A Modified Method for the Determination of the Carboxyl Groups in Fibers by Headspace Gas Chromatography

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ABSTRACT

This paper reports an improved headspace gas chromatographic method for the determination of carboxyl group content in wood fibers. Pretreatment of wood fibers was applied using dilute HCl to convert carboxyl groups to carboxylic acid groups and then using deionized water to wash fiber samples thoroughly. The samples were finally air dried. Sodium bicarbonate solution was used to react with carboxylic acid groups of the pretreated fibers in a closed testing vial to release carbon dioxide. The content of carboxyl groups in fibers was accurately quantified by determining the amount of carbon dioxide released by a headspace gas chromatograph equipped with a thermal conductivity detector. The modified process for fiber sample pretreatment increased the reliability and accuracy in measuring carboxylic acid groups. The present method is simple, accurate.

Key words: Carboxyl groups, Gas chromatography, Fiber sample

INTRODUCTION

Carboxylic acid groups (COOHs) in fibers play a very important role in cellulose fiber modification. The traditional methods for quantifying the carboxylic acid groups in wood fibers are mainly based on either acid-based titration[1-4] or complex titration[5] using EDTA. It was found[6] that these methods not only are complicated and time-consuming, but also exhibit a large variance among themselves even though they are conducted at the same laboratory.

Headspace gas chromatography (HSGC) has been widely used for analysis of volatile species in complex matrix samples. Many relative applications of HSGC have been published in the textbooks[7-9] and articles[10-13]. HSGC also can be applied to determine the content of nonvolatile species which can be converted to volatile components through chemical reactions. In a previous study[14], a phase reaction conversion (PRC) HSGC had been used for analyzing the carbonate content dissolved in black liquors, based on the conversion of carbonate to carbon dioxide through acidification and measurement of the carbon dioxide content in gaseous phase by chromatography using a thermal conductivity detector (TCD). We developed a PRC HSGC method to determine the total carboxyl group content in fibers of wood pulps[15]. This study presented some improvements of the pretreatment method of pulp samples and simplified the process of vialing a treated pulp sample for the measurement by HSGC, and compared the measurements results with our original method [15].

MEASUREMENT PRINCIPLE

The content of the species of interest in the condensed

phase can be determined through mass balance in a one-step reaction 1 using equation 2.

$$rR+bB\ (\text{condensed}) \leftrightarrow pP+qQ\ (\text{gas}) \quad (1)$$

$$C_B = \frac{k'}{a}\cdot\frac{b}{q}\cdot(V_T - V_L)A \quad (2)$$

The variables r and b are mole coefficients for reactants R and B, and p and q for products P and Q, respectively. C_B is the molar amount of condensed species to be analyzed in a condensed phase sample, a is the fraction of the analyzed species converted to gas Q, k' ($k'=C_Q/A$) is the calibration coefficient for the concentration of product Q with the HSGC detector signal peak area A. V_T and V_L are volume of sample vial and of the residual liquid sample in the vial. V_T-V_L is volume of the vial headspace. A is the measured HSGC detector signal peak area of product Q.

The carboxylates on fibers can be converted to carboxylic acid groups through the pulp pretreatment by dilute hydrochloric acid. After the pretreatment, it is required for the pulp to be washed thoroughly by deionized water in order to eliminate the impact of the residual acid in fibers on the measurements. The carbon dioxide generated through the following reaction of sodium bicarbonate with the carboxylic acid groups on fibers is released into the testing vial headspace and the signal peak area can be measured by the thermal conductivity detector (TCD) of the HSGC.

$$R-COOH + HCO_3^- \rightarrow R-COO^- + H_2O + CO_2\uparrow \quad (3)$$

The TCD signal peak area A_T of carbon dioxide within the testing vial headspace are contributed by the carboxylic acid groups on fibers, A_C, and the air within the testing vial, A_{Air}, i.e.

$$A_T = A_C + A_{Air} \quad (4)$$

If relating Equation 2 with Equation 4, we can obtain the following equation

$$C_B = \frac{k'b(V_T - V_L)}{aq}(A_T - A_{Air}) \quad (5)$$

Based on the assumption k = k'b/q, Equation 5 can be expressed as

$$C_B = \frac{k(V_T - V_L)}{a}(A_T - A_{Air}) \quad (6)$$

When the mass of the fibers in the vial is small (i.e. less than 0.1 grams) and the volume of aqueous reaction agent is large (i.e. 4 mL for a testing vial with 20 mL of volume), $V_T - V_L$, the volume difference between the vial and liquid within the vial, can be considered as a constant. Therefore, the equation 6 can be further simplified as

$$C_B = f(A_T - A_{Air}) \quad (7)$$

Where f is the calibration coefficient specific to the experiment and can be obtained through calibration. Assuming the air-dry weight of acid treated fiber sample is w, the carboxyl group content in fibers can be expressed as follows:

$$C_B = \frac{f}{w\times 0.9}(A_T - A_{Air}) \quad (\text{mmol/g}) \quad (8)$$

EXPERIMENTAL

Chemicals and Fiber Samples

All chemicals used in the experiments came from commercial sources. The standard bicarbonate solution consists of 0.0025 mol/L sodium bicarbonate and 0.10 mol/L sodium chloride, of which the deionized water with a specific resistance of not less than 17.4 MΩ·cm was used as the solvent. The deionized water was boiled for several minutes, and then poured into a conical flask and cooled quickly close to the room temperature prior to using. All fiber samples were collected from the laboratory alkaline pulping and bleaching process.

