

# *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 spectroscopy. Although mathematics were avoided as far as possible, a minimum amount was required to present correct explanations and to justify why some issues are tackled in one way rather than in another. We tried to keep technical explanations within the general scientific background that chemists receive in their careers. 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 overview of the most common atomic spectroscopic techniques. The very basics of the analytical techniques are discussed and, most importantly, pros and cons are presented to the reader. Practical difficulties are referred to, their solutions depicted and, when possible, multivariate chemometric solutions pointed out.

The second chapter 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 assess accuracy during any method development process. Typical methodologies are introduced and discussed, along with extensive literature reviews that combined objective optimization and atomic spectrometry.

Chapter three presents the basic ideas of classical univariate calibration. These constitute the standpoint from which the natural and intuitive extension of multiple linear regression (MLR) arises. Unfortunately, this generalisation is not suited to many current 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 four presents the most widely applied and, probably, most satisfactory multivariate regression method used nowadays: partial least squares. Graphical explanations of many concepts are given, along with the 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 standards, solutions with concomitants, *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 with his/her data and with the software capabilities. Validation is a key point that can never be stressed sufficiently strongly.

Finally, chapter five goes into a new regression paradigm: artificial neural networks. Quite different from the other regression methods presented in the book, they have gained acceptance because they can handle non-linear systems and/or noisy data. This step forward is introduced briefly and, once again, a review is presented with practical applications in the atomic spectroscopy field. Not surprisingly, most papers referred to deal with complex measurements (*e.g.*, non-linear calibration or concomitant-affected measurements in ETAAS) and/or new analytical atomic techniques (which, therefore, yield very complex data, *e.g.*, X-ray fluorescence in complex systems and several SIMS-based methodologies).

