

Hydrodynamic radius using Taylor dispersion

Gaussian variance due to Taylor dispersion (parabolic pressure-driven flow) is (in time units) given by

$$\tau_2^2 - \tau_1^2 = \frac{r^2(t_2 - t_1)}{24D} \quad (1)$$

where r is the radius of the tubing, t_1 and t_2 are the peak centre times at the first and second window respectively, τ_1^2 and τ_2^2 are the corresponding variances, and D is the diffusion coefficient of the analyte.

Rearrangement of equation 1 gives the diffusion coefficient as

$$D = \frac{r^2(t_2 - t_1)}{24(\tau_2^2 - \tau_1^2)} \quad (2)$$

The diffusion coefficient is related to the hydrodynamic radius, R_h , via the Stokes equation

$$D = \frac{k_B T}{6\pi\eta R_h} \quad (3)$$

where k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J K}^{-1}$), T the absolute temperature and η the viscosity.

Thus, combining equations 2 and 3

$$R_h = \frac{4k_B T (\tau_2^2 - \tau_1^2)}{\pi\eta r^2 (t_2 - t_1)} \quad (4)$$

Peaks registered in the windows before and after the loop are used in data analysis. An example of suitable peak fitting software is PeakFit, available from Systat Software. It is recommended that symmetric peaks are analysed with a Gaussian function, whilst those which exhibit asymmetry are best fitted with a Haarhoff van de Linde (HVL) function. The peak centres and standard deviations obtained from these functions, a_1 and a_2 , are t and τ respectively.



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in Denmark for Paraytec
www.md-scientific.dk
info@md-scientific.dk
Tel. 7027 8565