Moment theory for kinetic study of chromatography

Kanji Miyabe *

Department of Chemistry, Faculty of Science, Rikkyo University, 3-34-1, Nishi-Ikebukuro, Toshima, Tokyo 171-8501, Japan

ARTICLE INFO

ABSTRACT

It is required to study the mass transfer and reaction kinetics for well understanding some important characteristics and mechanisms of chromatography. A great number of studies have been pursued so far on the retention equilibrium in chromatography. On the contrary, some intrinsic difficulties prevent the progress of the kinetic study. Moment theory is one of effective strategies for analyzing chromatographic behavior from the kinetic point of view. In this review, at first, a framework of the moment analysis theory is explained. Then, the recent progress of some related research subjects is introduced.

© 2016 Elsevier B.V. All rights reserved.

Contents

1. Introduction

It must be essential to appropriately understand chromatographic behavior from various points of view, e.g., retention equilibrium, mass transfer and reaction kinetics, thermodynamics, and so on, for the further progress of chromatography. However, regarding the kinetic study on chromatography, there are some barriers preventing the research works. It seems to be more difficult to conduct the kinetic studies in comparison with the research works on the retention equilibrium.

Kinetic behavior in chromatography has frequently been studied on the basis of some ordinary rate equations [1–7]. It seems that the van Deemter equation is the most popular among them [3]. It was developed for chromatography under linear isotherm and nonideal conditions. The influence of some mass transfer processes, i.e., axial molecular diffusion and axial eddy diffusion in the mobile phase and mass transfer between the mobile and stationary phases, on band broadening was considered. Mass transfer rate was represented as a linear driving force model with an overall mass transfer coefficient. It was assumed that the column contained a large number of mixing stages and transfer units and that the heights for longitudinal diffusion and mass transfer could simply be added to yield HETP.

On the other hand, the general rate model of chromatography explains band broadening in chromatography in more detail. As indicated in Fig. 1, the contributions of several mass transfer and reaction processes in the column, e.g., axial dispersion (molecular and eddy diffusion), external (fluid-to-stationary phase) mass transfer, intra-stationary phase diffusion, and reaction kinetics, to band broadening is considered. Compared with the van Deemter equation, the mass transfer between the mobile and stationary phases is more accurately analyzed. A set of partially differential basic equations, which represent chromatographic behavior under linear isotherm conditions, is solved in the Laplace domain. Moment equations in the real time domain are mathematically derived from the analytical solution in the Laplace domain.

* Corresponding author: Tel.: 81-3-3985-2404.
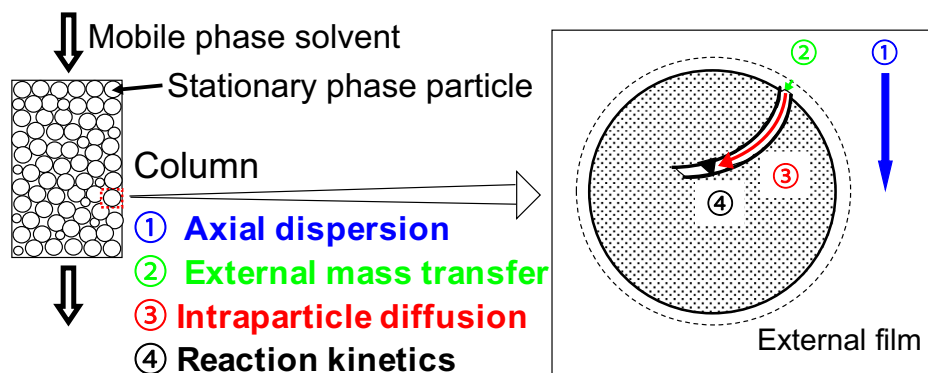*E-mail address:* kmiyabe@rikkyo.ac.jp.

Fig. 1. Schematic illustration of the mass transfer processes in a column.

