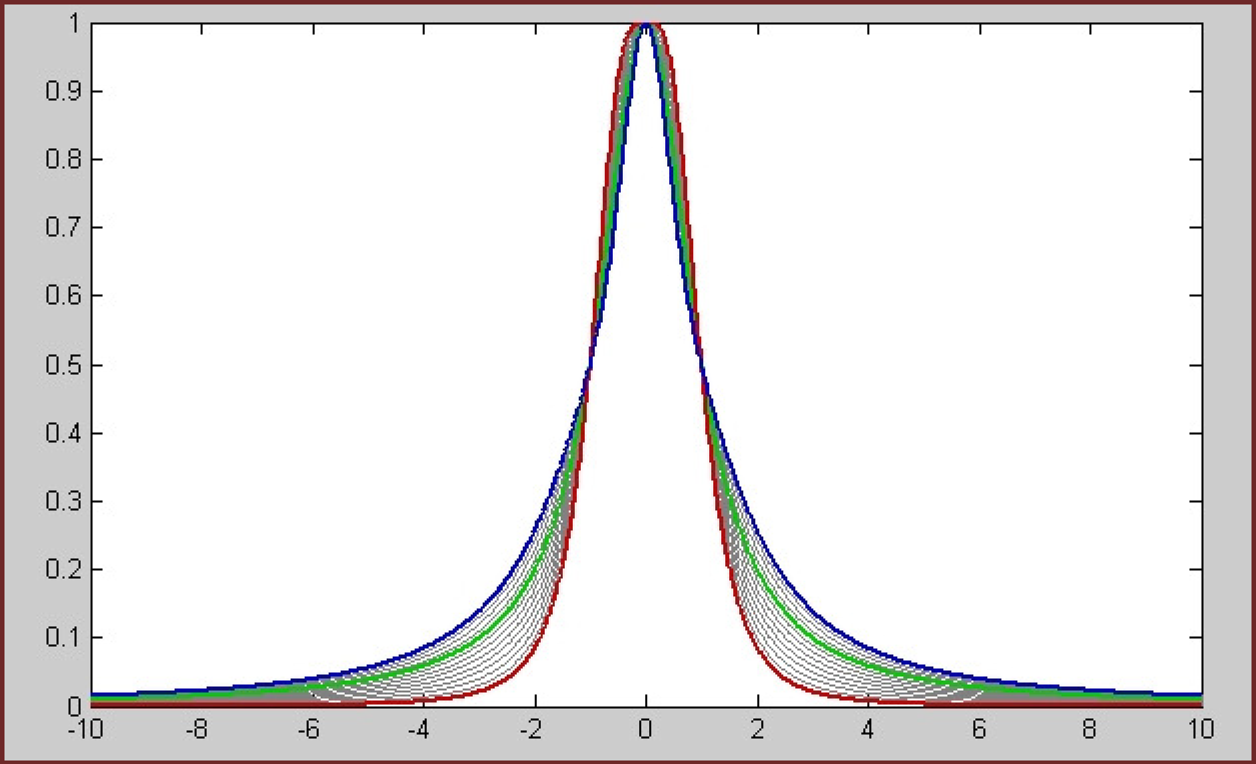
# Generalized Lorentzian lineshape

## with one new parameter for kurtosis fitting

Stan Sykora

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