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Review

# Mathematical functions for the representation of chromatographic peaks

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## Abstract

About ninety empirical functions for the representation of chromatographic peaks have been collected and tabulated. The table, based on almost 200 references, reports for every function: (1) the most used name; (2) the most convenient equation, with the existence intervals for the adjustable parameters and for the independent variable; (3) the applications; (4) the mathematical properties, in relation to the possible applications. The list includes also equations originally proposed to represent peaks obtained in other analytical techniques (e.g. in spectroscopy), which in many instances have proved useful in representing chromatographic peaks as well; the built-in functions employed in some commercial peak-fitting software packages were included, too. Some of the most important chromatographic functions, i.e. the Exponentially Modified Gaussian, the Poisson, the Log-normal, the Edgeworth/Cramér series and the Gram/Charlier series, have been reviewed and commented in more detail. © 2001 Elsevier Science B.V. All rights reserved

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## 1. Introduction

It is well known that there is no theoretic model for the exact description of the shape of chromatographic peaks. Several authors have proposed and/or used a number of empirical mathematical functions for the representation of these peaks [1,2,4–55,57–76,78–114,116–124,126–148,150–166,168–190]. A number of these functions have proved useful also to represent the shape of signals obtained from other analytical methods, as e.g. flow injection analysis, various spectroscopic methods, voltammetry, mass spectrometry, thermal analysis, etc.; conversely, several functions proposed for other techniques have demonstrated suitable to represent chromatographic peaks.

Perhaps the most frequent application of mathematical functions for peak shape representation is the so-called deconvolution of partially resolved peaks [4,6–10,12–16,18,23–25,29,30,39,40,44,45,48,49,54,55,57,58,61,63–66,68–70,78,80,84–88,95,99,103–105,117,126–128,133,137,152–154,156,157,159,161,163,164,166,168,171–174,182,189,190]: the analytical signal produced by the sum of  $n$  partially overlapping peaks is reproduced by optimising (generally using the least squares criterion) the parameters of the sum of  $n$  mathematical functions. In this way the explicit expression of each of the  $n$  functions is obtained, thus achieving an artificial resolution of the  $n$  peaks. The potentialities and the limits of this method have been extensively discussed by Maddams [116], Vandeginste and De Galan [177] and, recently, by Zhang et al. [189]; in the most recent applications the least-squares fitting is combined with other mathematical methods of data treatment (see e.g. [49,126,127,151,189]; although these papers deal mainly with spectroscopic data, the methods described and the relevant conclusions are completely applicable to chromatographic data as well).

Another important chromatographic application of data fitting techniques (with or without peak “deconvolution”) is the computation of the so-called “chromatographic figures of merit” (*cfom*) of peaks [21,26–28,36,41,50,52,71–73,89,91,96,101,118,129,130,134,135,137,138,141,144,145,150,151,166,169,175,178,186–188]. These include the first statistical moments, which allow to calculate the

peak area, mean/position, width, skew and excess (see also below), and also other less frequently computed parameters, as e.g. the number of theoretical plates [50,89]. The computation of these parameters leads to important information on the analyte itself (for example, the mean and the dispersion of the molecular mass of a polymer, in steric exclusion chromatography) and on its interactions in the chromatographic column (for example, the mass transport properties, and the activity, virial and diffusion coefficients). If the shape of the peak is represented and fitted by an explicit function, the *cfom* can be calculated with exact or approximate formulae which relate the fitted parameters of the function to the *cfom* [21,36,72,73,89,101,129,130,134,135,137,141,145,150,151,169,175,178,188]; if such formulae are not known, the fitting function can be analysed graphically. Both methods can be applied to overlapping peaks as well as to isolated ones, and are believed to be more accurate [89,100,129,137] than methods not based on peak fitting [11,26,27,50,52,71,91,96,129,137,138,186–188].

A third class of applications is represented by the study of the effect of one or more experimental parameters (e.g. eluent flow-rate, response time of the detector, etc.) on the shape of the peaks [1,19,62,76,120,121,142,143,155,160,178,179].

Another application is the production of simulated (artificial) peaks, either for didactic or commercial purposes [108,124,146] or, more frequently, to validate a proposed method for the treatment of experimental data [2,11,32,33,42,46,47,53,67,74,75,89,92,93,97,98,106,107,109,122,139,140,145,148,162,170,172,189,190].

Recently, the fitting of experimental data with suitable functions has been employed to improve the signal-to-noise ratio [41,43] and for the efficient and compact memorization of experimental data (see [5] and references therein).

As mentioned above, a large number of empirical functions have been proposed and used for all these applications. To our knowledge, an exhaustive list of suitable functions is not available in the literature. Several papers list their “names” without reporting further information [7,9,12,18,27,31,37,55,70,115,129,134,135,137,146,147,152,172,174,176,177]. In other cases the equations are reported and sometimes

commented [69,108,111,113,136,145,154,169]; however only a small number of functions are considered in each case. To our knowledge, the only paper which contains a systematic list of functions is a review by Maddams [116], who quotes and comments 13 functions (intended mainly for spectroscopy).

In some cases two equations representing the same function have been presented with different denominations; on the contrary, the same denomination has been sometimes applied to different functions. Several papers include equations affected by more or less serious printing errors, which sometimes appear to have propagated (see below).

In the present paper we try to present an archive as complete as possible of functions proposed in the literature for the representation of peaks. We have also attempted to present all the functions in a form as unambiguous and homogeneous as possible. On the basis of some mathematical properties, the functions have been criticized and evaluated in view of their possible use in peak fitting. The table with the list of the functions is presented and explained in detail in the following section.

## 2. Description of the table of the functions (Table 1)

The first column of Table 1 contains the denomination proposed for each function, which generally coincides with the one most frequently employed in the literature; other denominations are reported in brackets. For all the functions to which a specific name (like Gaussian, EMG, Poisson, etc.) appears to have not been assigned, we propose as the denomination the names of the Authors who, to our knowledge, have first proposed or used this function for the representation of peaks. The same rule has been followed in the cases in which the commonly used denomination appears too generic and potentially confusing (this is the case of names like “skewed gaussian”, “asymmetric gaussian”, etc.).

For a few of the functions the commonly employed denomination appeared to be improper, because in mathematics it usually refers to a different function; for example, this is the case of the Log-

normal and of the Gamma functions. We decided anyway to maintain the “chromatographic” (or “spectroscopic”) denomination.

In the table, the functions are ordered alphabetically according to their proposed names, with the exception of “similar” functions (as e.g. the several exponentially modified gaussians) which are grouped together.

The second column contains the mathematical equation of the function. If this equation appeared as such in the literature, the appropriate references are given in this column. Because very often a given function has been presented in the literature with different equations, we have tried to select the “best” one according to the following criteria:

- the “properties” (we have selected the equation with the best “properties”, as described below);
- the coherence of presentation (we have selected the equation which is most coherent with the others);
- the number of quotations (we have selected the most frequently quoted equation).

In reporting the equations, the symbols used for the variables and for the parameters have been uniformed according to the following scheme, to allow a more direct comparison between the different functions:

### (a) Variables

- $x$  the abscissa of the function, or the independent variable;
- $y$  the ordinate of the function, or the dependent variable;
- $t$  an auxiliary variable (e.g. an integration variable).

### (b) Parameters

It is advantageous to divide the adjustable parameters into two groups. The first group includes parameters which are directly correlated to one measurable property of the experimental peak (like height, width, retention time, etc.):

- $h$  parameter which is mainly or only related to the maximum height of the peak. For some functions  $h$  represents *exactly* the height, which conversely can be modified only by changing  $h$ ;

Table 1  
List of the functions

Most used name/s	Equation	Applications	Properties	References
Baker (4 <sup>th</sup> order Lorentzian)	$y = \frac{h}{1 + a(x-z)^2 + b(x-z)^3 + c(x-z)^4}$	1 spectroscopy	• symmetric only	[9,10] (rev. Maddams)
Beta	$y = hB_1^{1-s_1} B_2^{1-s_2} \left(B_1 + \frac{x-z}{w}\right)^{s_1-1} \left(B_2 + \frac{x-z}{w}\right)^{s_2-1}$ $y = 0$ $B_1 = \frac{s_1 - 1}{s_1 + s_2 - 2} \quad B_2 = \frac{s_2 - 1}{s_1 + s_2 - 2}$	4 chromatography spectroscopy	• single maximum • tailed only	[111,125,167]
Chesler–Cram – A (Gaussian-Triangular-Exponential)	$y = G(x)$ $y = G(x) + T(x)$ $y = G(x) + E(x)$ $G(x) = h \exp\left[-\frac{(x-z)^2}{2w^2}\right] \quad T(x) = a(x-b) \quad E(x) = a(c-b) \exp\left(-\frac{x-c}{d}\right)$ constraints: $a \geq 0, c > b$	4 chromatography	• parameter $z$ exact • fronted, symm. or tailed	[26,129]
Chesler–Cram – B (Gaussian-Hyperbolic-Exponential)	$y = h \left[ G(x) + \left(1 - \frac{H(x)}{2}\right) E(x) \right]$ $G(x) = \exp\left[-\frac{(x-z)^2}{2w^2}\right] \quad H(x) = 1 - \tanh[a(x-b)] \quad E(x) = c \exp\left[-\frac{d}{2}( x-e  + x-e)\right]$	2, 3, 4 chromatography	• parameter $z$ exact • fronted, symm. or tailed • stat. moments known ([130] exact, [27] approx.)	[27,76,125,130,145]
Cumulative	$y = \frac{h \left[ 1 + \operatorname{erf}\left(\frac{x-z+\frac{a}{2}}{w\sqrt{2}}\right) \right] \left[ 1 - \operatorname{erf}\left(\frac{x-z-\frac{a}{2}}{w\sqrt{2}}\right) \right]}{\left[ 1 + \operatorname{erf}\left(\frac{a}{2w\sqrt{2}}\right) \right]^2}$ constraints: $s > 0$	7 chromatography spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[167]
Asymmetric Cumulative	$y = \frac{h}{4} \left[ 1 + \operatorname{erf}\left(\frac{x-z+\frac{w}{2}}{s_1\sqrt{2}}\right) \right] \left[ 1 - \operatorname{erf}\left(\frac{x-z-\frac{w}{2}}{s_2\sqrt{2}}\right) \right]$ constraints: $s_1, s_2 > 0$	7 chromatography spectroscopy	• single maximum • parameters $z, s_1, s_2$ exact • fronted, symm. or tailed	[167]

