Rapid Determination of Formaldehyde in Sanitary Paper Napkins for Product Quality Control by Headspace Gas Chromatography

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This study reports on a headspace gas chromatographic method (HS-GC) for the determination of formaldehyde in sanitary napkin samples. The method is based on the reaction of formaldehyde and sodium borohydride in a concentrated potassium carbonate solution (824 g/L), in which formaldehyde is quantitatively converted to methanol at 105°C in 45 min. The methanol from the conversion is determined by HS-GC. The repeatability of the method had a relative standard deviation of less than 4.5%; the limit of quantification (LOQ) was 1.17 µg, and the recovery ranged from 96.8 – 106%. The present method is simple, rapid, and accurate. It is suitable for use in the batch testing for product quality control of tissue papers during the manufacturing process and in analysis of point-of-sale samples from commercial markets.

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Introduction

Formaldehyde is an important industrial commodity chemical that is widely used in the production of fertilizer, paper, plywood, and urea-formaldehyde resins.¹ However, since formaldehyde has been designated as a probable human carcinogen,^{2,3} it is important to minimize the concentration of formaldehyde in products, especially in products designed for consumer use. In China, the maximum allowed concentration of formaldehyde in textiles designed for use by infants and in direct skin contact are 20 and 75 ppm,⁴ respectively. There are a variety of paper products of tissue paper that directly come into contact with skin during use, such as sanitary napkins. Therefore, it is necessary to measure the formaldehyde content in such personal care paper products.

Formaldehyde is unstable in air and other gas phase matrices at temperatures below 150°C, where the chemical polymerizes rapidly to form dimers or trimers and/or combines with moisture in the air to produce methylene glycol.⁵ These chemical reactions are neither predictable nor complete, making it impossible to indirectly quantify the formaldehyde in a product based on the concentration of the dimer, trimer or methylene glycol species. For these reasons, most methods involve derivatizing formaldehyde either with hydrazines, followed by analysis with high performance liquid chromatography (HPLC), or with dinitrophenylhydrazine, followed by gas chromatography (GC). Compared with colorimetry,⁶⁻⁸ HPLC⁹⁻¹¹ and GC^{12,13} methods can effectively separate the coexisting interfering species and are adequately sensitive to detect very low amounts of formaldehyde in samples. However, these methods have the disadvantage that the derivatization procedures are complicated

and time-consuming, which not only make the methods less efficient but also introduce significant experimental errors.

In general, headspace based gas chromatographic methods, *e.g.*, conventional static headspace (HS) and headspace solid phase micro-extraction (HS-SPME), have a great advantage in determination of analyte(s) in complicated, non-volatile matrices.¹⁴ Usually, the HS-based methods require little or no sample pretreatment; typically, pretreatment consists of only filtration and/or extraction. Sugaya *et al.* have reported on a HS-GC/MS method for the determination of aldehydes in water, in which *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine was used as a derivatizing agent.¹⁵ However, it was noticed that only ~95% formaldehyde was derivatized under the suggested conditions (60 min at 60°C) and that the resulting product seemed to be unstable if a longer reaction time (>120 min) was applied. Different from derivatization reactions, oxidation and reduction reactions with inorganic reagents such as potassium permanganate and sodium borohydride (NaBH₄) are usually very fast and complete, especially at an elevated temperature. Recently, we have successfully developed a number of reaction-based HS-GC methods for the determination of carboxyl groups in pulps,¹⁶ carbonate and oxalate in pulping spent liquors.^{17,18} It is well known that formaldehyde can react with borohydride to form methanol in alkaline medium.¹⁹ However, since the conventional HS and HS-SPME are based on phase equilibrium techniques controlled by the partitioning coefficient, it is a big challenge to increase the detection sensitivity and the recovery for the quantification of the methanol that results from the conversion of the low levels of formaldehyde contained in tissue paper products. We reported previously that both salting-out effect and high headspace equilibration temperature are helpful for methanol to leave the aqueous phase (sample solution).²⁰⁻²² Thus, the detection sensitivity for methanol in tissue paper products can be improved even using a conventional GC flame ionization detector.

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In the present work, we report on a HS-GC method designed to rapidly determine formaldehyde in sanitary napkins. The research is aimed at optimizing the reaction conditions for the formaldehyde conversion and at improving the detection sensitivity for methanol in the headspace measurement.

Experimental

Chemicals and samples

All chemicals used in the experiment were of analytical grade and from commercial sources. A standard methanol solution (800 mg/L) was prepared by adding 20 μ L of methanol to 20 mL of distilled water. The concentration of the commercial aqueous solution of formaldehyde (~37% by weight) was accurately determined by iodometry. A standard formaldehyde solution (440 mg/L) was prepared by adding 1.0 g of the formaldehyde to 1 L of distilled water. A NaBH₄ solution (5 g/L) was prepared by adding 0.5 g of sodium borohydride to 100 mL of a solution containing 824 g/L of K₂CO₃, which was prepared by dissolving 1100 g of K₂CO₃ in 1 L of distilled water. A commercial sanitary napkin sample was used in this study.