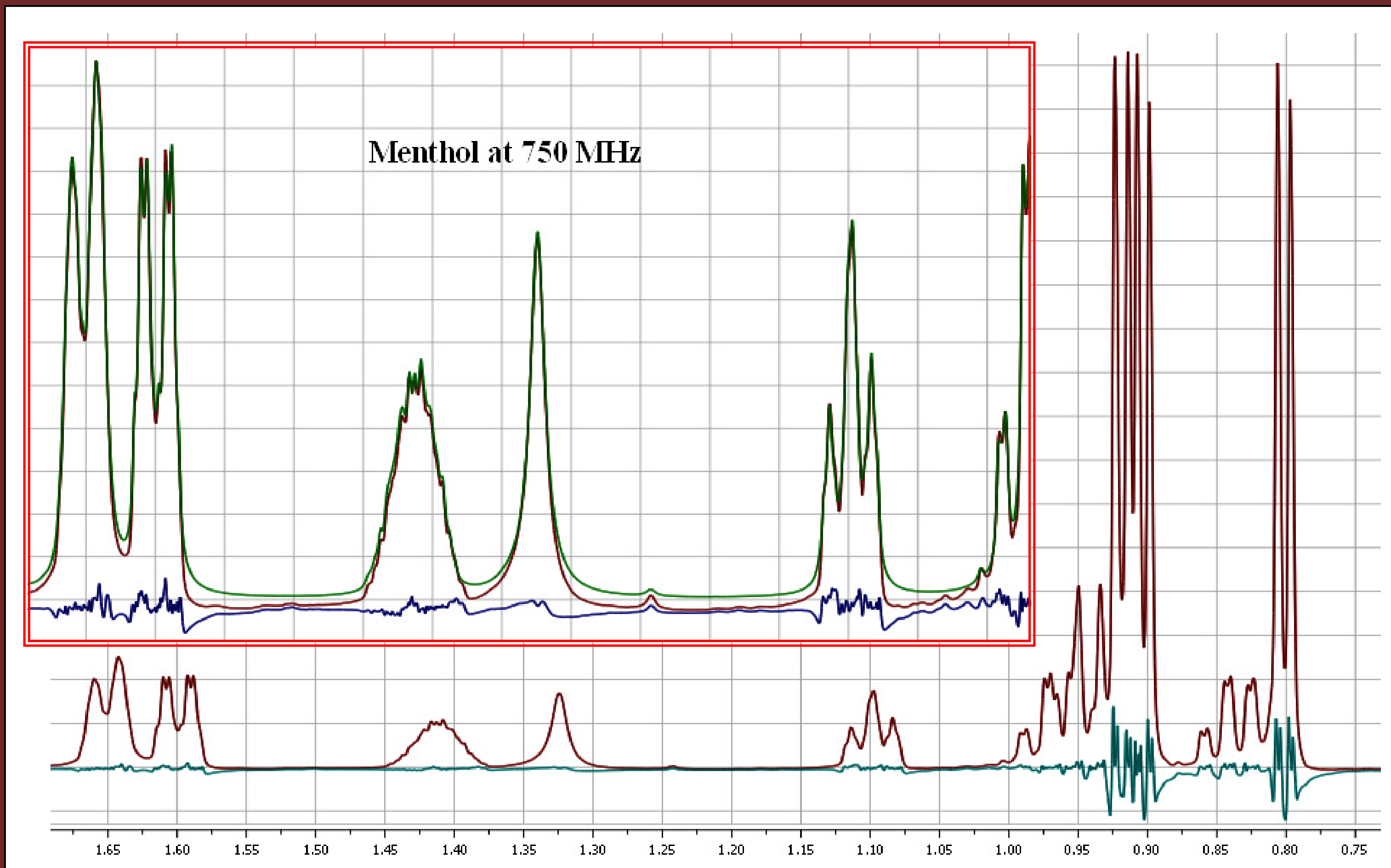
# GSD – Global Spectral Deconvolution

f-domain algorithm which automatically decomposes sets of superposed (near) *Lorentzians* and ends up with a

