehyde. Increasing the ratio of acetylactone above 1:1 also decreased the response; this appears to be a diffusion based problem. A strong yellow band appeared at the surface of the sol-gel indicating that all the reaction was taking place in the localized vicinity - rather than evenly through the sol-gel. The placement of the cuvette inside the UV spectrometer and the design of this equipment means that only the lower 2-3 mm of the sol-gel is actually measured. Therefore sensing time increases because the formaldehyde has to diffuse down through the upper part of the sol-gel to reach this active part and the high levels of acetylactone slow this down because all the formaldehyde is consumed in the upper part of the gel. At lower concentrations the reaction between the reagents is slower and enough formaldehyde manages to diffuse to the lower part of the gel to cause colour changes there as well. Comparison between sol-gels and aqueous acetylactone solution, indicated that the reaction in a 1:1 sol-gel and aqueous solution was not significantly different. The effect of sol-gel solution was also investigated by adding 10 μL of formaldehyde solution to 300 μL of sol-gel sensing solution (sol-gel: acetylactone, 1:1 v/v) and aqueous acetylactone solution. The absorbance after 2 h. (**Fig. 6.**) showed that the formaldehyde reacts with acetylactone in sol-gel without loss of sensitivity compared to aqueous sample.

Fig. 7. shows the absorbance change after exposing sol-gel sensors to 0.5 ppmv and 1.0 ppmv of formaldehyde vapour for 1-6 h. The absorbance increased with increasing exposure time. Due to the rather limited stability of the product of reaction with acetylactone, 6 h was selected as the standard sampling time. This period of time is also

convenient for daily measurement. The sampling time can however be shortened for environments that contain high concentrations of formaldehyde, for application, for example, within the adhesive industry - so long as appropriate calibration is performed.

The volume of sol-gel sensing material on the response to formaldehyde vapour was investigated to allow the smallest volume which could provide measurable responses. The sol-gel material (0.3-1.0 mL) was dispensed into disposable cuvettes and exposed to formaldehyde vapour for 6 hours. The results indicated that a volume of 0.3 mL was optimal and that the absorbance decreased with higher volumes of sol-gel sensing material while lower volumes led to low reproducibility. For example when a 1 ml solution was utilised, a yellow band developed at the top of the sol-gel, probably as a result of a diffusion controlled reaction i.e the formaldehyde is being consumed before reaching the lower parts of the sol-gel sample. Small changes in the spectra were observed since the UV beam was effectively passing beneath the active portion of the gel. When volumes below 0.3 ml were used, low levels of the sol-gel within the cuvette and the actual set-up of the UV spectrometer meant that only a portion of the beam was passing through the sample. 0.3 mL was therefore selected for calibration purposes.

3.4. Calibration curve, reproducibility and limit of detection

Calibration curves of the response to formaldehyde vapour under optimum conditions in the concentration range 0.05-1.2 ppmv are shown in **Fig. 8a**. A linear relationship is obtained in this range ($R^2=0.996$). Reproducibility of sol-gel sensors was investigated by measuring the absorbance of 15 sensors exposed to 0.2 and 1.0 ppmv of formaldehyde for 6 h. The relative standard deviations were 6.3% and 4.6%, respectively (Fig. 8b).

The limit of detection was found to be 0.03 ppmv (calculated as three times standard deviation of the blank signal (adsorption of sol-gel samples that have not undergone exposure

to formaldehyde) from 10 replicates divided by the slope of the calibration curve ($3S_b/m$).

These results indicate that this method allows for the determination of formaldehyde levels in air lower than the limiting value by both World Health Organization (0.08ppm) and Occupational Safety and Health Administration (0.75ppm).

3.5. Investigation of interferences

Carbonyl compounds *e.g.* aldehydes and ketones are common interfering substances for determination of formaldehyde. The reaction of acetaldehyde, benzaldehyde, acetone and butanone with sol-gel sensors were therefore investigated. Our findings showed that acetylaldehyde gave 6.5 % of the response of formaldehyde at the same concentration (0.1 mol L^{-1}) and the other compounds gave < 3 % of the formaldehyde response – thereby demonstrating a high selectivity for formaldehyde.

