



Short communication, Sample Preparation

A novel method for rapid determination of total solid content in viscous liquids by multiple headspace extraction gas chromatography

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ABSTRACT

This work demonstrates a novel method for rapid determination of total solid content in viscous liquid (polymer-enriched) samples. The method is based multiple headspace extraction gas chromatography (MHE-GC) on a headspace vial at a temperature above boiling point of water. Thus, the trend of water loss from the tested liquid due to evaporation can be followed. With the limited MHE-GC testing (e.g., 5 extractions) and a one-point calibration procedure (i.e., recording the weight difference before and after analysis), the total amount of water in the sample can be determined, from which the total solid contents in the liquid can be calculated. A number of black liquors were analyzed by the new method which yielded results that closely matched those of the reference method; i.e., the results of these two methods differed by no more than 2.3%. Compared with the reference method, the MHE-GC method is much simpler and more practical. Therefore, it is suitable for the rapid determination of the solid content in many polymer-containing liquid samples.

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1. Introduction

Total solid content is a measure of the combined content of non-volatile inorganic and organic substances contained in a liquid medium. Because total solid content is used in a wide range of scientific and technical areas, it is an important parameter in process and product quality control.

Traditionally, total solid content is simply measured by gravimetry [1], in which the water in samples is removed by evaporation at a temperature above the boiling point of water. By weighing the sample mass before and after drying, the amount of water loss can be obtained, and thus the total solid content of the sample can be calculated as the difference in the weight of the sample before and after the evaporation of the water. However, when the liquid samples contain significant amount of polymers, such as polymer latex and black liquor (pulping spent liquor, containing a significant amount of natural polymers), some precautions must be taken in the sample preparation [2,3]. For example, rapid water evaporation at high temperature can lead to the formation of a “peel” or “shell” on the surface of the sample during the drying process, forming a barrier that resists further removal of the water, a situation which can cause a significant error in the total solid content measurement.

In the case of black liquor, the sample must be well mixed with fine sand before heating (to increase the evaporation surface), and the drying process must be performed at 105 °C, a “moderate” temperature for at least 6 h [3]. Clearly, these procedures make the testing not only complicated but also very time-consuming.

Headspace gas chromatography (HS-GC) is an effective tool for determining volatile organic compounds (VOCs) in samples that have complicated matrix [4]. Equipped with a thermal conductivity detector (TCD), it can also be used to determine water content. Many commercial headspace auto-sampler systems can perform sample equilibration in a precisely temperature-controlled oven with a strong shaking mode. In addition, they can also obtain multiple headspace extraction (MHE) measurements on a given sample vial, in which the vapor phase is partly released as pressurized gas at each extraction. The strong shaking of the vial and partial removal of the vapor phase minimizes the formation of a “peel” or “shell” on the surface of the sample during the drying process. Since the time-course of water loss is recorded by MHE-GC, the complete water removal from sample can be extrapolated from the data measured during the relatively short period of the MHE process [4], resulting in a big saving of time. Therefore, we believe that MHE-GC could become an efficient method for the determination of total solid content of many polymer-containing samples.

The objective of the present study is to demonstrate a novel method for the determination of total solid content in polymer-containing liquid samples, based on a MHE-GC method. The work

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focuses on introducing the methodology and discussing the effect of the sample size, temperature, and mode of water removal from the vial on the water content measurement. As a specific application, black liquor samples with different total solid contents were measured by the present method and compared to results obtained by the reference method.

2. Experimental

2.1. Samples

The black liquor sample was obtained from a kraft pulp mill in southern China, and the liquor concentrating by evaporation was conducted in the laboratory. Liquors with different evaporation extent were obtained. Their total solid contents were determined by a reference method, TAPPI standard [3], i.e., the specimen is dried at 105 °C for a minimum of 6 h with inert surface extender and a controlled flow of dried air to increase drying rate and eliminate moisture entrapment. For the concentrated black liquors, they must be diluted to allow volumetric handling and to reduce scum formation.

2.2. Apparatus and operations

A GC system (Agilent GC 7890A, USA) and an automatic headspace sampler (DANI HS 86.50, Italy) were used for HS-GC measurement. The GC system was equipped with a thermal conductivity detector (TCD) and a 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. The headspace operating conditions were as follows: strong shaking for the sample vial at the temperature of 125 °C; vial pressurization time = 0.2 min; and sample loop fill time = 0.2 min. The volume of the headspace sample vials were 21.6 mL.