**GSD Peaks List**

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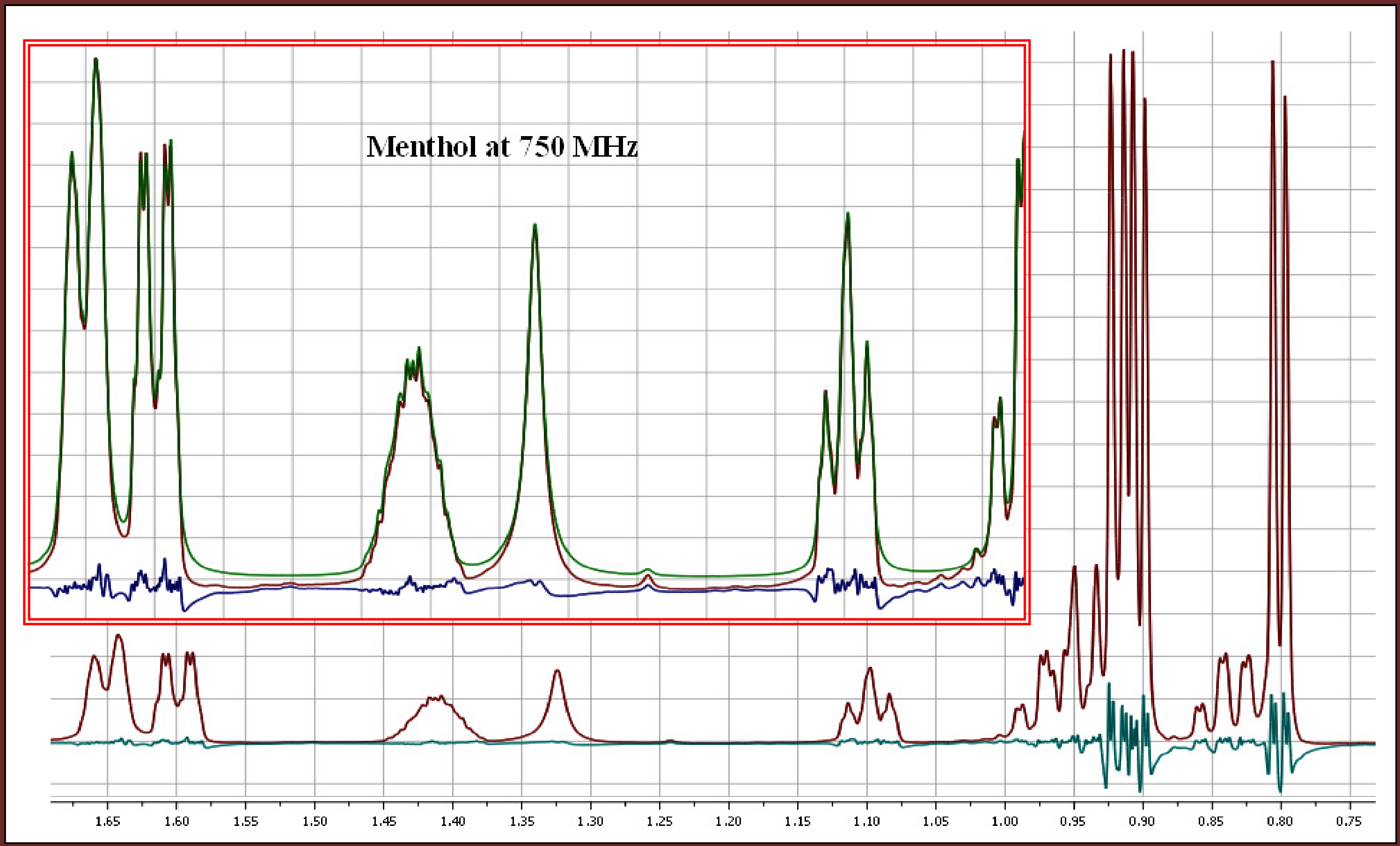
# The residuals comprise:

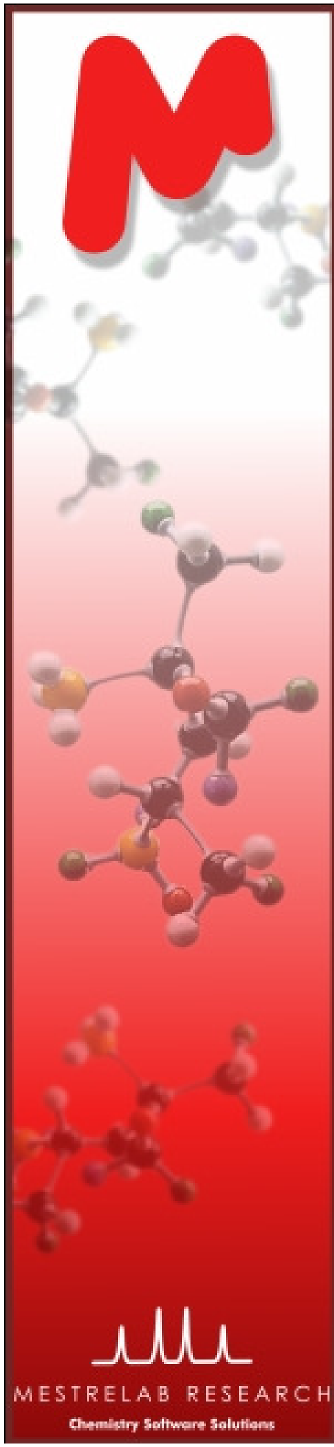
**Systematic components (reproducible):**

envelope of distinct transitions

**Non-systematic components (irreproducible):**

due to instrumental distortions shimming, decoupling, …)



