A novel solvent-assisted vapor absorption based headspace analysis technique for the determination of diffusion and solid–air partition coefficients of methanol in paper materials

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ABSTRACT

A novel method has been developed for the determination of the diffusion (D) and solid–air partition (K_d) coefficients of methanol in paper materials. The method used a solvent-assisted vapor absorption based headspace analysis technique to increase the driving force of the mass transfer process in the solid phase. Equations based on the established physical models described the process allowed the calculation of D and K_d of methanol in paper materials from the GC signals and experimental settings. The results showed that the amount of methanol transferred from the paper sheet can be significantly increased by the presence of the assisting triacetin. The solvent-assisted vapor absorption equilibrium can be obtained in 20 min. The method also generated equations allowing for the calculation of D and K_d of methanol in paper materials at any temperature. The present method is simpler and quicker than the chamber methods that are in widespread use today and should be of special interest to those concerned about the impact of food and beverage packaging on human health.

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1. Introduction

The intake of methanol (MeOH) is harmful to the human body due to its toxic metabolites; i.e., formaldehyde and formic acid [1–2]. Therefore, the methanol content in any potential source of human exposure, such as food, drinking water, and air in the workplace, are strictly regulated [3–6]. Recently, it was found that there is a significant amount of methanol entrapped in pulp and in final paper products [7–8]. The methanol in paper-based materials can migrate to foodstuffs through both direct contact and indirect contact; i.e., through the air, due to its volatility. Therefore, a potential risk to human health exists when paper-based materials are used in packaging.

Some techniques for paper surface treatment, such as sizing and coating, act as a barrier to limit the migration of methanol from paper materials. However, the effectiveness of these treatments on methanol mass transfer has not been evaluated. In addition to the initial methanol content in the paper, the mass transfer of the methanol is determined by two key parameters; i.e., the diffusion coefficient (D) and the solid–air partition coefficient (K_d) [9]. Therefore, it is important to determine these coefficients of methanol in the paper materials with different surface treatments in order to accurately assess the risk to human health posed by the use of these paper products in food packaging.

Several methods have been used for the determination of D and K_d of analyte(s) in packaging and building materials [10–13] based on chamber [14–18] and microbalance [19–20] approaches. In the chamber methods; e.g., dual-chamber and dynamic chamber, the time-dependent profiles of the concentration of the analyte in the chambers are recorded, from which D and K_d can be obtained by fitting the experimental data to established models [14–18]. In the microbalance methods, the amount of volatile analyte emitted is determined by the real-time detected weight loss of the samples. Here again, D and K_d are determined by fitting the experimental data to various models [19–20]. The major problem with these methods is that they employ custom-designed devices, which present difficulties when comparing results from different labs or applying for the method standardization.

Headspace measurement based gas chromatography (HS-GC) is an effective technique for analyzing volatile species in complicated matrices, including solids. There are many commercialized headspace auto-sampler systems available, in which the

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Nomenclature

A_1, A_2, A_3	The GC peak area of the three measurements, respectively
C_g^1, C_g^2, C_g^3	The methanol concentration in the vapor phase of the three measurements, respectively (μg/mL)
C_s^i, C_g^i, C_l^i	The methanol concentration on the solid, vapor and liquid interface, respectively (μg/mL)
C_s, C_g, C_l	The methanol concentration in the solid, vapor and liquid phase, respectively (μg/mL)
D	The diffusion coefficient (cm^2/h)
h	The thickness of the paper sheet (cm)
K_d, K	The dimensionless partition coefficient of solid–air and liquid–vapor phases, respectively
m_0	The initial mass weight of methanol in the paper sample (μg)
m_s, m_g, m_l	The mass weight of methanol in the solid, vapor, and liquid phase, respectively (μg)
S	The surface area of the paper sheet (cm^2)
t	The mass transfer time (h)
V_s, V_g, V_l	The volume of the solid, vapor, and liquid phase, respectively (mL)
V_g^1, V_g^2, V_g^3	The volume of vapor phase of the three measurements, respectively (mL)
α	The coefficient of Eq. (A.1) (h^{-1})
β	The coefficient of Eq. (A.1) (mL)

headspace sample vial can be regarded as a chamber and its temperature can be precisely controlled. In previous studies [21–24], a number of methods have been developed, based on HS-GC analysis, for the determination of the partition coefficients in systems in which the mass transfer rates are mainly partition-controlled; e.g., analyte(s) equilibrated between vapor phase and aqueous phase or between vapor phase and surface-absorbing solid phase. For the study of the mass transfer behavior of volatile analyte(s) in the diffusion-controlled systems; e.g., in the packaging or building materials, both diffusion coefficient and partition coefficient need to be considered. Although the conventional HS-GC method can be employed to monitor the mass transfer process, it is not suitable for the systems in which the release of the volatile species is very slow [7].