Apparatus and operations

All measurements were carried out using an Automatic Headspace Sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US) equipped with a flame ionization detector operated at 250°C. The flow rates of hydrogen and air were 30 and 400 mL/min, respectively. A DB-5 capillary column (30 m $\times$ 0.32 mm $\times$ 0.25 μ m) operated at a temperature of 30°C with nitrogen carrier gas (flow rate, 3.8 mL/min). Headspace operating conditions were as follows: equilibration temp., 105°C; needle and sampling coil temp., 115°C; transfer temp., 120°C; vial pressurization time, 0.2 min; sample loop fill time, 0.2 s; and sample loop volume, 3 mL.

Procedure of sample preparation

A 4.0-g sample from a sanitary napkin sample was accurately weighed and placed into a 250-mL jar containing 200 mL of K₂CO₃ (824 g/L) solution. The napkin sample was befibrated in the solution (the consistency of napkin fibers, 2%) by a high-speed disintegrator to obtain a uniform fiber suspension. Next, 5 mL of this fiber solution and 0.1 mL of the NaBH₄ solution were placed in a 20-mL headspace sample vial that was sealed immediately with a PTFE/butyl septum and aluminum cap. The vial was placed in the headspace sampler and allowed to equilibrate at 105°C for 45 min with fast shaking. Finally, a sample from the headspace was automatically withdrawn and measured by GC.

Results and Discussion

The present method is based on measuring the methanol that is quantitatively generated by the reaction of sodium borohydride with formaldehyde in an alkaline solution,¹⁹ *i.e.*,

The effects of the reaction conditions, *i.e.*, the dosage of sodium borohydride, the reaction temperature and time, on the completion of the conversion are discussed below.

Fig. 1 Effect of NaBH₄ dosage on the conversion of formaldehyde.

Fig. 2 Effect of the reaction time on the conversion.

Dosage of sodium borohydride

To insure complete conversion of formaldehyde (CH₂O) in Eq. (1), an excess amount of sodium borohydride is required. Figure 1 shows that for a sample of 0.00140 mmol of formaldehyde from the standard solution, a quantitative conversion can be achieved by 0.05 mg (~0.00132 mmol) of NaBH₄ under the given reaction conditions (in the presence of K₂CO₃ (824 g/L), an alkaline medium). It can be seen that NaBH₄ in a four-fold stoichiometric excess can drive the reaction to completion under these conditions. In the following study, a sufficient amount (0.5 mg) of NaBH₄ would be used in the reaction.

Reaction temperature and time

In general, a higher temperature accelerates chemical reactions. However, the conventional headspace analysis must be conducted at temperatures below the boiling point of the sample, because if the sample were to boil in the headspace vial, the sample liquid could be flushed into the sampling channel during the venting, which would contaminate or even block the sampling channel if there were non-volatile substances, such as cellulose fibers, present in the sample. In this case, the boiling point of the K₂CO₃ solution is ~110°C, so the experiments were conducted at 105°C.

As shown in Fig. 2, it takes about 40 min to reach complete

Table 1 Comparison of GC responses between the equal-molar methanol samples and the formaldehyde-converted-to-methanol samples

Amount of added/ $\mu\text{mol L}^{-1}$	GC signal		Difference, %
	Methanol	Methanol from formaldehyde	
5	10.2	10.1	-0.98
10	20.3	20.8	2.46
25	48.7	50.6	3.90
50	101	98.5	-2.48
100	206	210	1.94

Reaction in a K_2CO_3 solution containing 0.5 mg of NaBH_4 at 105°C for 45 min.

The GC signal count for the blank sanitary paper napkin is 5.32.

conversion of the formaldehyde when the fiber sample was used, which is marginally slower than what was observed in the fiber-free solution. To insure that quantitative conversion was achieved in all of the samples, 45 min was selected for use as the reaction time.

Confirmation of the completion of the conversion

In order to prove that the formaldehyde is completely converted to methanol under the above conditions, we analyzed two sets of samples with the similar molar amounts of formaldehyde or methanol. As seen in Table 1, the differences in the GC responses between the methanol samples and the formaldehyde-converted-to-methanol samples were small and did not indicate a consistent bias. Therefore, we conclude that the conversion reaction in this method is complete under the given conditions.

