Arabian Journal of Chemistry (2015) **8**, 487–494

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Spectrophotometric determination of formaldehyde based on the telomerization reaction of tryptamine

Nael G. Yasri *, Hasan Seddik, Maha A. Mosallb

Chemistry Department, Faculty of Science, University of Aleppo, Syria

Received 8 December 2010; accepted 2 February 2011
Available online 26 February 2011

KEYWORDS

Formaldehyde;
Tryptamine;
Spectrophotometery;
Environmental samples

Abstract A simple and sensitive spectrophotometric method for the determination of formaldehyde FA in different samples using tryptamine TA in a sulfuric acid medium was developed. A trace amount of sodium nitrite was added to enhance the production of a red violet colored product exhibiting an absorbance maximum at 558 nm. Beer's Law is obeyed for 0.80–23.00 μg mL^{-1} FA (r = 0.999), the recoveries are within the range of 96.25–100.66%, with percent relative standard deviations ranging from 1.02% to 2.73%. No interference was detected from commonly existing contaminates in the liquid samples e.g. phenol, aminoacids, sugars and related compounds. The method was applied successfully for the determination of formaldehyde in various environmental samples, such as rain water, wood products, and total cigarette smoke.

1. Introduction

Formaldehyde (FA), HCHO, is the most commonly found aldehyde in the environment (Liteplo et al., 2002). In general, formaldehyde enters the environment from natural sources, forest fires and from direct human pollution sources, such as fuel combustion, industrial on-site uses and off gassing from building materials and consumer products (Wakefield, 2008; Priority Existing Chemical Assessment, 2006).

Due to the high solubility (Heimlich, 2008), formaldehyde is found in natural rain, clouds, fog and steam, which paves its way as a pollutant. Moreover, the broad biological properties place formaldehyde among the significant industrial hazardous substances, with high impact on human health (Heimlich, 2008; Liteplo et al., 2002; Programme on Chemical Safety Formaldehyde Health and Guide, 1991). In air, formaldehyde is considered as immediately dangerous to life and health at a concentration level of 24 mg m^{-3}, and exposure limit of 90 g m^{-3} (Institute for Occupational Safety and Health, 1994).

Recently, there has been a tendency to determine the concentration of formaldehyde in the environmental samples for pollution control purposes and to provide strict regulatory restriction on the usage of consumer products. Therefore, a simple, rapid and highly sensitive determination method is urgently required (Heimlich, 2008).

* Corresponding author. Tel.: +963 933 685834.
E-mail address: naelyasri@hotmail.com (N.G. Yasri).
Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2011.02.005

Sensitive methods for formaldehyde determination include GC (Bianchi et al., 2007; Del Barrio et al., 2006; Reche et al., 2001; Velikonj et al., 1995; Davydova et al., 1986), voltammetry (Zhao et al., 2006), fluorometry (Zhang and Tian, 2004; Li et al., 2007), LC and HPLC (Possanzini and Di Palo, 2003; Witthauer et al., 1999; Isakau et al., 2009; Fu Liu et al., 2005; Huber and Fresenius, 1981; Chen et al., 2008). However, spectrophotometric based methods (Teixeira et al., 2004; Feng et al., 2004; Gigante et al., 2004; Tian et al., 2004; Cui et al., 2007; Jagadeesan and Gupta, 1979; Li et al., 2008; Gibson et al., 2008; Mohamed et al., 2008; Guo et al., 2006; Pinheiro et al., 2004) are among the relatively low-cost, simple and sensitive methods and are very popular. These methods are based on the reaction of formaldehyde with reagents, such as Schiff's reagent (Gibson et al., 2008), *p*-phenylenediamine (Mohamed et al., 2008), chromotropic acid (Gigante et al., 2004), brilliant cresyl blue (Guo et al., 2006) and fluoral P (Pinheiro et al., 2004).

The present work reports a simple, sensitive and accurate spectrophotometric method for the determination of formaldehyde in aqueous samples. The method is based on the formation of a colored telomere from the reaction of formaldehyde with indol-3-ethylamine (knows as tryptamine; TA), in a sulfuric acid medium. The method was optimized for the determination of unknown levels of formaldehyde in samples of rainwater, wooden products, and total cigarette smoke.

2. Material and methods

2.1. Apparatus

A Jasco V-630 spectrophotometer with 1.0 cm quartz cell was used for spectrophotometric measurements. An HPLC system (Merck-Hitachi) equipped with a diode array detector L-2455, quaternary pump L-2200 and column temperature regulator L-2350 was used. The analytical column used was a RP8 HI-BAR (250×4.6 mm ID 10 μm) from Merck. The chromatographic system was eluted by (45:55 v/v) acetonitrile:water solution as a mobile phase, with 20 μL injection volume at a flow rate of 1.0 mL min^{-1}, and a detector set at 345 nm wavelength. A digital Orion Research Model 601 analyzer provided with an Ingold U455 electrode was used for pH measurements.

2.2. Reagents and chemicals

Reagent-grade chemicals used were of the highest purity available from their sources. A stock FA solution of 1000 μg mL^{-1} was prepared by diluting a volume of 2.5 mL (37%) formaldehyde solution FA (SCP, super chemical produces) to 1000 mL with bidistilled water and standardized using the sulfite method (Annual Book of American Society for Testing and (ASTM) Standards, 1979). FA working standard solutions of 100 and 10 μg mL^{-1} were prepared daily from the stock standard solution by appropriate dilution. Tryptamine reagent TA 5×10^{-2} mol L^{-1} was prepared by dissolving 0.817 g (98% purity, Merck chemicals) tryptamine in 1% H_2SO_4 and then completing the volume to 100 mL using the same solvent. Sodium nitrite solution 2×10^{-3} mol L^{-1} was prepared by dissolving 0.139 g of 99% sodium nitrite (BDH England), in bidistilled water and diluting to 1000 mL in a volumetric flask. Sulfuric acid (98%), 2,4-dinitrophenylhydrazine (DNPH) were purchased from Merck and 5% (w/v) chromotropic acid from Mallinckrodt Chemical was freshly prepared in bidistilled water.

