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A New Headspace Gas Chromatographic Method for the Determination of Methanol Content in Paper Materials Used for Food and Drink Packaging

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ABSTRACT: This study reports on a method for determination of methanol in paper products by headspace gas chromatography (HS-GC). The method is based on the hydrolysis of the pulp or paper matrix, using a phosphoric acid solution (42.5%) as the medium at 120 °C in 5 h (excluding air contact) in order to release matrix-entrapped methanol, which is then determined by HS-GC. Data show that, under the given conditions of hydrolysis, no methanol was formed from the methoxyl groups in the material. Reproducibility tests of the method generated a relative standard deviation of <3.5%, with recovery in the range of 93.4−102%. The present method is reliable, accurate, and suitable for use in batch testing of the methanol content in paper-related materials. The method can play an important role in addressing food safety concerns that may be raised regarding the use of paper materials in food and beverage packaging.

KEYWORDS: *methanol, food packaging paper, phosphoric acid, headspace gas chromatography*

INTRODUCTION

Methanol is a light, volatile, colorless, and flammable liquid. When ingested, it is metabolized to formic acid and/or formate salts, which are poisonous to the central nervous system and, in extreme cases, can lead to blindness, coma, and death.[1,2] The European Union, the United States, and other countries have passed strict regulations to limit the amount of methanol in foods (less than 5−10 mg/kg), drinking water, and air in the workplace.[3−6]

Because of the presence of methoxyl groups on lignins and hemicelluloses in ligocellulosic pulping materials (wood and nonwood species), significant amounts of methanol are generated during pulping and bleaching processes.[7,8] Further, due to the hydrophilic groups in pulp fibers, a significant amount of methanol can be retained in the pulp and final paper products, even after pulp washing and drying procedures. Therefore, the investigation of methanol migration from paper packaging material to foods and beverages during their uses or storage is of great importance to the safety of human health, especially at a time of rising consumer concerns about the safety of the food they eat and feed to their children.

Even if methanol migration from paper products can be suppressed by the material treatment, such as surface coating and filling, it is important to quantify the original methanol content in the matrix of paper products since it is directly related to the amount of methanol that could conceivably migrate into packaged goods. This information is essential in evaluating the effectiveness of any material surface treatment or other methanol mitigation strategy that might be adopted.

Since methanol is a volatile organic compound (VOC), gas chromatography (GC) is a suitable technique for its quantification analysis. However, if the sample matrices are complex, such as pulping and bleaching spent effluents or solid samples, the GC method cannot be applied directly. These sample matrix problems can be largely eliminated by the proposed headspace (HS) sampling technique, coupled with analysis by gas chromatography (GC).[9] In the previous work,[10−12] we developed several methods for the determination of methanol in pulping spent liquor[10,11] and washing effluent[12] based on conventional, full-evaporation, and desiccated headspace gas chromatographic techniques (HS-GC). HS-GC is an ideal technique when the analyte(s) can be completely released or partially released from the liquid to the headspace under conditions of equilibrium. However, we found that the release of methanol from solid pulp fibers is extremely slow, taking several weeks or months to reach equilibrium. This is probably a result of the strong molecular interaction between methanol and the polar functional groups in pulp fibers.

A similar problem arises in the analysis of metals in pulp or paper products where the affinity of the paper matrix for metals interferes with the analysis. In those cases, the solution is to completely eliminate the paper matrix by hydrolysis using a strong acid.[13] Similarly, the methanol entrapped in the pulp and paper products could also be completely released if the paper matrix were to disappear through strong acid hydrolysis. Once released, the methanol can be quantified by HS-GC.[10−12]

In this work, we report on the development of an HS-GC method that is capable of quantifying the amount of methanol in pulp and paper products. The main focuses of the study were on the approach for hydrolyzing the paper matrix and the

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optimization of conditions for HS-GC testing. The precision and accuracy for the present method were also evaluated.

MATERIALS AND METHODS

Chemicals and Materials. All chemicals, including methanol, phosphoric acid (85% w/w), and alkaline lignin used in the experiment, were analytical grade and purchased from commercial sources. A series of phosphoric acid solutions, with concentrations ranging from 0% to 85% (w/w), was prepared by mixing appropriate amounts of phosphoric acid (85% w/w) with deionized water. An original standard methanol solution (1070 ppm) was prepared by adding 0.2684 g of pure methanol to 250 mL of phosphoric acid solution (42.5% w/w). A set of standard methanol solutions with various concentrations (1−100 ppm) were prepared by mixing the original standard methanol solution and phosphoric acid solution (42.5% w/w).

A base paper sample was obtained from a commercial source and used for food packaging material.

