Microfluidic Detection And Determination Of Formaldehyde : A Smart Tool

Dipali Jain¹, Sulbha Amlathe²

Department Of Chemistry, Uit Bu Bhopal, M.P., India 1.Research Scholar, 2. Supervisor And Hod Department Of Chemistry, Uit Bu Bhopal, M.P., India

Abstract

Formaldehyde (HCHO), is the most commonly found aldehyde in our environment owing to its toxicity, it has been classified as one of the major water pollutants. Formaldehyde enters the environment from natural sources which includes forests fires and direct human sources such as fuel combustion, on-site industrial uses, and released from building materials and cosmetic products .Although formaldehyde is necessary for many products and processes essential to the world's economy, but this dependence comes at a cost to public health. In the present communication a sensitive method is proposed for the detection and determination of formaldehyde. Formaldehyde reacts with phloroglucinol and 1-naphthylamine in alkaline medium forming a red color dye with an absorption maximum at 520 nm. The proposed sensor is linear range 20ppm to 320 ppm. The minimum detection limit found was 0.008 ppm for formaldehyde.

Key words: Formaldehyde, colorimetric method, microfluidic

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I. Introduction

Water pollution has become a global problem now a days. Pollutants is a substance which when introduced into environment causes undesirable products or spoiling of resources. Long or short term damage may be caused due to pollutant. These pollutants accumulate in environment with the passage of time. They only cause problem when their quantity increases ^[1-6]. Pollutant comes from factories it is also left as a by-product during various manufacturing process and it also plays a big role in pollution Hazardous waste may be in solid, liquid or in gaseous form.^[7-9] Formaldehyde is also one of them major pollutant, it is a colourless, strong-smelling chemical. It occurs naturally in the environment, including in foods and even inside our bodies, but it is also a widely used chemical in some industries^[11,12], It is used in making building materials and many household products, including Pressed-wood products, such as particleboard, plywood, and fibreboard, Glues and adhesives, Permanent-press fabrics, Paper product coatings, Certain insulation materials and cosmetics industries. When dissolved in water it is called formalin, which is commonly used as an industrial disinfectant and as a preservative in funeral homes and medical labs.^[14] It can also be used as a preservative in some products, such as antiseptics, medicines, and cosmetics^[17]. Sometimes, even formaldehyde is not an ingredient in a product, substances that release from them are formaldehyde. These have been found in cosmetics, soaps, shampoos, lotions, nail products and sunscreens, preservatives and cleaning products. NIOSH TLV value of formaldehyde for long exposure (TLV-TWA)0.12PPM, and short term exposure(TLV-STEL) is 0.3PPM, exposure over a short period. OSHA the legal airborne permissible exposure (PEL) is 0.75PPM and 2PPM not to be exceeded. ACGIH TLV is **0.3PPM**.^[19] People can be exposed to formaldehyde by Automobile exhaust, Pressed-wood products, unvented fuel-burning appliances, as a component of tobacco smoke^[18]. Absorbing it through the skin and Eating foods or drinking liquids containing formaldehyde. Exposure to excess of formaldehyde by any sources through the skin, Watery eyes, Burning sensations of the eyes, nose, and throat, Coughing, Wheezing, Nausea and Skin irritation and it can cause nasopharyngeal cancer and leukaemia. ^[13-15]. The International Agency for Research on Cancer (IARC) is part of the World Health Organization (WHO). One of its major goals is to identify causes of cancer. IARC has concluded that formaldehyde is "carcinogenic to humans" it can cause nasopharyngeal cancer and leukaemia.^[16] Spot test analysis for qualitative determination of materials on an absorbent material has been extensively studied for many years. Feigl and Anger have provided the basis for many such studies.^[20] Qualitative spot test analysis, however, is not very usual. Studies show that reflectance spectroscopy cannot yield precision better than 10% when used to obtain quantitative data directly from spot test analysis as mentioned by Kealey^[21] and thus results obtained were considered unreliable. Reflectance spectroscopy is considered qualitative and nonreproducible while transmittance spectroscopy is quantitative and reproducible analysis.^[22] Some other