3. Method

3.1. Spectrophotometric calibration curve

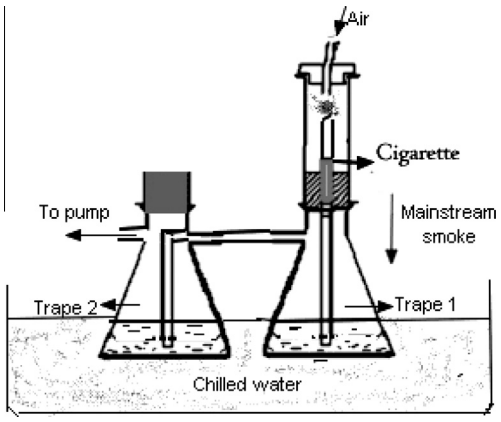
Proper volumes of the FA working standard solution were transferred to the stoppered test tubes to cover the concentration range of 0.80–23.00 μg mL^{-1}. The FA solution was diluted with water to 4.0 mL, the test tubes were replaced in the water bath at a constant temperature of 25 °C, followed by the addition of 4.0 mL concentrated H_2SO_4, the temperature was allowed to stabilize then 1.0 mL of the working TA solution was added followed by 1.0 mL sodium nitrite solution. All test tubes were then capped and left in the water bath for 35 min to ensure complete color development. A calibration graph was prepared by recording the absorbance of the resulting solutions at 558 nm against a similarly prepared reagent blank. All measured solutions were prepared in triplicates.

3.2. Formaldehyde determination in rain water

Some portions of countryside rain water (Aleppo City, Syria) were collected at two different time periods; each portion was about 100 mL volume. The first collection was in the first autumn rainfall in the second week of September 2009 and the second sample was collected from the same place after about one month. The collected rain water samples were immediately filtered through a 0.45 μm membrane filter from which a volume of 100 mL was heated, with continuous stirring, in a water bath at 80 °C for 10 min (Mohamed et al., 2008), in these conditions, the volatile acetaldehyde was expelled, and at the same time they have a little effect on FA (recoveries of FA $\geqslant$97%), which begin to drift with water vapor at $\geqslant$90 °C (Mohamed et al., 2008). The solution was left for a few minutes to cool after which bidistilled water was added to the volume to replace any evaporation.

In order to determine the low levels of FA a preconcentration procedure was performed by subjecting the resulting solution to a crystallization process with bisulfite. This was proceeded as follows: 5 g sodium bisulfite was added to 100 mL of the rain water, then the mixture was kept in an ice bath for one hour (ensuring a complete FA and bisulfite reaction), after which an accurate volume of 50 mL ethanol (95%) was added without stirring (the aqueous: ethanol ratio was 2:1 (v/v)). The mixture was then refrigerated (at −4 °C) for 30 min which lead to the formation of crystals from bisulfite addition compound. The crystals were then filtered using 0.45 μm membrane filter, and the filtrate was discarded. The crystals were kept at room temperature for solvent evaporation, followed by the dissolution of the dry crystals with suitable volume of 0.05 mol L^{-1} sulfuric acid, making the final FA concentration within the standard linear range of the suggested method. A 3 mL volume of the resulting solution was used in the proposed method for FA determination.

A separate FA preconcentration study with bisulfite crystals was performed to ensure higher recovery for trace FA level. The study included ethanol to water ratio, bisulfite quantity, and FA concentration.



Scheme 1 Home-made total cigarette smoke collection apparatus.

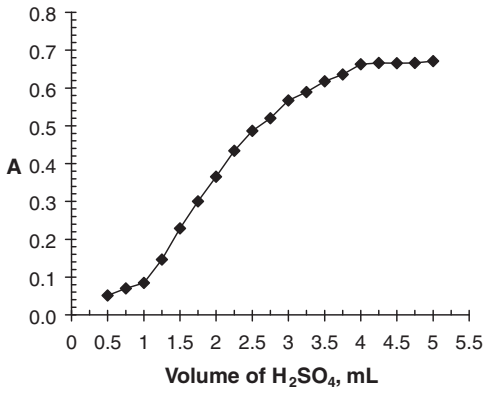


Figure 1 Effect of sulfuric acid volume on the absorbance values at 558 nm, Experimental conditions: 2.7×10^{-4} mol L^{-1} HCHO; 4×10^{-3} mol L^{-1} TA; 0.3×10^{-4} mol L^{-1} $NaNO_2$, at 25 °C and wait for 45 min; 10 mL final testing mixture.

3.3. Formaldehyde determination in total cigarette smoke

A procedure for total cigarette smoke (TSS) collection, described elsewhere (Mohamed et al., 2008), is applied for the FA determination in a local cigarette brand (Al Hamra long). The method in brief is as follows; a simple smoking apparatus was constructed as shown in Scheme 1, each trap (100 mL capacity) contained about 35 mL of chilled water. Just after smoking three cigarettes, the two trap solutions were combined, filtered through a 0.45 μm membrane filter and heated, with continuous stirring, in a water bath at 80 °C for 10 min, to expel volatile acetaldehyde (Mohamed et al., 2008). The remaining solution was then diluted to 250 mL in a volumetric flask and sample aliquots of 3 mL were promptly analyzed.

