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ORIGINAL ARTICLE

A simple spot test quantification method to determine formaldehyde in aqueous samples

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Abstract A simple, accurate, and economical method has been proposed to measure formaldehyde in aqueous samples. The method is based on quantification of classical chromotropic acid – formaldehyde violet spots developed on TLC. Different parameters such as concentration of chromotropic and sulfuric acid, time of heating and order of application of reagents have been studied to find out the optimum working procedure. Spots have been quantified by scanning the spotted TLC and analyzing the image in computer with Visual Basic 6.0 based graphic application. The study consisted of developing an appropriate calibration line, analyzing artificial and real samples, and comparing the new method with a standard spectrophotometric method (NIOSH Method-3500, 1994). It has been concluded that the present method had the capability for measuring formaldehyde in aqueous samples at trace level with high precision and accuracy, particularly when dealing with turbid and small volume samples where the standard method failed.

1. Introduction

Formaldehyde or methanal (HCHO) is the simplest aldehyde that is an important precursor to many chemical compounds. Yearly production of formaldehyde around the globe has exceeded 23 million tons during last few years (Lide, 2004). Formaldehyde is a gas at room temperature, but readily converts into a variety of other gaseous derivatives like trioxane. Formaldehyde occurs in the environment up to 0.03 ppm parts of air. Materials having formaldehyde, such as urea–formaldehyde foam insulation (UFFI) can release it in the form of gas or vapor. Pressed-wood products are the major source of formaldehyde indoor pollution. Cigarette smoke, gas stoves, wood-burning stoves, and kerosene heaters can also release formaldehyde. It is highly toxic to both plants and animals, and is particularly dangerous for the human eyes (Swenberg et al., 1980). When present in the air at levels exceeding 0.1 ppm, it causes severe irritation in the eyes, nose, and throat and usually results in watery eyes with burning sensations, coughing, wheezing, nausea, and skin irritation (Sakai et al., 2002). There is some

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evidence that formaldehyde become carcinogen when inhaled (Leonard, 1999). Epidemiological investigations of the fatality of factory workers following prolonged occupational exposure to formaldehyde showed a slight excess of lung cancer (Acheson et al., 1984a, b). Safe exposure limit to formaldehyde for 30 min is 100 $\mu g\ m^{-3}$ (0.08 ppm) (Sawada, 2006).

Formaldehyde in water comes mainly from oxidation of organic matter during ozonation (Glaze et al., 1989) and chlorination (Becher et al., 1992). In drinking water, it can arise from leaching from plastic fittings and water treatment processes. In the dissolved form, formaldehyde converts into a diol $CH_2(OH)_2$. An aqueous solution of formaldehyde is called formalin. Pure formalin is a saturated solution of formaldehyde in water (nearly 37% by weight) (Turoski, 1985; Keilson and Newell, 1990). It does not persist in water for long time because it is broken down within few hours by sunlight or by bacteria. However, when ingested to a level above 2.6 $mg\ l^{-1}$ (NOEL) via contaminated food or water, formaldehyde has been shown to cause vomiting, abdominal pain, dizziness, and in extreme cases can cause even death.

Li et al., 2007 developed a fluorophotometric method for formaldehyde determination in environmental waters, which was founded on the reaction of formaldehyde with acetoacetanilide and ammonia. The method was simple, rapid, economical, and highly sensitive. Różyo et al., 2002 determined the levels of formaldehyde in human saliva. Formaldehyde was determined as the dimedone adduct (formaldemethone) using OPLC. Tomkins et al., 1989 determined total formaldehyde in drinking water samples. Formaldehyde present in 1 liter water was derivatized with 2,4-dinitrophenylhydrazine in an acidic media and subsequently extracted with chloroform. After separation by solvent extraction, the product was quantified using reverse-phase liquid chromatography. Keyvanfard, 2010 proposed a simple and rapid catalytic kinetic method (based on the catalytic effect of formaldehyde on the oxidation of cresyl violet by bromate in the presence of sulfuric acid) for the determination of trace amount of formaldehyde. The method was exercised for the measurement of formaldehyde in water samples.