# Sources of peak-shape deviations from the Lorentzian shape

1. Magnetic field inhomogeneity (shimming)
2. Magnetic field noise (ebyte.it\library\docs\nmr06a\NMR_FieldNoise_Fid.html)
3. Sample spinning (dtto)
4. Sample temperature gradients (up to 0.01 ppm/deg)
5. FID weighting before FT (Voight and other profiles)
6. Distorsions due to Discrete Fourier Transform (cyclic condition)
7. Overlap of miriads of transitions in coupled spin systems
8. Relaxation effects (e.g: methyls contain 3 transitions of different widths)
9. Molecular dynamics effects (chemical exchange, limited mobility)
10. etc …

# Empirical (phenomenological) lineshapes

More fitted parameters
=> better peak approximation (always true)

Too many parameters
=> long execution times; convergence problems

Statistical correlation between parameters
=> big convergence problems, especially in the linearly swept mode used in GSD

# Lorentzian - Gaussian mixing

Gaussian profile is unnatural (see Stan's blog)

Plain linear LG combination implies two more parameters

Voight profile:

- Well justified, but only in some situations (LG apodization)
- Again two more parameters

In all LG approaches

- the new parameters correlate strongly with the old ones

**Conclusion: LG mixing is not very good**

# The Lorentz property

$$f(x) = 1 - \frac{1}{f(1/x)}$$

The physical meaning of this elegant mathematical property of the normalized Lorentzian line is not obvious

But it is nevertheless a good guiding principle

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# Rational functions sharing the Lorentz property

For every rational order (n | n+2) there exists a rational function which has the Lorentz property.

For n = 2 one obtains a rational lineshape with a single variable parameter p:

$$L_p(x) = (1-p)\frac{1}{1+x^2} + p\,\frac{1+x^2/2}{1+x^2+x^4}$$

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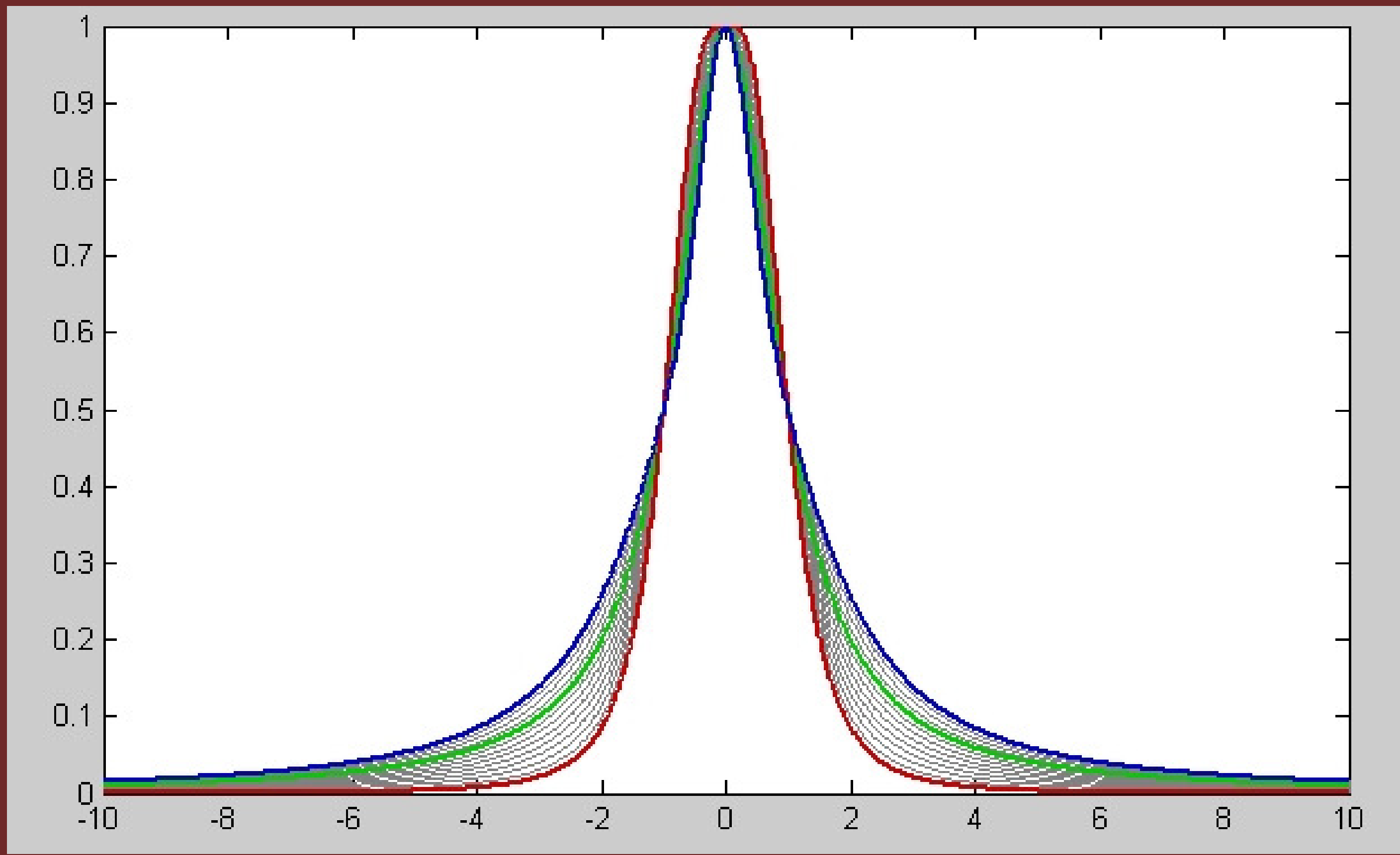
# Generalized Lorentzian Lineshape Plots