spectrophotometric methods for the determination and detection of formaldehyde was reported as well, Fabrícia Gasparini et al. spectrophotometric analytical method for determination of formaldehyde The method is based on formaldehyde reaction with chromotropic acid in the presence of magnesium sulphate producing a stable complex of Mg2+^[23].Determination of concentration of formaldehyde in high level waste during the destruction of nitric acid was reported by Suraj Mondal, Satya Narayan Das and others using The procedure is based on well-known condensation reaction between carbonyl compounds and hydrazine.^[24] Nurfathiyatul Izza & others study to analyze the content of formalin by using Schiff reagent and UV-Vis spectrophotometry. ^[25]Md. Bokthier Rahman, et al. Studied various methods on formaldehyde adulteration in food, [26] Yasri, N. G., Seddik, H., & Mosallb, M. A. reported spectrophotometric determination of formaldehyde based on the telomerization reaction of tryptamine^[27]Pratima Verma and V. K. Gupta described the spectrophotometric determination of formaldehyde using p-aminoazobenzene and sulphur dioxide in an acidic medium^[29]. The spectrophotometric method was developed by G.Sunita et al. using 2,4-D KMnO₄ in an alkaline medium to produce orange-red dye^[30]. A rapid monitoring method of formaldehyde in a new solid sorbent system was reported by M. Rai, K. N. Ramachandran, and V. K. Gupta using 1,3,5-trihydroxybezene, CaCl2, and NaOH in indicator tubes and cellulose fibres^[31]Previously, Amlathe and Gupta had developed indicator plates and tubes.^[32] Later on, using the same principle Abbaspour et al. introduced paptode, paptodes were similar to optodes in many features. In optodes, an ionophore is immobilized on a hydrophilic or hydrophobic polymer while in paptodes simply a paper or another ordinary porous material such as clay or cotton or even TLC can be used as a substrate support for the reagent. They have also developed method and disposable sensors for water pollutants like phenol, hydrazine, arsenic, lead, methyl parathion, cadmium .^[33-42] A coloured reaction product can be produced on the surface of a reagent impregnated inert support, by a single drop of solution of analyte, producing distinct flecks or rings. The degree of colour of the spot was found to be proportional to the concentration of the analyte. As in this method, the reflection properties of strips are observed.

II. Methodology

In the present communication a sensitive colorimetric method is proposed for the detection and determination of formaldehyde. Formaldehyde reacts with phloroglucinol and 1-naphthylamine in alkaline medium forming a red color dye with an absorption maximum at 520 nm and various parameters for analysis for has been studied.

III. Experimental

Apparatus

EI Double beam Spectrophotometer,

EI digital pH meter model 111

All Glass wares were used made up of 'A' grade Borosilicate glass.

Chemical and Reagent: all reagent used were analytical grade chemicals. Double Distilled water is used during the experiment.

Formaldehyde -A stock of 4000 ppm was prepared by using dissolved 1ml of formaldehyde in 100ml of double distilled water. The working standard is freshly prepared daily.

Phloroglucinol-1% of phloroglucinol solution is prepared by using 1gm of phloroglucinol dissolved in 100ml of double distilled water.

1-Naphthylamine-0.5% of 1-Naphthylamine is prepared by dissolved 0.5gm of 1-Naphthylamine in 10ml of glacial Acetic acid solution and make up the volume 100ml by double distilled water.

Sodium hydroxide -0.5 N solution of NaOH is prepared by dissolving 2gms in 100ml of double distilled water.

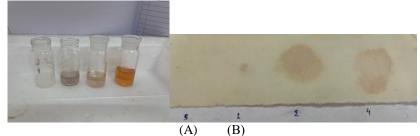
IV. Procedure

The known concentration of formaldehyde is taken in a graduated beaker then 1-Naphthylamine solution is added, after 5 minutes Phloroglucinol is added and shaken well. After 5 min sodium hydroxide solution is added and shaken well. A red colour dye appears indicating presence of formaldehyde. The absorbance is then measured at 520nm. A reagent blank was also prepared in the same manner. To construct the sensor strips for Whatman filter paper were immersed in 0.5% solution of **1**-Naphthylamine followed by immersing in 1% Phloroglucinol solution for few seconds and NaOH solutions well and then air dried. Aliquots of formaldehyde solutions of various concentration were injected on these strips to develop the spot.