Table 1. Continued

Most used name/s	Equation	Applications	Properties	References
Doniach Sunjic	$y = h \cos \left[ -\frac{\pi}{2} s + (1+s) \arctan \left( \frac{x-z}{w} \right) \right] \left[ 1 + \left( \frac{x-z}{w} \right)^2 \right]^{-(s+1)/2}$ <p>for <math>x \geq w \tan \left( -\frac{\pi}{2} \frac{1-s}{1+s} \right) + z</math></p> $y = 0$ <p>for <math>x &lt; w \tan \left( -\frac{\pi}{2} \frac{1-s}{1+s} \right) + z</math></p> <p>constraints: <math>s &gt; -1</math></p>	7 spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameter <math>s</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[113]
Edgeworth Cramér series	$y = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right]$ $\times \left\{ 1 + \sum_{i=1}^n \left\{ (-1)^i \sum_{j=1}^i \left\{ (-1)^j c_{i,j+2j}(i+2)! \sum_{k=0}^{\text{floor}(i+2j/2)} \left[ \frac{(-1)^k \left( \frac{x-z}{w} \right)^{i+2-2k}}{2^k k!(i+2-2k)!} \right] \right\} \right\} \right\}$ $c_{1,3} = \frac{s}{6}, \quad c_{2,4} = \frac{a}{24}, \quad c_{2,6} = \frac{a^2}{72}, \quad c_{3,5} = \frac{b}{120}, \quad c_{3,7} = \frac{sa}{144}, \quad c_{3,9} = \frac{s^3}{1296}, \quad n=3-8$ <p>(for the other coefficients see [134])</p> <p>floor(<math>t</math>) = the greatest integer <math>\leq t</math>, [125,134]</p>	2, 3 chromatography	<ul style="list-style-type: none"> <li>• fronted, symm. or tailed</li> <li>• stat. moments known (see all references)</li> </ul>	[36–38,111,125,126,134–137,155]
EMG (exponent. modified gaussian)	$y = \frac{hw}{s} \sqrt{\frac{\pi}{2}} \exp \left( \frac{w^2}{2s^2} - \frac{x-z}{s} \right) \left\{ 1 - \operatorname{erf} \left[ \frac{1}{\sqrt{2}} \left( \frac{w}{s} - \frac{x-z}{w} \right) \right] \right\}$ <p>constraints: <math>s &gt; 0</math></p>	1, 2, 3, 4, 5 chromatography FIA voltammetry	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known</li> </ul>	[7,11,17,19,20,23,27,32–35,42,43,46–48, 50,51 (and ref. therein), 52,58,61,62,65,66,71,75, 81,89,90 (and ref. therein), 91–94,96,100,108, 110–112,121,122,124,125,129,131,135–137,139–142, 145,146,154,156,160,162,167,173,183–188 (rev. Maddams)]
Generalized EMG	$y = \frac{hw}{ s } \sqrt{\frac{\pi}{2}} \exp \left( \frac{w^2}{2s^2} - \frac{x-z}{s} \right) \left\{ 1 - \operatorname{erf} \left[ \frac{1}{\sqrt{2}} \left( \frac{w}{ s } - \frac{x-z}{w s } \right) \right] \right\}$ <p>constraints: <math>s \neq 0</math></p>	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known (the same of EMG)</li> </ul>	[35,167]

Table 1. Continued

Most used name/s	Equation	Applications	Properties	References	
Simplified EMG	$y = \frac{hw}{s} \sqrt{2\pi} \frac{\exp\left(\frac{w^2}{2s^2} - \frac{x-z}{s}\right)}{1 + \exp\left[-\frac{2.4055}{\sqrt{2}}\left(\frac{x-z}{w} - \frac{w}{s}\right)\right]}$ <p>constraints: <math>s &gt; 0</math></p>	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known (practically the same of EMG in the range <math>s/w = 0.75 \div 3</math> [110])</li> </ul>	[110]	
Second simplified EMG	$y = \frac{hw}{s} \sqrt{\frac{\pi}{2}} \exp\left(\frac{w^2}{2s^2} - \frac{x-z}{s}\right) \times \left\{ \frac{1 - \exp\left(-\frac{3.3382}{\sqrt{2}}C(x)\right)}{1 + \exp\left(-\frac{3.3382}{\sqrt{2}}C(x)\right)} \{1 - 0.3328 \exp\{-0.61025[C(x)]^2\}\} \right\}$ $C(x) = \frac{x-z}{w} - \frac{w}{s}$ <p>constraints: <math>s &gt; 0</math></p>	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known (practically the same of EMG in the range <math>s/w = 0.75 \div 3</math> [110])</li> </ul>	[110] [110]	
Two time-constants EMG	$y = \frac{hw}{s_1 - s_2} \sqrt{\frac{\pi}{2}} [D(s_1) - D(s_2)]$ $y = \frac{hw^2}{s_1^2} \left\{ \exp\left[-\frac{(x-z)^2}{2w^2}\right] + \sqrt{\frac{\pi}{2}} C(s_1) D(s_1) \right\}$ $D(s) = \exp\left(\frac{w^2}{2s^2} - \frac{x-z}{s}\right) \left\{ 1 - \operatorname{erf}\left[-\frac{C(s)}{\sqrt{2}}\right] \right\}$ <p>constraints: <math>s_1, s_2 &gt; 0</math></p>	if $s_1 \neq s_2$  if $s_1 = s_2$	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• symm.<sup>a</sup> or tailed only</li> <li>• stat. moment zero (area) known (the same of EMG)</li> </ul>	[35]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Generalized two time-constants EMG	$y = \frac{hw}{s_1 - s_2} \sqrt{\frac{\pi}{2}} [D(s_1) - D(s_2)]$	if $s_1 \neq s_2$	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moment zero (area) known (the same of EMG)</li> </ul>	[35]
	$y = \frac{hw^2}{s_1^2} \left\{ \exp \left[ -\frac{(x-z)^2}{2w^2} \right] + \sqrt{\frac{\pi}{2}} C(s_1) D(s_1) \right\}$	if $s_1 = s_2$			
	$D(s) = \frac{s}{ s } \exp \left( \frac{w^2}{2s^2} - \frac{x-z}{s} \right) \left\{ 1 - \operatorname{erf} \left[ -\frac{C(s)}{\sqrt{2}} \frac{s}{ s } \right] \right\}$	$C(s) = \frac{x-z}{w} - \frac{w}{s}$			
	constraints: $s_1, s_2 \neq 0$				
Three time-constants EMG	$y = \frac{hw\sqrt{\pi}}{\sqrt{2}} [T_1 D(s_1) + T_2 D(s_2) + T_3 D(s_3)]$	if all $s_i$ differ	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• symm.<sup>a</sup> or tailed only</li> <li>• stat. moment zero (area) known (the same of EMG)</li> </ul>	[35]
	$y = \frac{h}{s_2 - s_1} \left\{ \frac{w^2}{s_2} \left\{ \sqrt{\frac{\pi}{2}} C(s_2) D(s_2) + \exp \left[ -\frac{(x-z)^2}{2w^2} \right] \right\} - \frac{s_1 w}{s_1 - s_2} \sqrt{\frac{\pi}{2}} (D(s_1) - D(s_2)) \right\}$	if two $s_i$ are equal			
	(this equation is valid for $s_1 = s_2$ . For $s_1 = s_3$ and for $s_2 = s_3$ simply substitute the given $s_i$ [35])				
	$y = \frac{hw^3}{2s_1^3} \left\{ \sqrt{\frac{\pi}{2}} D(s_1) + C(s_1) \left\{ \exp \left[ -\frac{(x-z)^2}{2w^2} \right] + C(s_1) \sqrt{\frac{\pi}{2}} D(s_1) \right\} \right\}$	if all $s_i$ are equal			
	$T_1 = \frac{s_1}{(s_2 - s_1)(s_3 - s_1)} \quad T_2 = \frac{s_2}{(s_1 - s_2)(s_3 - s_2)} \quad T_3 = \frac{s_3}{(s_1 - s_3)(s_2 - s_3)}$				
	$D(s) = \exp \left( \frac{w^2}{2s^2} - \frac{x-z}{s} \right) \left\{ 1 - \operatorname{erf} \left[ -\frac{C(s)}{\sqrt{2}} \right] \right\} \quad C(s) = \frac{x-z}{w} - \frac{w}{s}$				
	constraints: $s_1, s_2, s_3 > 0$				

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Generalized three time-constants EMG	$y = \frac{hw\sqrt{\pi}}{\sqrt{2}} [T_1 D(s_1) + T_2 D(s_2) + T_3 D(s_3)]$ $y = \frac{h}{s_2 - s_1} \left\{ \frac{w^2}{s_2} \left[ \sqrt{\frac{\pi}{2}} C(s_2) D(s_2) + \exp \left[ -\frac{(x-z)^2}{2w^2} \right] \right] - \frac{s_1 w}{s_1 - s_2} \sqrt{\frac{\pi}{2}} [D(s_1) - D(s_2)] \right\}$ <p>(this equation is valid for <math>s_1 = s_2</math>. For <math>s_1 = s_3</math> and for <math>s_2 = s_3</math> simply substitute the given <math>s_i</math> [35])</p> $y = \frac{hw^3}{2s_1^3} \left\{ \sqrt{\frac{\pi}{2}} D(s_1) + C(s_1) \left\{ \exp \left[ -\frac{(x-z)^2}{2w^2} \right] + C(s_1) \sqrt{\frac{\pi}{2}} D(s_1) \right\} \right\}$ $T_1 = \frac{s_1}{(s_2 - s_1)(s_3 - s_1)} \quad T_2 = \frac{s_2}{(s_1 - s_2)(s_3 - s_2)} \quad T_3 = \frac{s_3}{(s_1 - s_3)(s_2 - s_3)}$ $D(s) = \frac{s}{ s } \exp \left( \frac{w^2}{2s^2} - \frac{x-z}{s} \right) \left\{ 1 - \operatorname{erf} \left[ -\frac{C(s)}{\sqrt{2}} \frac{s}{ s } \right] \right\} \quad C(s) = \frac{x-z}{w} - \frac{w}{s}$ <p>constraints: <math>s_1, s_2, s_3 \neq 0</math></p>	<p>if all <math>s_i</math> differ</p> <p>if two <math>s_i</math> are equal</p> <p>if all <math>s_i</math> are equal</p>	<p>7 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• all parameters estimable</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moment zero (area) known (the same of EMG)</li> </ul>	[35]
EMG+GMG	$y = \left\{ \begin{array}{l} \frac{h}{4s_1} \exp \left( \frac{2s_1 z - 2s_1 x + w^2}{s_1^2} \right) \left[ 1 - \operatorname{erf} \left( \frac{s_1 z - s_1 x + w^2}{ws_1 \sqrt{2}} \right) \right] \\ h \exp \left[ -\frac{(x-z)^2}{2(w^2 + s_2^2)} \right] \left\{ 1 - \operatorname{erf} \left[ \frac{s_2(z-x)}{w\sqrt{2(w^2 + s_2^2)}} \right] \right\} \\ + \frac{\quad}{2\sqrt{2\pi}\sqrt{w^2 + s_2^2}} \end{array} \right\}$ <p>constraints: <math>s_1 &gt; 0</math></p>	[167]	<p>7 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[167]
EML (exponent modified lorentzian)	$y = h \int_0^\infty \left[ 1 + \left( \frac{x-z-t}{w} \right)^2 \right]^{-1} \exp \left( -\frac{t}{s} \right) dt$	[42]	<p>4 chromatography</p>	<p>properties unknown</p>	[42]



Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Erf	$y = h \left\{ 1 - \operatorname{erf} \left[ \left( \frac{x-z}{w} \right)^2 \right] \right\}$	[167]	7 chromatography spectroscopy	• single maximum • parameters $h, z, w$ exact • symmetric only	[167]
Error	$y = h \exp \left[ - \frac{ x-z ^{2/a}}{2w} \right]$ constraints: $a > 0$	[167]	7 chromatography spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[167]
Extreme value (extreme function in statistics)	$y = h \exp \left[ - \exp \left( - \frac{x-z}{w} \right) - \frac{x-z}{w} + 1 \right]$	[111,125,167]	4 chromatography	• single maximum • parameters $h, z, w$ exact • tailed only	[111,125,167]
Extreme value fronted	$y = h \exp \left[ \frac{x-z+w-wz \exp \left( \frac{x-z-w \ln s}{w} \right)}{ws} \right]$ constraints: $s > 0$	[167]	7 chromatography	• single maximum • parameters $h, z, s$ exact • fronted or symm only.	[167]
Extreme value tailed	$y = h \exp \left[ \frac{-x+z+w-wz \exp \left( - \frac{x-z+w \ln s}{w} \right)}{ws} \right]$ constraints: $s > 0$	[167]	7 chromatography	• single maximum • parameters $h, z, s$ exact • symm. or tailed only	[167]
Fahys	$y = h \left[ \cos \left( \pi \frac{x-z}{w} \right) \right]^a \frac{b^2}{b^2 + (x-z)^2}$ $y = 0$ constraints: $a > 0, b \neq 0$	for $z + s - \frac{w}{2} \leq x \leq z + s + \frac{w}{2}$ for $x < z + s - \frac{w}{2}$ and for $x > z + s + \frac{w}{2}$ [44]	1 spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[44] (rev. Maddams)
Asymmetric Fahys	$y = h \left[ \cos \left( \pi \frac{x-z-s}{w} \right) \right]^a \frac{b^2}{b^2 + (x-z)^2}$ $y = 0$ constraints: $a > 0, b \neq 0$	for $z + s - \frac{w}{2} \leq x \leq z + s + \frac{w}{2}$ for $x < z + s - \frac{w}{2}$ and for $x > z + s + \frac{w}{2}$ [44]	1 spectroscopy	• single maximum • fronted, symm. or tailed	[44] (rev. Maddams)

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
F-variance	$y = \frac{h \left( \frac{x-z}{w} + \frac{s_2(s_1-2)}{s_1(s_2+2)} \right)^{(s_1+s_2)/2} \left( 1 + \frac{s_1-2}{s_2+2} \right)^{(s_1+s_2)/2}}{\left\{ 1 + \frac{s_1 \left[ \frac{x-z}{w} + \frac{s_2(s_1-2)}{s_1(s_2+2)} \right]}{s_2} \right\}^{s_1+s_2/2} \left[ \frac{s_2(s_1-2)}{s_1(s_2+2)} \right]^{s_1/2-1}}$	<p>for <math>x \geq z - w \frac{s_2(s_1-2)}{s_1(s_2+2)}</math></p> <p>for <math>x &lt; z - w \frac{s_2(s_1-2)}{s_1(s_2+2)}</math></p>	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• <math>\text{symm.}^a</math> or tailed only</li> </ul>	[167]
	<p><math>y = 0</math></p> <p>constraints: <math>s_1 \geq 2, s_2 &gt; 0</math></p>	[167]			
Gamma (Chisquared)	$y = h \left[ -\frac{s-1 + \frac{x-z}{w}}{s-1} \right]^{s-1} \exp\left(-\frac{x-z}{w}\right)$	<p>for <math>x \geq w + z - sw</math></p> <p>for <math>x &lt; w + z - sw</math></p>	4 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• <math>\text{symm.}^a</math> or tailed only</li> </ul>	[111,167]
	<p><math>y = 0</math></p> <p>constraints: <math>s &gt; 1</math></p>	[111,167]			
Inverted Gamma	$y = \frac{hw \left( \frac{sx+x+w-zs-z}{w} \right)^{-s} \exp\left[ -\frac{(x-z)(s+1)^2}{sx+x+w-zs-z} \right]}{sx+x+w-zs-z}$	<p>for <math>x \geq \frac{z+sz-w}{s+1}</math></p> <p>for <math>x &lt; \frac{z+sz-w}{s+1}</math></p>	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• <math>\text{symm.}^{(a)}</math> or tailed only</li> </ul>	167
	<p><math>y = 0</math></p> <p>constraints: <math>s &gt; 0</math></p>	[167]			
Gaussian	$y = h \exp\left[ -\frac{(x-z)^2}{2w^2} \right]$	<p>[8,12,46,61,69, 105,106,120,122, 125,138,146,156, 157,160,162,167, 169,182]</p>	1, 2, 3, 4, 5, 6 chromatography FIA spectroscopy voltammetry mass spectrom.	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w</math> exact</li> <li>• symmetric only</li> <li>• stat. moments known (see e.g. [144])</li> </ul>	[1,4,5,7,8,12,13–15,22,24–26, 28,29,32,41,43,45,46,52,54–56, 58,61,63,67,68–70,84,88,97,98, 100,103,105–107,109,120,122, 124–128,131,133,135–139,144, 146,147,151,152,154,156–162, 166–171,182 (rev. Maddams)]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
bi-Gaussian	$y = h \exp \left[ -\frac{(x-z)^2}{2w_1^2} \right]$ $y = h \exp \left[ -\frac{(x-z)^2}{2w_2^2} \right]$	<p>for <math>x &lt; z</math></p> <p>for <math>x \geq z</math> [74,97,108,145,182]</p>	<p>1, 2, 4 chromatography spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w_1, w_2</math> exact</li> <li>• fronted, symm. or tailed</li> <li>• stat. moments known [21,74,145]</li> </ul>	<p>[21,63,74,97,108,141,145,146,164,182] (rev. Maddams)</p>
Constrained Gaussian	$y = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{zw_2 + w_1} \right)^2 \right]$	[167]	<p>7 spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• symmetric only</li> </ul>	[167]
Double Gaussian	$y = \frac{h}{\sqrt{2\pi}} \left\{ \frac{a}{w_1} \exp \left[ -\frac{1}{2} \left( \frac{x-z_1}{w_1} \right)^2 \right] + \frac{(1-a)}{w_2} \exp \left[ -\frac{1}{2} \left( \frac{x-z_2}{w_2} \right)^2 \right] \right\}$ <p>constraints: <math>1 \leq a \leq 0</math></p>	[141]	<p>2 chromatography</p>	<ul style="list-style-type: none"> <li>• parameters <math>z_1, z_2</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[141]
GEMG4 (4-parameter EMG-GMG hybrid)	$y = \frac{h \exp \left[ -\frac{(x-z+s)^2}{2(s^2+w^2)} \right] \left\{ -1 + \operatorname{erf} \left[ \frac{w^2 - s(x-z)}{w\sqrt{2(s^2+w^2)}} \right] \right\}}{\sqrt{2\pi(s^2+w^2)} \operatorname{erf} \left( \frac{\sqrt{2}}{2} - 1 \right)}$	[167]	<p>7 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[167]
GEMG5 (5-parameter EMG-GMG hybrid)	$y = \frac{h}{\sqrt{2\pi(s_1^2+w^2)} \operatorname{erf} \left( \frac{\sqrt{2}s_1}{2s_2} - 1 \right)} \exp \left[ -\frac{(s_2x - zs_2 + s_1^2)^2}{2s_2^2(s_1^2+w^2)} \right]$ $\times \left\{ -1 + \operatorname{erf} \left[ \frac{s_1(s_2x - zs_2 - w^2)}{ws_2\sqrt{2(s_1^2+w^2)}} \right] \right\}$ <p>constraints: <math>s_2 \neq 0</math></p>	[167]	<p>7 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[167]
GEX (generalized exponential function)	$y = h \exp \left\{ \frac{b-1}{a} \left[ 1 - \left( \frac{x-u}{z-u} \right)^a + a \ln \left( \frac{x-u}{z-u} \right) \right] \right\}$ <p><math>y = 0</math></p> <p>constraints: <math>a &gt; 0, b &gt; 1</math></p>	<p>for <math>x \geq u</math> for <math>x &lt; u</math> [83,174,175]</p>	<p>1, 2, 3 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known [83,175]</li> </ul>	[83,174,175]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Giddings	$y = \frac{h}{w} \sqrt{\frac{z}{x}} \left[ \exp\left(-\frac{x+z}{w}\right) \right] I_1\left(\frac{2\sqrt{zx}}{w}\right)$ $I_1(t) = \sum_{k=0}^{\infty} \frac{1}{k!(k+1)!} \left(\frac{t}{2}\right)^{2k+1} = \text{modified Bessel function of the first kind}$	[65,111,125,167]	4 chromatography	• single maximum • only symm. <sup>a</sup> or tailed	[37,38,59,60,65, 76,92,111,119, 125,167,178]
Gladney Dowden – A	$y = h \exp\left[-\frac{(x-z)^2}{2w^2 + s(x-z)}\right]$ $y = 0$	for $x > z - 2w^2/s$ (if $s > 0$ ) or $x < z - 2w^2/s$ (if $s < 0$ ) for $x \leq z - 2w^2/s$ (if $s > 0$ ) or $x \geq z - 2w^2/s$ (if $s < 0$ ) [61]	7 chromatography	• single maximum • parameters $h, z, s$ exact • fronted, symm. or tailed	[61]
Gladney Dowden – B	$y = [a(x-u) + b(x-u)^3] \exp\left[-\frac{(x-u)^2}{2w^2}\right]$ $y = 0$ <p>constraints: <math>a &gt; 0, b &gt; 0</math></p>	for $x \geq u$ for $x < u$	7 chromatography	• single maximum • parameter $u$ exact • tailed only	[61]
GMG (half-gauss. modified gaussian.)	$y = \frac{h \exp\left[-\frac{(x-z)^2}{2(s^2+w^2)}\right] \left\{ 1 + \operatorname{erf}\left[\frac{s(x-z)}{w\sqrt{2(s^2+w^2)}}\right] \right\}}{\sqrt{2\pi(s^2+w^2)}}$	[167]	7 chromatography	• single maximum • fronted, symm. or tailed	[167]
Gram Charlier series	$y = h \exp\left[-\frac{1}{2}\left(\frac{x-z}{w}\right)^2\right] \sum_{i=0}^n \left\{ (-1)^i c_i \sum_{j=0}^{\operatorname{floor}(i/2)} \left[ \frac{(-1)^j \left(\frac{x-z}{w}\right)^{i-2j}}{2^j j! (i-2j)!} \right] \right\}$ <p><math>c_0 = 1, c_1 = 0, c_2 = 0, c_3 = -s, c_4 = a, c_5 = -b</math> (for the other coefficients see [134]) floor(<math>t</math>) = the greatest integer <math>\leq t</math></p>	$n = 3-8$ [134]	1, 2, 3 chromatography	• parameter $w$ exact • for $n \geq 3$ fronted, symmetric or tailed, for $n < 3$ symmetric only • stat. moments known (see all references)	[36,72,73,119, 123,125,130,133, 137,178]
Haldna Pihl	$y = h \exp\left\{ -\frac{(x-z)^2}{w + \frac{s}{2}(x-z)\{1 + \tanh[1000(x-z)]\}} \right\}$ $y = 0$	always (if $s > 0$ ) for $a \tanh(-1 - 2w/s) < x < z - 2w/s$ (if $s < 0$ ) for $x \leq a \tanh(-1 - 2w/s)$ and for $x \geq z - 2w/s$ (if $s < 0$ ) [80]	1 Chromatography	• single maximum • parameters $h, z$ exact • fronted, symm. or tailed	[80]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
HVL (Haarhoff Van der Linde)	$y = \frac{hw}{zs\sqrt{2\pi}} \frac{\exp\left[-\frac{(x-z)^2}{2w^2}\right]}{\left[\exp\left(\frac{zs}{w^2}\right) - 1\right]^{-1} + \frac{1}{2} \left[1 + \operatorname{erf}\left(\frac{1}{\sqrt{2}} \frac{x-z}{w}\right)\right]}$	[65,167]	1, 2, 4 chromatography	• single maximum • fronted, symm. <sup>a</sup> or tailed • stat. moment zero (area) known [145]	[65,79,92,111, 136,145,167]
Intermediate	$y = \frac{h\{\exp[-a(x-u)] - \exp[-b(x-u)]\}}{b-a}$ $y = 0$ constraints: $a > 0, b > a$	for $x \geq u$ for $x < u$ [167]	7 chromatography spectroscopy	• single maximum • parameter $u$ exact • tailed only	[167]
Koskelo (modified gaussian)	$y = h \exp\left[\frac{s_2^2 2x - 2z + s_1^2}{2w^2}\right]$ $y = h \exp\left[-\frac{(x-z)^2}{2w^2}\right]$ $y = h \exp\left[\frac{s_2^2 2z - 2x + s_2^2}{2w^2}\right]$	for $x < z - s_1^2$ for $z - s_1^2 x z + s_2^2$ for $x > z + s_2^2$ [101]	1, 2 spectroscopy	• single maximum • parameters $h, z, s_1, s_2$ exact • fronted, symm. or tailed	[101,180]
Kowalski Isenhour	$y = h \left[ \operatorname{sech}\left(\frac{x-z}{w}\right) \right]^a$ constraints: $a > 0$		7 spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[102]
Laplace (double exp.)	$y = h \exp\left[-\frac{\sqrt{2} x-z }{w}\right]$	[167]	7 spectroscopy	• single maximum • parameters $h, z, w$ exact • symmetric only	[167]
Levy Martin	$y = h \exp\left\{-\frac{(x-z)^2}{2[w + s(x-z)]^2}\right\}$ $y = 0$ (this function can be considered a simplified Torres–Lapasio function. It has been used as the first part of a linear combination to represent polarographic peaks)	for $x > z - w/s$ (if $s \geq 0$ ) or for $x < z - w/s$ (if $s < 0$ ) for $x \leq z - w/s$ (if $s \geq 0$ ) or for $x \geq z - w/s$ (if $s < 0$ ) [78]	1 chromatography voltammetry	• single maximum • parameters $h, z, s$ exact • fronted, symm. or tailed	[78,172,173]
Li – A	$y = \frac{h[2\exp(-2) + 1]}{\exp\left(2\frac{z-w-x}{w}\right) + \exp\left(2\frac{x-z-w}{w}\right) + 1}$		7 chromatography	• single maximum • parameters $h, z, w$ exact • symmetric only	[111]