The shape parameter in this graph ranges from –1.00 (blue) to +2.00 (red). For 0.00 (green), the line is a perfect Lorentzian

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# Desirable properties of the new family of lineshapes

- Single extra parameter to be adjusted
- All members have the same
  position, height & half-height linewidth
- Hence: minimum correlation with the ‘old’ parameters
- The new parameter affects primarily the peak kurtosis

The Generalized Lorentzian lineshape is now operative in Mnova.

Users can configurate their systems to use
either the classical Lorentzian shape or the Generalized Lorentzian.

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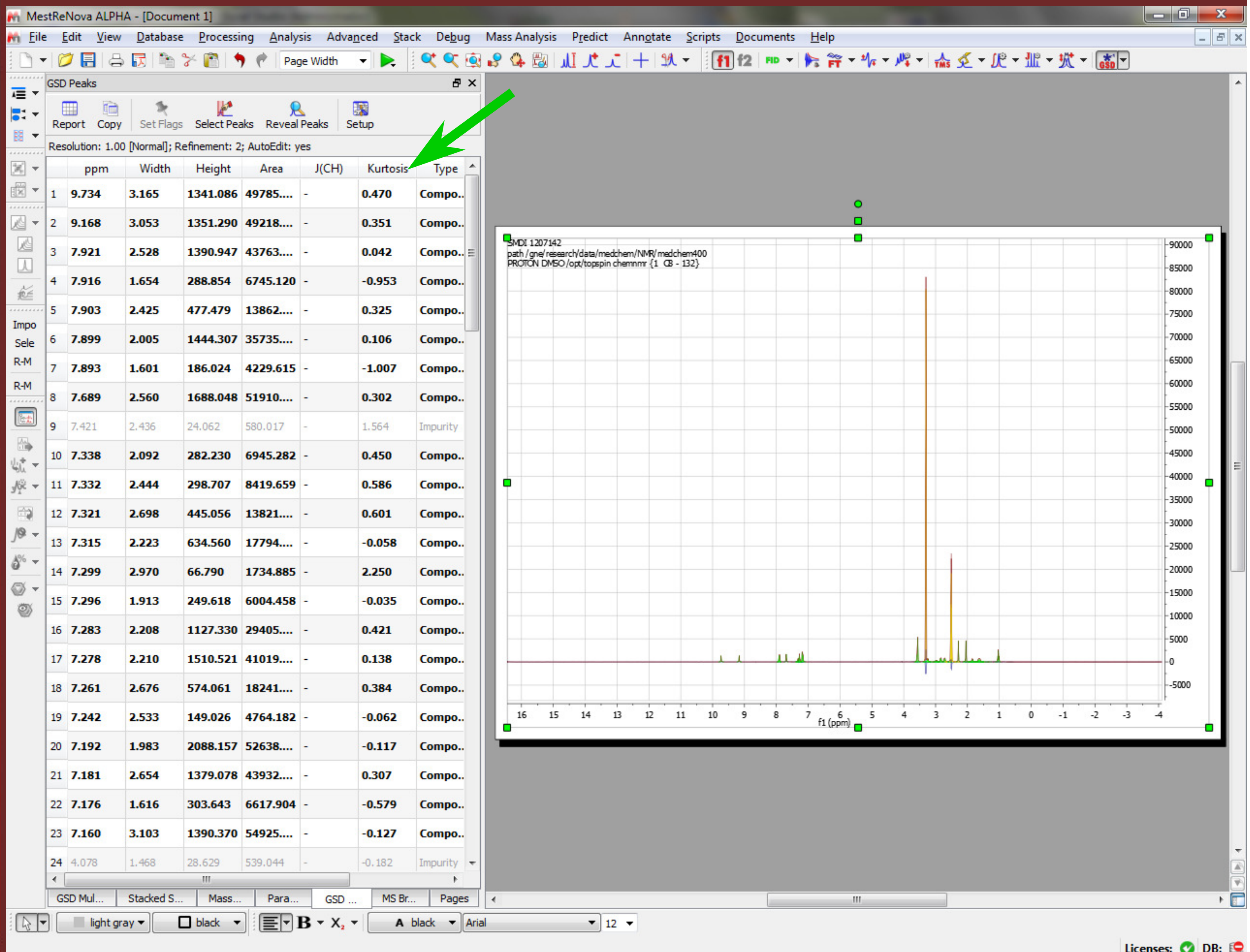
# Example of the UI interface