It is obligatory to develop simple and precise analytical methods to determine formaldehyde because of its widespread use, toxicity, and volatility. There are several methods available for the detection of formaldehyde in air and water. The most widely used methods for air samples are based on spectrophotometry, while for aqueous samples high-performance liquid chromatography (HPLC) is a preferred choice. Other methods include colorimetry, fluorimetry, polarography, gas chromatography (GC), infrared detection, flow injection analysis and gas detector tubes (Cogliano et al., 2004). HPLC or GC coupled with the mass spectrometer (MS) are most sensitive techniques. However, these techniques are very expensive. Besides, difficulties arise with the monitoring of turbid samples that can block columns or membranes or precipitations can demand considerable maintenance effort (Papaefstathiou et al., 1996).

This paper describes a simple, rapid, sensitive, selective, and reproducible analytical method of formaldehyde analysis based on the quantitative spot test technique. The violet–red spots of formaldehyde with chromotropic acid were developed on TLC. Chromotropic acid has been widely used as an analytical reagent in organic as well as in biological chemistry after the discovery of violet spots with formaldehyde in 1937 (Eegriwe, 1937). In view of the fact that the color density of spot is directly proportional to the concentration of formaldehyde, a simple analytical method has been developed for precise quantification of formaldehyde in aqueous samples at trace levels. The color densities of the spots were measured with simple software by taking the image of spotty TLC in computer subsequent to scanning. There are other techniques to quantify chromotropic acid – formaldehyde spots (Boyd and Logan, 1942; Boos, 1948); the present method is only one of its kind in terms of measuring, quantity of sample, simplicity and accuracy. The most appropriate application of the method is on-field analysis of trace amounts of formaldehyde in aqueous samples.

2. Materials and methods

2.1. Stock solution and standards

Stock solution of formaldehyde (1000 $mg\ l^{-1}$) was prepared by diluting analytical grade 10% formalin solution (Sigma–Aldrich, Inc.) with proper quantity of double distilled water. Standard solutions of desired concentrations (2–10 $mg\ l^{-1}$) were prepared by appropriate dilution of the stock solution.

2.2. Chemicals

Technical grade chromotropic acid disodium salt dihydrate, $(HO)_2C_{10}H_4(SO_3Na)_2{\cdot}2H_2O$ and reagent grade concentrated sulfuric acid (Sigma–Aldrich, Inc.), 95–98%, 1.840 $g\ ml^{-1}$ at 25 °C (lit.) were the chemicals that were used as it is or as doubled distilled water diluted solutions in order to evaluate the effect of these on color intensity of spots. Desired solutions of chromotropic acid were prepared in 50% sulfuric acid.

2.3. Procedure

TLC plate (Merck, Aluminum sheet, Silica gel $60F_{254}$, 3×5 cm) was used to develop spots since paper could not be employed (burnt because of concentrated sulfuric acid). One micro-liter drop of each, chromotropic acid, sulfuric acid and aldehyde solution was employed with micropipette (Pipettman) one over the other. The order of application of reagents and aldehyde solution was altered to check the effect on color density of the spot. Later, the TLC was placed in an oven for 2–20 min at 60 °C to notice the effect of time. Violet color spots intensifying on cooling were obtained.

2.4. Quantification of spots and analysis of samples

The spotty plate was scanned on a flatbed scanner (HP 3670 CCD Reflective Flatbed Scanner) and the image was imported in Visual Basic 6.0 based graphic application to measure the color density of spots. Detail of graphic application to read color densities of the spots is given in (Anwar et al., 2010). A calibration line was plotted taking concentration of formaldehyde's standards as abscissa against the corresponding color density of spots (ordinate). Slope, intercept, standard error of estimates and correlation coefficient were measured. Finally, synthetic as well as true aqueous samples of formaldehyde were analyzed using the same set of conditions by measuring their color densities and interpolating the corresponding concentrations from standards' calibration line.