Accurate determination of fiber water-retaining capability at process conditions by headspace gas chromatography

Shu-Xin Zhang [a], Xin-Sheng Chai [a,b,*], Liang He [a]

[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

ABSTRACT

This work reports on a method for the accurate determination of fiber water-retaining capability at process conditions by headspace gas chromatography (HS-GC) method. The method was based the HS-GC measurement of water vapor on a set closed vials containing in a given amount pulp with different amounts of water addition, from under-saturation to over-saturation. By plotting the equilibrated water vapor signal vs. the amount of water added in pulp, two different trend lines can be observed, in which the transition of the lines corresponds to fiber water-retaining capability. The results showed that the HS-GC method has good measurement precision (much better than the reference method) and good accuracy. The present method can be also used for determining pulp fiber water-retaining capability at the process temperatures in both laboratory research and mill applications.

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1. Introduction

Fiber water retaining, i.e., the capability for absorbing water, is an important property for papermaking process. Because the nature of fiber cell wall is modified when absorbing water, it improves the bonding between the fibers and thus the paper strength [1]. Moreover, the swollen fibers (due to water absorption) become plastic which can affect the degree of fiber fibrillation, efficiency of water removal [2,3], product quality [4,5], production rate, and consumption of energy during papermaking process [6]. Therefore, it is highly desired to have a method that can accurately determine the fiber retention capability at the process temperature conditions in both laboratory research and mill applications.

Currently, the fiber water retaining capability is commonly evaluated by a water retention value (WRV) measurement (based on centrifugation and weighing) in mill practice [7]. The major problem is that there is a large uncertainty in the sample centrifugal step, which could be affected by a number of factors such as the sample weight, centrifuge time and force, pore size of filters used in the measurement setup, and cellulosic or fibril sizes [8]. Moreover, the method is not suitable to be used for measuring the fiber WRV at elevated temperatures [7].

The fiber water retaining capability can be also evaluated by measuring the fiber saturation point, based on solute exclusion [9,10]. In this method, a number of sugars with different molecule sizes (e.g., xylans and dextrans) are used as the porous probe molecules. By measuring concentration changes for these sugar solutions, the amount of accessible and inaccessible water can be estimated [10,11]. This method is very complicated and time-consuming because the contents of these sugar compounds in the resulting solution must be pretreated and then quantified by various instruments, e.g., high performance liquid chromatography [12]. Similar to the WRV method, this fiber situation point method is operated at a room temperature condition, otherwise the leached species (lignins and sugars) from pulps due to high temperature can significantly affect the results in the sugars' quantification [13]. As the fiber water retaining capability at the process conditions is more interested in mill operation [13–16], it is important to develop a method that is suitable to do the testing at the elevated temperatures.

Headspace gas chromatography (HS-GC) is an effective technique to analyze the volatile species in the samples having complex matrices [17]. A distinguishing advantage of HS-GC is that it can perform an *in-situ* measurement at a precisely controlled temperature. In a previous work, we developed a HS-GC method for determining the water content in pulp and paper sheet, based on measuring the water vapor released from the sample at 105 °C [18]. Because of the bounding force between the water and fiber surface, the water vapor pressures (at the temperatures below water

* Corresponding author at: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China.
E-mail address: xschai@gmail.com (X.-S. Chai).

boiling-point) between the water absorbed by fibers and the free water should be different. Thus, it is expected that a significant change in water vapor pressure after the amount of water hold in pulp fibers is saturated, i.e., greater than its fiber saturation point. Therefore, by HS-GC measuring the water vapor pressure change for the pulp sample before and after the water saturation, a transition point, corresponding to the fiber water retaining capability, can be observed.

In this paper, we present a novel HS-GC method for determining the water retaining capability of pulp fibers. The major focuses were on the establishment of the methodology, and the selection of the conditions for the phase equilibrations during the testing. The method precision and accuracy were also evaluated.