Table 1. Continued

Most used name/s	Equation	Applications	Properties	References
Li – B	$y = \frac{h}{\left[1 + a_1 \exp\left(\frac{z-w-x}{w}\right)\right]^{a_2} + \left[1 + b_1 \exp\left(\frac{x-z-w}{w}\right)\right]^{b_2} - 1}$ constraints: $a_1, a_2, b_1, b_2 > 0$ [111]	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[111]
Li – C	$y = \frac{h}{\left[1 + a_1 \exp\left(\frac{z-w-x}{w}\right)\right]^{(z-w)/x a_2} + \left[1 + a_2 \exp\left(\frac{x-z-w}{w}\right)\right]^{(x/(z+w)) b_2} - 1}$ constraints: $a_1, a_2, b_1, b_2 > 0$ [111]	7 chromatography	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[111]
Littlewood	$y = h \sqrt{\frac{z}{x}} \exp\left[-\frac{2z}{w^2}(\sqrt{z} - \sqrt{x})^2\right]$ for $x > 0$ $y = 0$ for $x \leq 0$ [69]	1 chromatography	<ul style="list-style-type: none"> <li>• parameter <math>w</math> exact</li> <li>• tailed only</li> </ul>	[69,70,133,136]
Logistic (theoretical voltammetric peak)	$y = h \frac{4 \exp\left(-\frac{x-z}{w}\right)}{\left[1 + \exp\left(-\frac{x-z}{w}\right)\right]^2}$ [125,167]	1, 5 spectroscopy voltammetry	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w</math> exact</li> <li>• symmetric only</li> <li>• stat. moment zero (area) known [84]</li> </ul>	[43,84,125,167]
Asymmetric Logistic (logistic power)	$y = h \left[1 + \exp\left(-\frac{x+w \ln(s)-z}{w}\right)\right]^{-s-1} s^{-s} (s+1)^{s+1} \exp\left[-\frac{x+w \ln(s)-z}{w}\right]$ constraints: $s > 0$ [167]	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w, s</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[167]
Log-normal (skewed gaussian) (Fraser-Suzuki)	$y = h \exp\left\{-\frac{\ln r}{(\ln s_r)^2} \left\{\ln\left[\frac{(x-z)(s_r^2-1)}{w_r s_r} + 1\right]\right\}^2\right\}$ for $x > z - \frac{w_r s_r}{s_r^2 - 1}$ $y = 0$ for $x \leq z - \frac{w_r s_r}{s_r^2 - 1}$ constraints: $s_r > 0, s_r \neq 1, 1 < r < \infty$ [56 ( $r=2$ ), 58 ( $r=2$ ), 69 ( $r=2$ ), 71,111,135,137,165 ( $r=2$ ), 167 ( $r=2$ )]	1, 2, 4 chromatography FIA spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w, s_r</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known [71,135,145]</li> </ul>	[8,55,56,58,69–71,92, 109,111,133,135–137,145, 152,163–165,167,185]
3 parameters Log-normal	$y = \frac{h}{wx\sqrt{2\pi}} \exp\left[-\frac{\ln^2\left(\frac{x}{z}\right)}{2w^2}\right]$ [125]	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• tailed only</li> </ul>	[125,167]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Lorentzian (Cauchy)	$y = \frac{h}{1 + 4\left(\frac{x-z}{w}\right)^2}$	[2,5,39,40,54–56,84, 99,107,109,128,146]	1, 2, 3, 4, 5 chromatography spectroscopy voltammetry mass spectrom.	• single maximum • parameters $h, z, w$ exact • symmetric only	[1,2,4,5,25,39–41,43,53–56, 58,68,84,87,88,95,99,107, 109,113,125,128,144,146–148, 151,152,158,161,167–169,189] (rev. Maddams)
Lorentzian–Gaussian product	$y = h \frac{\exp\left[-(1-a)\frac{(x-z)^2}{2w^2}\right]}{1 + a\frac{(x-z)^2}{w^2}}$ constraints: $0 \leq a \leq 1$	[167]	1, 2, 3 spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[1,49,64,68,113,147,148,150,167] (rev. Maddams)
Asymmetric Lorentzian–Gaussian product	$y = h \frac{\exp\left\{-\frac{1-a}{2}\left\{\frac{x-z}{w[1+s(x-z)]}\right\}^2\right\}}{1 + a\left\{\frac{x-z}{w[1+s(x-z)]}\right\}^2}$ $y = 0$ constraints: $0 \leq a \leq 1$	for $x > z - 1/s$ (if $s \geq 0$ ) or for $x < z - 1/s$ (if $s < 0$ )  for $x \leq z - 1/s$ (if $s \geq 0$ ) or for $x \geq z - 1/s$ (if $s < 0$ )	7 spectroscopy	• single maximum • parameters $h, z$ exact • fronted, symm. or tailed	[113]
Lorentzian–Gaussian sum (linear combination) (Pseudo Voigt 1)	$y = h \left\{ a \exp\left[-4 \ln 2 \frac{(x-z)^2}{w^2}\right] + \frac{1-a}{1 + 4\frac{(x-z)^2}{w^2}} \right\}$ constraints: $0 \leq a \leq 1$	[55–57,150]	1, 2, 5 spectroscopy voltammetry	• single maximum • parameters $h, z$ exact • symmetric only	[13,43,49,55–57,63,64,117,118, 125,143,147,148,150,152,167, 169,171,176,177] (rev. Maddams)
Asymmetric Lorentzian–Gaussian sum (linear combination) (Pseudo Voigt 2)	$y = h \left\{ a \exp\left\{-\frac{\ln 2}{s^2} \left[\ln\left(\frac{2s(x-z)}{w} + 1\right)\right]^2\right\} + \frac{1-a}{1 + \frac{\left[\ln\left(\frac{2s(x-z)}{w} + 1\right)\right]^2}{s^2}} \right\}$ $y = 0$ constraints: $s \neq 0, 0 \leq a \leq 1$	[18,55]	1 chromatography spectroscopy voltammetry	• single maximum • parameters $h, z$ exact • fronted, symm. or tailed	[18,39,55,125]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
bi-Lorentzian–Gaussian sum	$y = h \left\{ a \exp \left[ -\frac{(x-z)^2}{2w_1^2} \right] + (1-a) \left[ 1 + \frac{(x-z)^2}{w_1^2} \right]^{-1} \right\}$ $y = h \left\{ b \exp \left[ -\frac{(x-z)^2}{2w_2^2} \right] + (1-b) \left[ 1 + \frac{(x-z)^2}{w_2^2} \right]^{-1} \right\}$ <p>constraints: <math>0 \leq a \leq 1, 0 \leq b \leq 1</math></p>	<p>for <math>x &lt; z</math></p> <p>for <math>x \geq z</math></p> <p>[145]</p>	<p>2, 4 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w_1, w_2</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[145]
Mixed Lorentzian–Gaussian	$y = h \exp \left[ -\frac{(x-z)^2}{2w_1^2} \right]$ $y = h \left[ 1 + \left( \frac{x-z}{w_2} \right)^2 \right]^{-1}$	<p>for <math>x &lt; z</math></p> <p>for <math>x \geq z</math></p>	<p>4 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w_1, w_2</math> exact</li> <li>• fronted or tailed only</li> </ul>	[108]
Losev – A	$y = \frac{h}{\exp \left( -\frac{x-z}{w_1} \right) + \exp \left( \frac{x-z}{w_2} \right)}$		<p>7 spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>w_1, w_2</math> exact</li> <li>• fronted, symm. or tailed</li> <li>• stat. moments known [114]</li> </ul>	[113,114]
Losev – B	$y = \frac{h}{\left[ \exp \left( -\frac{x-z}{w_1} \right) + \exp \left( \frac{x-z}{w_2} \right) \right]^a}$ <p>constraints: <math>a &gt; 0</math></p>		<p>7 spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>w_1, w_2</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[113]
NLC (Non-linear chromatogr.)	$y = \frac{h}{ws} \left[ 1 - \exp \left( -\frac{s}{w} \right) \right] \frac{\sqrt{\frac{z}{x}} I_1 \left( \frac{2\sqrt{zx}}{w} \right) \exp \left( \frac{-x-z}{w} \right)}{1 - \left[ 1 - \exp \left( -\frac{s}{w} \right) \right] T \left( \frac{z}{w}, \frac{x}{w} \right)}$ $T(r, v) = \exp(-v) \int_0^r \exp(-t) I_0(2\sqrt{vt}) dt$ $I_n(t) = \sum_{k=0}^{\infty} \frac{1}{k!(k+n)!} \left( \frac{t}{2} \right)^{2k+n} = \text{modified Bessel function of kind } n$	[65,111]	<p>1, 4 chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[65,91,111,167,181]
Parabola	$y = h \left[ 1 - \left( \frac{x-z}{w} \right)^2 \right]$ <p><math>y = 0</math></p>	<p>for <math>z-w \leq x \leq z+w</math></p> <p>for <math>x &lt; z-w</math> and for <math>x &gt; z+w</math></p>	<p>4 chromatography spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w</math> exact</li> <li>• symmetric only</li> </ul>	[53,146,169]



