Journal of Chromatography A, 1443 (2016) 62–65

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Rapid determination of moisture content in paper materials by multiple headspace extraction gas chromatography

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ARTICLE INFO

Article history:
Received 7 February 2016
Received in revised form 20 March 2016
Accepted 21 March 2016
Available online 24 March 2016

Keywords:
Moisture content
Multiple headspace extraction
Gas chromatography
Paper materials

ABSTRACT

This paper describes a new method for the rapid determination of the moisture content in paper materials. The method is based on multiple headspace extraction gas chromatography (MHE-GC) at a temperature above the boiling point of water, from which an integrated water loss from the tested sample due to evaporation can be measured and from which the moisture content in the sample can be determined. The results show that the new method has a good precision (with the relative standard deviation <0.96%), high sensitivity (the limit of quantitation = 0.005%) and good accuracy (the relative differences <1.4%). Therefore, the method is quite suitable for many uses in research and industrial applications.

1. Introduction

The moisture content in paper materials can affect many physical properties of paper (such as stiffness, smoothness, and tensile strength), which are important to the performance of the products in their applications [1]. Therefore, analytical methods that can efficiently and accurately determine the moisture content in the paper materials and products play an important role in process control and optimization of industrial applications.

Two approaches have been traditionally used for measuring the moisture content in paper materials; i.e., the oven-drying method and the toluene distillation method [2]. In the oven-drying method, the moisture content of the sample is obtained by simply measuring the weight loss of the sample before and after drying at 105 °C for >6 h. Because other volatile substances (e.g., residual monomers in the coating chemicals) are also removed during the drying process, the moisture content of the sample can be easily overestimated. In the distillation method, toluene is used as a solvent to carry water out of the paper materials. Since there are two phases (i.e., organic and water phases) that clearly separate in the collected condensate, the amount of water can be measured. Although any volatile substances present in the paper have no effect on this distillation method, a significant amount of paper material (500–1000 g) is required in order to achieve the desired accuracy for the measurement. Moreover, toluene is a toxic, flammable chemical, and safety measures must be taken to protect the operators during the process.

In more recent years, instruments such as near infrared spectroscopy (NIR), microwave moisture meter and gas chromatography (GC), have been used to quantify the moisture content in various types of samples [3–5]. The major problems with the NIR and microwave techniques are the precision and accuracy of the moisture content measurement, especially for samples with complicated matrices. In the GC method, a sample extraction pretreatment, using a water-soluble organic solvent (e.g., methanol or ethanol) is required. Therefore, the method is complicated, time-consuming and can easily introduce significant errors in the pretreatment stages.

Headspace gas chromatography (HS-GC) is an effective technique for analyzing volatile species in liquid samples that have complicated matrices [6]. However, the conventional HS-GC analysis is difficult to use for the determination of water content in solid samples because the vapor-solid partitioning of water varies among samples with different matrices, which introduces difficulties in the calibration of the method. Moreover, an internal standard calibration method is not suitable for the solid materials because it has a difficulty to spike a standard that can be evenly distributed in the sample.

Multiple headspace extraction (MHE) [6,7] (i.e., repeatedly analyzing (in a stepwise fashion) the vapor phase in a given sample vial is now available in many commercial headspace auto-samplers. In each headspace extraction, the vapor phase (which includes the analyte(s)) is partly removed from the vial for GC testing. If the analyte in the sample is nearly completely vaporized from the vial,

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http://dx.doi.org/10.1016/j.chroma.2016.03.059
0021-9673/

the total amount of analyte can be determined by integrating its contents during MHEs. In this way, the sample matrix effect is no longer a problem.

The objective of the present study is to develop a MHE-GC method for rapidly determining the of moisture content of paper materials. The major foci in this work were to establish the MHE-GC methodology and explore the preferred conditions, such as the headspace equilibration temperature, the extraction interval time, the number of extractions and the sample size. The precision and accuracy of the method were also evaluated.

