



Rapid determination of methanol content in paper materials by alkaline extraction, coupled with headspace analysis



Chun-Yun Zhang^a, Ling-Ling Li^a, Xin-Sheng Chai^{a,b,*}, Donald G. Barnes^c

^a State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China

^b National Paper Products Quality Supervision Inspection Center, Dongguan, China

^c School of Environment and Energy, South China University of Technology, Guangzhou, China

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ABSTRACT

This study reports on a rapid method for the determination of methanol in paper-based materials by alkaline extraction, coupled with headspace analysis. Methanol partition equilibria between solid–liquid phases and vapor–liquid phases were conducted in two separate containers, from which an equation for calculating the total methanol content in the original paper sample was derived. It was found that the extraction equilibrium of methanol from solid sample could be achieved within 5 min at room temperature using a high-speed disintegrator, and a subsequent neutralization step is an effective way to prevent methanol from being regenerated at high temperature during headspace equilibration. The results showed that the relative standard deviations for reproducibility tests were in the range of 1.86–6.03%, and the recoveries were in the range of 92.3–107%. The present method is simple and practical; it can be an efficient tool for quantifying the methanol content in paper-based materials and thus play an important role in the investigation of methanol migration behavior in food and beverage packaging.

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1. Introduction

Ingestion of methanol has proven to be harmful to the human body through its metabolism to formaldehyde or formic acid, both of which are poisonous to the central nervous system. In extreme cases, the result has been blindness, coma, or even death [1,2]. A series of strict regulations has been passed to limit the amount of methanol that enters exposed human bodies, directly and indirectly, through such sources as food, drinking water and air in the workplace [3–6]. In the paper industry, methanol is generated from the addition of a methyl group to lignin and/or hemicellulose in wood and non-wood materials during the alkali-rich processes of pulping and bleaching processes [7]. Recently, we found that methanol produced in these processes is mainly released to the process effluents [7,8]. However, a significant amount of methanol may remain entrapped in the pulps and the final paper products [9]. Therefore, the quantification of methanol remaining in paper products is important in the investigation of possible migration

of methanol from paper products to humans, especially to those products used for food packaging and personal hygiene.

There are several methods available for the determination of methanol in beverage [10] and air [11] that are based mainly on gas chromatography (GC). For samples in non-volatile matrices; e.g., salts and polymers, pretreatment procedures (typically solvent extraction) are required before measurement by GC. However, in spite of the complicated and time-consuming pretreatment procedure, the contamination problem of the GC system cannot be completely eliminated because some of the non-volatile organic compounds are also transferred into the solvent phase. In order to address this problem more effectively, we have developed a number of headspace (HS) GC methods that could be used for the quantification of volatile analytes in samples with complicated matrices; e.g., methanol in pulping [12,13], oxygen delignification [12,13] and pulp washing effluents [14]. These different headspace techniques; i.e., the conventional, full evaporation, and water removal by hydrate formation, have been described in the cited works.

However, the HS-GC methods cannot simply be applied to the volatile analytes entrapped in a solid sample; e.g., the methanol content in pulp fiber or paper-based products. As reported earlier, the release of methanol from solid pulp fibers is a very slow process, taking several weeks or months to reach equilibrium [9]. In order to release methanol from the solid phase, we proposed a sample

* Corresponding author at: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China. Tel.: +86 20 87113713; fax: +86 20 87113713.

E-mail address: xschai@gmail.com (X.-S. Chai).

pretreatment procedure to hydrolyze the paper matrix in a phosphoric acid medium [9]. Then the methanol in the hydrolysis medium is determined by HS-GC. It was found that the paper matrix can be completely dissolved in 5 h at 120 °C. However, special precautions must be taken, otherwise the existing oxygen in the purging gas can react methoxyl groups (O–CH₃) in pulp fibers in the acidic medium leading to formation of methanol, thus causing a positive error in the quantification. Although this was the first method that could quantify the methanol content in pulp and paper products, the method is not very efficient because of the time-consuming hydrolysis involved.

Alkali was reported to be an important swelling and extracting agent for separating hemicellulose from lignocellulosic materials, since alkali solutions can penetrate deep into the inner sites of fibers [15,16]. Thus, the methanol that is bound to pulp fibers can be easily released to the alkaline medium and measured by HS-GC based on either the vapor–liquid equilibrium [12] or the full evaporation mode [13]. From our feasibility study, we observed that the methanol bound to pulp fibers is partially released; i.e., some methanol molecules remain in the fibers (solid phase), during the alkaline extraction. As a result, there is a need to develop a HS-GC method for determining the methanol content in pulp and paper products by a one-step equilibrium in a three-phase system or in a two-step process in two containers; i.e., to conduct the equilibrations of the solid–liquid and vapor–liquid phases separately.