Table 1. Continued

Most used name/s	Equation	Applications	Properties	References
Pearson IV	$y = h \exp \left\{ -s_2 \left[ \tan^{-1} \left( \frac{x - \frac{ws_2}{2s_1} - z}{w^2} \right) + \tan^{-1} \left( \frac{s_2}{2s_1} \right) \right] \right\}$ $\times \left( 1 + \frac{s_2^2}{4s_1^2} \right)^{s_1} \left[ 1 + \frac{\left( x - \frac{ws_2}{2s_1} - z \right)^2}{w^2} \right]^{-s_1}$ <p>constraints: <math>s_1 &gt; 0</math> [167]</p>	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> </ul>	[167]
Pearson IVa	$y = \frac{hs}{w} \exp \left[ s \tan^{-1} \left( \frac{x + \frac{ws}{2} - z}{w} \right) \right] \left[ 1 + \frac{\left( x + \frac{ws}{2} - z \right)^2}{w^2} \right]^{-1} \left[ \exp \left( \frac{s\pi}{2} \right) - \exp \left( -\frac{s\pi}{2} \right) \right]^{-1}$ <p>constraints: <math>s \neq 0</math> [167]</p>	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>z, s</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> </ul>	[167]
Pearson IVb	$y = \frac{hs}{2w} \exp \left( \frac{s\pi}{2} \right) (4 + s^2) \exp \left[ s \tan^{-1} \left( \frac{x + \frac{ws}{4} - z}{w} \right) \right] \left[ 1 + \frac{\left( x + \frac{ws}{4} - z \right)^2}{w^2} \right]^{-2} (\exp(s\pi) - 1)^{-1}$ <p>constraints: <math>s \neq 0</math> [167]</p>	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>z, s</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> </ul>	[167]
Pearson VII (Fraser Suzuki)	$y = h \left[ 1 + 4 \left( \frac{x - z}{w} \right)^2 (2^{1/a} - 1) \right]^{-a}$ <p>constraints: <math>a &gt; 0</math> [30,56,84,167]</p>	1 spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• symmetric only</li> <li>• stat. moment zero (area) known [55,84]</li> </ul>	[30,55,56,84,125,167,169] (rev. Maddams)
Asymmetric Pearson VII (asymmetric Fraser Suzuki)	$y = \frac{h}{\left\{ 1 + \frac{2a^2 - 1}{s^2} \left\{ \ln \left[ \frac{2s(x - z)}{w} + 1 \right] \right\}^2 \right\}^{a-2}}$ <p>for <math>x &gt; z - w/2s</math> (if <math>s &gt; 0</math>) or <math>x &lt; z - w/2s</math> (if <math>s &lt; 0</math>)</p> $y = 0$ <p>for <math>x \leq z - w/2s</math> (if <math>s &gt; 0</math>) or <math>x \geq z - w/2s</math> (if <math>s &lt; 0</math>)</p> <p>constraints: <math>0 &lt; a &lt; \sqrt{2}, s \neq 0</math> [55]</p>	1 spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> </ul>	[55] (rev. Maddams)

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Poisson (Gamma) (Martin–Singe)	$y = h \exp\left\{(1-a)\left[\frac{x}{z} - \ln\left(\frac{x}{z}\right) - 1\right]\right\}$ $y = 0$ constraints: $a > 1$	for $x \geq 0$ for $x < 0$ [69]	1, 2, 4 chromatography	• single maximum • parameters $h, z$ exact • tailed only • stat. moments known [74]	[21,31,37,69,70,74, 111,133,136,137, 146,154,178,184]
Inverse Polynomial	$y = h \left[1 + a\left(2\frac{x-z}{w}\right)^2 + b\left(2\frac{x-z}{w}\right)^4 + c\left(2\frac{x-z}{w}\right)^6\right]^{-1}$ constraints: $a > 0, b > 0, c > 0$	[125]	7 spectroscopy	• single maximum • parameters $h, z$ exact • symmetric only	[125]
Pulse	$y = 4h \exp\left(-\frac{x-u}{w}\right) \left[1 - \exp\left(-\frac{x-u}{w}\right)\right]$ $y = 0$	for $x \geq u$ for $x < u$ [167]	7 chromatography spectroscopy	• single maximum • parameters $u, w$ exact • tailed only	[167]
Pulse with power term	$y = h \exp\left(-\frac{x-u}{w}\right) \left[1 - \exp\left(-\frac{x-u}{w}\right)\right]^a$ $y = 0$	for $x \geq u$ for $x < u$ [125]	7 chromatography spectroscopy	• single maximum • parameter $w$ exact • tailed only	[125,167]
Sherwood	$y = h\{GL(x) + [1 - GL(x)]T(x)\}$ $GL(x)$ =Lorentzian–Gaussian sum or product $T(x) = b \exp\left[- x-z \frac{(1-c)^d}{c^e}\right]$ $T(x) = 0$ constraints: $0 \leq b \leq 1, c \cong 0.3, d \cong 1, e \cong 0.2$	for $x > z$ (tailed peaks) or for $x < z$ (fronted peaks) for $x \leq z$ (tailed peaks) or for $x \geq z$ (fronted peaks)	2 spectroscopy	• single maximum • parameters $h, z$ exact • fronted or tailed only	[113,150]
Symmetric double Sigmoid	$y = \frac{h \left[1 + \exp\left(-\frac{w}{2s}\right)\right] \left[1 + \exp\left(\frac{w}{2s}\right)\right] \exp\left(-\frac{x-z}{w}\right)}{\left[1 + \exp\left(-\frac{x-z+\frac{w}{2}}{s}\right)\right] \left[1 + \exp\left(-\frac{x-z-\frac{w}{2}}{s}\right)\right]}$	[167]	7 chromatography spectroscopy	• single maximum • tailed only	[167]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Asymmetric double Sigmoid	$y = h \left[ 1 + \exp \left( - \frac{x-z+\frac{w}{2}}{s_1} \right) \right]^{-1} \left\{ 1 - \left[ 1 + \exp \left( - \frac{x-z-\frac{w}{2}}{s_2} \right) \right]^{-1} \right\}$	[125,167]	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• fronted, symm. or tailed</li> </ul>	[125,167]
Square Sine	$y = h \left[ \sin \left( \frac{\pi}{2} \frac{x-u}{z-u} \right) \right]^2$ <p><math>y = 0</math> constraints: <math>z &gt; u</math></p>	<p>for <math>u \leq x \leq 2z - u</math></p> <p>for <math>x &lt; u</math> and for <math>x &gt; 2z - u</math> [53,125,169]</p>	4 spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, u</math> exact</li> <li>• symmetric only</li> </ul>	[53,125,169]
Student (4° order Lorentzian)	$y = \frac{h}{\left[ 1 + 4 \frac{(x-z)^2}{w^2} \right]^2}$	[128]	1 spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w</math> exact</li> <li>• symmetric only</li> </ul>	[9,10,128] (rev. Maddams)
Student $t$	$y = \frac{h}{\left[ 1 + \frac{(x-z)^2}{sw^2} \right]^{(s/2)+(1/2)}}$ <p>constraints: <math>s &gt; 0</math></p>	[167]	7 chromatography spectroscopy	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• symmetric only</li> </ul>	[167]
Torres–Lapasio	$y = h \exp \left\{ - \frac{(x-z)^2}{2 \left[ w + \sum_{i=1}^n s_i (x-z)^i \right]^2} \right\}$	[172]	4 chromatography	<p>for <math>n = 0</math> see Gaussian</p> <p>for <math>n = 1</math> see Levy/Martin</p> <p>for <math>n &gt; 1</math>:</p> <ul style="list-style-type: none"> <li>• parameters <math>h, z</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[172,173]