3.6. Stability of sol-gel sensing

The stability of sol-gel sensors were evaluated by storage at -20°C , 4°C and 20°C (room temperature). The composition of the sol-gel was found to change depending on temperature. The sol-gels were found to lose $3.7\pm 1.4\%$, $46.4\pm 3.1\%$ and $82.0\pm 0.5\%$ by weight after storing 1 week in the -20°C , 4°C and 20°C , respectively. However, sampling time at room temperature for 6 h was not affected by the evaporation of the sol-gel components. Storage of sol-gel at 20°C for 1 day can cause a loss of $9.0\pm 0.7\%$ by weight. The shrinkage of sol-gel can cause variation of the spectral response due to poor contact between the sol-gel and the cuvette walls. However it could be seen by visual checking that the colour changes still occurred. This results indicated that the stability of sol-gel sensors were more affected by the initial sol-gel composition than by the loss of the sensing reagents.

Storage of sol-gel formaldehyde sensors in the freezer is therefore recommended to avoid the evaporation of the sol-gel components.

3.7. Determination of formaldehyde in the air

The acetylacetone sol-gel entrapped material was evaluated for the determination of formaldehyde inside a cupboard. Four separate batches of five cuvettes containing acetylacetone entrapped sol-gel were placed inside new MDF cabinets for 6 h (MDF, especially when new emits formaldehyde). After six hours the cuvettes were removed and the absorbance at 410 nm determined by spectrophotometry. Since the reaction is cumulative, the absorbance of the sol-gels could be related directly to the average formaldehyde concentrations within the cabinet. Results as shown in **Table 2** demonstrated that the average concentrations of formaldehyde inside the cabinets varied between 0.13 and 0.25 ppmv and there were good agreements seen between individual samples of the same batch (RSD's from 6-12%).

4. Conclusion

A sol-gel based sensor with entrapped acetylacetone reagent is reported for the determination of formaldehyde in the air. The developed sensing device can be used as a qualitative and screening method for on site analysis in the presence of formaldehyde. Although not capable of giving the rapid response obtained from many semiconductor based sensors such as reviewed here [45], they are capable of measuring cumulative doses over, for example, an 8 hour working day and can give faster responses in response to high levels of formaldehyde. The responses can be qualitatively observed visually, without the need for any equipment and if quantification is required this can be done by UV spectroscopy. The proposed method is simple, inexpensive, portable, contains no overly aggressive chemicals,

consumes a small amount of low toxicity reagent, operates at room temperature and requires no post sample preparation. Moreover, this method was found to offer good selectivity, sensitivity and reproducibility. Potential applications for this include as an exposure badge, similar to the radiation counter badges used by workers in the nuclear industry. Alternatively the sol-gels could be used in remote optical sensors where they are connected via optical fibres to a centrally located spectrometer.

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Figure captions

Fig. 1. The reaction mechanism of formaldehyde with acetylacetone and methyl acetoacetate in the presence of ammonium acetate and acetic acid and a schematic of the experimental set-up for the exposure of the sol-gel to formaldehyde.

Fig. 2. The response of the reaction of formaldehyde with acetylacetone (a) and methyl acetoacetate (b) over time in the presence of 2 mol L^{-1} ammonium acetate and 2 % acetic acid at room temperature. Formaldehyde concentrations; (\blacktriangle) 0.005 mol L^{-1} ; (\blacklozenge) 0.01 mol L^{-1} ; (\bullet) 0.02 mol L^{-1} . Adsorption measured for acetylacetone at 410 nm, methyl acetoacetate at 376 nm. (c) UV spectra of the adducts of acetylacetone and methyl acetoacetate with formaldehyde.

Fig. 3. The stability of lutidine formed by the reaction of formaldehyde with acetylacetone at room temperature. Formaldehyde concentrations; (\blacktriangle) 0.005 mol L^{-1} ; (\blacklozenge) 0.01 mol L^{-1} ; (\bullet) 0.02 mol L^{-1} .

