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Thermogravimetric analysis for rapid assessment of moisture diffusivity in polydisperse powder and thin film matrices

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ABSTRACT

Accurate description of moisture diffusivity is key to precisely understand and predict moisture transfer behaviour in a matrix. Unfortunately, measuring moisture diffusivity is not trivial, especially at low moisture values and/or elevated temperatures. This paper presents a novel experimental procedure to accurately measure moisture diffusivity based on thermogravimetric approach. The procedure is capable to measure diffusivity even at elevated temperatures (> 70 °C) and low moisture values (> 1%). Diffusivity was extracted from experimental data based on "regular regime approach". The approach was tailored to determine diffusivity from thin film and from poly-dispersed powdered samples. Subsequently, measured diffusivity was validated by comparing to available literature data, showing good agreement. Ability of this approach to accurately measure diffusivity at a wider range of temperatures provides better insight on temperature dependency of diffusivity. Thus, this approach can be crucial to ensure good accuracy of moisture transfer description/prediction especially when involving elevated temperatures.

1. Introduction

Proper understanding of moisture transfer is essential to design and/or develop processes or products in food or pharmaceutical industries. An example of when moisture transfer becomes crucial is drying. Drying is widely implemented in foods and pharmaceutical industries e.g. to encapsulate sensitive ingredients such as enzymes (Perdana, Fox, Schutyser, & Boom, 2012; Zhang, Chen, Boom, & Schutyser, 2017), probiotics (Huang et al., 2016, 2017; Perdana et al., 2012; Perdana, Fox, Siwei, Boom, & Schutyser, 2014; Schutyser, Perdana, & Boom, 2012; Wang, Huang, Fu, Jeantet, & Chen, 2016; Zheng, Fu, Huang, Jeantet, & Chen, 2016), active pharmaceutical ingredients (Broeckx, Vandenheuvel, Claes, Lebeer, & Kiekens, 2016; Ubbink & Krüger, 2006), or simply to transform the products into powdered or dried form to improve product physical stability or to be used in further application (Putranto, Xiao, Chen, & Webley, 2011; Vuataz, 2002). Here, mastering moisture transfer can provide dramatic win to avoid e.g. process-related problems/stoppages or product quality issues (Carpin et al., 2016; Perdana, Fox, Boom, & Schutyser, 2015; Putranto, Chen, & Mercadé-Prieto, 2015; Schmitz-Schug, Gianfrancesco, Foerst, & Kulozik, 2013; Turchiuli, Gianfrancesco, Palzer, & Dumoulin, 2011).

Understanding and predicting drying processes require complete and accurate diffusivity data as function of moisture content and temperature. A small error in diffusivity value can contribute to large errors in the modelling of drying behaviour (Perdana, Aguirre Zubia, Kutahya, Schutyser, & Fox, 2015; Perdana, Fox, Schutyser, & Boom, 2013; Straatsma, Van Houwelingen, Steenbergen, & De Jong, 1999). Here, availability of diffusivity data at temperatures relevant to drying is of great relevance. Unfortunately, these data are often scarce. Scarcity of the data is likely due to limitation of the measurement techniques, either gravimetric method (Coumans, 1987; Gianfrancesco, Vuataz, Mesnier, & Meunier, 2012; Räderer, Besson, & Sommer, 2002; Yamamoto, 2001), nuclear magnetic resonance (NMR) spectroscopy (Jin et al., 2012; Marcone et al., 2013), fluorescence recovery after photo-bleaching (FRAP), or diffusion wave spectroscopy (DWS) (Weinbreck, Rollema, Tromp, & de Kruif, 2004).

In this paper we present a gravimetric technique to measure moisture diffusivity suitable for elevated temperatures. Thermogravimetric Analysis (TGA) was employed to establish a drying curve from which moisture diffusivity was extracted using the regular regime (RR) approach. According to Schoeber (1976), the regular regime can be defined as the period during unstationary drying after

