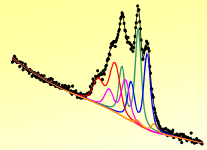
Product or sum: what is the better alternative for approximating the convolution of Lorentzian and Gaussian functions for fitting x-ray photoelectron spectra?



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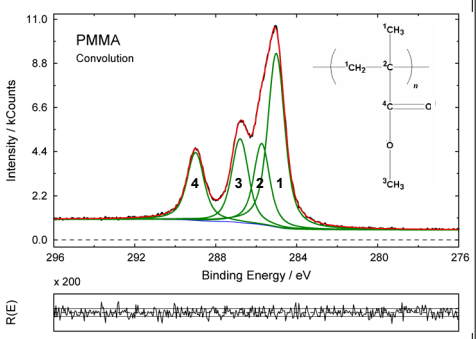
Abstract:
A comparative study for fitting of x-ray photoelectron spectra using different model functions is presented. The synthetically generated test spectrum PMMA and the real measured Cu 3p spectrum are fitted with three generally used models: product, sum and convolution of Gaussian and Lorentzian functions. It was found that the sum function is the definitely better alternative than the product function compared with the perfect approach using the convolution procedure. All spectra were fitted with the modified software UNIFIT 2006.

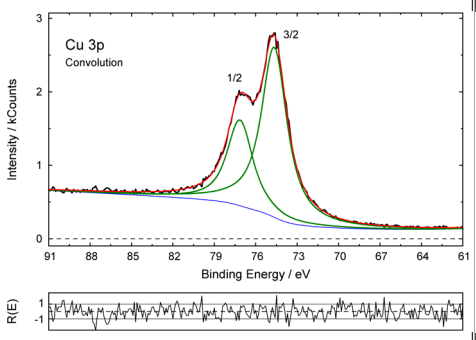
Fit of a synthetic test spectrum PMMA and the measured Cu 3p spectrum:

- The test spectra PMMA [poly(methyl methacrylate)] was generated using the convolution routine of MICROCAL ORIGIN© with the peak width of the Lorentzian *L(E)* and Gaussian *G(E)* functions of 0.6 eV. The relative intensities of the four components were **16.8% (289.0 eV)**, **20.8% (286.8 eV)**, **20.8% (285.7 eV)** and 4**1.6% (285.0 eV)**. The background was simulated with a combination of constant and Shirley type background. Finally a statistical noise was superimposed over the spectrum.
- The Cu 3p spectrum was recorded with the ESCALAB 220 iXL, Al-mono source, Large area XL mode and 10 eV pass energy. The peaks were fitted with two independent single lines and an adjustable background consisting of a polynomial 3rd degree and a Shirley background. The theoretically expected intensity ratio of the **$3p_{3/2}/3p_{1/2}$** is **2:1**.

Convolution

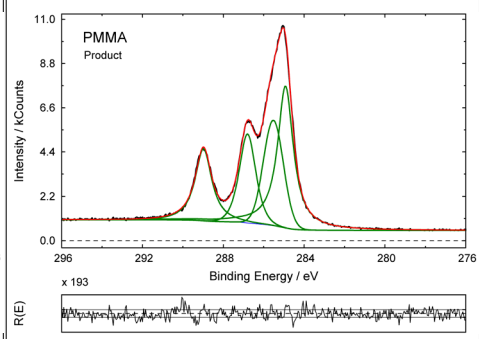


Parameter	Peak number 4		3		2		1	
	Value	Error	Value	Error	Value	Error	Value	Error
Rel. intensity/%	17.23	2.6	20.15	3.2	19.36	6.9	43.26	4.0
Peak position/eV	289.00	0.00	286.80	0.00	285.73	0.03	285.01	0.01

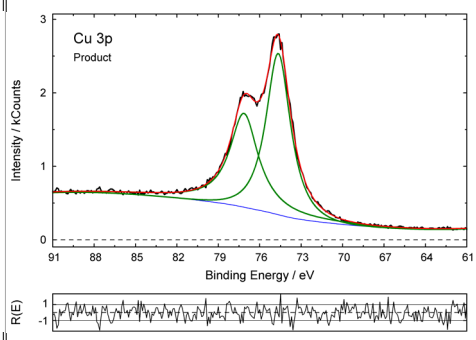


Area ratio Cu $3p_{3/2}$/Cu $3p_{1/2}$:
2.04

Product

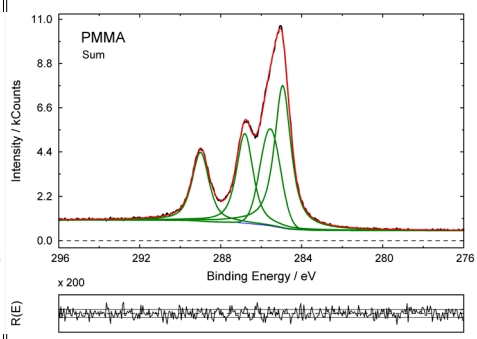


Parameter	Peak number 4		3		2		1	
	Value	Error	Value	Error	Value	Error	Value	Error
Rel. intensity/%	17.89	6.5	18.58	10.7	24.89	19.7	38.64	7.3
Peak position/eV	288.98	0.02	286.80	0.00	285.52	0.18	284.92	0.08

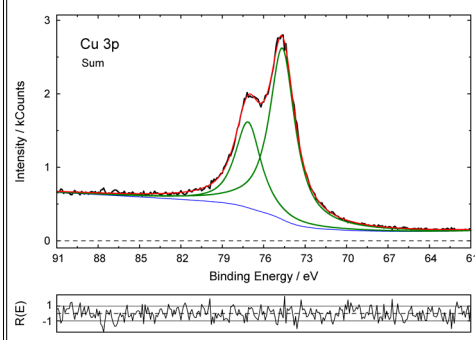


Area ratio Cu $3p_{3/2}$/Cu $3p_{1/2}$:
1.23

Sum



Parameter	Peak number 4		3		2		1	
	Value	Error	Value	Error	Value	Error	Value	Error
Rel. intensity/%	17.33	3.2	22.28	7.2	22.95	10.4	37.45	10.0
Peak position/eV	289.00	0.00	286.81	0.01	285.56	0.14	284.94	0.06



Area ratio Cu $3p_{3/2}$/Cu $3p_{1/2}$:
2.06

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