Fig. 4. Effect of ammonium acetate and acetic acid on the response of sol-gel formaldehyde sensing. (\blacklozenge) acetic acid; (\bullet) ammonium acetate.

Fig. 5. Effect of ratio of sol-gel solution to acetylacetone and without sol-gel.

Fig. 6. Comparison between acetylacetone and acetylacetone mixed sol gel (1:1). (\blacklozenge) acetylacetone:sol-gel, (1:1); (\bullet) acetylacetone.

Fig. 7. Response of sol-gel formaldehyde sensing exposed to formaldehyde vapour over time (1-6 h). (\blacklozenge) 0.5 ppmv; (\bullet) 1.0 ppmv.

Fig. 8. (a) Standard calibration curve of sol-gel sensing after exposed to formaldehyde vapour 0.05-1.2 ppmv for 6 h (b) actual results for groups of 15 sensors exposed to either 0.2 ppmv or 1.0 ppmv formaldehyde.

Figure 1.

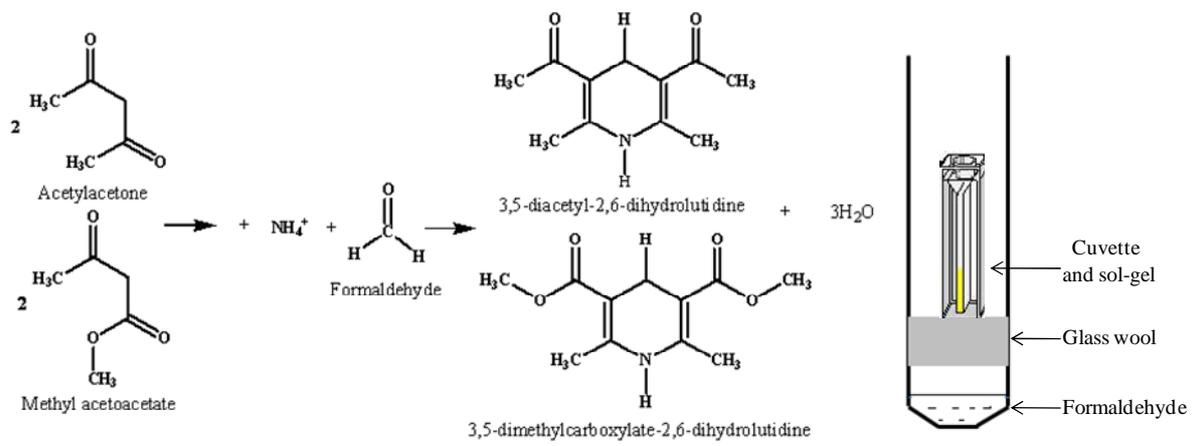


Figure 2.