3.4. Formaldehyde determination in wood products

FA in wood products, such as in medium density fiberboard (MDF) and chipboard, was determined by applying the suggested method. To each 1 g ground sample of MDF, chipboard was added intermittently as very small pieces, 50 mL of bidistilled water was added and the mixture was agitated using an ultrasound bath for 10 min at 80 °C. This ensured the removal of acetaldehyde if present (Mohamed et al., 2008), and the complete dissolution of free FA from the sample (British Standards Institution, 1995), total FA, however, could be obtained by soaking the sample in a sulfuric acid medium, (Chrastil and Reinhardt, 1986). The solution was then left for a few minutes to cool, filtered then a 3 mL volume of the filtrate was used in the proposed method for FA determination.

4. Results and discussion

4.1. Effect of various concentrated acids

The addition of FA with TA, in the sulfuric acid medium, developed a violet colored product with a clear absorbance maximum at 558 nm. The effect of various volumes of concentrated sulfuric acid was studied using 3 mL of 8 μg mL^{-1} (2.7×10^{-4} mol L^{-1}) FA concentration. The results, (Fig. 1), show that the increases of acid volume, within the range 0.5–4.0 mL, show an increase in the absorbance. Increasing the acid concentration to volumes above this range shows good and nearly constant absorbance values.

For the same acidifying propose, various concentrated acids, such as nitric acid (70%) hydrochloride acid (37%), acetic acid (99%) and phosphoric acid (85%) were individually tested using a volume of 4 mL from each acid and using the same experimental conditions. The results show, no color development in the solution by using the above mentioned acids. An addition of 0.5 mL of 1.0×10^{-2} mol L^{-1} H_2O_2 to the previously tested phosphoric acid gave a violet colored product with a broad peak at 566 nm (Fig. 2). The color development using H_3PO_4 and H_2O_2 took approximately 3 h to establish a stable colored product. Despite a low potential hazard of H_3PO_4 as compared with H_2SO_4, a longer period of time taken by the former to develop a colored product lead to the preference of the cautious use of H_2SO_4.

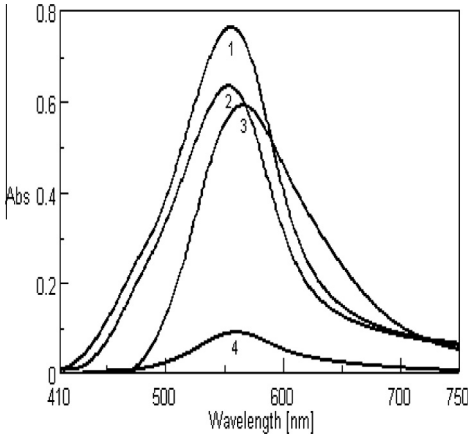


Figure 2 Absorption spectra show the effect of; (1) sulfuric acid with sodium nitrite using 8 μg L^{-1} HCHO, (2) sulfuric acid using 8 μg L^{-1} HCHO, (3) phosphoric acid using 8 μg L^{-1} HCHO, (4) sulfuric acid with sodium nitrite using 1 μg L^{-1} HCHO.

4.2. Effect of sodium nitrite concentration and other oxidants material

It has been noticed during preliminary testing experiments that the addition of trace amount of oxidants, e.g. H_2O_2 and Fe^{3+} [as $Fe_2(SO_4)_3$], increases the reaction speed with no effect on the total absorbance value. Adding a trace amount of sodium nitrite to the sulfuric acid media containing FA and TA, however, caused an increase in both, the absorbance (Fig. 2) and in the reaction speed.

The effect of $NaNO_2$ concentration was studied within the range of 0.5×10^{-5}–1.4×10^{-3} mol L^{-1}. The results (Fig. 3) show that the absorbance increased rapidly with increasing $NaNO_2$ concentration with a maximum at 2×10^{-4} mol L^{-1}. Further increases in the $NaNO_2$ concentration to a value more than 9×10^{-4} mol L^{-1}, may lead to a decrease in the absorption value. Thereafter, a concentration of 2×10^{-4} mol L^{-1} of $NaNO_2$ was adopted for further experiments.

Taking into consideration the color development period, the absorbance of the color was monitored for 8 h both in the absence and in the presence of $NaNO_2$. In the absence of sodium nitrite, the result (Fig. 4) shows that the colored product formation increased gradually during the first 3 h of the reaction time and a maximum was reached after 6 h. Alternatively, the presence of 2×10^{-4} mol L^{-1} $NaNO_2$ enhanced the reaction rate with a nearly stable colored product formation after 35 min that remained for 6 h.

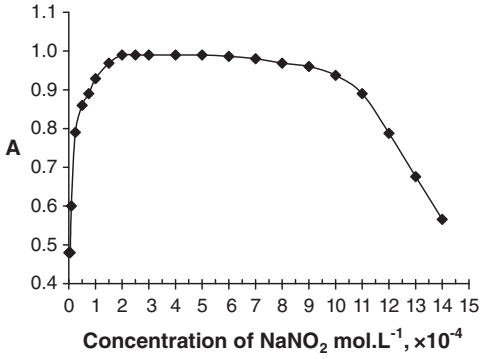


Figure 3 The effect of sodium nitrite concentration on the absorbance values at 558 nm. Experimental conditions: HCHO 2.7×10^{-4} mol L^{-1}; TA 5×10^{-3} mol L^{-1}; 4 mL H_2SO_4 (98%); at 25 °C and wait for 30 min; 10 mL final testing mixture.