Table 1. Continued

Most used name/s	Equation		Applications	Properties	References
Triangle	$y = h \left( 1 - \frac{ x-z }{w} \right)$ $y = 0$	<p>for <math>z-w \leq x \leq z+w</math></p> <p>for <math>x &gt; z+w</math> or <math>x &lt; z-w</math></p> <p>[146]</p>	<p>4</p> <p>chromatography</p> <p>spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, w</math> exact</li> <li>• symmetric only</li> </ul>	[53,146,169]
V. Haverbeke Brown	$y = h \left\{ a \exp \left\{ -\ln 2 \left[ \frac{x-z}{w} - s \left  \frac{x-z}{w} \right  \right]^2 \right\} + \frac{1-a}{1 + \left[ \frac{x-z}{w} - s \left  \frac{x-z}{w} \right  \right]^2} \right\}$ <p>constraints: <math>0 \leq a \leq 1</math></p>	[176]	<p>7</p> <p>spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, s</math> exact</li> <li>• fronted, symm. or tailed</li> </ul>	[176] (rev. Maddams)
Voigt (Gaussian- Lorentzian convolut.)	$y = \frac{2h\sqrt{2}}{w_1 w_2 \sqrt{3\pi^3}} \int_{-\infty}^{\infty} \exp \left[ -2 \left( \frac{t-z}{w_1} \right)^2 \right] \left[ 1 + \frac{4}{3} \left( \frac{x-t}{w_2} \right) \right]^{-1} dt$	[143]	<p>1, 3</p> <p>spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameter <math>z</math> exact</li> <li>• symmetric only</li> </ul>	[28,56,64,68,99,125,143 (and ref. therein) 147 (and ref. therein), 158, 167]
Weibull	$y = h \exp \left\{ \frac{a-1}{a} \left[ 1 - \left( \frac{x-u}{z-u} \right)^a + a \ln \left( \frac{x-u}{z-u} \right) \right] \right\}$ $y = 0$ <p>constraints: <math>a &gt; 1</math></p>	<p>for <math>x &gt; u</math></p> <p>for <math>x \leq u</math></p> <p>[69]</p>	<p>1</p> <p>chromatography</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z, u</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> <li>• stat. moments known (see GEX)</li> </ul>	[69,70,133,136,137,167]
Weibull 3 (Weibull)	$y = h \left( \frac{a-1}{a} \right)^{(1-a)/a} \left[ \frac{x-z}{w} + \left( \frac{a-1}{a} \right)^{1/a} \right]^{a-1}$ $\times \exp \left\{ - \left[ \frac{x-z}{w} + \left( \frac{a-1}{a} \right)^{1/a} \right]^a + \frac{a-1}{a} \right\}$ $y = 0$	<p>for <math>x &gt; z - \left( \frac{a-1}{a} \right)^{1/a}</math></p> <p>for <math>x \leq z - \left( \frac{a-1}{a} \right)^{1/a}</math></p> <p>[125,167]</p>	<p>7</p> <p>chromatography</p> <p>spectroscopy</p>	<ul style="list-style-type: none"> <li>• single maximum</li> <li>• parameters <math>h, z</math> exact</li> <li>• fronted, symm.<sup>a</sup> or tailed</li> </ul>	[125,167]

<sup>a</sup> Not exactly but practically symmetric.

for some other functions the height depends also on other parameters.

- z* parameter which is mainly or only related to the retention time of the peak. For some functions *z* represents *exactly* the retention time, which conversely can be modified only by changing *z*; for some other functions the retention time depends also on other parameters.
- u* parameter which is mainly or only related to the abscissa of the peak start. For some functions *u* represents *exactly* this abscissa, which conversely can be modified only by changing *u*; for some other functions the peak start depends also on other parameters.
- w* parameter which is mainly or only related to the width of the peak. For different functions the value of *w* may be related to the width at different heights of the peak. For some functions the width can be modified only by changing *w*, but more commonly it depends also on other parameters.
- s* parameter which is mainly or only related to the symmetry of the peak; ideally, *s* should be positive for fronted, zero for symmetric and negative for tailed peaks (or vice versa), but this is the case only for some functions: as for *w*, the exact “physical meaning” of *s* is peculiar to each function. For some functions the symmetry can be modified only by changing *s*, for some others it depends also on other parameters.

All the parameters quoted above (with the exception of *s*) are always positive for “positive” peaks, like those usually encountered in chromatography. Negative peaks can be fitted simply by changing the sign of the appropriate parameter.

The second group includes parameters which (usually) cannot be directly correlated to a measurable property of the experimental peak, and often affect the peak shape in a complex way. The value of this kind of parameters (which have been indicated with lower-case letters, *a*, *b*, etc.) is generally difficult to estimate; this fact can negatively affect the convergence of a least-squares non-linear fitting algorithm to the true minimum [149]. In addition, parameters of this kind are often strongly correlated to one or more of the other ones, thus further

impairing the convergence [149]. For these reasons, we decided to avoid, if possible, adopting equations which contain a large number of parameters of this kind. For example, in the case of the Giddings function, Eq. (2) has been preferred to Eq. (1), although the former has been used to a lesser extent:

$$y = \sqrt{\frac{ab}{x}} \exp(-ax - b) I_1(\sqrt{4abx}) \quad (1)$$

$$y = \frac{h}{w} \sqrt{\frac{z}{x}} \left[ \exp\left(-\frac{x+z}{w}\right) \right] I_1\left(\frac{2\sqrt{zx}}{w}\right) \quad (2)$$

(in both equations,  $I_1(t)$  represents the modified Bessel function of the first kind, see Table 1). In other cases the change of the parameters had mainly the goal of uniforming the symbolism of the equations (see above), as e.g. in the case of the Losev functions, which has been changed from (3) to (4):

$$y = \frac{h}{\exp[-a(x-z)] + \exp[b(x-z)]} \quad (3)$$

$$y = \frac{h}{\exp\left(-\frac{x-z}{w_1}\right) + \exp\left(\frac{x-z}{w_2}\right)} \quad (4)$$

If a function is defined, or if it can be employed, only in a finite interval of values of the independent variable and/or of some of the optimisable parameters, the extremes of these intervals are reported; however, the fact that *x*, *h*, *z*, *u* and *w* must always be positive is implied.

In the third column of the table we report the techniques, in which the functions have been employed, and the applications; the latter are coded as follows:

1. peak fitting and/or “deconvolution” of poorly resolved peaks;
2. calculation of statistical moments and *cfom* in general;
3. effect of one or more experimental parameters on the shape of the peaks;
4. simulations;
5. improvement of the signal-to-noise ratio;
6. memorization of chromatograms/spectra;
7. function proposed for peak representation but, to our knowledge, not used till now.

In the fourth column of the table, some favourable mathematical properties of the functions are re-

ported. The properties considered (which refer to the chosen equation and are valid only within the reported existence intervals of the independent variable and of the optimisable parameters) are the following:

- *single maximum*: the function is unimodal (has a single maximum) for every combination of the parameters. The possibility for a function to exhibit more than one maximum could impair the results in some applications (especially in the “deconvolution” of poorly resolved peaks).
- *parameters (. . .) exact*: the listed parameters are not merely related to the height, retention time, abscissa of the start, width and skew of the peak, respectively (see above), but they represent exactly, and only, these peak shape characteristics; conversely these characteristic can be modified only by changing the corresponding parameter. Therefore, the listed parameters can be accurately estimated from the shape of the experimental peak. This property is generally welcome in the fitting procedure.
- *fronted, symmetric or tailed*: the function is sufficiently flexible and can assume all the possible chromatographic shapes. This property is welcome for a more general use of the function.
- *statistical moments known*: the relations between the parameters of the function and the statistical moments are reported in the literature; in this case, the references are given. We just remember that the statistical moments of a function  $f(x, h, z, \dots)$  are defined by the equations:

area (moment zero):

$$m_0(h, z, \dots) = \int_p^q f(x, h, z, \dots) dx$$

mean (first moment):

$$m_1(h, z, \dots) = \int_p^q \frac{x \cdot f(x, h, z, \dots)}{m_0(h, z, \dots)} dx$$

$i$ th central moment:

$$m_i(h, z, \dots) = \int_p^q \frac{[x - m_1(h, z, \dots)]^i \cdot f(x, h, z, \dots)}{m_0(h, z, \dots)} dx$$

$(i = 2, 3, \dots)$

( $p$  and  $q$  represent the extremes of the interval in which the function is defined) and in principle they can be obtained in explicit form if  $f(x, h, z, \dots)$  is known. The resolution of these integrals can however be difficult, also with the help of powerful mathematical softwares, and in many cases only approximate solutions can be obtained. As a consequence, in the latter cases the direct calculations of the statistical moments with curve fitting could be not very accurate.

These properties represent an “a priori” measure of the usefulness of a given function and allow to anticipate if it can be used for a specific application. However, the “usefulness” of a function depends also on a property which cannot be evaluated a priori: its ability to represent the instrumental data, i.e. the attainable goodness-of-fit. This property could be defined only on a statistical basis, by fitting the function to a large number of experimental peaks obtained at the different experimental conditions.