Apparatus

All measurements were carried out using an HP-7694 automatic headspace sampler and model HP-6890 capillary gas chromatograph equipped with a thermal conductivity detector (Agilent Technologies, Palo Alto, CA). GC conditions were as follows: capillary column

with ID = 0.53 mm and length of 30 m (model GS-Q, J&W Scientific Inc., Folsom, CA) at 30 °C, carrier gas helium flow rate of 3.1 mL/min. The GC was run in splitless mode. Headspace sampler operating conditions were as follows: oven temperature of 60 °C, vial pressurized by helium and pressurization time of 0.2 min, sample-loop fill time of 0.2 min, loop equilibration time of 0.05 min, vial equilibration time of 10 min with strong shaking, and loop fill time of 1.0 min.

Procedures

The fiber samples were firstly pretreated with 0.10mol/L hydrochloric acid solution for 1 hour at room temperature, magnetically stirring at a constant speed. The concentration of the fiber suspension was about 1.2%. After finishing the acid pretreatment, the suspension was filtered, and fiber sample was washed thoroughly using deionized water with a specific resistance of not less than 17.4 MΩ·cm until the pH value of the filtrate was close to that of the deionized water. The fiber samples finally were air-dried in an air conditioned room.

Depending on the estimated content of the carboxyl groups, 0.0300- 0.0750 grams of air-dried fiber sample were weighed out and placed directly into the headspace testing vial. Four milliliters of 0.0025 mol/L standard sodium bicarbonate solution mixed with 0.10 mol/L sodium chloride was added into the vial. Then the vial was quickly sealed and shaken properly in order to keep the fiber sample well dispersed. The headspace testing vial well prepared for analyzing in HSGC is shown as Fig.1.

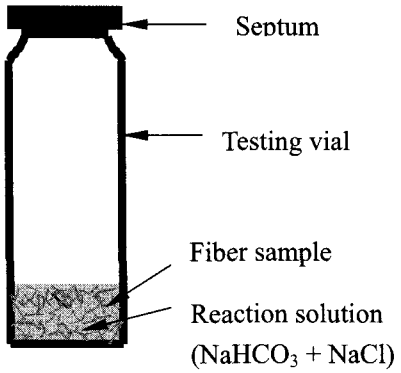

Fig. 1. Schematic diagram of the headspace

Calibration

To facilitate the experimental calibration, no attempt was made to conduct the calibration experiments using standard carboxylic acid solutions. Calibration was achieved through the reaction of standard hydrochloric acid solution with sodium bicarbonate. Taking a set of headspace testing vials with a 75 mm high and 20 mL of each volume, of which there was 4 mL of reaction agent (0.0025 mol/L $NaHCO_3$ + 0.10 mol/L NaCl), and injecting different volumes ranging from 0 to 60 μL of 0.100 mol/L hydrochloric acid solution into the vials using a microsyringe. The molar range of the standard hydrochloric acid should cover the molar range of carboxyl groups in fiber samples to be determined. The molar amount of the reaction agent applied was overdosed during the whole reaction. The GC signal peak area and the molar amount of standard hydrochloric acid added in the vial were recorded. According to eq.7, we obtained $f = 4.563\times10^{-5}$ ($mmol^{-1}$), $A_{Air} = 8.95$, through the linear regression, with R^2 = 0.9989 (Figure 2) by assuming complete reaction between hydrochloric acid and the reaction agent.

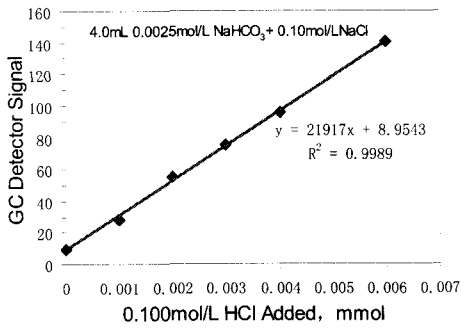

Fig. 2. Calibration of GC detector signals.

RESULTS AND DISCUSSION

Converting ratio of carboxyl groups to carbon dioxide

As described in our original study, achieving a constant or near complete conversion of carboxylic acid groups in fibers to carbon dioxide is very important to the accuracy of the measurements. It was found that the reaction rate was very low at room temperature. To increase forward reaction, one can increase the dosage of bicarbonate

properly, extends reaction time, and increases reaction temperature. It was found an increase in reaction temperature was very effective to increase reaction rate. A constant conversion from carboxylic acid groups to carbon dioxide can be achieved within 10 minutes at 60 °C (Figure 3).

The effect of carbon dioxide in ambient air

The contribution of carbon dioxide in ambient air to the measured GC detector signal should be excluded especially in measuring fiber samples with low content of carboxyl groups. The GC signal peak area contributed by ambient air was found to be 8.95 as shown in calibration (Figure 2), i.e., $A_{Air} = 8.95$.

