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Evaluation of analytical calibration based on least-squares linear regression for instrumental techniques: A tutorial review

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ABSTRACT

The analytical calibration of an instrumental method is very important, being considered as a key point in method validation. There are different validation guidelines; showing that analytical calibration process variety prevails in terms of nomenclature, methodology employed and acceptance criteria. Very common mistakes in the analytical calibration process are the use of correlation and/or determination coefficients as a test for linearity, the negligence in the heteroscedasticity of the experimental data and selection of appropriate weighting factor, misunderstanding about the regression through the origin and using zero-point calibration. Once the calibration function is established, their linearity can be confirmed by using different procedures such as graphical plots, statistical significance tests and numerical parameters. In particular, deviation from back-calculated concentrations expressed in the form of percentage of relative error (*%RE*) can be considered very useful for unambiguous linearity evaluation. Some case studies were included to explain the linearity assessment from a practical viewpoint.

Contents

Abbreviations: AIC, Akaikes information criterion; ADL, average deviation from linearity; AOAC, association of official analytical chemists; ANOVA, analysis of variance; AUT, automatically; BC, back-calculated; Cal-VG, calibration section of validation guidelines; C.I, confidence interval; CS, case study; CVDL, coefficient of variation of deviations from linearity; DOF, degree of freedom; DEV, deviation from back-calculated concentrations; EMA, European medicines agency; ESTD, external standard; GOF, goodness of fit; GRA, graphical; H_A, alternative hypothesis; H_0, null hypothesis; ICH, international conference of harmonization; ICP, inductive coupled plasma; INAB, Irish national accreditation board; ISTD, internal standard; IUPAC, International union of pure and applied chemistry; *j*, calibration levels; JRC-FCM, Joint research centre-food contact material; *k*, calibration replicates; LIN, linearity; LLQ, lowest limit of quantification; LOF, lack-of-fit; N, number of calibration data; MAN, Mandel; NATA, national association of testing authorities of Australia; OLS, ordinary least-squares; PAR, peak area ratio; PE, pure error; QC, quality coefficient; *r*, correlation coefficient; R^2, determination coefficient; RE, relative error; REG, regression; RES, residuals; RR, relative residual; RSE, residual standard error; RTO, regression through origin; SE, standard error; SSDL, sum of squares of deviations from linearity; SLO, slope; SQT, significance of quadratic term; STA, statistically; SWGTOX, scientific working group for forensic toxicology; TOST, two-one sided test; US FDA, United States food and drug administration; USP, United States pharmacopeia; VFAs, volatile fatty acids; WF, weighting factor; WLS, weighted least squares; ZPC, zero point calibration.

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1. Introduction

The validation is required in analytical chemistry to demonstrate the performance of the method and the reliability and consistency of the analytical results. Therefore, before an analytical method can be implemented for routine use, it must first be validated to demonstrate that it is suitable for its intended purpose. Several chemical organizations have developed at national or international level different validation guidelines in the field of analytical chemistry. Among them, some international well known validation references are provided by the Association of Official Analytical Chemists (AOAC) [1], the International Union of Pure and Applied Chemistry (IUPAC) [2], the analytical chemistry group EURACHEM [3,4] and the European Medicines Agency (EMA) [5]. On the other hand, some validation guidelines have been published at national level by regulatory authorities such as US FDA (the United States Food and Drug Administration) [6], USP (the United States Pharmacopeia) [7], ANVISA (National Health Surveillance Agency of Brazil) [8], INAB (Irish National Accreditation Board) [9] and NATA (National Association of Testing Authorities of Australia)