The moment equations provide some items of important information about the retention equilibrium and mass transfer and reaction kinetics in the column from the first absolute moment (μ_1) and the second central moment (μ_2') of elution peak profiles experimentally measured [8–22]. The physical meanings of all the parameters included in the moment equations are clearly defined because they are derived on the basis of the general rate model of chromatography. Quantitative information about the mass transfer and reaction kinetics in the column and in the stationary phase can be obtained with physically sound justification. This is the most significant difference between the method of moments and the ordinary rate analysis using the conventional rate equations, e.g., van Deemter equation. They do not quantitatively provide the kinetic information from the curved profile of the flow rate dependence of HETP.

In both the cases of the kinetic study using the ordinary rate equations and the moment equations, it is required, in principle, to acquire far more experimental data than the study on the retention equilibrium. We need to experimentally measure chromatographic peaks as many as possible because the whole profile of the curved correlation between HETP and the mobile phase flow velocity is essential for the accurate kinetic study.

Additionally, in the moment theory, as indicated in Fig. 2, it is required to integrate an elution peak profile in the range of time for accurately determining μ_1 and μ_2'. The integration time range required for the determination of μ_2' is wider than that of μ_1. However, the noise of baseline far from the peak more significantly affects μ_2' than μ_1. It is more difficult to accurately measure μ_2' in comparison with μ_1. The difficulty in the measurement of the accurate value of μ_2' leads to the error concerning the second moment analysis. The accurate measurement of the flow rate dependence of HETP is originally more difficult than the determination of retention factor (k) and retention equilibrium constant (K_a).

Moment analysis (MA) method is one of effective strategies for quantitatively analyzing chromatographic behavior. However, it is not recognized for many chromatographers that the MA method is an effective approach for the kinetic study of chromatographic behavior because it is not necessarily familiar for them. Quantitative studies about the mass transfer processes, e.g., determination and estimation of related kinetic parameters (diffusivity and mass
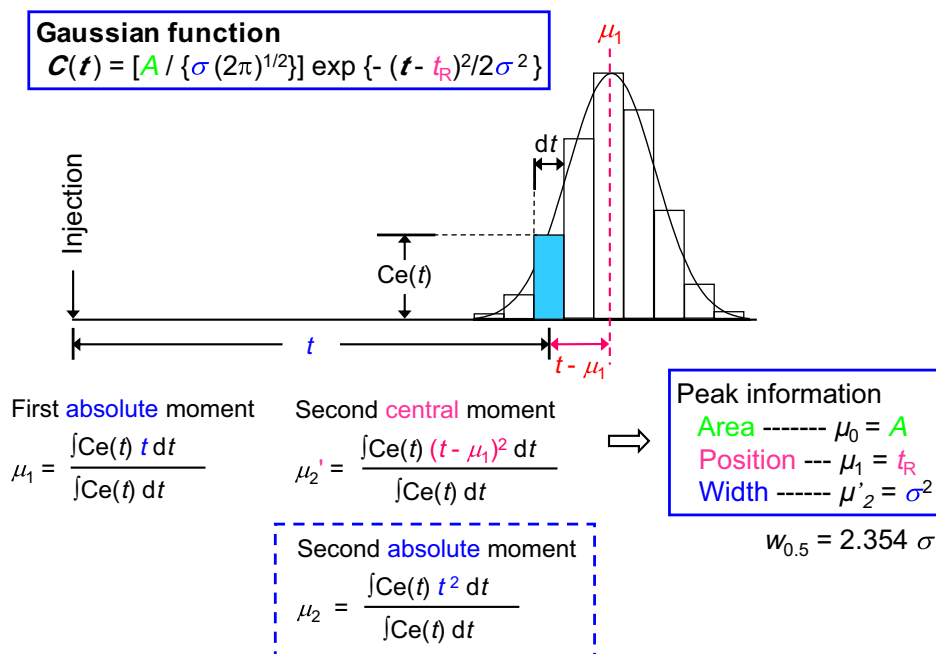

Fig. 2. Definition of first absolute moment (μ_1) and second central moment (μ_2').