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Note

Analytical solution for the area under chromatographic peaks obtained from the deconvolution method of Vaidya and Hester

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In a recent paper[1], Vaidya and Hester have proposed deconvolution of overlapping chromatographic peaks using a constrained non-linear optimization method developed by Box[2].

For this purpose, a modified version of the generalized exponential function (GEX) is used to fit both the original and deconvoluted chromatographic peaks. The GEX function, h, is given by

$$h = h_m v^{b-1} \exp \left[\frac{b-1}{a} (1 - v^a) \right] \quad (1)$$

where

$$v = \frac{V - V_0}{V_m - V_0}$$

Each peak is defined by the values of five parameters: V_0, the elution volume where the detector output signal (h) positively deviates from the baseline; V_m, the elution volume at the maximum detector output (h_m); h_m, itself; and the shape parameters a and b.

In this note, we report an analytical solution for the integral of the GEX function. Thus, once a chromatogram has been deconvoluted by the method of Vaidya and Hester, the relative contribution of each peak to the total chromatogram can quickly and easily be calculated.

The area, A, of each peak is given by eqn. 2.

$$A = \int_0^\infty h \, dv = \int_0^\infty h_m v^{b-1} \exp \left[\frac{b-1}{a} (1 - v^a) \right] dv \quad (2)$$

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Substituting w for v^a yields:

$$A = \frac{h_m}{a} \exp\left(\frac{b-1}{a}\right) \int_0^{\infty} w^{\frac{b-a}{a}} \exp\left(-\frac{b-1}{a} w\right) dw \tag{3}$$

The integration of eqn. 3 gives[3]:

$$A = \frac{h_m}{a} \left[\exp\left(\frac{b-1}{a}\right)\right] \left(\frac{a}{b-1}\right)^n \Gamma(n) \tag{4}$$

where $n = (b/a)$.

In order to obtain eqn. 4 from eqn. 3, the two conditions

$$n > 0 \tag{5}$$

$$\frac{b-1}{a} > 0 \tag{6}$$

must be satisfied. As explained in the paper of Vaidya and Hester, fitting positive peaks with the GEX function always yields a positive value for a and a value of b greater than one. Therefore, the conditions in eqns. 5 and 6 are always satisfied for GEX obtained in the deconvolution of positive peaks.

This is not the case with negative peaks since the value of a in a GEX function fitted to a negative peak is negative and eqns. 5 and 6 are not satisfied. This computational obstacle to calculating the area via eqn. 4 can be overcome by fitting the inverse of a negative peak with another GEX function. The value of a for the newly fitted GEX function will be positive.

Thus, a fused peak is described by a sum and a difference of positive GEX functions instead of a sum of both positive and negative GEX functions:

$$h = \Sigma\, \text{GEXP}_i - \Sigma\, \text{GEXN}_j \tag{7}$$

where GEXP_i are positive GEX functions fitted to positive peaks and GEXN_j are positive GEX functions fitted to the inverse of the negative peaks. With this method, both positive and negative peaks are described by GEX functions with positive values of a and the analytical solution given by eqn. 4 can be used for peak area calculations.

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REFERENCES

1 R. A. Vaidya and R. D. Hester, *J. Chromatogr.*, 287 (1984) 231–244.
2 M. J. Box, *Comput. J.*, 8 (1965) 42–52.
3 W. H. Beyer and S. M. Selby, *Standard Mathematical Tables*, CRC Press, Cleveland, OH, 1976, 24th ed., p. 386.