Apparatus and Operations. HS-GC measurements were carried out with an automatic 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 30 °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 = 2.0 bar; carrier gas pressure = 1.5 bar; vial pressurization time = 15 s; sample loop fill time = 20 s; and transfer time = 20 s.

Procedures of Sample Preparation. A 1.50 g sample, based on oven-dried weight, from an air-dried eucalyptus pulp was accurately weighed and placed into a 250 mL flask containing 150 mL of phosphoric acid solution (42.5% w/w). The pulp sample was defibrated in the solution (the consistency of pulp fibers, 1%) using a high-speed disintegrator to obtain a uniform fiber suspension. After 15 mL of fiber suspension was added to a 20 mL headspace vial, the air above fiber suspension of sample vial was purged using nitrogen at a 300 mL/min of flow rate for one minute. After the purging tube was withdrawn, the sample vial was immediately sealed with a PTFE/silicone septum and aluminum cap. The prepared sample vial was placed in an air-dry oven, where the pulp fiber was hydrolyzed at a temperature of 120 °C for five hours.

HS-GC Analysis. The hydrolyzed sample was removed from the oven and cooled to room temperature. After the hydrolysate was filtered through a membrane filter (0.45 μm), a 1 mL sample of filtrate was placed in a headspace vial. The HS-GC analysis of the vials was conducted after 30 min at a 105 °C to reach equilibrium.

RESULTS AND DISCUSSION

Release of Methanol from Pulp and Paper to Air by Increasing the Temperature. Figure 1a shows the time-dependent methanol release from a pulp sample at different temperatures. It can be seen that the release of methanol from pulp sample is a very slow process, especially at a low temperature. However, even at 105 °C, the trend of methanol release was still increasing after 28 h, as shown in Figure 1b. Although the exposure surface area in the base paper is larger than that of the pulp lump used in the testing, the complete release of methanol was still not achieved. Therefore, both the temperature and the exposure surface area of sample cannot be relied upon as the means of efficiently releasing the methanol entrapped in pulp or paper products.

Release of Methanol by Dissolving Sample Matrix and Effect of Hydrolysis Medium. Methanol can completely be released into the solution if the paper matrix, i.e., the carbohydrate (solid) phase, disappears. In the present work, several liquid mediums that are commonly used for dissolving

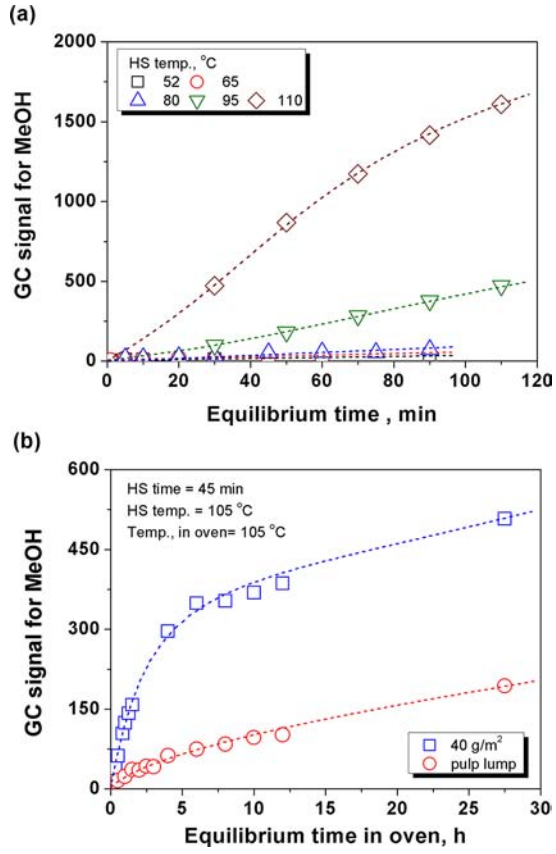

Figure 1. Release of methanol from pulp and paper to air in a closed system (sample size = 0.10 g).

or hydrolyzing carbohydrates; such as cupriethylenediamine solution,[14] ionic liquid,[15] strong nitrate acid, and sulfuric acid,[16] were considered for use in this application. The results showed that although the carbohydrates can be completely dissolved or hydrolyzed, there were significant amounts of methanol, more than expected, generated during the processes, which were detected by the HS-GC measurement. The additional methanol could have resulted from conversion of methoxyl groups in the carbohydrates and/or lignins of pulps to methanol during the processes. However, when phosphoric acid (42.5%) was used as the reaction medium, the amount of methanol released was much less, and it leveled off after reacting for 5 h at 120 °C under anaerobic conditions (see Figure 2a). Although higher temperatures could speed up the hydrolysis, as shown in Figure 2b, it would create cause a potential leakage problem in headspace sample vial due to the higher pressure.