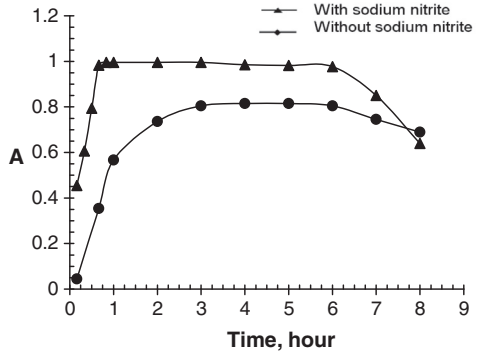


Figure 4 The absorbance variation at 558 nm during 8 h time in the absence and in 2.7×10^{-4} mol L^{-1} HCHO: the present of 2×10^{-4} mol L^{-1} $NaNO_2$. Experimental conditions: 5×10^{-3} mol L^{-1} TA; 4 mL H_2SO_4 (98%); at 25 °C; 10 mL final testing mixture.

It has been known that $NaNO_2$ in acidic solution gives nitrous acid which decomposed with the evolution of nitrogen oxides, but at these reaction conditions of temperature and order of material addition (FA, H_2SO_4, TA, and then $NaNO_2$), the absorption and the reaction speed were surprisingly increased, even at a temperature reaching 25 °C.

It is suggested that the presence of $NaNO_2$ could enhance the formation of a hydrated semi oxidized species of formaldehyde that have more efficiency to condense with indole and its derivatives.

4.3. Constitution of the colored product

The nature of the binary colored product (FA-TA) was determined by performing two studies, the first using continuous variation method (Likussar and Boltz, 1971). In this method, a series of solutions were prepared, with that the concentration of FA plus TA were held constant at 1.0×10^{-3} mol L^{-1}. A graph was prepared by plotting absorbance against the ratio [FA]/[FA] + [TA]. The result of applying this method, (Fig. 5), indicated that the (TA:FA) ratio is 2:1.

The second study used a molar ratio method (Meyer and Ayres, 1957), this was performed by increasing the TA concentration within the range of (1.3×10^{-3}–2.1×10^{-4}) mol L^{-1}, for the formation of the colored product with constant FA concentration of 2.7×10^{-4} mol L^{-1}.

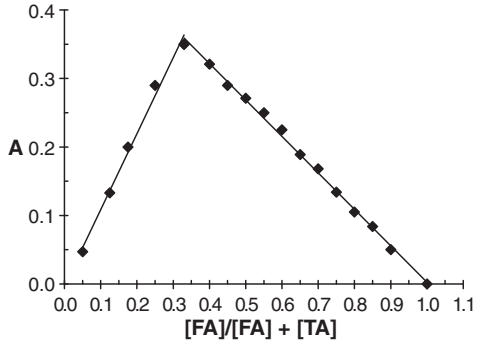
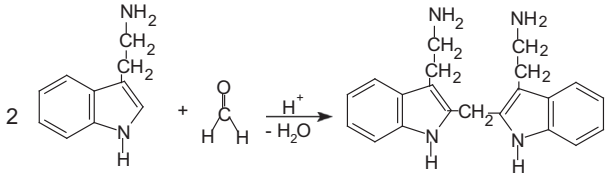


Figure 5 Continuous variation method for FA-TA colored production at 558 nm. Experimental conditions: 2×10^{-4} mol L^{-1} $NaNO_2$; 4 mL H_2SO_4 (98%); at 25 °C and wait for 30 min; 10 mL final testing mixture.



Scheme 2 Possible telomerization reaction of formaldehyde with tryptamine.

The result shows rapid increases in the absorbance with increasing TA concentration (maxima at 5×10^{-3} mol L^{-1}), with an intersection point of 2 on the [TA]/[FA] axes versus absorption. Hence, according to these results and the Hopkins-Cole biochemical reaction (Berg et al., 2006), which is used for qualitative determination of tryptophan, the composition of the binary colored product formed TA-FA, may be expressed as 2:1 (Scheme 2).

4.4. Effect of temperature

The effect of temperature was studied within the range 5–95 °C. In these set of experiments the mixture was prepared in test tubes placed in a water bath at a defined temperature for a period of 30 min after which the ambient temperature was maintained.

The result (Fig. 6), demonstrated that the colored product formed at a temperature in the range of 5–25 °C exhibited nearly stable absorbance, whereas increasing the temperature within the range of 26–35 °C showed a decrease in the absorbance (around 2%). Increasing the temperature within the range of 40–90 °C, caused the absorbance to decrease dramatically with the dissociation of the colored product, resulting in uncontrollable conditions of the reaction. Thus, the method should be performed at a temperature less than or equal to 25 °C.

4.5. Method validation

Beer's Law is obeyed within FA concentration range of (0.80–23.00) mg L^{-1} (r = 0.999). The calibration graph is described by the equation: $Y = bX + m$, obtained by the method of least squares (where Y = absorbance, m = intercept, b = slope and X = concentration in μg mL^{-1}). Correlation coefficient, intercept and slope for the calibration data, as well as, the sensitivity parameters such as apparent molar absorptivity and Sandell's sensitivity values, the limits of detection and quantification are calculated and summarized in (Table 1). The LOD and LOQ were calculated according to the same guidelines using the formulae: LOD = 3.3 SD/b and LOQ = 10 SD/b, where SD is the standard deviation of five reagent blank determinations and b is the slope of the calibration curve (Miller and Miller, 1993).

