Carboxyl Groups in Wood Fibers. 1. Determination of Carboxyl Groups by Headspace Gas Chromatography

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Determination of Carboxyl Groups in Wood Fibers by Headspace Gas Chromatography

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ABSTRACT

The phase reaction conversion (PRC) headspace gas chromatographic (HSGC) technique was employed to develop a method for the determination of the content of carboxyl groups in wood fibers. Acid treatment of the wood fibers using hydrochloric was applied to convert carboxyl groups to carboxyl acids. Bicarbonate solution is then used to react with carboxyl acids on the treated fibers in the headspace of a testing vial to form carbon dioxide that is analyzed by a thermal conductivity detector using gas chromatography. The conversion reaction was conducted at 60°C for about 10 minutes to achieve near complete conversion. The contribution to GC detector signal from carbon dioxide formed by residual hydrochloric acid on wood fibers can be accounted for from the known experimental parameters. The effect of carbon dioxide in the headspace of the testing vial air was calibrated or can be eliminated by purging the testing vial using nitrogen before experiment. The measured contents of carboxyl groups in 8 wood fiber samples were in good agreement with those measured by a titration method. The present method is accurate, rapid, and automated.

INTRODUCTION

Carboxylic acid groups, COOH, represent the ion-exchange capacity of cellulose materials, i.e., the ability to absorb metallic cations during processing and are responsible for wood fiber swelling, conformability, and thus contribute to the bounding of fibers. They also have the ability to improve the adsorption of retention aids in papermaking. The stability and electric properties of paper depend on the amount of metal ions bound by the carboxyl groups on wood fibers. On the other hand, the absorbed cations by the carboxylic acid groups contribute to a discoloration mechanism for fiber and paper during paper drying. These acid groups also play an important role for wood fiber modification since they are fairly reactive and strategic sites for addition and substitution reactions. Finally, they can increase viscosity and decrease fiber solubility of specialty grade dissolving pulps. Therefore, the quantification of carboxyl groups on wood fibers is of paramount importance for both fundamental and applied studies.

The traditional methods for quantifying the total carboxylic acid group concentration in wood fibers or polymers are mainly based on either acid-based titration [1-4], or complex titration using EDTA [5]. A detailed comparison of carboxylic acid group content in wood fibers measured by these methods was reviewed by Wilson [6]. It was found that all these methods are not only complicated and time-consuming, but also demonstrated large variance among themselves even when they were conducted within the same laboratory.

Headspace gas chromatography (HSGC) has been widely used for analysis of volatile species in complex matrix samples. Many applications based on HSGC have been published in the textbooks [7-9] and review articles [10-12]. HSGC can also be applied to analyze some nonvolatile species that could be converted to volatile specie through chemical reactions. In a previous study [13], we have reported a phase reaction conversion (PRC) HSGC method for the determination of carbonate, a nonvolatile species, in wood pulping spent liquors, based on converting the carbonate in the sample liquor into carbon dioxide through acidification and measured by gas chromatography equipped with a thermal conductivity detector (TCD).

METHDOLOGY

The phase reaction headspace GC method along with other technical issues have been described and discussed in detail in our previous study [13]. The key is to convert the species of interest in the condensed phase into gas phase that can be analyzed by GC in a headspace. The content of the species of interest in a condensed phase can be determined through mass balance in a one step reaction (1) using eq. (2).

$$r\mathrm{R} + b\mathrm{B}(\text{condensed}) \leftrightarrow p\mathrm{P} + q\mathrm{Q}(\text{gas}) \quad (1)$$

$$A = \frac{\alpha}{k(V_T - V_L)} \cdot \frac{q}{b} \cdot n_B \quad (2)$$

Where n_B is the molar amount of condensed species B to be analyzed in the condensed phase sample, α is the fraction of the species to be analyzed converted to gas Q, A is the measured GC detector peak area of product gas Q, k (= C_Q/A) is the calibration coefficient of the GC system for concentration of product gas, C_Q, with GC detector signal peak area, A, and w is the weight of the condensed material sample participated in reaction (1). It was found that carboxylic acid groups on wood fibers can be converted to carbon dioxide using bicarbonate after the fiber is acid treated with hydrochloric acid. The following reaction describes the conversion reaction.

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

The carbon dioxide generated from the reaction of carboxyl groups with bicarbonate is released into the headspace of a testing vial and can be quantified by GC with a thermal conductivity detector (TCD).