The effect of fiber sample size

The fiber sample size involves two issues. One is related to the sensitivity of GC detector, which means too small a fiber sample may approach the detection limit of the GC detector. For the experiment conditions established in the present study, the detection limit is estimated to be around 0.5 μmol of carboxylic acid groups. Decreasing the headspace volume or enlarging the volume of bicarbonate solution can increase the detection limit. Another issue related to the sample size is the effect of the fiber sample on the total volume of the reaction system and on the mixing of the fiber sample with the bicarbonate solution, i.e., how much the volume of the reaction solution changes after the sample is mixed and reacted with the bicarbonate solution.

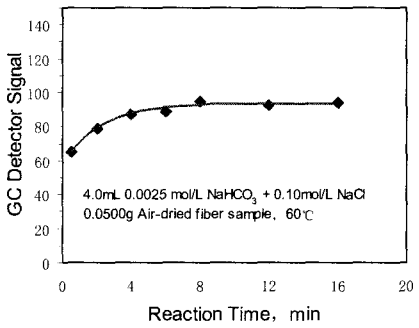

Fig. 3. Effect of rection time on GC detector signal of CO_2 in the testing vial

Because 4 mL of the reaction system was fixed during the calibration experiment, any unknown volume deviation in the reaction solution from 4 mL can change the partial pressure in the headspace and cause measurement errors. The effect of sample size variation on measurement accuracy due to the variations of headspace partial pressure was thoroughly studied in our previous research on phase reaction conversion (PRC) HSGC technique.[14] The right amount of fiber sample can facilitate better mixing of the fiber sample with the bicarbonate solution in the vial during the reaction. It was found in this experiment that less than 2.5% of the fiber consistency based on weight will not affect the measurement accuracy of the present method.

The effect of ion strength

Sodium chloride was used to increase the ionic strength of the reaction solution in the present method. It was found that the intensity of the GC detector signal can be increased when sodium chloride was added into the reaction solution. This is because the sodium ions can facilitate the release of hydrogen ion from the carboxylic acid groups in fibers.[3] Furthermore, the solubility of carbon dioxide in liquid phase may be reduced due to the addition of sodium salt, which may help the removal of carbon dioxide from liquid phase to the headspace and improve the sensitivity of GC detecting. It was also found that the intensity of GC signal reaches a constant level after 0.10 or more mol/L of sodium chloride is added into the reaction solution. Therefore, the standard bicarbonate solution used in the present study contains 0.10 mol/L of sodium chloride.

Reproducibility

The experimental reproducibility was conducted using five 0.0300 g samples of sample A, 0.0750 g samples of sample B. Table 1 lists the measured GC detector signal peak areas for the two samples using two different fiber sample pretreatment methods. The results show that the relative standard deviations (RSTD) of four separate sets of experiment using two different fiber sample pretreatment methods with fiber sample A and B are less than 4.0 %, of which a smaller RSTD was obtained using method A than that obtained using method B. The present method, that is, method A, has a better

reproducibility and measurement reliability.

Method comparison

The detailed comparison between HSGC method and the traditional acid-base titration method has been presented.[15] The HSGC method is accurate, rapid, and automated in comparison with the traditional titration method.

Table 1. Reproducibility of the two methods

	GC detector signal, peak area			
	Sample A (0.0300 g)		Sample B (0.0750 g)	
	Method A	Method B	Method A	Method B
1	51.5	49.9	126.0	120.5
2	48.6	49.4	131.6	127.8
3	52.1	53.9	129.8	126.9
4	50.4	51.4	126.5	130.3
5	49.7	53.2	127.1	131.4
Mean	50.5	51.6	128.2	127.4
RSTD,%	2.77	3.83	1.87	3.34

Method A and B represent the present and original[15] methods, respectively.

For the HSGC method, however, the fiber sample pretreatment process has been modified in the present study. As described in the Experimental, after the hydrochloric acid pretreatment, fiber samples was washed with deionized water thoroughly and finally air-dried in an air conditioned room, different from our original method[15]. After modifying the fiber pretreatment method, it is unnecessary to determine the residual hydrochloric acid on the fibers and to hold the fiber sample using a needle while vialing in our original method, the vialing process can be greatly simplified. As a result, the vialing time was reduced, and besides, the human experiment error caused by the vialing process in our original method can be eliminated. While using the present fiber pretreatment process for the two samples in Table 1, the RSTD can be decreased by 27 and 44 % for samples A and B, respectively.

Furthermore, it is necessary to use the deionized water with a higher specific resistance in order to avoid the impact of water quality on the measurement. It was found that the quality of the deionized water has no influence on the measurement when the specific resistance is greater than 17.4 MΩ·cm.

CONCLUSIONS

The modified method for the determination of carboxyl groups in fibers by headspace gas chromatography was presented in this study.. The method of acid pretreatment followed by deionized water washing is superior to our previous method without deionized water washing. The modified HSGC method can increase the reliability of the measurement. The present method is simple and accurate compared with our original one.

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