Table 1 Sensitivity and regression parameters.

Parameter	Proposed method
λ_{max} (nm)	553
Linear range (μg mL^{-1})	0.80–23.00
Molar absorptivity (ε) (L mol^{-1} cm^{-1})	2972.2
Sandell sensitivity[a] (μg cm^{-2})	0.1
Limit of detection (LOD) (ng mL^{-1})	290
Limit of quantification (LOQ) (μg mL^{-1})	0.88
Intercept (a)	0.003
Slope (b)	0.109
Regression coefficient (r)	0.999

[a] Limit of determination as the weight in μg mL^{-1} of solution which corresponds to an absorbance of A = 0.01 measured in a cuvette of cross-sectional area 1 cm^2 and l = 1 cm. $Y = a + b\,X$, where Y is the absorbance, X is the concentration in μg mL^{-1}, a is the intercept, b is the slope.

The precision and accuracy were assessed according to the IUPAC recommendations (Miller and Miller, 1993) by analyzing 0.08, 0.10, 0.30, 0.50, 0.80, 1.0, 5.0, 10.00, 15.00, 18.00, 20.00, and 23.00 μg mL^{-1} FA in aqueous solutions (Table 2). The relative accuracy R% was within the range of 96.25–100.60%, with RSD% ⩽2.73%, indicating a good accuracy with high precision of the method. The reproducibility of the method also known as the inter precision was evaluated by performing replicate analyses solution over a period of five days. The inter day RSD values were less than or equal to 3.90% reflecting the usefulness of the method in routine analysis.

Method robustness was tested by making small incremental changes in either TA concentration, H_2SO_4 concentration, $NaNO_2$ concentration or temperature. To check the ruggedness, an analysis was performed by three different analysts and on three different spectrophotometers by the same analyst. The robustness and the ruggedness were checked at three different concentrations of FA. The intermediate precision, expressed as RSD percent, which is a measure of robustness and ruggedness was within the acceptable limits as shown in the Table 3.

4.6. Interference study

The influence of various ions, some of organic and inorganic compounds, commonly found with FA in the aqueous environment was examined within the concentration range of 15–1000 μg mL^{-1}. A relative error of ±5% on the concentration of FA was considered tolerable. No interference within the testing range of concentration was observed from sugars, such as glucose and fructose, ketones as acetone, aminoacids as leucine, urea, phenol and the following ions Na^+, K^+, Ca^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Fe^{2+}, Zn^{2+} Cl^-, and NH^{4+}. However,

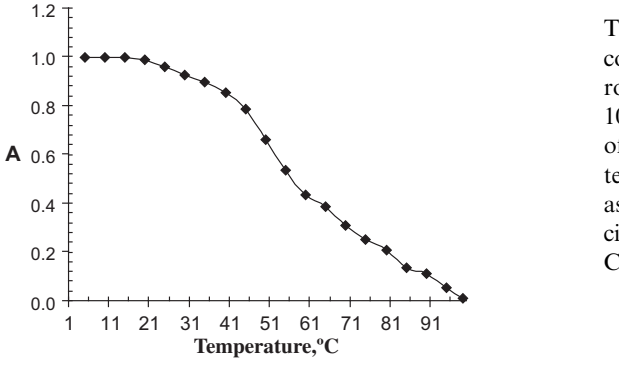
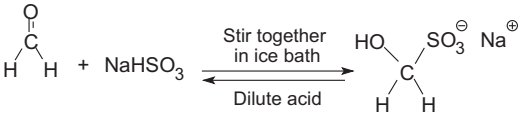


Figure 6 Effect of temperature on the absorbance values at 558 nm. Experimental conditions: 2.7×10^{-4} mol L^{-1} HCHO; 5×10^{-3} mol L^{-1} TA; 4 mL H_2SO_4 (98%); 2×10^{-4} mol L^{-1} $NaNO_2$; 10 mL final testing mixture.



Scheme 3 Reaction of bisulfite with formaldehyde.

Table 2 Evaluation of precision and accuracy for FA determination.[a]

FA taken (μg mL^{-1})	Intra-day accuracy and precision			Inter-day accuracy and precision		
	FA μg mL^{-1} (n = 6)			FA μg mL^{-1} (n = 5)		
	Found ± SD	R%	RSD%	Found ± SD	R%	RSD%
0.80	0.77 ± 0.021	96.25	2.73	0.76 ± 0.030	95.62	3.90
1.00	0.97 ± 0.024	97.00	2.47	0.96 ± 0.031	96.50	3.25
5.00	4.95 ± 0.109	99.00	2.20	4.87 ± 0.140	97.40	2.87
10.00	10.02 ± 0.160	100.20	1.60	10.00 ± 0.256	100.00	2.56
15.00	15.10 ± 0.172	100.60	1.14	14.98 ± 0.277	99.87	1.85
20.00	19.84 ± 0.202	99.20	1.02	19.82 ± 0.287	99.10	1.45
23.00	22.70 ± 0.232	98.69	1.02	22.64 ± 0.265	98.43	1.17

[a] The experiments were performed using the optimum conditions of 5×10^{-3} mol L^{-1} TA, 4 mL H_2SO_4 (98%) with final testing mixture volume at 10 mL (or 39.2% (w/w)) and 2×10^{-4} mol L^{-1} $NaNO_2$.

Table 3 Robustness and ruggedness expressed as intermediate precision.