Any residual hydrochloric acid on fibers after pretreatment can also react with bicarbonate to form carbon dioxide as shown in reaction (4).

$$H^+ + HCO_3^- = H_2O + CO_2 \quad (4)$$

Furthermore, carbon dioxide in air will also contribute to the total carbon dioxide within the headspace of the testing vial. Therefore, the actual measured GC peak area A_{exp} of carbon dioxide in the vial headspace can be expressed as,

$$A_{\exp} = A_{carboxyl} + A_{HCl} + A_{Air} \quad (5)$$

Based on Eq. (2), we can rewrite eq. (5) to relate the measured GC peak area A_{exp} to the molar amount of carboxyl group content, $n_{carboxyl}$, in fibers, as follows,

$$n_{carboxyl} = \frac{k(V_T - V_L)}{\alpha}(A_{\exp} - A_{air}) - \frac{\beta}{\alpha}(1-\gamma)\cdot w \cdot C_{HCl} \quad (6)$$

where w is the weight of the testing fiber sample, γ is the consistency of the fiber sample, α and β are the conversion fractions of reactions (3) and (4), respectively, C_{HCl} is the concentration of hydrochloric in the solution used for fiber acid treatment, A_{air} is the GC signal of ambient carbon dioxide in the testing vial. Eq. (6) can be simplified as follows,

$$n_{carboxyl} = f(A_{\exp} - A_{air})/\alpha - f_1 \quad (7)$$

where $f = k(V_T\text{-}V_L)$ and $f_1 = (1 - \gamma)\cdot w\cdot C_{HCl}\cdot\beta/\alpha$ are calibration constants and can be obtained through calibration. f_1 can also be calculated by assuming $\beta/\alpha = 1$ and using the known concentration of hydrochloric in the acid solution for fiber treatment and the measured consistency of the fiber sample.

It is expected that measurement accuracy can be improved if the hydrochloric acid treated fibers are dried to vaporize all the residual hydrochloric on fibers before allowing the fibers to react with bicarbonate and the testing vial is de-aired.

EXPERIMENTAL

Chemicals and fiber samples

All chemicals used in the experiment were obtained from commercial sources. A standard bicarbonate solution consists of 0.005 mol/L sodium bicarbonate and 0.1 mol/L sodium chloride was prepared from source chemicals. All fiber samples were collected from our laboratory alkaline pulping and bleaching processes.

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, USA.). GC conditions were: capillary column with an ID = 0.53 mm and a length of 30 m (model GS-Q, J&W Scientific Inc., Folsom, CA, USA) at 30°C, carrier gas helium flow rate of 3.1 mL/min. Headspace Sampler operating conditions were: 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 first pretreated using a 0.10 mol/L hydrochloric acid (HCl) solution for one hour at room temperature under magnetically stirring at a constant speed. The fiber sample was then dewatered (thickened) in a centrifugal juice extractor. The consistency of the dewatered fibers was determined. Thus, the amount of hydrochloric acid remaining in the dewatered fibers can be determined. 4 mL of 0.005 mol/L standard bicarbonate solution was added into a headspace testing vial. A one inch long needle was placed through the septum of the testing vial. About 0.15 gram of dewatered fibers is weighted. The weighted fiber sample is held by the needle on the inner face side of the septum. Therefore, when the testing vial is not completed sealed by the septum, the fiber sample hung over in the vial without contacting (or reacting with) the bicarbonate solution as shown in Fig. 1. After the testing vial is completely sealed, the needle is pulled out of the septum so that the fiber sample falls into the solution. Therefore, reaction will not start before the testing vial is sealed to avoid any reaction products leak out of the testing vial.

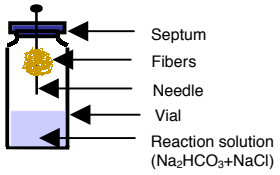

Fig. 1 A schematic diagram shows the method of placing acid treated wood fibers into the testing vial for GC measurement.

Conductometric titration was used to determine the amount of total acid groups in fibers [4]. 1.5-2.2 g fibers was added into a 300mL 0.1 mol/L NaOH solution and the suspension was stirred for 1 hour, ensuring that all of the carboxylic acid were in protonated form. The fibers were filtered using a fritted glass filter funnel and washed completely with deionized water. The filtered fibers were quantitatively transferred into a beaker to which was added 250 mL of 0.001 mol/L NaCl and 1.5 ml 0.1 mol/L HCl. The solution was stirred and sparged with argon for several minutes. The solution was then titrated with 0.05 mol/L NaOH in 0.25ml aliquots, taking conductivity readings after each addition. A plot of the conductivity versus the volume of NaOH was obtained in which the intersection point of the "V" shaped curve corresponded to the acid group concentration.