The fifth column contains the references. The lists include also several papers in which the relevant equation has been merely used, without discussing its properties; these papers are included because they could be helpful in evaluating the quality of the results obtained with the function for a given application.

The citation of a given function by Maddams in his review [116] is underlined in this same column.

### 3. Remarks on some functions

Five of the functions reported in Table 1, i.e. the Exponentially Modified Gaussian (EMG), Poisson, Log-normal, Gram–Charlier series and Edgeworth–Cramér series, will now be shortly reviewed and commented:

#### 3.1. The EMG (Exponentially Modified Gaussian)

The literature on EMG is quite large, including three reviews [51,81,90] and a number of papers dealing with its calculation [3,17,22,33,34,110]. The model from which the function has been obtained is rather simple and verisimilar [17,94,160], and the goodness-of-fit obtained for experimental peaks is generally good (see e.g. [20,131]). This explains the popularity of the EMG, which is by far the most

frequently used function in chromatography and in flow injection analysis.

The equation proposed here (Table 1) has never been used in the literature, but it is rather simple and compact, and includes explicitly the error function (erf) which is available in most graphical and mathematical software packages (on the contrary, most of the equations reported in the literature include the error function implicitly, as a definite integral). We must remark that in the EMG the value of  $s$  must be larger than zero. This fact has two disadvantages: first, the function can be used to represent only tailed and not fronted peaks; second, at least with some equations (including the one we propose), the computations can lead to an overflow error at very low values of asymmetry ( $s \approx 0$ ) [3,33,34,110]. This latter difficulty can easily be overcome by using “high precision” variables. The first limitation is overcome by the so-called “generalized” EMG which, strangely enough, has been only marginally employed.

In Table 2 all the other formulae for the EMG reported in the literature (almost 20) are listed. Between them, the equations from 1 to 7 are all mathematically equivalent each other; the ones from 8 to 12 are approximate expressions, equivalent to the “true” EMG only in the case (generally true) in which  $z$  is much larger than  $s$  [81]. The other equations, starting from the 13th to the end, represent functions which are all different each from the other and also from the first 12: in these cases, there has been one or more printing errors (the presence in the literature of EMG equations with printing errors has been also noticed by Foley [51] and by Hanggi [81]).

### 3.2. The Poisson function

The Poisson function has been frequently employed to represent chromatographic peaks. A lot of equations are reported in the literature, since practically every author who used this function proposed a different equation (Table 3). We have chosen the equation of Grimalt et al. [69], because its parameters are less mutually correlated than for the other equations. Moreover, it is very simple and does not require the calculation of the factorial, which for non-integer arguments requires the calculation of the gamma function ( $\Gamma$ ).

It is useful to notice that the two names assigned

to this function, Poisson and Gamma, could be confusing. In fact, the equation chosen by us and the one marked “(2)” (see Table 3), which usually have been called “Gamma”, are apparently very different from all the others, which usually have been called “Poisson” (or “Martin-Singe”), leading to the conclusion that they are two different functions. On the contrary, they are identical, as it has been noticed also by Wu et al. [184]. We recommend to use only the name “Poisson” (even if Wu et al. proposed “Gamma”) to avoid the confusion with a different function proposed by Li et al. [111] and called “Gamma” ( $\gamma$ ) by these authors.

### 3.3. The Log-normal function

The Log-normal function has been used quite often to represent mainly chromatographic and FIA peaks and sometimes spectroscopic peaks too (see references in Table 1). The Log-normal is a very good function for chromatographic peaks, so that some authors have preferred to use it instead of the EMG itself [69–71,133,135–137]. This function is often called also “Skewed gaussian” or “Fraser-Suzuki”. It can be noticed that very recently two different equations of the Log-normal have been considered to be two different functions [145] because of the different names. We recommend to use only the name “Log-normal”.

In Table 4 we list all the other equations reported in the literature, which are all mathematically equivalent each other. The first of these is identical to our proposed equation with a different definition for  $s$  and with  $r = 2$  ( $r$  is the ratio between  $h$  and the height at which  $w$  and  $s$  are computed). The properties of the two equations are the same; therefore, the choice was only due to the fact that the former appears to have been cited (slightly) more frequently.

### 3.4. The Edgeworth/Cramér series and the Gram/Charlier series

These series have been used largely for the evaluation of statistical moments in chromatography. A large number of different equations are reported in the literature, see Tables 5 and 6. Our proposed equations, first reported by Olive et al. [134], appear to be very complicated but, unlike the others, they

Table 2  
Equations and references for the EMG

$$y = \frac{hw}{s} \sqrt{\frac{\pi}{2}} \exp\left(\frac{w^2}{2s^2} - \frac{x-z}{s}\right) \left\{ 1 - \operatorname{erf}\left[\frac{1}{\sqrt{2}}\left(\frac{w}{s} - \frac{x-z}{w}\right)\right] \right\}$$


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Other equations and references	Notes
(1) $y = \frac{h}{ws\sqrt{2\pi}} \int_0^\infty [G(x)E] dt$	[7,32,33,42,62,75,108,112,141,142,154,186,188] $A(x) = \frac{x-z}{w\sqrt{2}}$
(2) $y = \frac{hw\sqrt{2}}{s} \exp[B^2 - 2A(x)B] \int_{-\infty}^{A(x)-B} \exp(-t^2) dt$	[50,51,58,61,75,121,122,129,156,183,185] $B = \frac{w}{s\sqrt{2}}$ $C(x) = \sqrt{2}[A(x) - B]$
(3) $y = \frac{h}{s\sqrt{2\pi}} \exp[B^2 - 2A(x)B] \int_{-\infty}^{C(x)} \exp\left(\frac{-t^2}{2}\right) dt$	[23,52,89–91,124,125,146,162] $G(x) = \exp\left[-\frac{1}{2}\left(\frac{x-z-t}{w}\right)^2\right]$
(4) $y = \frac{h}{2s} \exp[B^2 - 2A(x)B] \left\{ 1 - \operatorname{erf}\left[-\frac{C(x)}{\sqrt{2}}\right] \right\}$	[47,48,65,111,187] $E = \exp\left(-\frac{t}{s}\right)$
(5) $y = \frac{hw}{s} \exp[B^2 - 2A(x)B] \int_{-C(x)}^\infty \exp\left(\frac{-t^2}{2}\right) dt$	[33–35,172] $G^1 = \exp\left[-\frac{1}{2}\left(\frac{t-z}{w}\right)^2\right]$
(6) $y = \frac{h}{s\sqrt{\pi}} \exp[B^2 - 2A(x)B] \int_{-\infty}^{A(x)-B} \exp(-t^2) dt$	[90,108] $E^1(x) = \exp\left(-\frac{x-t}{s}\right)$
(7) $y = \frac{hw}{s} \exp[B^2 - 2A(x)B] \int_{-\infty}^{C(x)} \exp\left(\frac{-t^2}{2}\right) dt$	[50,51] $E^{11}(x) = \exp\left(-\frac{x-t+z}{s}\right)$
(8) $y = \frac{h}{ws\sqrt{2\pi}} \int_0^x [G^1 E^1(x)] dt$	[17,81,100]
(9) $y = \frac{h}{2s} \exp[B^2 - 2A(x)B] \left[ \operatorname{erf}\left(\frac{z}{w\sqrt{2}} + B\right) + \operatorname{erf}\left(\frac{C(x)}{\sqrt{2}}\right) \right]$	[81,131]
(10) $y = \frac{h}{ws\sqrt{2\pi}} \int_0^x [G(x)E] dt$	[81,131]
(11) $y = \frac{hw}{s} \exp[B^2 - 2A(x)B] \int_{-z/w}^{\sqrt{2}A(x)} \exp\left[-\frac{C^2(x)}{2}\right] \sqrt{2} dA(x)$	[160]
(12) $y = \frac{h}{s\sqrt{\pi}} \exp[B^2 - 2A(x)B] \int_{C(x=0)/\sqrt{2}}^{C(x)/\sqrt{2}} \exp(-t^2) dt$	[110]
(13) $y = \frac{h}{s} \int_{-\infty}^x [G^1 E^{11}(x)] dt$	[27,61,146]
(14) $y = \frac{hw}{s} \sqrt{\frac{\pi}{2}} \exp[B^2 - A(x)B] \operatorname{erf}\left(\frac{C(x)}{\sqrt{2}}\right)$	[7,11]
(15) $y = \frac{hw}{s} \sqrt{\frac{\pi}{2}} \exp[B^2 - 2A(x)B] \{1 + \operatorname{erf}(B - A(x))\}$	[46,145]
(16) $y = \frac{h}{ws\sqrt{2}} \left\{ \operatorname{erf}\left(\frac{z}{w} + \sqrt{2}B\right) + \operatorname{erf}(A(x) - \sqrt{2}B) \right\}$	[17]
(17) $y = \frac{hw}{s} \exp\{-[A(x)]^2\} \left\{ \sqrt{\frac{\pi}{2}} \exp\left\{\frac{[C(x)]^2}{2}\right\} + C(x) + \frac{[C(x)]^3}{3} + \frac{[C(x)]^5}{3.5} + K \right\}$	[34]
(18) $y = \frac{h}{w\sqrt{2\pi}} \int_0^x [G^1 E^1(x)] dt$	[43]

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Table 4  
Equations and references for the Log-normal

	$y = h \exp \left\{ - \frac{\ln r}{(\ln s_r)^2} \left\{ \ln \left[ \frac{(x-z)(s_r^2-1)}{w_r s_r} + 1 \right] \right\}^2 \right\}$		
(1)	$y = h \exp \left\{ - \frac{\ln 2}{s^2} \left\{ \ln \left[ \frac{2s(x-z)}{w} + 1 \right] \right\}^2 \right\}$		[8,55,109,145,163]
(2)	$y = h \exp \left\{ - \frac{\ln 2}{\left(\ln \frac{s}{w}\right)^2} \left\{ \ln \left[ \frac{(x-z) \left( \left(\frac{s}{w}\right)^2 - 1 \right)}{(s+w) \left(\frac{s}{w}\right)} + 1 \right] \right\}^2 \right\}$		[145]
(3)	$y = h \frac{b}{x-a} \exp(-c^2) \exp \left\{ - \frac{1}{2c^2} \left[ \ln \left( \frac{x-a}{b} \right) \right]^2 \right\}$		[164]
(4)	$y = \frac{h \sqrt{\ln 2} (s^2-1)}{sw \ln(s) \sqrt{\pi} \exp \left[ \frac{\ln(s^2)}{4 \ln 2} \right]} \exp \left\{ - \frac{\ln 2}{\ln(s)^2} \ln \left[ \frac{(x-z)(s^2-1)}{ws} + 1 \right]^2 \right\}$		[167]

require neither the derivation of the Gauss function nor the computation of the Hermite polynomials.

