Deciphering the Temporal Shift Puzzle

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Abstract

Time-based observation of a moving object will always lead to a distorted shape and a shift of position. The shift has been solved by rigorous mathematical derivation in this work by a convolution process of the results from Fick's Law for a sample traveling in a narrow flow channel. An empirical constant has been defined which can be acquired from experiments. It corrects the spatially-false image and can be further applied in the design of analytical instruments.

Introduction

In many chemical instruments (e.g. flow injection analysis or chromatography) the results are customarily presented as peaks on a recorder chart. The peak shape looks like but is usually not a symmetrical Gaussian curve. It is now understood that the peak apex (t_p*) does not reveal the actual arrival time (t_p) but with an illusion shift in the time coordinate (denoted as Φ, $\Phi = t_p - t_p{*}$). The scale of the temporal shift is correlated to the expanding coefficient of a flow system. In flow injection analysis the shift can be approximated as $\Phi = D/u^2$ where D is the axial dispersion coefficient and u the average flow speed. In chromatography, this shift is influenced by the dynamic partition coefficient k", and the solution is $\Phi = k''f/2 + D(k''+1)^2/u^2$. In practice, the shift can be estimated by a recursion calculation of the apparent position. It can also be obtained by other approaches, e.g. from the time for mean peak area (t_a*) and the temporal first moment(t_r*). The former can be estimated by letting $\int C(t)dt\big|_{t=t_a*} = A_t/2$ and the solution is estimated as: $t_a{*} \approx t_p + \Phi$. The latter parameter can be calculated by $t_r{*} = 1/A_t \int tC(t)dt = t_p + 2\Phi$. With the empirical Φ, the theoretical peak function can then implemented as: $C(t) = A_t/(\sqrt{4\Phi\pi t})\exp[-(t - t_p{*} - \Phi)^2/(4\Phi t)]$. It has been successfully applied to predict flow injection peak shapes and the results are satisfactory.

References

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