2. Experimental

2.1. Samples

The coated paper samples were collected from several laboratories and manufacturers in China. The moisture contents in these samples were determined by the TAPPI standard over-drying method [2].

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 (flow rate = 3.8 mL/min). 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 each headspace sample vial was 21.6 mL.

2.3. Measurement procedures

About 0.50 g of a coated paper sample was placed in an empty headspace vial. By weighing the vial (including a PTFE/butyl and aluminum septum) before and after sample addition, the exact weight of the sample was determined, after which 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. The GC signal (peak area) of water measured by GC at each headspace extraction was recorded.

3. Results and discussion

3.1. Methodology

When a paper sample is placed in a container (headspace vial) and heated at an elevated temperature, some of the water in the paper sample is transfered to the vapor phase. Because the container is completely sealed, a phase equilibrium is established between the water in the vapor phase and the water remaining in the paper, described by vapor-solid partitioning coefficient (K_d);

$$K_d = C_s/C_g \tag{1}$$

where C_s (g/g) and C_g (g/mL) are, respectively, the concentration of water in the solid sample and in the vapor phase at the equilibrium.

In a headspace vial that contains a paper sample, the amount of water can be expressed as:.

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

where m_w (g) is the total amount of water in the original sample. w and V_g are, respectively, the weight (g) of the paper and the volume (mL) of the vial (assuming that the volume of the solid sample is negligible). Merging Eqs. (1) and (2), we have, at equilibrium,

$$m_w = \left(K_d w + V_g\right) C_g \tag{3}$$

where the vapor-solid partitioning coefficient (K_d) is a parameter that is characteristic of a particular type of paper, reflecting differences in the specification and processing approaches used in making different kinds of paper.

In the multiple headspace extraction (MHE) process, the amount of water extracted from the sample in each headspace extraction can be expressed as [8,9]

$$\Delta m = \varphi C_g V_g \tag{4}$$

where φ is the volume ratio constant of headspace sampling [8].

The total amount of water in the original sample is the sum of water extracted out of the sample vial; i.e.,

$$m_w = \Delta m_1 + \Delta m_2 + \ldots + \Delta m_n = \sum_{1}^{n\to\infty} \Delta m_i \tag{5}$$

According to Eqs. (4) and (5) and the relationship between the GC signal (A) and C_g; i.e., $C_g = kA$, we can obtain

$$m_w = \sum_{1}^{n\to\infty} \Delta m_i = K \sum_{1}^{n\to\infty} A_i \tag{6}$$

where $K = \varphi k V_g$.

The relationship between the GC signal A and its extraction number in MHE can be described as [6]

$$\log(A_n) = \log(A_0) - bn \tag{7}$$

or

$$\frac{A_n}{A_0} = 10^{-bn} \tag{8}$$

where b is a ratio constant of the headspace extraction.

Assuming that

$$10^{-b} = q \tag{8-1}$$

Eq. (8) can be written as

$$q = \frac{A_1}{A_0} = \frac{A_2}{A_/} = \ldots = \frac{A_n}{A_{n-1}} \quad (q < 1) \tag{9}$$

According to Eq. (9) and the approximation of infinite series, the integrated GC signal in the MHE can be expressed as

$$\sum_{1}^{n\to\infty} A_i = A_1 + A_2 + \ldots A_n = A_1 + A_1 q + \ldots + A_1 q^{n-1} = \lim_{n\to\infty} \frac{A_1(1-q^n)}{1-q} = \frac{A_1}{1-q} \tag{10}$$

Substituting Eq. (10) to Eq. (6), we have

$$m_w = K \frac{A_1}{1-q} \tag{11}$$

Since the ratio constant b in Eq. (7) is experimentally obtained by the MHE measurement, the total amount of water in the sample can be determined. Thus, the moisture content in the sample can be calculated by

$$C_w = \frac{m_w}{w} \times 100\% \tag{12}$$

where C_w is the moisture content in the sample and w is the sample weight.