V. Results and Discussion

Formaldehyde reacts with phloroglucinol and 1-Naphthylamine in alkaline medium to produce a red coloured product. Thus even the tube contains both the reagent but no colour production takes place until the formaldehyde sample is added. 1-Naphthylamine itself is slightly purple coloured and could become turbid if a large amount is used, therefore, a small amount of reagent should be used, if we use excess of NaOH and the

solution become clear and red coloured disappears. If we used excess of Phloroglucinol solution become turbid. The pH of red dye is 13.07 is observed by pH meter.



Photograph : colour developed at different concentration of formaldehyde (A) Colour variation in tubes (B) colour variation on paper strips

Effect of reagent concentration.

In order to study the effect of Phloroglucinol and 1-Naphthylaminne concentration, solutions with various concentrations of reagents were prepared and studied these were plotted absorbance vs. concentrations Fig. 1 and 2 shows the effect of Phloroglucinol and 1-Naphthylamine concentration respectively. Fig. 1 shows, at 0.5% of 1-Naphthylamine maximum colour intensity was observed and Fig. 2 shows that, at 1% of Phloroglucinol maximum colour intensity was observed .Therefore, 1% Phloroglucinol and 0.5% of 1-Naphthylamine were selected as the optimum.

Effect of temperature

Fig. 3 shows the effect of temperature, various series were prepared and studied at many temperature range 0° C to 35° C, the optimum temperature which required to colour development is between 15-18°C.

Response time, stability and detection limit of the system

The response time of the system was evaluated under optimum conditions for 80ppm of formaldehyde . It was calculated by measuring the time required to achieve a steady colour intensity. The response time of 10-12 minutes was achieved. To study the stability of the colour. The colour intensity remains nearly constant for the period of 15-20 minutes . After that the colour start change.

Effect of foreign species

The effect of various interferents commonly found in polluted water during the determination of formaldehyde. As the reaction is carried out in a strongly alkaline medium, metal ions such as Sn^{2+} , $Cu^{2+}Ni^{2+}$, Ca^{2+} and Ag^+ , Mg^{2+} which form hydroxides will interfere by precipitation. Para-substituted phenols such as p-cresol, p-nitrophenol and p-chlorophenol did not interfere.

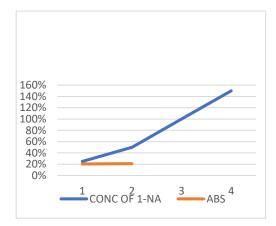
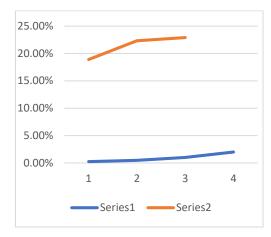
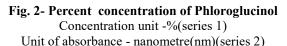


Fig.1 Percent concentration of 1-Naphthylamine Concentration unit -%(series 1) Unit of absorbance -nanometre(nm) (series 2)





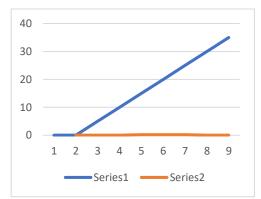


Figure 3 effect of temperature , Where Temperature unit ° c (series 1), Unit of absorbance - nanometre(nm)(series 2)

VI. Applications

The proposed method has been applied successfully for the determination of formaldehyde in industrial waste water and biological samples. The samples were spiked by adding known amounts of Formaldehyde. A recovery test of HCHO was performed to compare the developed method with the official analysis method (DNPH method^[43]). The developed method was used to determine the HCHO levels in several water samples. The results obtained are given in the Table. The data show that the recovery of formaldehyde is quantitative and hence the method can be satisfactorily applied to hygiene work.

Formaldenyde lound", p.p.m.			
Concentration of	Proposed	DNPH	Recovery, %
Formaldehyde	method(p.p.m.)	method(p.p.m.)	
added(p.p.m.)			
3	2.71	2.90	90.3
5	4.53	4.35	90.7
8	7.26	8.00	90.8
12	10.92	11.00	91.0
15	13.72	14.80	91.4
18	16.47	17.10	91.5

 Table 1. Determination of Formaldehyde in spiked waste water samples

 Formaldehyde found*, p.p.m.

* Mean of three repeated determinations.

VII. Conclusions

The described method in the present paper has many advantages as it does not need many instruments, it is very simple ,selective and rapid. Its range is much wider as compared to other methods for determination of formaldehyde. Immobilization of reagents is very simple.

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