To determine whether any of the methanol released into the headspace came from converted methoxyl groups in the pulp fibers, the methoxyl content of a pulp and a pure lignin sample was measured before and after phosphoric acid hydrolysis, by a HS-GC method developed previously.[17] The results (see Table 1) showed that the amount of methoxyl groups in these samples was unchanged by the phosphoric acid hydrolysis. These data confirm that no methanol was converted from either base paper or lignin in the proposed hydrolysis conditions.

HS-GC Conditions for Methanol Testing. *Sample Volume.* In general, a large sample volume can increase the detection sensitivity in a HS-GC measurement. However, the lager sample volume also requires a longer headspace

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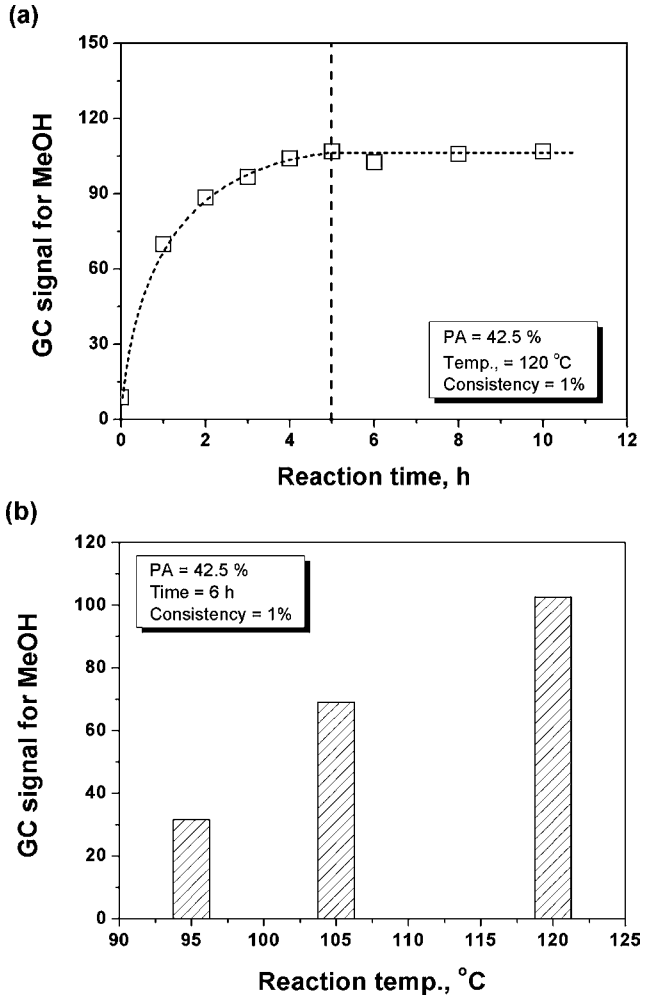

Figure 2. Effect of the (a) equilibration time and (b) temperature on the methanol release to the headspace.

Table 1. Comparison of Methoxyl Content in the Samples before and after Hydrolysis with Phosphoric Acid

	methoxyl content, g/kg		
samples	before	after	difference, %
base paper	2.78	2.94	5.8
lignin	53.3	55.1	3.4

equilibration time,[9] which makes HS-GC measurement less efficient. As shown in Figure 3, the detection sensitivity for methanol testing by the present method can be dramatically increased by increasing the sample volume up to about 1 mL. After that the detection sensitivity improvement for methanol testing is less significant. Therefore, 1 mL was chosen as the appropriate sample size to use in this HS-GC method.

Headspace Equilibration Temperature and Time. As reported earlier,[18] the vapor and liquid phase equilibrium (VLE) of methanol can be achieved within 30 min at 70 °C when a 10 mL aqueous solution is used. The VLE could be reached more quickly if a small sample volume or high equilibration temperature were selected.[19,20] As shown in Figure 4, the time for methanol to reach VLE in the present medium is about 30 min, much longer than expected. We believe that this is due to the high viscosity of the concentrated phosphoric acid medium.[21] Therefore, we chose 30 min and

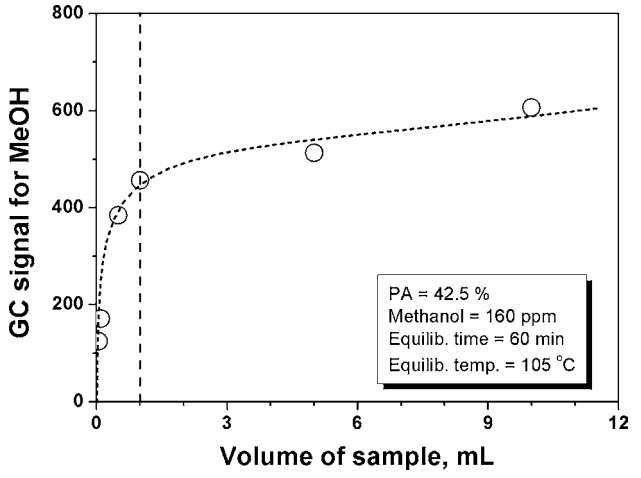

Figure 3. Effect of sample volume on the methanol measurement.