FA taken (μg mL^{-1})	Method robustness		Method ruggedness	
	Parameter altered RSD% (n = 3)		Inter-analysists RSD% (n = 3)	Inter-instruments RSD% (n = 3)
	TA (mol L^{-1})[a]	Acid (w/w%)[b]		
1.0	2.12	3.30	2.08	1.89
10.0	2.49	2.98	1.97	1.54
20.0	1.01	1.20	0.98	0.87
	Temperature (°C)[c]	$NaNO_2$ (mol L^{-1})[d]		
1.0	2.26	2.71		
10.0	2.15	2.51		
20.0	1.07	0.97		

[a] TA concentrations used were (4, 5, 6) $\times 10^{-3}$ mol L^{-1}.
[B] Sulfuric acid used were 37.0, 39.2, and 41.0 w/w%.
[c] Temperature used were 27, 25, and 23 °C.
[d] $NaNO_2$ concentrations used were (1.5, 2.0, 2.5) $\times 10^{-4}$ mol L^{-1}.

Table 4 Tolerable concentration of foreign species in the determination of 1.66×10^{-4} mol L^{-1} FA.

Interference substances	Tolerable limit[a] ([species]/[HCHO])	Tolerable concentration (mol L^{-1})	$A_{(I)}/A$[b]
Acetaldehyde	4.2	6.9×10^{-4}	1.050877
H_2O_2	24	4.0×10^{-3}	0.948823
Fe^{3+}	48	7.9×10^{-3}	0.935002
Ni^{2+}	54	8.9×10^{-3}	0.949123
Co^{2+}	54	8.9×10^{-3}	0.940344

[a] Defined as ± 5% relative error.
[b] $A_{(I)}$: absorbance in the presence of interference substances; A: absorbance without the interference.

interference was observed, (Table 4), from acetaldehyde (4.2-fold) and oxidant material as hydrogen peroxide (24-fold) which causes dissociation of the colored product. Interferences were also observed with ions, such as Fe(III) at 48 fold, Ni(II) and Co(II) up to 54-fold.

4.7. Preconcentration with bisulfite crystals

Considering that the concentration of FA found in samples, such as in rain water, could be less than the limit of the suggested method, a procedure for FA collection from these samples is needed. A modified FA crystallization collection method with sodium bisulfite ($NaHSO_3$) was performed in order to determine FA. This crystallization method was used to collect formaldehyde from air samples (U.S. Department of Health and Services, 1994). The method depends on the crystallization of aldehydes and ketones with bisulfite in aqueous media (Scheme 3) (Clayden et al., 2000). This method in brief included the addition of excess of bisulfite to the collected rainwater, forming a dissolved compound with FA, and addition of ethanol caused the compound to crystallize.

The optimum experimental conditions were determined for the concentrations of FA which are lower than the linearity range of the suggested method (these concentrations were not capable for the analysis by applying the suggested method.

Varying the bisulfite quantity for the preconcentration of 0.1 μg mL^{-1} FA present in 100 mL of bidistilled water, after which the analysis procedure was performed, reveals higher recoveries of 95%, with a relative standard deviation RSD of 2.8%, by using 5 g bisulfite. Increasing the bisulfite quantity up to 8 g/100 mL shows no variation in the recovery value. On the other hand, using 1.0, 2.0, 3.0, 4.0 g/100 mL of bisulfite gives a recovery of 50%, 61%, 79%, and 84%, respectively.

For the same preconcentration purpose, and for the same FA concentration, varying the ethanol (95%):water ratio as

Table 5 Determination of formaldehyde in different testing samples.

Sample[a]			Proposed method (n = 5)		Reference method (n = 5)
No	Type	HCHO added (μg mL^{-1})	HCHO (found ± S.D)[b]	R%[e]	Found ± S.D (μg mL^{-1})
1	Rain[c]	–	1.58 ± 0.037	–	1.57 ± 0.050
		0.5	2.06 ± 0.032	96.00	F = 1.82
		1.5	3.06 ± 0.041	98.67	t = 0.60
2	Rain [d]	–	0.87 ± 0.024	–	0.85 ± 0.032
		0.5	1.36 ± 0.028	98.00	F = 1.77
		1.5	2.36 ± 0.039	99.33	t = 1.85
3	TSS	–	18.31 ± 0.188	–	18.17 ± 0.202
		1	19.31 ± 0.201	100.00	F = 1.15
		3	21.28 ± 0.232	99.00	t = 1.66
4	Wood (MDF)	–	5.10 ± 0.076	–	5.14 ± 0.103
		0.5	5.58 ± 0.095	96.00	F = 1.84
		1.5	6.58 ± 0.110	98.66	t = 1.17
5	Wood	–	6.50 ± 0.116	–	6.48 ± 0.124
		0.5	6.99 ± 0.104	98.00	F = 1.14
		1.5	7.98 ± 0.111	98.67	t = 0.38

The value of t (tabulated) at 95% confidence level and for four degrees of freedom is 2.78.
The value of F (tabulated) at 95% confidence level and for four degrees of freedom is 6.39.
[a] All of the analytical samples had unknown FA concentration.
[b] Expressed for TSS in μg per cigarette, and μg mL^{-1} the for other samples.
[c] Collected from the first rain (countryside, Aleppo city, Syria) and preconcentrated twice.
[d] Collected after a period of one month (countryside, Aleppo, Syria) and preconcentrated 10 times.
[e] The recovery values for added FA concentrations.

