Non-linear Calibration Leads to Improved Correspondence Between Uncertainties

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Keywords: Quality assurance; Precision; Accuracy; Uncertainty; Non-linear calibration

Although calibrations are routine procedures of instrumental analysis and quality assurance, the working curve is rarely applied to the determination of the uncertainty budget, most likely owing to the difficulties associated with the calculation of uncertainties. The present work provides an investigation of an uncomplicated expression of the non-linear working curve that is well suited for an assessment of predicted uncertainties. At small concentrations, the working curve reduces to a straight line that corresponds to the conventional calibration line. If no interferences were disturbing the analysis, the calculation of uncertainties of calibrations must correspond to the uncertainties of unknowns that were determined by many repetitions. Thus, by introducing an average value of the law-of-propagation of errors (LPE) and observing the conditions of the central limit theorem, an excellent correspondence was obtained between predicted uncertainties and measured uncertainties. In order to validate the method, experiments were applied of flame atomic absorption spectrometry (FAAS) for the analysis of Co and Pt, and experiments of electrothermal atomic absorption spectrometry (ETAAS) for the analysis of Fe. A ten fold extension of the calibration range was identified, as represented by a lower limit of analysis (LLA) and an upper limit of analysis (ULA), which were defined by the properties of the detection system of the apparatus. It was thus found that the uncertainty of the detector dominated the contributions to the uncertainty budget, and it was proposed that a full analysis of the instrument ought to be performed before determination of every single analyte. Following this investigation, the homoscedasticity or heteroscedasticity may be identified by residuals of calibration.