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Note

Deconvolution of overlapping chromatograms

II. Analytical solution to the moments of the GEX function

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In a recent paper[1], we have demonstrated a powerful new method for deconvolution of overlapping chromatograms using constrained, non-linear optimization and the GEX function. Subsequently, an analyutical solution for areas under peaks modeled by GEX functions has been reported[2]. In this paper, we wish to demonstrate that the previous integration of the GEX function can lead to false results when used to calculate the fraction of the area occupied by a given peak in an overlapped chromatogram. We also present a general analytical solution to obtain all the moments of a GEX function.

As presented previously[1], a chromatographic peak may be represented by a GEX function given by:

$$h = \mathrm{f}(X) = h_{\mathrm{m}}\, V^{b-1} \exp\left\{\frac{\mathrm{b}-1}{a}(1 - V^{a})\right\} \tag{1}$$

$$V = \frac{X - V_0}{V_{\mathrm{m}} - V_0}$$

Fig. 1 graphically describes such a GEX peak. The n^{th} moment about an axis parallel to the h axis at X equal to A is given by:

$$\gamma_n^A = \int_{V_0}^{\infty} \mathrm{f}(X) \cdot (X - A)^n \mathrm{d}X \tag{2}$$

The above integral can be solved* and the final result is

$$\gamma_n^A = \sum_{r=0}^{n} \Theta_r \left(\frac{a}{b-1}\right)^{\left(\frac{b+r}{a}\right)} \Gamma\left(\frac{b+r}{a}\right) \tag{3}$$

* For a copy of the detailed mathematics, please contact the authors.

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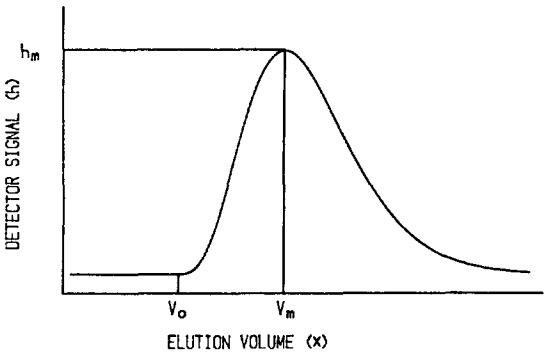

Fig. 1. A single GEX peak.

where

$$\Theta_r = \frac{h_m \exp\left(\frac{b-1}{a}\right)}{a} \cdot {}^nC_r \beta^{r+1} \alpha^{n-r}$$

$$\beta = V_m - V_0$$

$$\alpha = V_0 - A$$

$${}^nC_r = \frac{n!}{r!\,(n-r)!}$$

Eqn. 3 may be used to compute various characteristics of a peak. Table I shows a list of formulae to calculate several such criteria. The formulae in eqn. 3 and Table I can be incorporated into a small subprogram to calculate individual peak characteristics after deconvolution by our method.

Fig. 2 shows a chromatogram containing three fused peaks. This chromatogram has been deconvoluted using our method[1], and the "best fit" parameters for the three GEX functions are presented in Table II. Table III presents the results of calculating peak areas for the three individual peaks by numerical integration, the formulae presented here, and the formula reported previously by other researchers[2]. As can be clearly seen, the formula presented previously leads to erroneous results.

TABLE I

USING MOMENTS TO CALCULATE PEAK CHARACTERISTICS[3]

Characteristic	*Method of calculation*
Area	$\gamma_{n=0}^{A=0}$
Mean	$\gamma_{n=1}^{A=0}$/area
Variance	$\gamma_{n=2}^{A=\text{mean}}$/area
Skewness	$\gamma_{n=3}^{A=\text{mean}}/\{\text{area}*(\sqrt{\text{variance}})^3\}$
Kurtosis	$\gamma_{n=4}^{A=\text{mean}}/\{\text{area}*(\text{variance})^2\}$

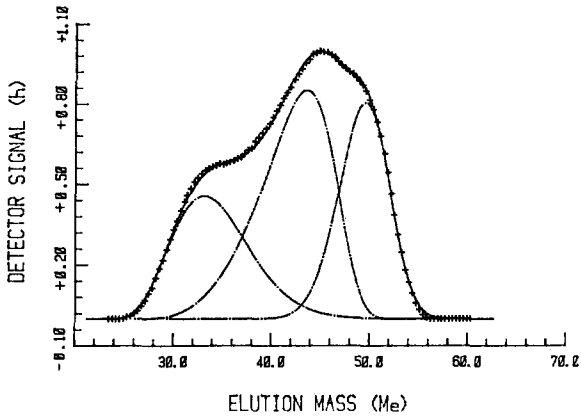

Fig. 2. Deconvolution of data file 7283B using program PEKSEP. Key: + = data points; solid line = fitted function (sum of three GEX functions); broken lines = individual deconvoluted peaks.

TABLE II

BEST FIT GEX PARAMETERS FOR THE CHROMATOGRAM PRESENTED IN FIG. 2

Parameter	*Peak number*		
	1	*2*	*3*
V_0	23.384	26.572	27.284
b	4.8572	3.7824	16.129
a	1.5534	8.2552	5.0472
V_m	33.125	43.620	49.505
h_m	0.4569	0.8533	0.8066

TABLE III

PEAK AREAS FOR THE INDIVIDUAL PEAKS IN THE CHROMATOGRAM PRESENTED IN FIG. 2

Peak number	*Numerical integration*		*Formulae presented in this paper*		*Formula reported in ref. 2*	
	Peak area	*% of total*	*Peak area*	*% of total*	*Peak area*	*% of total*
1	4.5052	25.79	4.5084	25.73	0.46282	40.07
2	7.7931	44.62	7.8529	44.81	0.46064	39.88
3	5.1658	29.59	5.1629	29.46	0.23151	20.05

SYMBOLS

h detector signal
h_m detector signal at peak maximum
V_0 elution volume at peak threshold
V_m elution volume at peak maximum
a shape parameter always greater than zero
b shape parameter, always greater than one
n order of a moment
A axis for a moment (axis $\equiv X = A$)
X elution volume
V dummy variable in GEX function
r index variable

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