2.3. Measurement procedures

About 0.50 g of a liquor sample was added into an empty headspace vial. By weighing the vial (including a PTFE/butyl septum and aluminum) before and after sample addition, the exact weight of the sample was determined. The sample vial was immediately sealed. The vial was equilibrated at 125 °C in the headspace sampler and allowed to proceed with a MHE-GC measurement at an interval time of 5 min. After testing, the vial was weighed again. The difference of the weights before and after MHE measurement represents the amount of water loss in the experiment. Accordingly, the GC signals (peak area) of water measured by GC at each headspace extraction were recorded.

3. Results and discussion

3.1. Profile of water loss of the tested sample during MHE

According to the partitioning equilibration, the content of water in the vapor phase is a function of the content of water in the liquid phase, i.e.,

$$C_G = KC_L \quad (1)$$

where K is a partitioning coefficient of water between vapor and liquid phase and C_L is the water content in the samples. Since the GC signal in the headspace measurement is proportional to the amount of water vapor (i.e., $A = kC_G$) and C_L is proportional to the mass of water (m_w) in sample, Eq. (1) can be written as:

$$A = km_w \quad (2)$$

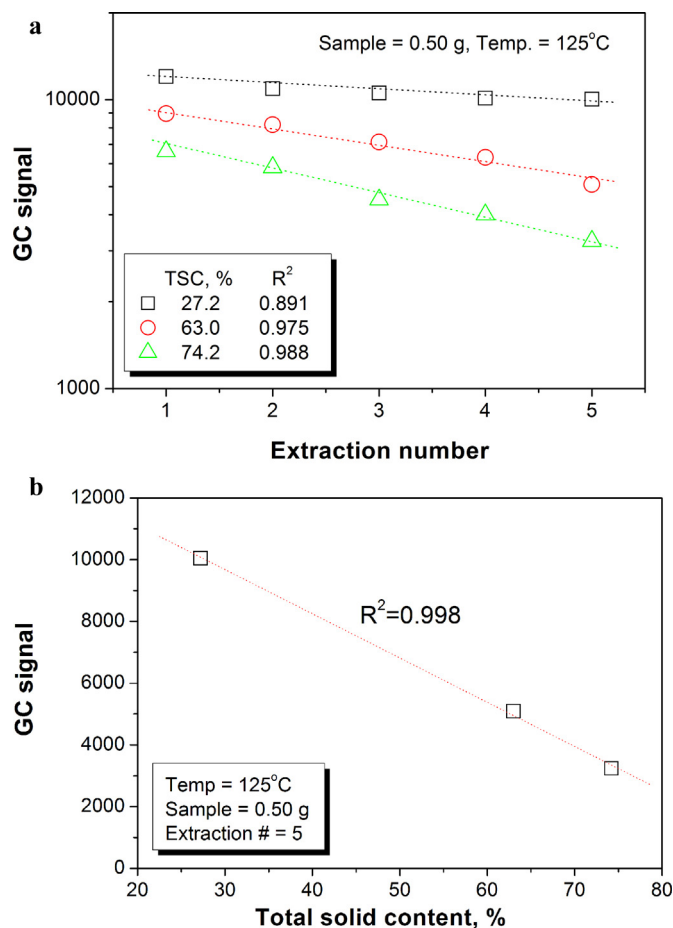


Fig. 1. (a) Profiles of water removal during MHE; (b) the relationship between the GC signal and the total solid content of samples at the 5th headspace extraction.

As shown in Fig. 1a, the amount of water loss during the MHE is exponentially decreased at the given conditions. Therefore, the relationship between the amount of water in the vial (m_w) and MHE number (n) can be written as,

$$\log(A) = a' - bn \quad (n = 0, \dots, i) \quad (3a)$$

or

$$\log(m_w) = a - bn, \quad (3b)$$

in which

$$a' = \log(A_0) \quad \text{or} \quad a = \log(m_w^0) \quad (\text{when } n = 0) \quad (3c)$$

and

$$t = qn \quad (3d)$$

where t represents the equilibration time, and q is the interval of time between two adjacent headspace extractions. Therefore, the complete water removal from the tested sample can be predicted with the limited headspace extraction according to Eq. (3a) or (3b).

It is also seen from Fig. 1a that for the given sample weight (0.50 g), the water removal is quicker for the sample with high total solid content, which also means the trend of water loss is slow if the tested sample contains more water. Fig. 1b shows the GC signal

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