Effect of potassium carbonate on the detection sensitivity for methanol

Due to the low concentration of formaldehyde in paper issue products, the methanol detection sensitivity of the method is also important. As reported previously,²² the effect of salting-out on the Henry's law constant of methanol is significant. Thus, in addition to raising the boiling point of the solution to achieve a higher reaction temperature, the presence of K_2CO_3 is also helpful in enhancing the detection sensitivity of methanol in the HS-GC method because of the salting-out effect. As shown in Fig. 3, for the given amount of methanol (1.1 mg/L), the GC response is dramatically increased in solutions containing K_2CO_3 up nearly to its solubility limit.²³ It should be noted that the solubility of K_2CO_3 in water is much higher than that of Na_2CO_3 ,²³ which also allows the reaction to be performed at a higher temperature (e.g., 105°C in the present case) due to a greater elevation of the boiling point. In the present work, an 842 g/L concentration of K_2CO_3 was selected for the make-up sample in the formaldehyde analysis.

Method calibration, precision, and validation

The method calibration was performed by placing different amounts ($0 - 10 \text{ mg/L}$) of the standard formaldehyde solution into a set of headspace sample vials that were tested by the present method, from which a standard calibration curve was obtained, i.e.,

$$A = 2.33(\pm 1.27) + 12.9(\pm 0.059)C \quad (n = 7, r^2 = 0.9999) \quad (2)$$

Fig. 3 Effect of K_2CO_3 concentration on methanol detection in HS-GC.

where A and C represent, respectively, the GC signal response for methanol and the formaldehyde content (in μg) added in the headspace sample vial.

Calculated by Eq. (3),²⁴ the limit of quantitation (LOQ) in the present method is $1.17 \mu\text{g}$, which equals 11.7 ppm when a 5-mL of solution with a 2% sanitary napkins consistency was used in the testing. Thus, the LOQ of the present method can meet the government requirements for the formaldehyde test in products designed for use by infants or in direct skin contact.⁴

$$\text{LOQ} = \frac{a + 10 \times |\Delta a|}{s} \quad (3)$$

where a , Δa and s represent the intercept, uncertainty of the intercept, and the slope in Eq. (2), respectively.

The formaldehyde content, C_F , in the sanitary napkin sample, can be calculated by the following equation, i.e.,

$$C_F (\text{ppm}) = \frac{A_0 - 2.33}{12.9w} \quad (4)$$

where w is the weight (in grams) of sanitary napkin in the suspension solution. A_0 represents the net GC signal counts for methanol (by subtracting the signal counts from a blank testing).

The repeatability testing of the present method was investigated by the quintuplicate determination of formaldehyde in a sanitary napkin. The results show that the relative standard deviations were less than 4.5% .

To verify the present method, we prepared a set of spiked sample solutions by adding different amounts ($0 - 11 \mu\text{g}$) of formaldehyde to a set of 5 mL of sanitary napkin suspension solutions in headspace sample vials, each of which contained 842 g/L of K_2CO_3 and 0.5 mg of NaBH_4 . The samples were then measured by the present HS-GC method. An unspiked sample of the napkin suspension served as the reference. The amounts of formaldehyde in the samples were calculated by Eq. (2). Thus, the net contribution from the added formaldehyde in the GC measurements in these spiked samples can be determined. Table 2 shows that the recoveries achieved in the present method are in the range of $95.5 - 106\%$, which is appropriate for many purposes.

Table 2 Method validation

Sample No.	Formaldehyde content/ μg		Recovery, %
	Added	Measured	
1	0.550	0.585	106
2	1.10	1.13	103
3	2.75	2.84	103
4	5.50	5.25	95.5
5	11.0	10.7	96.8

The formaldehyde content in the unspiked suspension of sanitary napkin was 2.85 μg .

HS-GC measurement time for multiple sample analysis

Although 45 min was chosen for the formaldehyde conversion reaction, the time for the analysis of multiple samples can be significantly reduced by the use of the overlapping constant mode of thermostating in the present headspace sampler system.¹⁴ Specifically, since the methanol determination by GC can be completed within 3 min, a GC cycle time of 5 min was selected. When testing multiple samples is desired, the first sample vial testing begins its reaction time (RT, 45 min) to complete the conversion of formaldehyde in the sample to methanol, followed by the chromatographic cycle time of 5 min. Throughput time can be minimized, if the second sample enters the RT phase with a time lag of 5 min, so that the second sample enters the GC testing phase immediately after the first sample is finished. As a result, the total analysis time for multiple samples can be drastically reduced compared to an *ad seriatum* approach to analysis.

Conclusions

A HS-GC technique for the determination of formaldehyde in sanitary napkin samples has been developed, based on the determination of the methanol generated from formaldehyde using NaBH_4 as the reducing agent. The presence of K_2CO_3 not only provides the alkaline environment required for the reaction but also enhances the methanol detection sensitivity in headspace analysis by both boiling point elevation and a salting-out effect. The method is simple, rapid, and accurate, and can be automated.

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