0.5:2, 0.75:2, 1:2, 1.25:2, 1.5:2, and 2:2 gives recoveries of 50.2%, 94.5%, 95.3%, 94.7%, 30.7%, and 0.0%, respectively, with that, the excess of ethanol to a ratio more than 1:2 caused re-dissolution of the crystal.

Similar treatment of a solution containing trace formaldehyde levels of 0.08, 0.05, and 0.03 μg mL^{-1} gives (recovery ± RSD)% of (95.25 ± 2.9)%, (94.80 ± 3.1)%, and (94.07 ± 3.7%) respectively.

5. Application

The analytical results of FA with the suggested method in rain water were compared with the result obtained by HPLC measurement (Tsai et al., 2003), and are in good agreement. The HPLC measurement depended on the derivatization of FA with 0.1% of 2,4-dinitrophenylhydrazine reagent (DNPH). While the analytical results for the other samples of wood products, and TSS samples were compared with the standard chromotropic acid method adopted by NIOSH (Institute for Occupational Safety and Health, 1994). The obtained analytical results, Table 5, gave quantitative recoveries in the range of 96.0–100.0%. The test of significance shows that Student's t-test values and F-values at 95% confidence level are less than the theoretical values, indicating that there is a good agreement between the results obtained by the proposed method and the reference method with respect to accuracy and precision. These results prove the validity and reliability of the proposed method to analyze different aqueous samples.

In rainwater, however, the concentration of FA is different according to the area, gas emission and of pollutants present (Reeve, 2002). The first autumn rain collection contained more pollutants, due to the washing out of the dissolvable substances present in air, moreover, the concentration levels of FA in the two rain water samples analyzed indicate high levels of FA pollutant, which demand more attention and control of the pollutant's emission in the region.

6. Conclusion

A spectrophotometric method has been developed for the determination of low level formaldehyde. The developed method depends on the formation of a red violet colored product from the telomerization of FA with TA in the presence of concentrated sulfuric acid and trace $NaNO_2$ amounts. The method is shown to be selective, sensitive, simple and easy to perform. The colored product that has been formed is stable at a temperature less than or equal to 25 °C, and does not interfere with substances normally present as pollutants. The method validation proved the accuracy and precision for the routine application of low level formaldehyde determination.

Acknowledgment

The authors thank Dr Zaib HUSSAIN, PUNJAB University (Pakistan), for technical assistance.

References

Annual Book of American Society for Testing and Material (ASTM) Standards, Part (29), D2194, 1979, pp. 65–71.
Berg, J.M., Tymoczko J.L., Stryer, L., Biochemistry, 16th Ed., The Tripe Helix, 2006.
Bianchi, F., Careri, M., Musci, M., Mangi, A., 2007. Fish and food safety: determination of formaldehyde in 12 fish, species by SPME extraction and GC–MS analysis. Food Chem. 100, 1049–1053.

British Standards Institution, Formaldehyde in textiles. Part 2. "Method for determination of free formaldehyde", British Standard, BS 6782, Part 7, 1995, p. 12.

Chen, L., Jin, H., Wang, L., Sun, L., Xu, H., Ding, L., Yu, A., Zhang, H., 2008. Dynamic ultrasound-assisted extraction coupled on-line with solid support derivatization and high-performance liquid chromatography for the determination of formaldehyde in textiles. J. Chromatography 1192, 89–94.

Chrastil, J., Reinhardt, R.M., 1986. Direct colorimetric determination of formaldehyde in textile fabrics and other materials. Anal. Chern. 58, 2848–2850.

Clayden, J., Greeves, N., Warrer, S., Wothers, P., 2000. Organic Chemistry. Oxford University.

Cui, X., Fang, G., Jiang, L., Wang, S., 2007. Kinetic spectrophotometric method for rapid determination of trace formaldehyde in foods. Anal. Chem. Acta 590, 253–259.

Davydova, E.A., Stolyanova, A.G., Ostrovskaya, E.G., 1986. Comparative assessment of gas-chromatographic and photometric methods to determine formaldehyde in laboratory studies on construction polymers. Gig-Sanit. 3, 56.

Del Barrio, M.A., Hu, J., Zhou, P., Cauchon, N., 2006. Simultaneous determination of formic acid and formaldehyde in pharmaceutical excipients using headspace GC/MS. J. Pharm. Biomed. Anal. 41, 738–743.

Feng, S., Fan, J., Wang, A., Chen, X., Hu, Z., 2004. Kinetic spectrophotometric determination of formaldehyde in fabrics and air by sequential-injection analysis. Anal. Lett. 37, 2545–2555.

Fu Liu, J., Peng, J.F., Chi, Y.G., Jiang, G.B., 2005. Determination of formaldehyde in shiitake mushroom by ionic liquid-based liquid-phase microextraction coupled with liquid chromatography. Talanta 65, 705–709.

Gibson, L.T., Kerr, W.J., Nordon, A., Reglinski, J., Robertson, C., Turnbull, L., Watt, C.M., Cheung, A., Johnstone, W., 2008. On-site determination of formaldehyde: a low cost measurement device for museum environments. Anal. Chem. Acta 623, 109–116.

Gigante, A., Gotardo, M., Tognolli, J., Pezza, L., Pezza, H., 2004. Spectrophotometric determination of formaldehyde with chromotropic acid in phosphoric acid medium assisted by microwave oven. Microchem. J. 77, 47–51.

Guo, Y., Yan, H.T., Pei, R.H., Jia, S.Y., 2006. Kinetic spectrophotometric determination of formaldehyde by catalytic oxidation of brilliant cresyl blue with sodium bromate. Fenxi-Shiyanshi 25, 92–94.

