Structure of the Book

It was very clear from the beginning that the main objective of this project would be to present atomic spectroscopists with the basis of the most widely applied multivariate regression techniques. We did not want just '*another book on chemometrics*' and, instead, we challenged ourselves to present some practical material with clear links to common problems in atomic spectrometry. Although complex mathematics were avoided as far as possible, a minimum amount was required to present the correct explanations and to justify why some issues were tackled in one way rather than in another. We tried to keep technical explanations within the general scientific background that chemists receive in their career. Besides, in our opinion, atomic spectroscopists should be conscious that things are changing so rapidly in analytical chemistry that some sound background on chemometrics is highly advisable. Please, consider it as another tool to be combined with your instruments, not as an end in itself.

In this respect, the first chapter is devoted to a general view of the most common atomic techniques. The very basics of the analytical techniques are discussed and, most importantly, pros, cons and some basic troubleshooting are presented to the reader. Practical difficulties are referred to, their solutions depicted and, when possible, multivariate chemometric solutions pointed out.

The second chapter reviews univariate calibration. Although this might seem trivial for researchers it is observed too frequently, even in papers published in prestigious journals, that fundamental issues have been overlooked and, therefore, the results might be questionable. Chemists must be aware of some fundamental problems caused by the way in which we use the regression line obtained using the well-known (?) least-squares criterion. It happens that we do not have an exact mathematical solution and, therefore, we are forced to use approximations, which are acceptable under some restricted conditions. Further, different equations are published in literature and their differences/similarities not always explained. We have tried to present a unified approach. In this

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chapter a small amount of mathematics was included because the overall matter sounds familiar to most users and because univariate regression is a critical tool in every laboratory which delivers results and evaluates their uncertainty.

Chapter 3 deals with a critical statement that any analyst and chemometrician has to remember: no good chemometric analysis can be obtained unless the original data are trustworthy. One of the key objectives of chemometrics is to obtain relevant information from the data, but this is possible if, and only if, the data are correct. To obtain reliable data, we can use a suite of dedicated chemometric tools aimed at developing good analytical methodologies. Thus, experimental design, optimization and robustness are cornerstones to assessing accuracy during any process of method development. Typical methodologies are introduced and discussed, along with extensive literature reviews that combine objective optimization and atomic spectrometry.

Chapter 4 retrieves the basic ideas of classical univariate calibration as the standpoint from which the natural and intuitive extension of multiple linear regression (MLR), arises. Unfortunately, this generalization is not suited to many laboratory tasks and, therefore, the problems associated with its use are explained in some detail. Such problems justify the use of other more advanced techniques. The explanation of what the multivariate space looks like and how principal components analysis can tackle it is the next step forward. This constitutes the root of the regression methodology presented in the following chapter.

Chapter 5 presents the most widely applied and, probably, most satisfactory multivariate regression method used nowadays: partial least squares regression. Graphical explanations of many concepts are given, along with a more formal mathematical background. Several common approaches to solve current problems are suggested, along with the golden rule that '*there is not a golden rule*'. The development of a satisfactory regression model can alleviate the typical laboratory workload (preparation of many calibration solutions, using a large number of solutions with different concomitants at different levels of concentration, *etc*.), but only when a strict and serious job is performed with the regression software. Iteration is the key word here, as the analyst has to iterate within his/her data and within the software capabilities. Validation is a key point that will never be stressed sufficiently enough. In this 2nd edition we included a comprehensive approach to derive typical figures-of-merit from multivariate models. This includes the new alternatives given by the International Organization for Standardization (ISO) and the European Union to the former 'limit of detection' and 'limit of quantification'. Many discussions here are based on the excellent work from the research group of Professors Luis Sarabia and María Cruz Ortíz (University of Burgos).

Finally, Chapter 6 goes into two new regression paradigms: artificial neural networks and support vector machines. Quite different from the other regression methods presented in the book, they are gaining acceptance because they can handle non-linear systems and/or noisy data. This step forward is introduced briefly and, once more, a review is presented with practical applications in the atomic spectroscopy field. Not surprisingly, most papers deal with complex measurements [*e.g.* non-linear calibration or

concomitants-affected measurements in electrothermal atomic absorption spectroscopy (ETAAS)] and/or new analytical atomic techniques [which, therefore, yield very complex data; *e.g.* X-ray fluorescence in complex systems, laser-induced breakdown spectrometry (LIBS) and several secondary ion mass spectrometry (SIMS)-based methodologies].

Two distinctive features of this new edition are that more worked examples are included in the book, and that the same dataset is used throughout the chapters dealing with multivariate calibration. It is the authors' desire that these will help the reader to visualize the different models that can be obtained using different regression methods.

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