USER-FRIENDLY TUTORIAL AND SPREADSHEET FOR THE BOTTOM-UP EVALUATION OF LEAST-SQUARES CALIBRATIONS

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The top-down evaluation of the measurement uncertainty based on intralaboratory data is very popular since it only requires an adequate evaluation of measurement intermediate precision and trueness. However, in some cases, estimated performance data is not representative of performance over the analytical range due to precision and trueness variations in this range.

Since the top-down approach tends to overestimate the measurement uncertainty, small performance variations in the analytical range can be somehow masked by the uncertainty overestimation. However, in some cases and for some portions of the analytical range, the simplified evaluation of the measurement uncertainty can drive to bad estimates. Occasional and not explained bad performance in proficiency test can be caused by these inconsistencies. A careful bottom-up evaluation of the measurement uncertainty can more easily ensure reported uncertainty is adequate for the all analytical range.

In measurements based on an instrumental method of analysis, uncertainty is frequently underestimated in bottom-up evaluations due to the inadequate assessment of calibrators value uncertainty. If the Least-Squares regression model is used, calibrators quality must be adequate for the regression process and taken into account in the uncertainty budget. The frequently reported correlation between calibrators signals (i.e. the smaller deviation between signal replicates than to the regression line - Figure) results from poor calibrators quality.

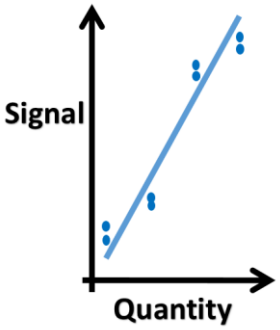

Figure: Correlated calibrators signals

The detailed validation of regression model assumptions can be also useful for top-down evaluations of the measurement uncertainty since bias become controlled throughout the calibration range.

This communication presents a tutorial for the design, validation and quality control of analytical calibrations. The tutorial includes the definition of the calibration range and calibrators preparation procedure, the assessment of regression model assumptions, the estimation of the limits of detection and quantification, the evaluation of the measurement uncertainty and calibration quality control. This tutorial is implemented in a user-friendly and validated MS-Excel spreadsheet.

The application of this tutorial to the quantification of nitrites in drinking water by molecular spectroscopy, between 0.1 mg L^{-1} and 0.4 mg L^{-1}, with an expanded relative uncertainty ranging from 2.1 % to 3.1 % is presented. Measurement uncertainty estimation quality was checked through the analysis of four control standards distributed along the calibration range, in ten independent calibrations performed in different days summing up 40 controls. The metrological compatibility of estimated and reference values of control standards proved the adequacy of the measurement model.

[1] Ricardo J. N. Bettencourt da Silva, Spreadsheet for designing valid least-squares calibrations: A tutorial, Talanta 148 (2016) 177-190.