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Nomenclature

a	power parameter to describe the diffusion coefficient dependency on water content, –
d_{10}	arithmetic mean diameter, m
d_{32}	surface-volume mean diameter, m
d_{43}	volume-moment mean diameter, m
d	density, kg m^{-3}
D	mutual diffusion coefficient of water in solute, $m^2 s^{-1}$
D_r	dimensionless (reduced) diffusion coefficient, –
D_a	apparent moisture diffusion coefficient in solute-fixed coordinate, $m^2 s^{-1}$
F	dimensionless flux parameter, –
L	characteristic length, m
m	concentration, kg m^{-3}
r	absolute distance coordinate, m
Sh_d	Sherwood number of the dispersed phase, –
t	time, s
T	temperature, °C or K
T_g	glass transition temperature, K
T_{iso}	isothermal heating temperature, °C
u	mass concentration on dry matter mass basis, kg kg dry-solid^{-1}
v	molar volume, m^3 $mole^{-1}$
w	weight
x	molar fraction, m $mole^{-1}$
X	dimensionless surface area, –
z	reference component mass-centered coordinate, –
Z	thickness of the thin film in complete dry condition, m

Greek symbols

η	Boltzmann parameter, –
λ	hollowness degree, –
υ	shape parameter, –
ϕ	dimensionless space coordinate, –
ρ	mass concentration, kg m^{-3}
τ	dimensionless time coordinate, –

Subscripts:

0	initial
end	final
m	moisture (water)
iso	isothermal
s	solid/solute
ss	surface

which the influence of the initial condition can be neglected, but during which the concentrations will still evolve. Thus, in this regime the drying behaviour can be regarded as an intrinsic property of the material, enabling the extraction of diffusivity (Coumans, 1987). The advantages of regular regime approach include the possibility to extract diffusivity values across wide moisture content values covered by the drying experiments. The RR approach was tailored to enable extraction of diffusivity from both thin film and (polydisperse) powder samples.

There is a large chance of error when residual moisture content is determined *off-line*. Error/shift in determining moisture content will stir systematic error in relating moisture diffusivity against moisture content. The impact of this error is magnified at low moisture content where moisture diffusivity becomes particularly sensitive to moisture values (Perdana, van der Sman, Fox, Boom, & Schutyser, 2014). In contrast, measurement with TGA enables an accurate *in-line* determination of moisture content from the sample (2010). This ensures that the moisture diffusivity is accurately correlated with the moisture content.

2. Materials and methods

2.1. Materials

Maltodextrin DE 17-19 (Cargill Deutschland GmbH, Germany, later referred to as “maltodextrin”) and native corn starch (Agrana Staerke GmbH, Austria, later referred to as “corn starch”) were used as received.

2.2. Sample preparation

Thin films were prepared by dissolving 20 g maltodextrin and 1 g agar in 79 g demineralised water. The mixture was allowed to boil in a heating plate. Then, the mixture was cast in a mould (to prepare a film with a thickness of 1 mm) and slowly cooled down to solidify at room temperature. It was reported that addition of agar has negligible effect on the diffusivity of water in the film (Coumans, 1987). Solidification with agar was reported to suppress moisture transfer due to convection (Räderer et al., 2002).

An aluminium crucible medium (100 µL volume, Mettler-Toledo, USA) and an aluminium piercing lid (Mettler-Toledo, USA) were weighed using an AX-205 balance (Mettler-Toledo, USA); recorded with 0.01 mg accuracy. Approximately 20 µg of powdered sample or thin film sample (cut into circular shape with diameter of 3.5 mm) was placed in the aluminium crucible. Then, the crucible was hermetically sealed with the aluminium piercing lid. The sealed crucible was re-weighed. Sample weight was thus determined as mass difference between the first and second weighing.

Sample crucibles were then placed in an auto-sampler turntable of Thermogravimetric Analysis-Differential Scanning Calorimetry (TGA-DSC1, Mettler-Toledo, USA). The auto-sampler was equipped with a piercing kit, which automatically pierced the crucible immediately before transferring the crucible into the TGA measuring cell.

2.3. Drying experiments in a thermogravimetric analysis

For this particular TGA apparatus, prior to sample measurement, a blank measurement should be carried out. An empty aluminium crucible medium was sealed with an aluminium piercing lid and weighed. Then, blank measurement was performed with the TGA method that will be applied to the samples.

The TGA method consists of three steps (see Supplementary Information):

1. Rapid ramp heating from ambient temperature to the desired isothermal heating temperature
2. Isothermal heating, from which the drying curve will be established. The isothermal heating temperatures (T_{iso}) were varied between 50 and 105 °C.
3. Second ramp heating for *in-situ* determination of residual moisture content at the end of the isothermal heating step. The procedure follows the method developed by Vuataz, Meunier, and Andrieux (2010).

During measurement, sample weight, sample temperature, and the involved heat-flow were recorded every second. Measurements were carried out in triplicate.