



Spreadsheet for designing valid least-squares calibrations: A tutorial



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ABSTRACT

Instrumental methods of analysis are used to define the price of goods, the compliance of products with a regulation, or the outcome of fundamental or applied research. These methods can only play their role properly if reported information is objective and their quality is fit for the intended use. If measurement results are reported with an adequately small measurement uncertainty both of these goals are achieved. The evaluation of the measurement uncertainty can be performed by the bottom-up approach, that involves a detailed description of the measurement process, or using a pragmatic top-down approach that quantify major uncertainty components from global performance data. The bottom-up approach is not so frequently used due to the need to master the quantification of individual components responsible for random and systematic effects that affect measurement results. This work presents a tutorial that can be easily used by non-experts in the accurate evaluation of the measurement uncertainty of instrumental methods of analysis calibrated using least-squares regressions. The tutorial includes the definition of the calibration interval, the assessments of instrumental response homoscedasticity, the definition of calibrators preparation procedure required for least-squares regression model application, the assessment of instrumental response linearity and the evaluation of measurement uncertainty. The developed measurement model is only applicable in calibration ranges where signal precision is constant. A MS-Excel file is made available to allow the easy application of the tutorial. This tool can be useful for cases where top-down approaches cannot produce results with adequately low measurement uncertainty. An example of the application of this tool to the determination of nitrate in water by ion chromatography is presented.

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1. Introduction

Many important decisions are based on results from instrumental methods of analysis such as the price of goods, the compliance of products with legal requirements or the outcome of fundamental and applied research based on chemical analysis. Instrumental methods of analysis can be divided in selective and separation methods. Selective methods involve the presentation of the whole sample to the detection system that collects a characteristic property of the analyte. Molecular spectrometry after a selective colorimetric reaction, atomic spectrometry and potentiometry are the most commonly used selective instrumental methods of analysis. Separation method involve the separation of sample components before their presentation to a detector that can have limited selectivity. Chromatographic and electrophoretic methods are the most popular separation techniques. These methods provide qualitative and quantitative information about the analyte and/or analysed item. Whenever instrumental methods of analysis are undoubtedly selective due to the characteristics

of the instrumental signal given the complexity of sample matrix, analysts have to care the quantitative information reported by the instrument. The more general terms for a quantitative determination is “measurement” and for analytical method is “measurement procedure” and therefore are used throughout the text [1].

A measurement procedure can only play its role properly if the reported information is objective and has the required quality. The reporting of measurement with uncertainty [1,2] makes information objective and the measurement quality quantified by its uncertainty is only adequate if uncertainty is low enough for the trend or difference that needs to be distinguished [3,4]. For instance, if a relative difference between the quantities of an analyte in two samples larger or equal to 10% must be detected, measurements standard uncertainty should not be larger than 2.4% [3,4]. The maximum admissible uncertainty is designated “target uncertainty” [1]. Therefore, a measurement uncertainty is fit for an intended use if proven not larger than the defined target value. The decision of measurement fitness for the intended use also depends on measurement traceability; i.e. on the adequacy of the used reference for the measurement such as a certified reference material [3].

Different strategies can be used to evaluate the measurement uncertainty. The subanalytical approach [5] (also known as

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“bottom-up” [6] or “modelling” approach [7]) involves dissecting the measurement procedure in individual uncertainty components responsible for random or systematic effects, the quantification of these components and the determination of the combined effect of the various components using the uncertainty propagation law or numerical methods [8,9]. In the end, the analyst will have a detailed model of the measurement that allows the accurate estimation of the measurement uncertainty and the optimisation of the uncertainty or cost of analysis. Although this strategy for the evaluation of the measurement uncertainty is easy to understand, its application is not straightforward for complex measurements [5]. Some alternatives to this approach are available, such as the supralaboratory approach [5] (also known as “top-down” [6] or “interlaboratory validation approach” [7]) or the supra-analytical approach [5] (also known as “single-laboratory validation” approach [7]) that estimates most uncertainty components from the dispersion of results of various laboratories or from intermediate precision and bias estimated in-house respectively.

This work presents a tutorial for the validation of quantifications performed by instrumental methods of analysis based on calibrations built from the least-squares regression model. The validation includes the evaluation of the measurement uncertainty using the sub-analytical approach. The developed measurement model requires that instrumental signal precision is constant throughout the calibration range.

The tutorial comprises 1) the definition of the calibration interval, 2) the definition of the procedure for calibrators preparation (also known as “calibration standards”), 3) the validation of the adequacy of the regression model to describe the calibration curve and 4) the evaluation of measurement uncertainty. The various stages of the tutorial are described in detail and a user-friendly MS-Excel spreadsheet is made available for its application (see Electronic Supplementary material). This tool was developed to be applied by any analysts regardless of his/her experience and to guarantee the production of metrologically sound information. Any queries associated with the application of the tutorial can be directed to the author.