In this work, we report on the development of a novel method for rapidly quantifying the methanol content in pulp and paper materials, which is based on both alkali extraction and HS-GC measurement. The main focus is on the validation of the solid–liquid partition equilibrium for deriving an equation that can be used to calculate the total methanol content in the original paper materials and to determine the proper time, temperature and procedures for the alkali extraction and the HS-GC measurement, making sure that no methanol regeneration is introduced. The precision and accuracy for the method were also evaluated.

2. Materials and methods

2.1. Chemicals and materials

All chemicals, including sodium hydroxide, acetic acid, methanol used in the experiment, were analytical grade and purchased from commercial sources without further purification. Sodium hydroxide solution (8%, w/w) was prepared in a 1000 mL flask by dissolving 83.3 g of sodium hydroxide (>96% pure) into a measured amount of distilled water. The acetic acid solution (24%, w/w) used as a neutralizer was prepared in a 100 mL flask by dissolving 24.1 g of acetic acid (>99.5% pure) into a measured amount of distilled water. A set of standard methanol solutions with concentrations ranging from 0 to 63.4 ppm were prepared by diluting the original standard methanol solution (63.4 ppm, obtained by dissolving 63.4 mg of pure methanol in 1000 mL of distilled water) with appropriate amounts of distilled water. The standard methanol solution with concentration of 1584 ppm was prepared by dissolving 158.4 mg of pure methanol in 100 mL of distilled water.

Bleached chemical thermal mechanical pulp (BCTMP) of crystal cypress and bleached kraft pulp of eucalyptus was obtained Hongta Tobacco Co., Ltd., China. Paper cups and paper tissues were purchased from commercial sources.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automated headspace sampler (DANI HS 86.50, Italy) and a GC system

(Agilent GC 7890A, US) equipped with a flame ionization detector and a DB-5 capillary column, operating at a temperature of 40 °C with nitrogen carrier gas (flow rate = 3.8 mL/min). Headspace operating conditions were as follows: 30 min of strong shaking for the sample equilibration at 105 °C; sample loop temperature = 110 °C; transfer line temperature = 115 °C; pressurization pressure = 2.00 bar; carrier gas pressure = 1.5 bar; vial pressurization time = 15 s; sample loop fill time = 25 s; and transfer time = 20 s.

2.3. Sample preparation

A 1.00 g sample of oven-dried BCTMP was weighed and placed in a container equipped by the high-speed (18,000–25,000 rpm) disintegrator. 100.0 mL of the extraction agent (8%, w/w sodium hydroxide solution) was added to the container with a pulp consistency of 1% (w/v). The pulp sample was then defibrated in the solution by treatment with the disintegrator for 1 min. After the fiber suspension was filtered through a membrane filter (0.45 μm), 660 μL of filtrate was placed in a headspace vial. Then, 340 μL of acetic acid (24%, w/w) was added to bring the total volume of liquid up to 1 mL. The sample vial was immediately sealed with a PTFE/silicone septum and an aluminum cap for HS-GC analysis at 105 °C for 30 min.

The same procedure was followed for the internal standard calibration test, the only difference being that the sample was spiked with 1 mL of the methanol standard solution (1584 ppm).

3. Results and discussion

In order to obtain a good dispersion of fibers in the liquid medium, we conducted the equilibration in two separate containers. The first container, equipped a high-speed disintegrator, was used for dispersing sample fibers in the alkaline solution and for the methanol extraction. After equilibrium was achieved, the filtrate of the extraction solution was transferred to a second container (the headspace sample vial) for vapor–liquid phase equilibration which was then measured by HS-GC. Therefore, the quantification of the methanol in the original sample in this method involves two equilibriums, which will be discussed below.

3.1. Methanol equilibrium in alkaline solution and fiber system

Fig. 1 shows the relationship between the amounts of methanol added to the paper sample and the net amounts of methanol in the equilibrated liquid phase in the first container, measured by HS-GC after being transferred to the second container. It can be seen that the amount of methanol found in the filtrates of the extraction medium are lower (only about 57%) than those

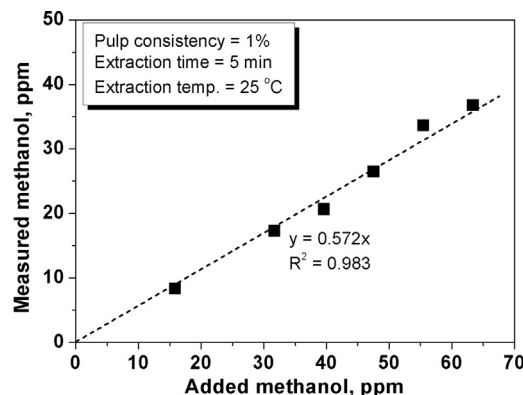


Fig. 1. Relationship between the amounts of methanol added to the paper samples and the amount detected by HS analysis.

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