



Short communication

Extension of Golay plate height equation for open-tubular columns



Leonid M. Blumberg

Advachrom, P.O. Box 1243, Wilmington, DE 19801, USA

ARTICLE INFO

Article history:

Received 21 June 2017

Received in revised form 29 August 2017

Accepted 11 October 2017

Available online 12 October 2017

Keywords:

Plate height

OTC

PLOT columns

ABSTRACT

Golay plate height equation with its B-term equal to $2D_m/u$ (D_m is molecular diffusivity of a solute in the carrier gas and u is the gas velocity) has been developed for WCOT (wall-coated open-tubular) GC columns with liquid stationary phases. In a more general case of OTC (open tubular columns) such as the PLOT (porous layer open-tubular) columns and others, the B-term is $2(D_m + kD_s)/u$ (D_s and k are the solute net diffusivity in the stationary zone and the retention factor, respectively) which can be substantially larger than $2D_m/u$. A simple proof is provided together with other adjustments in Golay equation, and its interpretation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Golay pioneering plate height theory [1] was developed for WCOT (wall-coated open-tubular) GC columns in which a solute retention takes place in *absorptive* stationary film coating the internal wall of a column tubing. The theory did not address other currently important classes of OTC (open-tubular columns) such as the PLOT (porous layer open-tubular) ones in GC and LC, and others.

As Golay stated and as it is clear from the theory [1], it is “applicable [only] to columns of uniform cross-sections in which the input to exit pressure ratio is near unity”. Following the constraint in the original theory, the **uniform** (the same at any longitudinal locations) OTC and their operational conditions (temperature, mobile phase density, etc.) are assumed below. In addition to the *plate height* (the rate of increasing the variance, σ^2 , of a solute band within a column as a function of the distance, x , traveled by the solute along a column) Golay also evaluated the *dynamic diffusivity* [1] (the rate of increasing σ^2 as a function of time, t , traveled by the solute). If dt , dx and $d\sigma^2$ are the increments in t , x and σ^2 , respectively, and if D_m and k are the solute molecular diffusivity in the carrier gas and the retention factor, respectively, then [1]:

$$d\sigma^2 = \left(2D_{\text{eff}} + \frac{Cu^2}{1+k} \right) dt \quad (1)$$

$$d\sigma^2 = \left(\frac{B}{u} + Cu \right) dx \quad (2)$$

where

$$D_{\text{eff}} = \frac{D_m}{1+k} \quad (3)$$

$$B = 2D_{\text{eff}}(1+k) \quad (4)$$

where u is the gas velocity, and where D_{eff} and the quantities in parentheses of Eqs. (1) and (2) are, respectively, the *effective diffusivity* [2], the dynamic diffusivity and the plate height corresponding to a given solute in a given column. Together, Eqs. (3) and (4) yield:

$$B = 2D_m \quad (5)$$

At $u=0$, Eq. (1) becomes:

$$d\sigma^2 = 2D_{\text{eff}}dt, (atu = 0) \quad (6)$$

Let D_s be the solute diffusivity in the stationary phase [1]. A no-flow case of Eq. (6) in combination with $D_s=0$ highlights the relationship between D_m and D_{eff} in Eq. (3). Indeed, quantity $1/(1+k)$ in Eq. (3) is the fraction of the total solute amount that resides in the column open space filled with carrier gas. In the absence of flow, the longitudinal variance (σ_{open}^2) of that fraction increases with time as [3,4] $d\sigma_{\text{open}}^2 = 2D_m dt$. As the rest of the solute, i.e. its $k/(1+k)$ fraction, resides in the stationary phase where it does not diffuse ($D_s=0$), and as the equilibrium between the phases is continuously maintained, the net increment ($d\sigma^2$) in the variance (σ^2) of all solute material is $(1+k)$ times smaller than $d\sigma_{\text{open}}^2$. The relation of D_{eff} to D_m in Eq. (3) reflects this fact. This observation also suggests that, if D_s is comparable with D_m like can be D_s in porous layer of a PLOT column then D_{eff} can be substantially larger than $D_m/(1+k)$ in Eq. (3).

E-mail address: leon@advachrom.com

The main focus of this study is evaluation of parameter B in Eqs. (2) extended to OTC in general. A class of OTC for which the original theory [1] was not intended was the PLOT columns, although the original idea of the PLOT columns was proposed in the same work [1] as a way of increasing the amount of absorptive stationary phase without increasing the C-term in Eqs. (1) and (2) due to the slow diffusion in the phase. Later Golay developed an extension [5,6] to the plate height theory [1] accommodating the C-term to PLOT columns. However, the effect of the porous layer on the B-term was not considered.

The B-term evaluation in this report is based mostly on published material typically discussed in the context of the effect of the obstruction to molecular diffusion in packed LC columns [2,7–12]. It follows from the published material [2,9–13] that, when Eqs. (2) is extended to OTC in general, quantity D_{eff} in Eq. (4) for B can be expressed as:

$$D_{\text{eff}} = \frac{D_m + kD_s}{1 + k} \quad (7)$$

where D_s is the solute net diffusivity in the stationary zone [10,12,14–16] and k is the solute retention factor defined as the ratio:

$$k = \frac{m_s}{m_{\text{open}}} \quad (8)$$

of its amounts, m_{open} and m_s , in the open space and in stationary zone of OTC, respectively. In PLOT columns, the latter includes the solute amount in the porous layer pores.

Unfortunately, the known derivations of the relations leading to Eq. (7) are either sketchy and difficult to verify, or involve several sources, or when detailed and developed in one source [10,13], are too complex because the derivation of D_{eff} was just one of several topics of broader study of factors affecting the plate height in packed or other columns. On the other hand, when it targets narrower but more basic issue of the effect of D_s on the B-term in the plate height equation for OTC in general, the derivation can be substantially simplified.