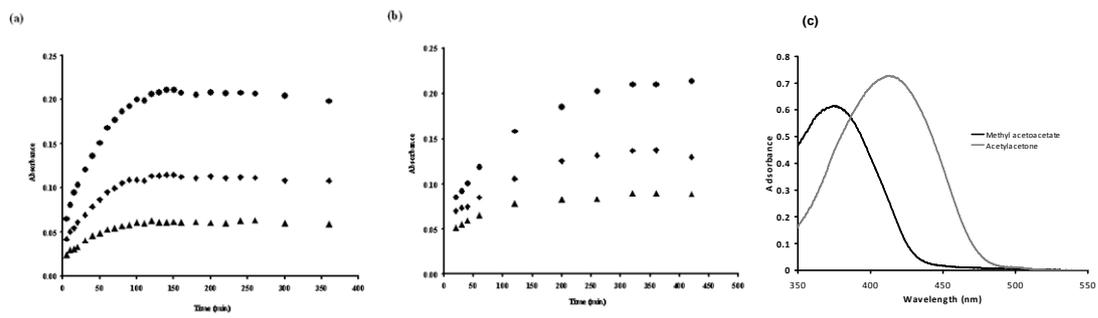


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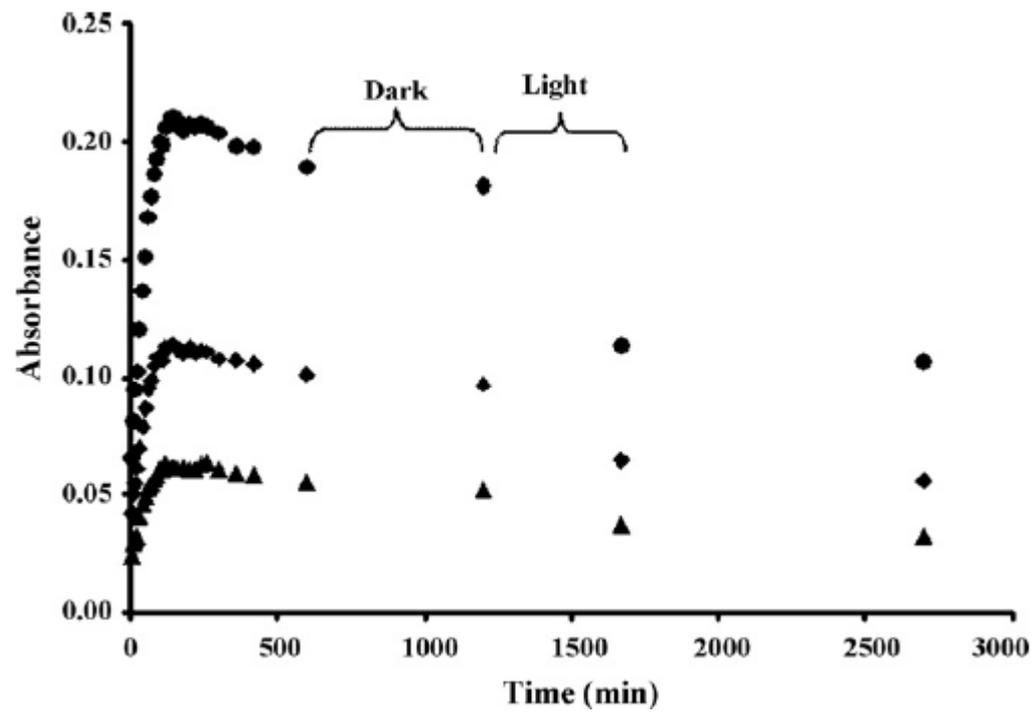


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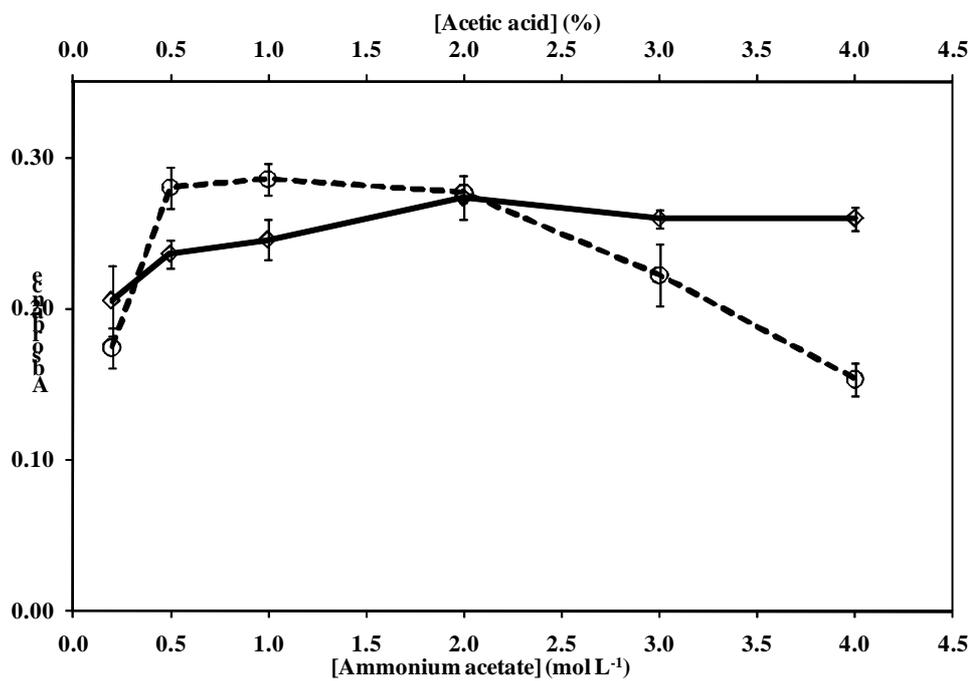


