Uncertainty in fatty acid methyl ester
Reference material characterization

Camilo D Aleman, Yolby M. Rodriguez & Immer M. Caicedo
Mol Labs Quimiométricas
quimiometria@mollabs.com

The usual uncertainty estimation from the EURACHEM Guide CG04 applied to assigned values of fatty acids for a edible oil CRM to be accredited, results in low values compared to the reference, a higher hierarchy material used for calibration (MRC DMR 528a CENAM). So, we use the model for uncertainties associated with the x_i and the y_i, from the ISO/TS 28037:2010. Here we show detailed data for oleic acid and final results for our (finally !) accredited CRM.

Model: EURACHEM/CITAC CG04 Appendix E.4. linear least squares

The mathematical modeling was defined as:

$$\hat{Y} = \widehat{\beta_0} + \widehat{\beta_1} x_i$$

The regression for oleic acid showed results:

$$\widehat{Y} = 125{,}68 + 5068{,}14\, x_i$$

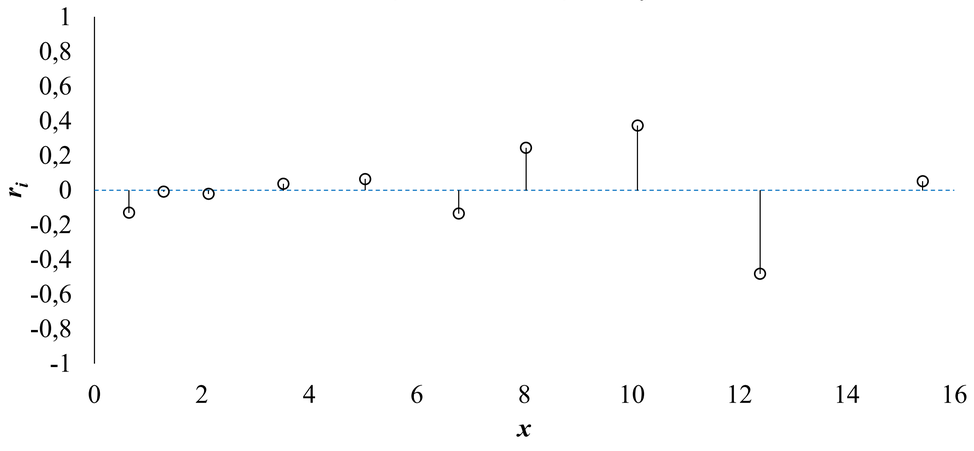

Figure 1- Weighted residuals r_i obtained - linear least squares

The calculation of the uncertainty $u(c_0)$ associated with the linear least square is estimated as:

$$u(c_0) = \frac{S}{B_1}\sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_0 - \bar{c})^2}{s_{XX}}}$$

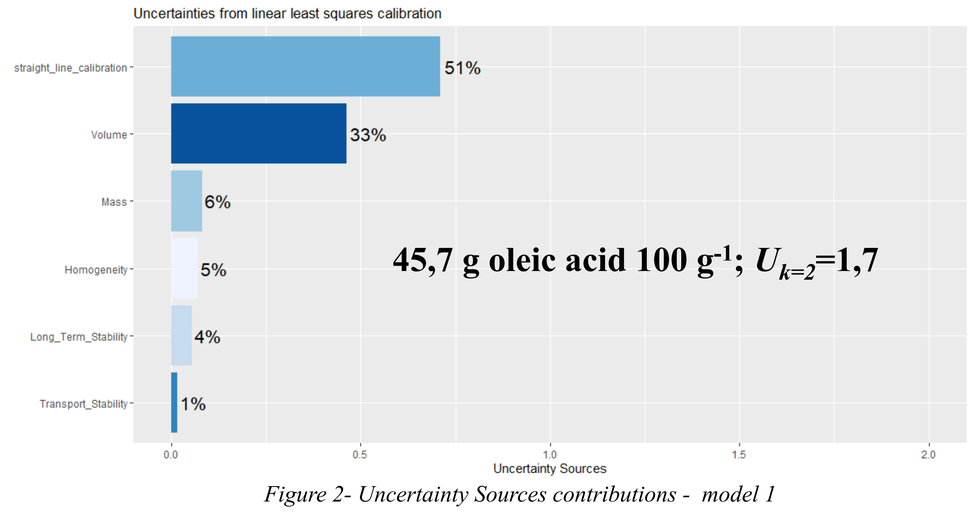

Figure 2- Uncertainty Sources contributions - model 1

Model: ISO/TS 28037:2010 chapter 7. Uncertainties associated with the x_i and the y_i

The case corresponds to that described by the statistical model:

$$x_i = X_i^* + d_i \qquad y_i = Y_i^* + e_i \qquad Y_i^* = A^* + B^* X_i^* \quad \text{i} = 1, \ldots, \text{m}$$

With,

$$\boldsymbol{a} = \begin{bmatrix} -526{,}62 \\ 5234{,}02 \end{bmatrix}, \qquad \boldsymbol{U_a} = \begin{bmatrix} 23427{,}96 & -8704{,}66 \\ -8704{,}66 & 7772{,}00 \end{bmatrix}$$

