A new, simple approximation for the deconvolution of instrumental broadening in spectroscopic band profiles

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The deconvolution of instrumental influences in measured band profiles is an important aspect of quantitative or semi-quantitative Raman and photoluminescence spectroscopic analysis. The instrument profile function (IPF) of dispersive, visible-light spectrometers is typically very close to a Gaussian function, whereas most pure Raman and photoluminescence band shapes of solids show a Lorentzian profile. As a result, when the band widths (full width at half maximum, FWHM) of the IPF and the spectral bands are roughly on the same order of magnitude, the measured band profiles exhibit a shape which is the convolution of Gaussian and Lorentzian functions, i.e., the Voigt function. The analytically correct calculation of the Voigt function is complicated, and most spectroscopy programs, especially those bundled with instruments, do not provide a full analytical Voigt implementation that would allow the deconvolution of instrumental broadening and true spectroscopic band widths (as done e.g. in Sundius 1973). Therefore, there has been an urge to approximate both the Voigt function (e.g., by the pseudo-Voigt profile) and the deconvolution procedure (e.g. Olivero and Longbothum 1977, and references therein) by simpler numerical methods. This contribution presents a new, simple approximation to calculate IPF-deconvoluted spectroscopic FWHMs from fitted Voigt or pseudo-Voigt profiles.

The area form of the Voigt function can be written as:

$$y = \frac{A\gamma}{2\pi\sqrt{\pi}\sigma^2}\int_{-\infty}^{\infty}\frac{e^{-t^2}}{\frac{\gamma^2}{2\sigma^2}+\left(\frac{x-x_c}{\sqrt{2}\sigma}-t\right)^2}dt, \qquad (1)$$

where A is the integrated area, γ is the Lorentzian half-width, σ is the Gaussian width parameter ($FWHM_{Gauss} = 2.3548\ \sigma$), x_c is the centre parameter of the symmetric Voigt profile. Suitable programs (e.g. PeakFit) can thus provide a direct calculation of the Lorentzian contribution if the Gaussian width, i.e. the IPF, is kept constant during the fitting procedure.

Other Voigt parametrisations, as well as the pseudo-Voigt function (sometimes referred to as the Gauss-Lorentz sum), while performing adequately in obtaining experimental band parameters through fitting, leave us without numerical values for the deconcolved band widths. Previous attempts to approximate numerically the Lorentzian FWHM using a known IPF include e.g. Olivero and Longbothum (1977) for Gaussian and Dijkman and van der Maas (1976) (also Irmer 1985) for triangular IPFs.

The new method presented here relies on series of computer-generated Voigt profiles using known Gaussian and Lorentzian contributions. The aim is to find an empirical approximation for the *difference* between the Voigt experimental FWHM (w_V) and the pure physical Lorentzian FWHM (w_L) in the knowledge of the Gaussian IPF's σ or FWHM (w_G), so that finally a simple subtraction can replace the deconvolution procedure. From the generated datasets, values of ($w_V - w_L$) were plotted against ($w_V - w_G$) for each fixed w_G (see Fig. 1a). The use of ($w_V - w_G$) caused all trends to start at $w_V - w_G = 0$, making curve fitting more consistent. All ($w_V - w_L$) vs. ($w_V - w_G$) curves were fitted using the so-called dose response function, sometimes referred to as a four-parameter logistic (4PL) function:

$$y = \frac{A_1 - A_2}{1 + (x/x_0)^p} + A_2, \qquad (2)$$

where A_1 and A_2 are start and end values, respectively, on the y axis, x_0 is a centre parameter and the exponent p controls the steepness of the curve. The equation used for curve fitting becomes the following after fixing $A_1 = w_G$ and $A_2 = 0$:

$$w_V - w_L = \frac{w_G}{1 + \left(\frac{w_V - w_G}{x_0} \right)^p}, \tag{3}$$

which means only the parameters x_0 and p remain to be determined. This dose response function gives a very good approximation to the ($w_V - w_L$) vs. ($w_V - w_G$) curves (Fig.1a), despite not being an analytical solution (Fig. 1b). The refined parameters are $x_0 = 1.11261\ w_G$ and $p = 1.011$ for all five simulated datasets. The results allow the approximation of these values by $x_0 \approx {}^{10}\!/_{9}\ w_G$ and $p \approx 1$ (the latter meaning the omission of the exponent). Substituting into Eqn. 3, the expression proposed for the correction of the IPF contribution becomes

$$w_V - w_L \approx \frac{w_G}{1 + \left(\frac{w_V - w_G}{{}^{10}\!/_{9}\, w_G} \right)} = \frac{w_G}{0.9\frac{w_V}{w_G} + 0.1}. \tag{4}$$

Figure 1A shows the simulated discreet values and the fitted curves according to Eqn. 4. As a demonstration, another, arbitrary w_G data series is used to compare analytically generated ($w_V - w_L$) values to those calculated using Eqn. 4 (Fig. 1B). The misfit is typically not more than 2.5% of the IPF correction necessary in all cases, i.e. probably less than the uncertainty associated with peak fitting real-world (e.g. noisy, high-background) spectra.

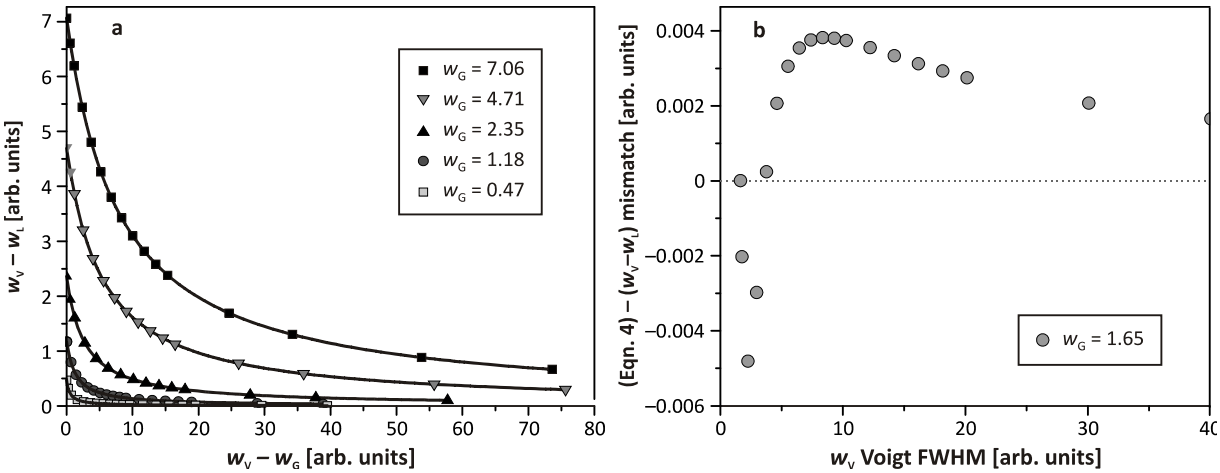

Fig. 1. *(**a**) Simulated datasets (markers) and curves fitted to them using Eqn. 4. (**b**) Misfit of simulated ($w_V - w_L$) and approximated correction (Eqn. 4) in a test dataset ($\sigma = 0.7$). All axes share the same spectroscopic unit.*

The simple formula in Eqn. 4 yields the number to be subtracted from experimentally determined w_V values. This method has the desirable property of only using experimentally derived quantities (Voigt or pseudo-Voigt width and IPF) and can be calculated by a very simple mathematical formula. The calculation and subtraction are very easily done in any spreadsheet or plotting software; furthermore, it can be done on each pixel of an FWHM map.

Acknowledgement: *The author wishes to thank Lutz Nasdala for his generous support.*

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