According to the Fick's first law [25] i.e.,

$$J = D\frac{dC}{dx} \tag{1}$$

The mass transfer flux (J) from the sample matrix can be increased by raising the temperature (affecting the diffusion coefficient (D)) and/or increasing the concentration difference of the analyte(s) (i.e., dC) between the bulk solid phase and the solid interface (dx). In the closed headspace sample vial, the driving force (dC) at a given temperature is reduced by the increasing concentration of volatile species in the vapor phase. Therefore, reducing the concentration of the analyte in the vapor phase will increase its mass transfer from the tested matrix. We believe that the reduction of the analyte in the vapor in the vial can be realized by using a solvent (i.e., the "assisting solvent") to absorb the gaseous species in the system. Because much more amount of analyte(s) can be transferred out from the studied material if a vapor absorption trapper is placed in the system, the measurement accuracy for these coefficients (based on the diffusion model [26–28]) could be greatly improved.

In this paper, we report on such a solvent-assisted vapor absorption based HS-GC method for simultaneously determining the diffusion and solid–air partition coefficients of methanol in paper materials. The main focuses are on (a) the derivation of the equations for calculating D and K_d and (b) the selection of the optimal conditions for the methanol release. The D and K_d of methanol in several commercial paper samples are determined by the new method and presented as a demonstration of the utility of the method.

2. Experimental

2.1. Chemicals and materials

All chemicals, including methanol and triacetin, were analytical grade and purchased from commercial sources without further purification. Two sets of standard methanol solutions with concentrations ranging from 0 to 79.2 ppm (as mg/L) were prepared by diluting the pure methanol (>99.5% w/w) with appropriate amounts of distilled water and pure triacetin (>99.5% w/w), respectively.

The paper samples, including base-paper sheet, coated paper sheet, cup paper, bowl paper and cigarette wrapping paper, were purchased from commercial sources.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automated headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US) equipped with a flame ionization detector and a DB-5 capillary column, operating at a temperature of 30 °C with nitrogen carrier gas (flow rate = 3.8 mL/min). Headspace operating conditions were as follows: 2 h and 1 h of strong shaking for the mass transfer at 60 °C, 70 °C and 80 °C, 90 °C, respectively; sample loop temperature = 105 °C; transfer line temperature = 10 °C; pressurization pressure = 2.00 bar; carrier gas pressure = 1.5 bar; vial pressurization time = 15 s; sample loop fill time = 10 s; and transfer time = 20 s.

2.3. Sample preparation

Fig. 1 is a schematic diagram of the system used in the present method. The test paper sheet (5×15 cm^2) was rolled and placed in a headspace sample vial (21.6 mL) that includes a small tube containing a desired volume of pure triacetin (as the solvent). The vial was immediately sealed with a PTFE/silicone septum and equilibrated conducted in the headspace instrument at the temperature of interest. The HS-GC measurement was performed at the desired time-length. In general, longer time (2 h) is required for the equilibration at lower temperatures (e.g., 60 °C) in order to
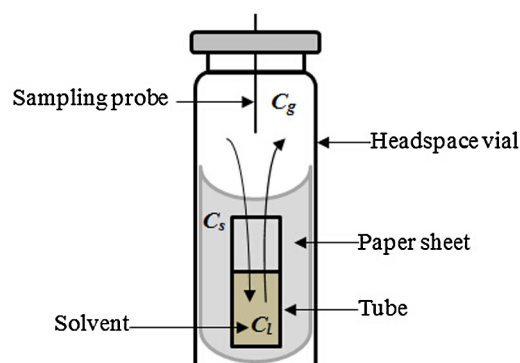

Fig. 1. The schematic diagram of the system for the present method.