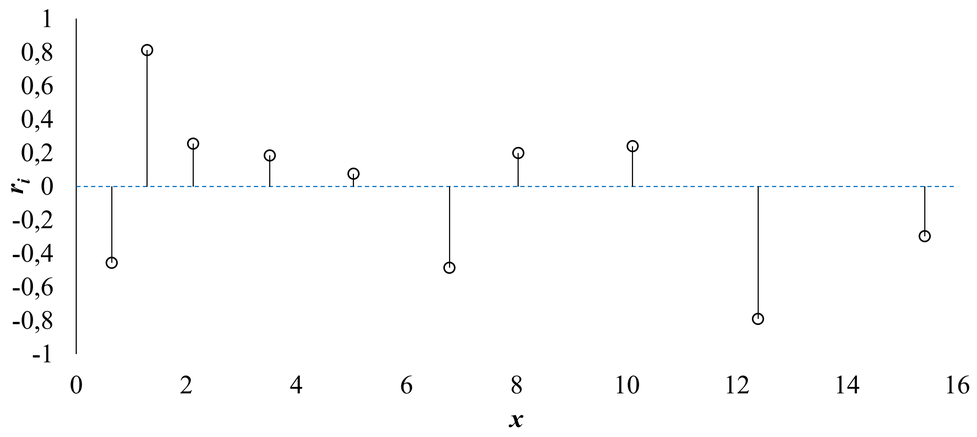

Figure 3- Weighted residuals r_i obtained - Uncertainties associated with the x_i and the y_i

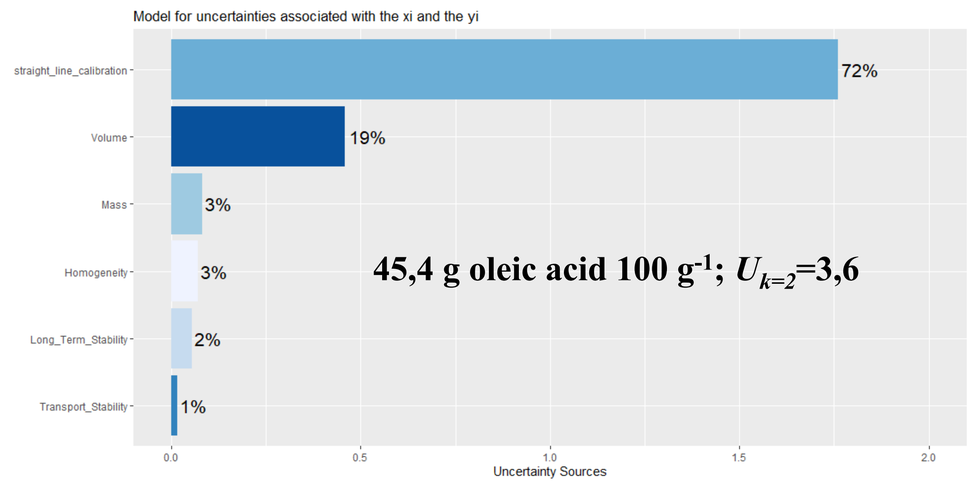

Figure 4- Uncertainty Sources contributions - model 2

Final results

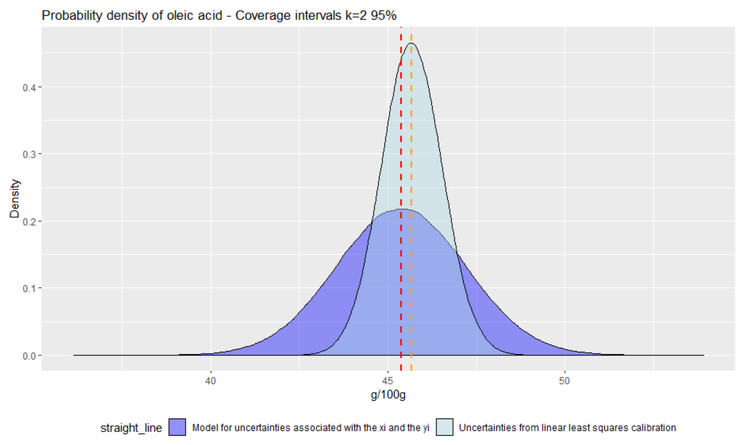

Figure 5- Density probability plot for two models

Table 1- Assigned value g 100 g^{-1} and uncertainty for all characterized fatty acids

	Uncertainties from linear least squares calibration	Model for uncertainties associated with the xi and the yi
Stearic acid	2,16 $U_{k=2}$= 0,12	2,12 $U_{k=2}$= 0,33
Palmitic acid	4,32 $U_{k=2}$= 0,19	4,27 $U_{k=2}$= 0,53
Linoleic acid	15,01 $U_{k=2}$= 0,59	14,9 $U_{k=2}$= 1,6
Oleic acid	45,7 $U_{k=2}$= 1,7	45,4 $U_{k=2}$= 3,6

Conclusions:

- ***R*** and ***Excel*** calculations for uncertainties associated with the x_i and the y_i, are easy to compute. So, it will be safe and effective to use them: same results of linear least squares for negligible x_i contributions.

References:

1. EURACHEM/CITAC. “Guide CG04 Quantifying Uncertainty in Analytical Measurement”. Third Edition 2012.
2. International Organization for Standardization (ISO). “Technical Specification ISO/TS 28037, Determination and use of straight-line calibration functions”. First edition 2010-09-01. Switzerland.
3. International Organization for Standardization (ISO). “ISO Guide 35:2017, Reference materials – Guidance for characterization and assessment of homogeneity and stability”. Four editions. 2017-08. Switzerland.

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