Heimlich J.E., 2008. Formaldehyde; The Invisible Environment Fact, Sheet Series, The Ohio State University, CDFS-198-08.

Huber, W., Fresenius, Z., 1981. Mechanization of photometric analysis with the component parts of liquid chromatography. II. Fast precise determination of formaldehyde. Anal. Chem. 309, 386–390.

National Institute for Occupational Safety and Health, NIOSH Manual of Analytical Methods, 4th ed., Department of Health and Human Services, NIOSH, Cincinnati OH, USA, 1994.

Isakau, H., Robert, M., Shingel, K.I., 2009. A novel derivatization-free method of formaldehyde and propylene glycol determination in hydrogels by liquid chromatography with, refractometric detection. J. Pharm. Biomed. Anal. 49, 594–600.

Jagadeesan, N., Gupta, V., 1979. New spectrophotometric method for determination of formaldehyde in air. Talanta 26, 962–963.

Li, Q., Oshima, M., Motomizu, S., 2007. Flow-injection spectrofluorometric determination of trace amounts of formaldehyde in water after derivatization with acetoacetanilide. Talanta 72, 1675–1680.

Li, Q., Sritharathikhum, P., Oshima, M., Motomizu, S., 2008. Development of novel detection reagent for simple and sensitive determination of trace amounts of formaldehyde and its application to flow injection spectrophotometric analysis. Anal. Chem. Acta. 612, 165–172.

Likussar, W., Boltz, D.F., 1971. Theory of continuous variations plots and a new method for spectrophotometric determination of extraction and formation constants. Anal. Chem. 43 (10), 1265–1272.

Liteplo, R.G., Beauchamp, R., Meek, M.E., 2002. Report by International Programme on Chemical Safety IPCS. Canadian Centre for Occupational Health and Safety (CCOHS).

Liteplo, R.G., Beauchamp, R., Meek, M.E., 2002. Health Canada, Ottawa, Canada, and R. Chénier, World Health Organization, Geneva

Meyer, A.S.J., Ayres, G.H., 1957. The mole ratio method for spectrophotometric determination of complexes in solution. J. Am. Chem. Soc. 79 (1), 49–53.

Miller, J.C., Miller, J.N., 1993. Statistical in Analytical Chemistry, 3rd ed. Ellis Horwood.

Mohamed, A.A., Mubarak, A.T., Marestani, Z.M.H., Fawy, K.F., 2008. Highly sensitive and selective catalytic determination of formaldehyde and acetaldehyde. Talanta 74, 578–585.

Pinheiro, H.C., Valéria de Andrade, M., Afonso de Paula Pereira, P., de Andrade, J.B., 2004. Spectrofluorimetric determination of formaldehyde in air after collection onto silica cartridges coated with Fluoral P. Microchem. J. 78, 15–20.

Possanzini, M., Di Palo, V., 2003. Simultaneous determination of HCHO, CH_3 CHO and O(x) in ambient air by hydrazine reagent and HPLC. Ann. Chim. 93 (1-2), 149–156.

Priority Existing Chemical Assessment, Report No. 28, Report by National Industrial Chemicals Notification and Assessment Scheme (NICNAS), Common wealth of Australia (2006).

International Programme on Chemical Safety; Formaldehyde Health and Safety Guide n. 57, World Health Organization, Geneva, 1991, p. 48.

Reche, F., Garrigos, M., Sanchez, A., Jimenez, A., 2001. Determination of formaldehyde in finger-paints for children use by SFE combined with spectrophotometric and chromatographic techniques. Anal. Lett. 34, 1311–1322.

Reeve, N.R., 2002. Introduction to environmental analysis. John Wiley & Sons Ltd, University of Sunderland, UK.

Teixeira, L., Leao, E., Dantas, A., Pinheiro, H., Costa, A., de-Andrade, J., 2004. Determination of formaldehyde in Brazilian alcohol fuels by flow-injection solid phase spectrophotometry. Talanta 64, 711–715.

Tian, L., Zhang, A., Zhai, Y., 2004. Determination of trace formaldehyde in air by fast spectrophotometry with acetylacetone. Fenxi-Shiyanshi 23, 63–65.

Tsai, C., Shiau, H., Lee, S., Chou, S., 2003. Determination of low molecule weight aldehydes in packed drinking water by high performance liquid chromatography. J. Food Drug Anal. 11, 46–52.

U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods. 4th ed. Methods A-Z & Supplements. Washington, DC: U.S. Government Printing Office, Aug 1994.

Velikonj, S., Jarc, I., Zupancic, L.K., Marsel, J., 1995. Comparison of gas-chromatographic and spectrophotometric techniques for the determination of formaldehyde in water. J. Chromatography 704, 449–454.

J.C. Wakefield, Formaldehyde-General information, Report by Health Protection Agency, CHAPD HQ, HPA Version 1, 2008.

Witthauer, J., Heilemann, K.J., Bischof, W., 1999. The applicability of DNPH active collectors as passive collectors for the determination of formaldehyde in indoor air. Gefahrstoffe-Reinhalt Luft. 59 (10), 369–373.

Zhang, A.M., Tian, L.Q., 2004. Kinetic spectrophotometric and spectrofluorimetric determination of trace formaldehyde. Fenxi-Kexue-Xuebao 20, 519–521.

Zhao, C., Li, M., Jiao, K., 2006. Determination of formaldehyde by staircase voltammetry based on its electrocatalytic oxidation at a nickel electrode. J. Anal. Chem. 61, 1204–1208.