The number  $n$  of terms to be included in the calculation of the series is not univocally defined: in the literature,  $n$  is usually in the range 2–8 for the Edgeworth/Cramér, and 3–8 for the Gram/Charlier. It has been demonstrated [36,38,134] that  $n$  depends on the skew of the given experimental peak.

#### 4. Commercial softwares

Although generic mathematical or graphic softwares could be used in principle for the purpose of peak fitting, a number of specific programmes have been described in the literature for the treatment of chromatograms and spectrograms [4,7,8,16,24,25,31,41,45,51,56–58,61,63,82,84,86,99,101,104,106,

Table 3  
Equations and references for the Poisson

$y = h \exp \left\{ (1-a) \left[ \frac{x}{z} - \ln \left( \frac{x}{z} \right) - 1 \right] \right\}$					
(1)	$y = \frac{x^b}{a^{b+1} b!} \exp \left( - \frac{x}{a} \right)$	[21,37,74]	(6)	$y = \frac{h}{\sqrt{2\pi(a-1)}} \left( \frac{x}{z} \right)^{a-1} \frac{a^a}{(a-1)^{a-1}} \exp \left[ - \frac{ax}{z} + a - 1 \right]$	[178]
(2)	$y = h \left( \frac{x}{z} \right)^{a-1} \exp[-b(x-z)]$	[184]	(7)	$y = h \frac{a(x-u)}{a!} \exp(-x+u)$	[154]
(3)	$y = \frac{[b(x-u)]^a}{a!} \exp[-b(x-u)]$	[31]	(8)	$y = h \frac{b^a}{\Gamma(a)} (x-u)^{a-1} \exp[-b(x-u)]$	[184]
(4)	$y = \frac{[a+b(x-z)]^a}{a!} \exp[-a-b(x-z)]$	[31]	(9)	$y = h \exp\{a[\exp(ix) - 1]\}$	[146]
(5)	$y = \left[ 1 + \frac{b}{a}(x-z)^a \right] \exp[-b(x-z)]$	[31]	(10)	$y = \frac{x^b}{a^b b!} \exp \left( - \frac{x}{a} \right)$	[111]

110, 124, 125, 132, 146, 149, 152, 153, 161, 163, 167, 168, 173, 188].

These programmes were mainly written ad hoc for “personal” use. There are however some commercial softwares which can be bought alone or as modules together with other more general programs. To our knowledge, the existing softwares are “Peak-solve” (Galactic) [56], “Peakfitter” (Microcal) [125], and “Peakfit” (SPSS) [167]. These softwares have been reviewed in the literature (see e.g. [16,77,82]); therefore we will simply report here how many and which “built-in” functions are included in the database of each programme.

Galactic “Peaksolve” contains only a small number of built-in functions: Gaussian, Log-normal, Lorentzian, Lorentzian–Gaussian sum, Pearson VII, Voigt. The absence of the most frequently employed chromatographic function, the EMG, has to be underlined.

Microcal “Peakfitter” divides the “built-in” functions in “chromatographic” (Chesler/Cram–B, Edgeworth/Cramér series, EMG, Gaussian, Giddings, Gram/Charlier series), “spectroscopic” (Gaussian, Lorentzian, Lorentzian–Gaussian sum, asymmetric Lorentzian–Gaussian sum, Lorentzian, Pearson VII, inverse Polynomial, Voigt), “generic peak” (Beta, Extreme Value, Gaussian, Logistic, 3-parameters Log-normal, Lorentzian, Lorentzian–Gaussian sum, asymmetric Lorentzian–Gaussian sum, Pearson VII, inverse Polynomial, asymmetric double Sigmoid, Weibull 3) and “other type” (exponential, trigonometric, etc.; between them, only the square Sine can assume a “peak-like” shape).

SPSS “Peakfit” lists the highest number of built-in functions, which as for Peakfitter are classified in different groups: “chromatographic” (generalized EMG, EMG+GMG, Extreme Value fronted, Extreme Value tailed, Gaussian, GEMG4, GEMG5, Giddings, GMG, HVL, Log-normal, NLC), “spectroscopic” (Gaussian, constrained Gaussian, Lorentzian, Lorentzian–Gaussian product, Lorentzian–Gaussian sum, Pearson VII, Voigt), “miscellaneous peak” (Cumulative, asymmetric Cumulative, Erf, Intermediate, asymmetric Logistic, Logistic power, Pulse, Pulse with power term, symmetric double Sigmoid, asymmetric double Sigmoid), “statistical” (Beta, Error, 4-parameters Extreme Value, Extreme Value fronted, Extreme Value tailed,

F-variance, Gamma, inverted Gamma, Gaussian, Laplace, Logistic, Log-normal, 3-parameters Log-normal, Lorentzian, Pearson IV, Pearson IVa, Pearson IVb, Student *t*, Weibull 3), and “transition” (sigmoid-like functions). Unlike the latter, the statistical functions actually possess a reasonably good “peak-like” shape and they therefore were included in Table 1, even if not specifically proposed for chromatography or spectroscopy. “Peakfit” includes two equations (with the same denomination) for several functions, in one case *h* representing the maximum height and in the other case the area. In a few cases, however, pairs of mathematically equivalent functions have been presented with two different denominations.

In general, two apparently contradictory observations can be done regarding the built-in functions included in these three commercial softwares. First, a number of equations employed in the literature for peak representation are not made available (note, however, that it is always possible to create a “personal” function and use it instead of a built-in one). Second, to our knowledge, several built-in functions (especially those of SPSS “Peakfit”) have never been considered in the literature for peak fitting purposes.

## 5. Conclusions

In this paper, we collected and tabulated 86 functions proposed for the representation of chromatographic peaks. The most used name, the most convenient equation, the applications, the mathematical properties (in relation to the possible applications) and a list of references are reported for each function (Table 1). The built-in functions employed in some commercial peak-fitting software packages have been included, too.

An important objective of this work has been the individuation and elimination of a number of ambiguities, which sometimes appear to have propagated, in the denomination of the reported functions. Quite often the same name has been assigned to different functions, or conversely a single function has been designated with different names. We underlined these cases, which especially (but not only)

Table 5  
Equations and references for the Edgeworth/Cramér series

$$y = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right] \left\{ 1 + \sum_{i=1}^n \left\{ (-1)^i \sum_{j=1}^i \left\{ (-1)^i c_{i,i+2j} (i+2j)! \sum_{k=0}^{\text{floor}((i+2j)/2)} \left[ \frac{(-1)^k \left( \frac{x-z}{w} \right)^{i+2-2k}}{2^k k! (i+2-2k)!} \right] \right\} \right\} \right\}$$

Other equations and references		Notes
(1)	$y = G(t) + \sum_{i=1}^n Q_i(-t)$	[36–38,111,155] $Q_i(-t)$ : see [36]
(2)	$y = G(t) \left\{ 1 + \sum_{i=1}^n \left\{ (-1)^i \sum_{j=1}^i \left[ (-1)^i c_{i,i+2j} H_{i+2j}(x) \right] \right\} \right\}$	[134] $c_{i,i+2j}$ : see [134]
(3)	$y = G(t) + \sum_{i=1}^n \left\{ (-1)^i \sum_{j=1}^i \left[ c_{i,i+2j} G^{(i+2j)}(t) \right] \right\}$	[134] $H_i(t) = (-1)^i \frac{G^{(i)}(t)}{G(t)}$ (Hermite pol.)  $G(t) = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right]$  or $\frac{h}{w\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right]$

regard the Gamma, Giddings, Log-normal and Poisson functions, and proposed unambiguous names.

Some of the most important chromatographic functions, i.e. the Exponentially Modified Gaussian (EMG), the Poisson, the Log-normal, the Edgeworth/Cramér series and the Gram/Charlier series, have been reviewed and commented in more detail. Tables 2–6 list all the equations which have been used to represent these functions. Several of the equations employed in the literature for the EMG

appear to be affected by (printing?) errors; these erroneous equations are reported in Table 2 in addition to the “correct” ones.

As a final conclusion, it is worth remarking that the representation of chromatographic peaks (as well as of peaks produced by other techniques) has been generally achieved using a limited number of functions, as it is indicated by the number of citations reported in the last column of Table 1. These functions are primarily the EMG and the Gaussian,

Table 6  
Equations and references for the Gram/Charlier series

$$y = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right] \sum_{i=0}^n \left\{ (-1)^i c_i \sum_{j=0}^{\text{floor}(i/2)} \left[ \frac{(-1)^j \left( \frac{x-z}{w} \right)^{i-2j}}{2^j j! (i-2j)!} \right] \right\}$$

Other equations and references		Notes
(1)	$y = G(t) \sum_{i=0}^n \left[ (-1)^i c_i \frac{H_i(t)}{i!} \right]$	[36,73,123,134] $c_i$ : see [134]
(2)	$y = G(t) \left\{ 1 + \sum_{i=3}^n \left[ (-1)^i c_i \frac{H_i(t)}{i!} \right] \right\}$	[72,125,130,178] $H_i(t) = (-1)^i \frac{G^{(i)}(t)}{G(t)}$ (Hermite pol.)
(3)	$y = \sum_{i=0}^n \left\{ \frac{c_i G^{(i)}(t)}{i!} \right\}$	[119,134] $G(t) = h \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right]$  or $\frac{h}{w\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x-z}{w} \right)^2 \right]$

and to a lesser (although significant) extent also the Edgeworth/Cramér, Giddings, Gram/Charlier, HVL, Log-normal, Poisson, Weibull, Lorentzian, Lorentzian–Gaussian product, Lorentzian–Gaussian sum, Pearson VII and Voigt (the latter five in spectroscopy). All the remaining functions have been more or less ignored in the literature. Several of them appear to be only partially suitable to represent chromatographic peaks, for example because they cannot assume a skewed shape, or because their optimizable parameters are difficult to estimate. Some other functions, however, possess good properties and/or have been demonstrated to be good models for real chromatographic peaks; there seems to be no specific reason for their lack of popularity, which probably is merely due to the tendency of researchers to continue to use traditional, well studied and frequently cited functions at the expense of the newer ones.

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