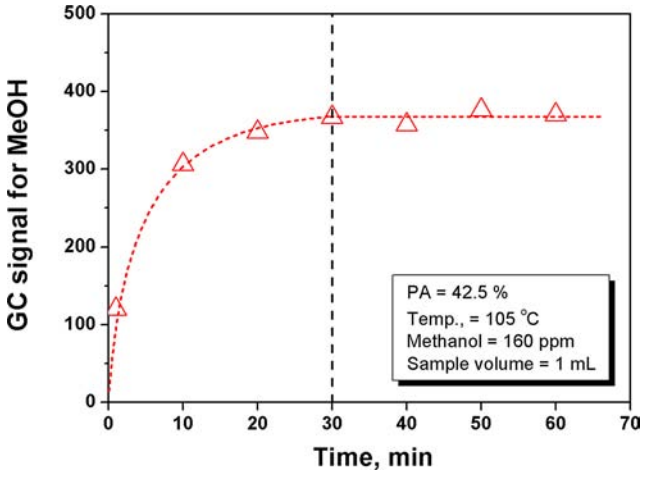

Figure 4. Effect of equilibration time in the methanol testing.

105 °C for the headspace equilibration in the present method. It should be pointed out that although 30 min was chosen for the methanol headspace equilibration, the actual time for the analysis of multiple samples can be significantly reduced, because there is a so-called overlapping constant mode of thermostatting available in many commercial headspace autosampler systems.[9]

Method Evaluation. *Calibration.* The method calibration was performed by adding various concentrations (1−100 ppm) of the standard methanol solution (phosphoric acid = 42.5%) into a set of headspace vials, and then subjecting them to the hydrolysis and HS-GC measurement procedures. A standard calibration curve was obtained which can be expressed as

$$A = 3.03(\pm 0.54) + 3.17(\pm 0.03)C \quad (n = 7, R^2 = 0.999) \tag{1}$$

where A and C represent, respectively, the GC signal (peak area) and the methanol concentration (in ppm) in the phosphoric acid solution placed in the headspace sample vials.

Based on eq 1, the methanol content, C_{MeOH}, in the pulp and paper sample can be calculated by the following equation:

$$C_{MeOH} = \frac{A - 3.033}{3.170\theta} \tag{2}$$

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where θ is the consistency of pulp or paper matrix in the suspension solution, and A represents the GC signal for methanol.

Precision. The reproducibility of the present method was investigated by the quintuplicate determination of methanol in a base paper sample. The results show that the reproducibility was more than 96.5%.

Validation. To validate this method, a set of spiked sample solutions was analyzed by adding different amounts (0−60 ppm) of methanol to a set of 15 mL of paper (fibers) suspension in headspace sample vials, each of which was hydrolyzed at temperature of 120 °C for five hours. The filtrates were then measured by the present HS-GC method. An unspiked sample of the paper suspension served as the reference. The contents of methanol in the samples were obtained using eq 1. Thus, the net contribution from the added methanol in the HS-GC measurements of these spiked samples can be detected. Table 2 shows that the recoveries achieved in the present method are in the range of 93.4−102%, which is appropriate for many purposes.

Table 2. Method Validation[a]

	methanol, ppm		
sample no.	added	measured	recovery, %
1	5.31	4.96	93.4
2	10.6	10.8	102
3	31.8	30.7	96.5
4	42.5	41.5	97.6
5	53.1	52.6	99.1

[a]The amount of methanol in the original paper suspension sample was 32.2 ppm.

In summary, a HS-GC technique for the determination of methanol in paper materials has been developed. The sample was dissolved in a phosphate acid medium in the absence of oxygen in order to remove the complex matrix and release the entrapped methanol without converting any of the methoxyl groups to methanol during the sample hydrolysis. The method is reliable, accurate, and suitable for use in batch testing of paper-related materials. The method can play an important role in addressing food safety concerns that may be raised regarding the use of paper materials in food and beverage packaging.

Future related research opportunities include the following:

a. Investigation of performance of methanol mitigation measures in the pulping process.
b. Methanol migration studies in various food packaging under various conditions.
c. Collaborative efforts in method standardization to ensure comparability of results from different laboratories.
d. Assessment of health and ecological risks posed by the presence of methanol in food packaging materials.

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Notes

The authors declare no competing financial interest.

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