Calibration

To ease the experimental calibration, an attempt was not made to conduct calibration experiments using standard carboxylic acid groups. Calibration was achieved through the reaction of standard hydrochloric acid with bicarbonate. Different volumes range from 1-50 μL of 0.100 mol/L of standard hydrochloric acid solution was injected into a set of 4 mL 0.005 mol/L of sodium bicarbonate solutions with using a micro-syringe. The volume of the bicarbonate solution was 4 mL (same as that used for measuring fiber samples). The range of the molar amount of the standard hydrochloric acid should cover the range of the molar amount of carboxyl groups in fiber samples to be tested. The total application of the molar amount of bicarbonate is overdosed. The GC signal peak area and the molar amount of hydrochloric applied were recorded. By assuming complete reaction

between hydrochloric acid and bicarbonate, Eq. (6) can be written as follows,

$$n_{HCl} = f(A_{\exp} - A_{air}) \quad (8)$$

From the recorded GC signal peak areas and molar amounts hydrochloric acid applied during calibration experiments, we obtained $f = 4.49\text{X}10^{-5}$, $A_{air} = 9.3$ through linear regression with $R^2=0.9983$. Carboxyl groups content can now be determined using Eq. (6) or (7).

RESULTS AND DISCUSSION

Test of constant rate of conversion from carboxylic acid groups to carbon dioxide

As discussed in our previous study [13], achieving constant or near complete conversion of carboxyl groups to carbon dioxide in reaction (3) is important to the success of the present HSGC method. It was found that the reaction rate of reaction (3) was very low at room temperature due to the nature of solid-liquid reaction, i.e., hydrogen ions of carboxylic acid groups in a solid phase (fibers) and bicarbonate ions in a solution. It was recommended that an over dosage of bicarbonate should be used to mix with fiber sample to insure near complete reaction. It was found that an increase in reaction temperature was effective to increase reaction rate because that an increase in temperature not only increases the diffusion rate of bicarbonate into wood fibers, but also increases the removal rate of carbon dioxide produced by the reactions into the headspace. It was also found that a constant conversion of carboxyl groups into carbon dioxide can be achieved within 10 minutes of reaction at a temperature of 60°C as shown in Fig. 2.

The effect of carbon dioxide in air

The effect of carbon dioxide in the air was accounted for through calibration. The GC signal in terms of peak area contributed by carbon dioxide in ambient air was found to be 9.3 as shown in calibration. To eliminate the effect of carbon dioxide in the air on the accuracy of measurements, the air in the testing vials can be removed by deaeration techniques, such as purging the air in the vial with nitrogen. As will be discussed later, it was found that measurements with air free testing vials gave better reproducibility.

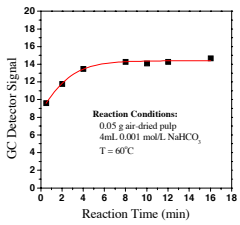

Fig. 2 The effect of reaction time on measured GC signal of carbon dioxide in the testing vial headspace produced by the reaction of carboxyl groups and bicarbonate solution.

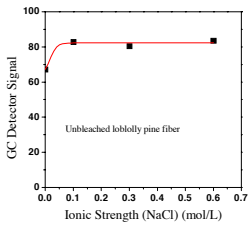

Fig. 3 The effect of ionic strength of the bicarbonate solution on measured GC signal of carbon dioxide in the testing vial headspace produced by the reaction of carboxyl groups and bicarbonate solution.

Effect of sample size

There are two issues associated with sample size. One is related to measurement sensitivity, i.e., too small of a sample may approach the detection limit of the GC detector. For the experimental conditions established in the present study, the detection limit is estimated around 0.5 μmol carboxylic acid groups based on the calibration experiments. One can use a smaller headspace volume (or large volume of bicarbonate solution) to increase the detection limit. Another issue related to sample size is the effect of the fiber sample on the total volume of the reaction system, i.e., how much the volume of the reaction solution changes after the fiber sample is mixed and reacted with the bicarbonate solution? The issue is raised due to the fact that the volume of the reaction system was fixed at 4 mL during calibration (the volume of hydrochloric acid solution added is negligible), any unknown deviation in the volume of the reaction solution from 4 mL in experiments can cause measurement error. Furthermore, the right amount of fiber sample facilitated better mixing of the fiber sample with the bicarbonate solution. It was found in this experiment that a maximum fiber consistency of 3.5% based on the weight of dewatered fibers (not the weight of the dried fibers) and the volume of the bicarbonate solution of 4 mL will not affect the accuracy of the present method.