| | ppm | Width | Height | Area | J(CH) | Kurtosis | Type |
|---|---|---|---|---|---|---|---|
| 1 | 9.734 | 3.165 | 1341.086 | 49785.... | - | 0.470 | Compo.. |
| 2 | 9.168 | 3.053 | 1351.290 | 49218.... | - | 0.351 | Compo.. |
| 3 | 7.921 | 2.528 | 1390.947 | 43763.... | - | 0.042 | Compo.. |
| 4 | 7.916 | 1.654 | 288.854 | 6745.120 | - | -0.953 | Compo.. |
| 5 | 7.903 | 2.425 | 477.479 | 13862.... | - | 0.325 | Compo.. |
| 6 | 7.899 | 2.005 | 1444.307 | 35735.... | - | 0.106 | Compo.. |
| 7 | 7.893 | 1.601 | 186.024 | 4229.615 | - | -1.007 | Compo.. |
| 8 | 7.689 | 2.560 | 1688.048 | 51910.... | - | 0.302 | Compo.. |
| 9 | 7.421 | 2.436 | 24.062 | 580.017 | - | 1.564 | Impurity |
| 10 | 7.338 | 2.092 | 282.230 | 6945.282 | - | 0.450 | Compo.. |
| 11 | 7.332 | 2.444 | 298.707 | 8419.659 | - | 0.586 | Compo.. |
| 12 | 7.321 | 2.698 | 445.056 | 13821.... | - | 0.601 | Compo.. |
| 13 | 7.315 | 2.223 | 634.560 | 17794.... | - | -0.058 | Compo.. |
| 14 | 7.299 | 2.970 | 66.790 | 1734.885 | - | 2.250 | Compo.. |
| 15 | 7.296 | 1.913 | 249.618 | 6004.458 | - | -0.035 | Compo.. |
| 16 | 7.283 | 2.208 | 1127.330 | 29405.... | - | 0.421 | Compo.. |
| 17 | 7.278 | 2.210 | 1510.521 | 41019.... | - | 0.138 | Compo.. |
| 18 | 7.261 | 2.676 | 574.061 | 18241.... | - | 0.384 | Compo.. |
| 19 | 7.242 | 2.533 | 149.026 | 4764.182 | - | -0.062 | Compo.. |
| 20 | 7.192 | 1.983 | 2088.157 | 52638.... | - | -0.117 | Compo.. |
| 21 | 7.181 | 2.654 | 1379.078 | 43932.... | - | 0.307 | Compo.. |
| 22 | 7.176 | 1.616 | 303.643 | 6617.904 | - | -0.579 | Compo.. |
| 23 | 7.160 | 3.103 | 1390.370 | 54925.... | - | -0.127 | Compo.. |
| 24 | 4.078 | 1.468 | 28.629 | 539.044 | - | -0.182 | Impurity |

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# Applications

✓ Improved quantitation of peaks

✓ Work in progress:

Additional parameter for Auto-Edit
(in particular for labile & water peaks scoring)

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# Thank You for your Patience

Any Questions ?

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