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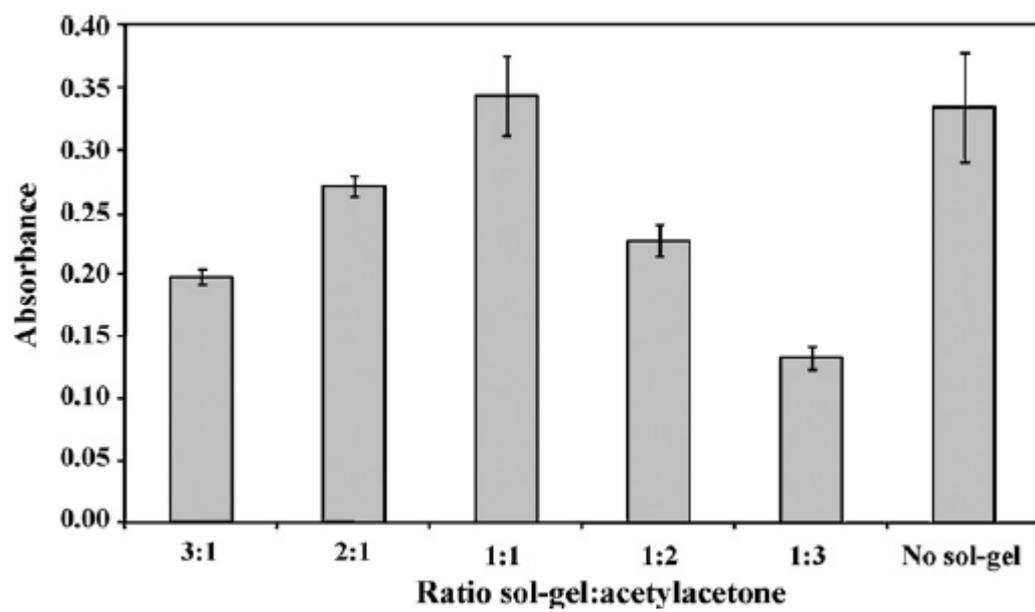