Effect of ionic strength

It was found that GC signal intensity can be increased when sodium chloride was added into the reaction solution. This is because the sodium ions facilitate the release of hydrogen ions from carboxyl groups in fibers [3]. Furthermore, the solubility of carbon dioxide in the solution may be reduced due to the addition of salt. Therefore, the detecting sensitivity for the present method can be improved with the addition of sodium chloride. However, it was found that the detection sensitivity reaches a constant level after the concentration of sodium chloride reaches 0.1 mol/L as shown in Fig. 3. Therefore, the standard bicarbonate solution used in the present study contains 0.1 mol/L of sodium chloride.

Measurement precision

The reproducibility tests of the present method were conducted using five 0.030 g of fiber sample A, five 0.075 g of fiber sample B, and five 0.05 g of fiber sample C. These fiber samples were air-dried after acid pretreatment using hydrochloric acid solution. Table I lists the measured GC detector signal peak areas of the measurements for the two samples. The results show that the relative standard deviations of two separate sets of experiments with fiber sample A and B are less than 4.0% without nitrogen purge of the air in the headspace of the testing vial. It was found that the precision of the method was greatly improved when reaction and measurement were performed in air-free testing vials using air-dried fiber sample C where the effect of carbon dioxide in the ambient air can be eliminated to reduce one more source of error in Eq. (7). A relative standard

deviation of less than 1% was achieved with nitrogen purge of the testing vial before usage when a fiber sample C was used as shown in Table I. The results shown in Table I indicate the excellent reproducibility of the present method.

Table I. Reproducibility of the present PRC-HSGC method

Replica	GC Detector Signal, *Peak Area*		
	Sample A* (0.03 g)	Sample B* (0.075 g)	Sample C† (0.05 g)
1	49.9	120.5	22.2
2	49.4	127.8	22.3
3	53.9	126.9	22.6
4	51.4	130.3	22.2
5	53.2	131.4	22.2
Mean	**51.6**	**127.4**	**22.2**
RSTD	**3.83%**	**3.34%**	**0.78%**

* without N_2 purge and † with N_2 purge of the testing vials

Method comparison

The carboxyl groups in eight fiber samples from kraft pulping and different bleaching processes were determined by both the present method and a reference method. The reference method is based on acid-base titration described in the experimental section. The comparison results of the measured carboxylic acid groups contents in these fiber samples are listed in Table II. The results indicate that good agreement between the two methods was obtained with the relative differences for 5 samples less than 1% and maximum relative difference is within 9%. The standard deviations of the two methods of 4% for the present method and 8% for the titration method well explains the difference between the two methods. The comparison results indicate the validity of the present method. Since both methods rely on acid-base neutralization chemistry to ascertain carboxylic acid groups, the fundamental measurement criterion is the same, but they differ on the manner in which the data is collected. The standard titration method is conductometric in nature, meaning that it relies on ionization step changes that are plotted in two dimensions, and the neutralization point must be discriminated in the two dimensions, leading to errors approaching 5-10%. However, this new method relies on measurement of the carbon dioxide resulting from a decarboxylation reaction that is carried to completion. Its precision is certainly better since the only error would be in the conversion efficiency of the decarboxylation, since HSGC is already known from our work to have a high level of accuracy in measuring infinitesimal levels of analytes.

CONCLUSIONS

A novel method for the determination of carboxylic acid groups content in fibers using HSGC technique has been developed. The method is based on the conversion of carboxylic acid groups into carbon dioxide through the reaction with bicarbonate after wood fiber treatment with hydrochloric acid solution. The carbon dioxide is then measured by HSGC using TCD. The conversion reaction was conducted at 60°C in a headspace testing vial. A constant conversion fraction was achieved about 10 minutes into the reaction process. The contribution to GC detector signal from carbon dioxide formed by residual hydrochloric acid on wood fibers can be corrected through calibration. The effect of carbon dioxide in the headspace of the testing vial air can be quantified through headspace measurements or eliminated by purging the testing vial using nitrogen before experiment. The measured contents of carboxyl groups in 8 wood fiber samples were in good agreement with those measured by a titration method. In addition, the present method is rapid and automated.

Table II. Comparisons of the contents of carboxyl groups in 8 fiber samples measured by the present PRC-HSGC method and those by a conductivity titration method using a standard sodium hydroxide solution.

Sample	Content of carboxyl groups in fibers (mmol/g)		
	PRC-HSGC	Titration	Relative Difference (%)
1	0.0789	0.0786	0.35
2	0.0682	0.0739	-7.71
3	0.0413	0.0415	-0.57
4	0.0695	0.0694	0.04
5	0.0815	0.0755	8.01
6	0.0611	0.0610	0.10
7	0.0225	0.0241	-6.87
8	0.0577	0.0581	-0.69

About 0.1 – 0.25 gram of fiber samples (30% consistency) after acidic treatment were accurately weighted for each measurement.

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