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Review

Univariate analytical calibration methods and procedures. A review

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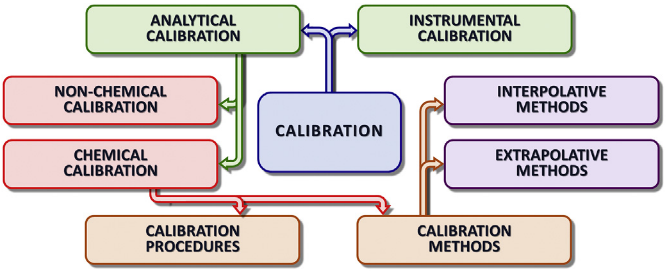
HIGHLIGHTS

- Fundamental terms related to univariate calibration are defined.
- Classification of calibration methods is presented.
- Calibration methods and procedures are reviewed.
- Real and potential possibility of combining analytical methods is provided.

GRAPHICAL ABSTRACT



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ABSTRACT

An original focus on univariate calibration as an experimental process of quantitative analysis is presented. A novel classification system is introduced against the background of the present situation concerning nomenclature of calibration methods. Namely, it has been revealed that four methods well-known in analytical chemistry: the conventional method, the internal standard method, the indirect method and the dilution method, can be split into those carried out in both the interpolative and the extrapolative mode. It is then shown that the basic procedures of all these methods can be modified including different approaches, such as matrix-matched technique, spiking the sample with a reactant, bracketing calibration, and others. For the first time (as compared to monographies dealing with univariate calibration) it is reviewed how the methods are mixed and integrated with one another thereby creating new calibration strategies of extended capabilities in terms of enhanced resistance to the interference and non-linear effects – as the main sources of systematic calibration errors. As additional novelty, rationally possible combinations of the calibration methods – not met hitherto in the literature – have been predicted. Finally, some general rules relating to calibration are formulated and the main calibration problems that still need to be solved are displayed.

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1. Introduction

In spite of broad improvements in methods and instrumentation, analytical calibration still remains a key element in analytical chemistry. Calibration is a crucial step in almost every chemical procedure leading to evaluation of the concentration of a determined substance (analyte) in a sample. This is so because the instruments used for chemical analysis provide, in principle, information in the form of an intensity of the analytical signal that only corresponds to the analyte concentration but does not directly determine this concentration. The main task of calibration is thus to transform the signal intensity into the analyte concentration as accurately and precisely as possible.

Although billions of chemical analyses are performed every day all over the world and the great majority of them lead to the determination of analytes on the basis of univariate calibration, this kind of analytical calibration is not very popular among analysts as an individual, methodologically and practically interesting subject. In particular, the most recent literature comprehensively dealing with calibration problems is related to multivariate analysis [1–4] with special attention paid to elaboration of the calibration data with the use of chemometric methods. The last article relating broadly to the methodological aspects of univariate calibration appeared in 2001 [5] and it covered the subject in the context of chemical standards rather than generally. In some other papers the fundamental issues of univariate calibration were reviewed either from metrological [6] and statistical [7–9] points of view or in relation to individual analytical methods, including mainly chromatography [10,11] and ICP-MS [12]. Specific calibration approaches that are applied when a sample is analyzed by flow techniques [13–15] or is prepared by solid phase micro-extraction [16] have also been summarized recently.

The above situation motivated us to write the present paper, in which we have attempted to discuss univariate calibration methodologies and strategies in analytical chemistry more generally and comprehensively. The main goal of this paper is to present the advantages and potential applicability of a wide range of various calibration methods, including those which have been forgotten to some extent or exploited very rarely in practice. It was decided to reveal the possibilities of how they can be performed in two essentially different modes (interpolative and extrapolative) and in accordance with different modified procedures, as well as how they can be mixed and integrated with each other. The calibration methods and procedures are primarily discussed from the perspective of their capability of overcoming the interference effects as the principal source of systematic errors that can occur during the calibration process.

The article is essentially focused on purely practical and chemical calibration aspects, whilst bypassing mathematical and metrological approaches to the subject. Our own experiences in calibration – in comparison with other works – are widely presented and some of our own concepts and ideas are suggested and put forward for general review.

The paper is organized as follows: the principles of analytical calibration are first described, along with a discussion on calibration classification. Then, examples of various calibration procedures and methods exploited in both batch and flow analysis are then presented and discussed. The final section is dedicated to more specific calibration approaches, which are however widely applied in particular analytical areas.

2. Calibration methods

According to the last recommendation of the Joint Committee for Guides in Metrology *calibration* is defined as “operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication” [17]. This general definition can be adapted to analytical practice and purposes through the following expression: “calibration is a process encompassing *modeling* of the theoretical relationship. i.e. *calibration dependence*, between the intensity of the analytical signal and the concentration of a substance (usually an analyte) in the form of an experimental dependence, i.e. *calibration function (plotted as calibration graph)*, formulated with the use of chemical standards and *transformation* of the intensity of the signal measured for a sample assayed into the analyte concentration in the sample [18].

The purely analytical character of above definition can be understood by drawing an analogy with the relationship between calibration dependence and calibration function and the real (true) and found (experimental) concentration of the analyte in a sample: the calibration dependence, like the real analyte concentration, can only be experimentally evaluated but never ideally accurately determined. Another relationship is as follows: the better (more accurate) the modeling of the calibration dependence by means of a calibration function, the greater the accuracy of the analyte concentration in a sample.

From a practical point of view, the calibration process consists of four stages: the preparative stage (i.e., the preparation of sample and standards), the measurement stage (i.e., reading the signal intensities for sample and standards), the modeling stage (formulation of the calibration function), and the transformation stage (calculation of the analytical result) [15]. As the great majority of analyses are performed with the use of liquid samples and standards (even if solid or gaseous samples are originally to be analyzed) as well as the samples are sometimes prepared together with and not separately from the standards, the term “calibration solutions” instead of “sample and standards” will be used throughout the paper.

In the analytical literature, two further useful terms relating to calibration are also often encountered: *calibration procedure* and *calibration method*. Unfortunately, they are not strictly defined and distinguished in any relevant official documents or unofficial articles. In our approach [19], *the calibration procedure* is a detailed mode of performing all the above-mentioned four stages of the