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ORIGINAL ARTICLE

Spectrophotometric determination of formaldehyde based on the telomerization reaction of tryptamine

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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).

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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 HIBAR (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.