TUTORIALS AND SPREADSHEETS FOR DESIGNING VALID LEAST SQUARES CALIBRATIONS

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Problem: The bottom-up approach for the evaluation of the measurement uncertainty produce accurate uncertainty estimations but their application to complex measurements is not trivial.

Methodology: Tutorials and spreadsheets for the bottom-up evaluation of the uncertainty of measurements based on least square calibrations were developed.

Scope: Measurement based on least square calibration of analytical instrumentation.

Definition of the calibration interval

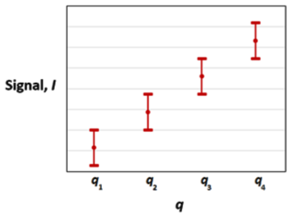
The calibrators should produce univocal signals.

Input:

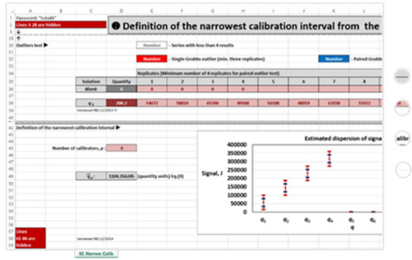
- Concentration of the lowest calibrator except the blank, q_1;
- 10 replicate signals of the blank and q_1;
- Total number of calibrators.

Output:

- Largest concentration of the narrowest calibration interval.



Calibrators with univocal signals.



Homoscedasticity and Linearity

The homoscedasticity of the variance of signals is assessed through an F-test of the variances at the lower and higher concentrations of the calibration interval (i.e. q_1 and q_p).

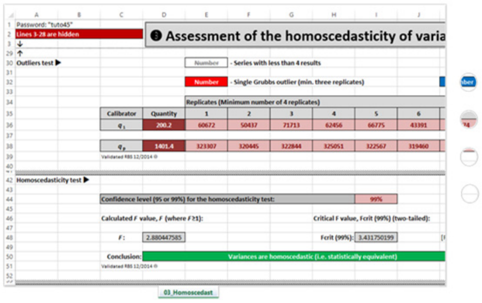
The linearity of signal variation with the concentration is tested by the ANOVA lack-of-fit test.

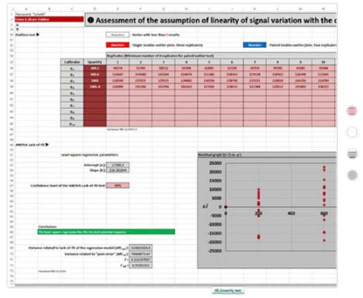
Input:

- Replicate signals of calibrators.

Output:

- Decision about the applicability of the least square model.





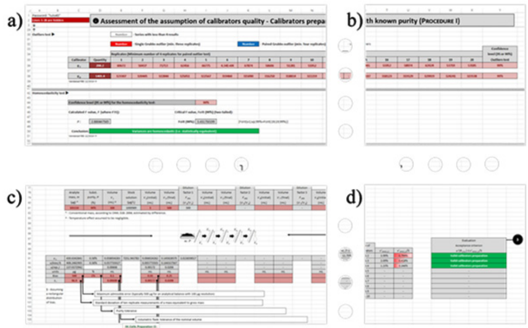
Calibrators quality

The least square regression model requires that the relative positioning of calibrators concentrations is affected by a negligible uncertainty given signal precision.

This assumption is assessed by proving that the relative standard uncertainty of the ratio of the concentration of any pair of calibrators, u'_R, is smaller than one fifth of the relative standard deviation of signals repeatability, s'_r.

$$u'_R \leq s'_r/5$$

Print-screen of different stages of the use of the sheet:
a) & b) enter the signals of calibrators q_1 and q_p;
c) enter the details of calibrators preparation;
d) comparison of u'_R with s'_r;
a) report the final conclusion about the validity of calibrators preparation scheme [box in the bottom of a].



Measurement uncertainty

After the validation of the strategy for instrument calibration, it is used in the analysis of unknown samples.

The relative standard uncertainty of sample concentration, u'_S, results from the combination of the relative standard uncertainty of sample signal interpolation, u'_{Int}, with the relative standard uncertainty of stock solution concentration, u'_{stk}:

$$u'_S = \sqrt{u'^2_{Int} + u'^2_{stk}}$$

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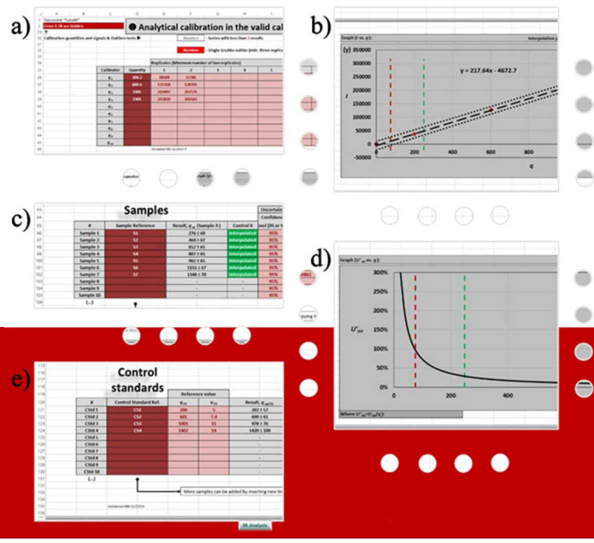
Print-screen of different section of the sheet: a) is used to entre calibrators signals, c) to entre sample signals and collect results, e) to entre control sample signals and known quantities and to collect quality control results, and section b) and d) represent the absolute and relative interpolation uncertainties.



Conclusion:

The developed tutorial and respective spreadsheet allows the easy design of the calibration of instrumental methods of analysis and the accurate estimation of their uncertainty.

Acknowledgements
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