This paper is divided in the tutorial, an application example and the final conclusion. A glossary of acronyms and symbols is presented after references.

2. Tutorial

The description of each main stage of the tutorial starts with their principles and subsequently the respective procedure and spreadsheet is presented. A user-friendly MS-Excel spreadsheet (CalibTut.xls) for the application of the tutorial is available as “Electronic Supplementary material”. This file is divided in sheets where data processing of the various stages of the tutorial can be performed. Fig. 1 outlines the different stages of the tutorial and presents their inputs.

Throughout the text the generic term “quantity” (e.g. quantity of analyte) is used instead of some examples of quantities such as “concentration (mol L⁻¹)”, “mass concentration (mg L⁻¹)”, “mass fraction (mg kg⁻¹)” and “mass (mg)”.

2.1. Definition of the calibration interval

The calibration interval should start in the “analytical zero” or in a quantity above the limit of detection, LOD, and ends at a quantity that allows the adequate accommodation of calibrators positioned between the lowest and highest calibration level. The latest edition of the International Vocabulary of Metrology (VIM) [1] defines LOD as the “measured quantity value, obtained by a given measurement procedure, for which the probability of falsely claiming the absence of a component in a material is α , given a probability β of falsely claiming its presence”. The International Union of Pure and Applied Chemistry (IUPAC) recommends default values for α and β equal to 0.05 [1].

Usually, in spectrometric methods of analysis the calibration interval starts in the “analytical zero” with the signal of a “blank” (i.e. an item with no analyte or the studied characteristics). In separation methods calibration interval usually starts with the signal of a calibrator with a quantity equal or larger than the LOD, since usually blank has no analyte peak. Peaks are observed in blanks contaminated with the analyte.

According to the latest IUPAC recommendations, if measurements results are normally distributed the LOD is estimated by Eq. (1) [10]:

$$LOD = t_{\nu_{bk}}^{95\%;one} s_{bk} \left(\frac{4\nu_{bk}}{4\nu_{bk} + 1} \right) + t_{\nu_{LOD}}^{95\%;one} s_{LOD} \left(\frac{4\nu_{LOD}}{4\nu_{LOD} + 1} \right) \quad (1)$$

where s_{bk} and s_{LOD} are the repeatability standard deviations of measurements of a blank item and an item with a quantity close to the LOD (reported in quantity units) estimated for ν_{bk} and ν_{LOD}

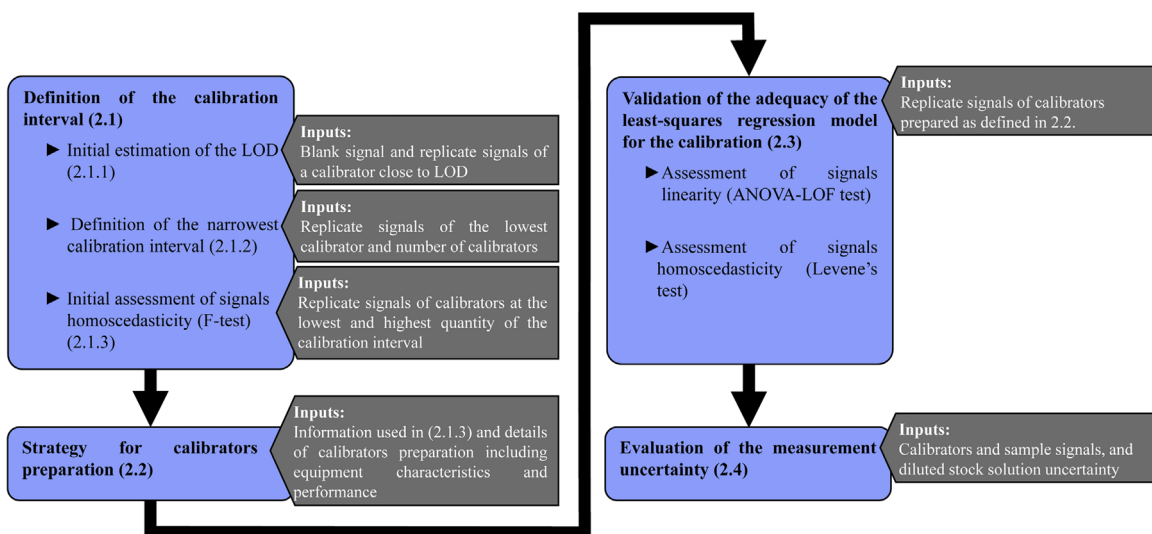


Fig. 1. Outline of the tutorial and inputs of their stages.

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