The goals for this report are (a) to demonstrate that, generally, quantity D_{eff} in Eq. (4) for the local plate height in OTC is described by Eq. (7), (b) to provide a simple proof of that, (c) to rearrange other terms in Golay equation to make it directly suitable for a broad class of round-tubing OTC – the open-tubular columns with absorptive and adsorptive porous and non-porous wall coating.

2. Theory

2.1. Proof of Eq. (7)

Consider a uniform tube concentrically filled with two homogeneous media, 1 (internal) and 2 (external). If necessary to prevent the loss of the filling material, the tube can be sealed at both ends. The fills are uniform, and the filling materials cannot diffuse in each other or change in time or distance in any way. If another material, a solute, is (somehow) injected in the middle of the tube, its distribution between the two media might change with time (t) and with distance (x) along the tube.

Let

$$m = m_1 + m_2 \quad (9)$$

where $m_1 = m_1(x,t)$ and $m_2 = m_2(x,t)$ are the distance- and the time-dependent amounts of the solute per unit length in media 1 and 2, respectively, and let, as in Golay theory [1], the ratio:

$$k = \frac{m_2}{m_1} \quad (10)$$

(possibly different for different solutes) be *uniform* (independent of x), *linear* (independent of the total amount), and *time-invariant*

(independent of t). The effective diffusivity (D_{eff}) of the entire solute along the tube, i.e. the parameter D_{eff} in the second Fick's law of the longitudinal diffusion [17,18] in the tube:

$$\frac{\partial m}{\partial t} = D_{\text{eff}} \frac{\partial^2 m}{\partial x^2} \quad (11)$$

can be found from the mass balance equations for each media. Expressing quantities m_1 in m_2 as the fractions:

$$f_1 = \frac{m_1}{m}, f_2 = \frac{m_2}{m} \quad (12)$$

of the total helps to simplify the mass-balance equations.

Let D_1 and D_2 be the diffusivities of the solute in media 1 and 2, respectively, and suppose that the solute distribution between the media was prevented. The mass-balances in each media would be independent of each other and would be governed by the Fick's second law of diffusion:

$$\frac{\partial m_1}{\partial t} = D_1 \frac{\partial^2 m_1}{\partial x^2}, \quad \frac{\partial m_2}{\partial t} = D_2 \frac{\partial^2 m_2}{\partial x^2} \quad (13)$$

On the other hand, in the presence of the solute distribution between media 1 and 2, the net change, $\partial m_1(x,t)$ in $m_1(x,t)$ during a short time interval ∂t is the fraction f_1 of the sum of the diffusive changes in $m_1(x,t)$ and $m_2(x,t)$. Similarly, the net change, $\partial m_2(x,t)$ in $m_2(x,t)$ during the same time interval is the fraction f_2 of the same sum, i.e.:

$$\frac{\partial m_1}{\partial t} = f_1 \cdot \left(D_1 \frac{\partial^2 m_1}{\partial x^2} + D_2 \frac{\partial^2 m_2}{\partial x^2} \right) \quad (14)$$

$$\frac{\partial m_2}{\partial t} = f_2 \cdot \left(D_1 \frac{\partial^2 m_1}{\partial x^2} + D_2 \frac{\partial^2 m_2}{\partial x^2} \right) \quad (15)$$

In this section, the last two equations are the only ones that were introduced by reasoning. All preceding expressions were either the definitions or expressions of known physical relations, and the rest of the derivations is based on purely mathematical transformations.

Together with Eq. (9), Eqs. (14) and (15) yield:

$$\begin{aligned} \frac{\partial m}{\partial t} &= \frac{\partial m_1}{\partial t} + \frac{\partial m_2}{\partial t} = f_1 \cdot \left(D_1 \frac{\partial^2 m_1}{\partial x^2} + D_2 \frac{\partial^2 m_2}{\partial x^2} \right) \\ &+ f_2 \cdot \left(D_1 \frac{\partial^2 m_1}{\partial x^2} + D_2 \frac{\partial^2 m_2}{\partial x^2} \right) \end{aligned} \quad (16)$$

Accounting further for Eq. (12), one has:

$$\frac{\partial m}{\partial t} = f_1 \cdot \left(D_1 \frac{\partial^2 f_1 m}{\partial x^2} + D_2 \frac{\partial^2 f_2 m}{\partial x^2} \right) + f_2 \cdot \left(D_1 \frac{\partial^2 f_1 m}{\partial x^2} + D_2 \frac{\partial^2 f_2 m}{\partial x^2} \right) \quad (17)$$

$$\frac{\partial m}{\partial t} = (f_1 f_1 D_1 + f_1 f_2 D_1 + f_1 f_2 D_2 + f_2 f_2 D_2) \frac{\partial^2 m}{\partial x^2} \quad (18)$$

Comparison of the latter with Eq. (11) leads to conclusion:

$$D_{\text{eff}} = f_1 f_1 D_1 + f_1 f_2 D_1 + f_1 f_2 D_2 + f_2 f_2 D_2 \quad (19)$$

Due to Eqs. (10) (9) and (12), quantities f_1 and f_2 can be expressed as:

$$f_1 = \frac{1}{1+k}, f_2 = \frac{k}{1+k} \quad (20)$$

Substitution of these relations in Eq. (19) yields:

$$D_{\text{eff}} = \frac{D_1 + kD_2}{1+k} \quad (21)$$

According to Einstein theory of Brownian motions [3,4], this D_{eff} is the same as the one in Eq. (6). Therefore, in the context of OTC, the

Download English Version:

<https://daneshyari.com/en/article/7609729>

Download Persian Version:

<https://daneshyari.com/article/7609729>

[Daneshyari.com](https://daneshyari.com)