Figure 6

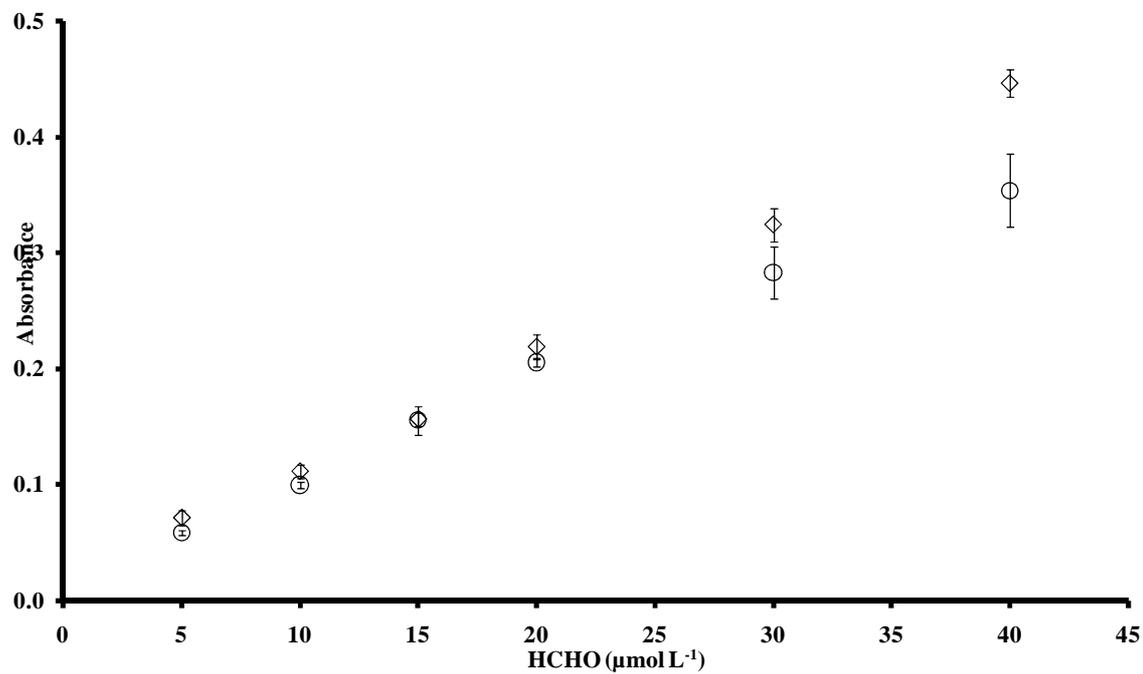


Figure 7

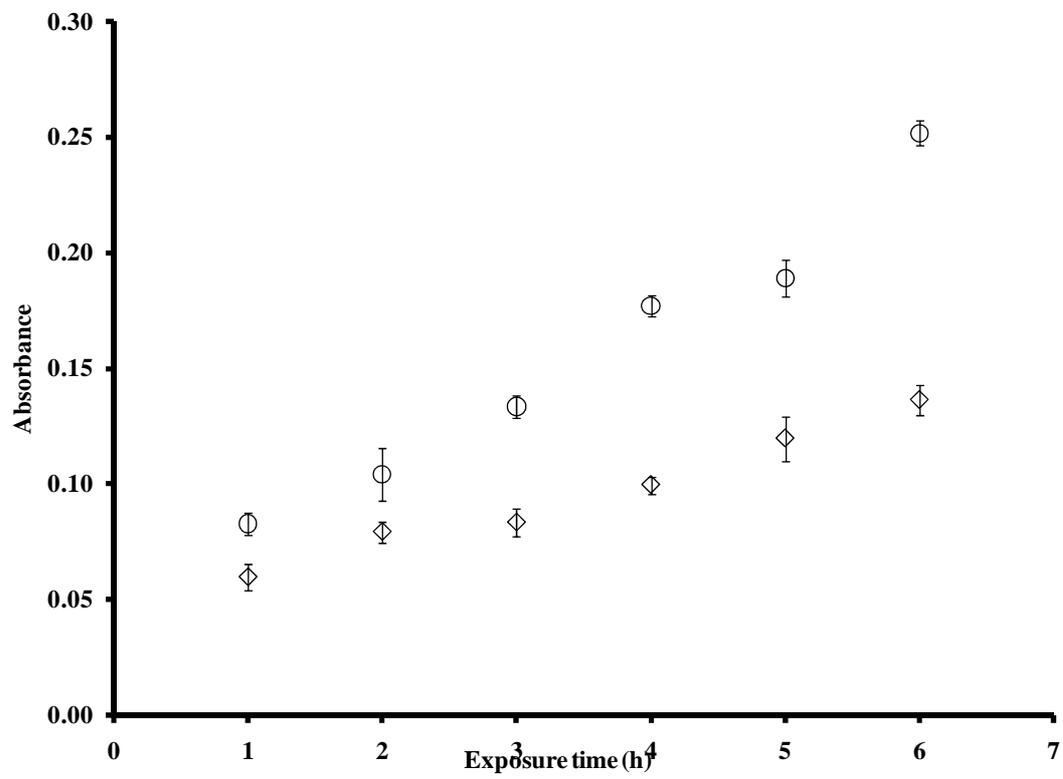


Figure 8