2. Experimental

2.1. Samples

All pulps were purchased from the manufacture sources in China.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automated headspace sampler (Thermo HS TriPlus 300, US) and a GC system (Agilent GC 7890A, US) equipped with a thermal conductivity detector (TCD) and GS-Q capillary column with an i.d. of 0.53 mm and a length of 30 m (J&W Scientific, USA) operating at a temperature of 105 °C with nitrogen carrier gas (flowrate = 3.8 mL/min). Headspace operating conditions were as follows: 30 min of strong shaking to allow sample equilibration at the temperature of interest, pressurization pressure = 1.00 bar, carrier gas pressure = 1.50 bar, vial pressurization time = 15 s, sample loop fill time = 10 s, and transfer time = 20 s. The volumes of the sample loop and the headspace sample vials used in the test were 3 mL and 21.6 mL, respectively.

2.3. Procedures in sample preparation and measurement

The sample preparation and measurement procedures were as follows: Weight 0.200 g of pulp sample into a set of headspace sample vials (20 mL), then add the different quantities of distilled water in these vials. The vials were sealed and placed in a water bath for 60 min to equilibrate the water absorption in pulp fibers at the desired temperature. After that, the vials were placed in the headspace sampler tray for automatic HS-GC measurement.

3. Results and discussion

3.1. Principle of the method

For a pulp sample placed in a closed vial, the fiber-absorbed water partitioning coefficient (K_0) between the vapor-solid (fiber) phase before the saturation point can be described as

$$K_0 = \frac{C_s}{C_g} \tag{1}$$

where all symbols are defined in Table 1.

The total mass of water in the closed vial can be written as

$$m_w = m_s + m_g = C_s w + C_g V_g \tag{2}$$

Merging Eqs. (1) with (2) and making an arrangement, we have

$$C_g = \frac{m_w}{K_0 w + V_g} \tag{3}$$

Table 1
Symbols and definitions.

Symbols	Definition
K_0	partitioning coefficient
C_g	concentration of water in the vapor phase
C_s	concentration of water in the pulp fibers
m_w	the mass of water added in the vial
m_s	the mass of the water in the pulp fibers
m_g	the mass of the water in the vapor phase
w	the mass of the pulp fibers in the vial
V_g	the volume of the vapor phase
A	GC signal
ΔH_m	enthalpy of vaporization
a	integration constant
b	coefficient
f	response factor of HS-GC signal to water content
S_1	coefficient
T	temperature in the vial
P	saturated vapor pressure of liquid
R	gas constant
T	equilibrium temperature

Since the GC signal is linearly proportional to the concentration of the water content in the headspace, i.e., $A = fC_g$ [17], Eq. (3) can be expressed as

$$A = \frac{fm_w}{K_0 w + V_g} = S_1 m_w \tag{4}$$

with

$$S_1 = \frac{f}{K_0 w + V_g} \tag{4-1}$$

It can be seen from Eq. (4) that the GC signal for the water content in the headspace (corresponding to the water vapor pressure) is proportional to the amount of water added in the vial. Until the amount of water added is greater than the fiber saturation point, Eqs. (3) and (4) are no longer valid. At this time, the water content in the headspace is mainly contributed by the amount of free (or excess) water because the fiber surface is fully covered by the free water. According to Claperon-Clasius Equation [19], the vapor pressure change of a solvent is proportional to the temperature change, i.e.,

$$\frac{d\ln P}{dT} = \frac{\Delta H_m}{RT^2} \tag{5}$$

Integrating Eq. (5) to have

$$P = e^{a - \frac{b}{T}} \tag{5-1}$$

According the Ideal Gas Law [19], the water vapor pressure is proportional its content, i.e.,

$$P = C_g RT \tag{6}$$

Merge Eqs. (5-1) with (6) to have

$$C_g = \frac{1}{RT} e^{a - \frac{b}{T}} \tag{7}$$

and thus the GC signal in the headspace measurement after fiber water saturation point can be written as

$$A = \frac{f}{RT} e^{a - \frac{b}{T}} \tag{8}$$

Eq. (8) indicates that the GC signal for the water vapor is constant at the given temperature, once the headspace vial contains the free water.

Therefore, by plotting GC signal for the water content in headspace vs. the amount of water added to the pulp fibers before and after saturation, a transition point that corresponding to the fiber water retaining capability can be determined.