Brazilian Journal of Analytical Chemistry
2021, Volume 8, Issue 32, pp 13-15
doi: 10.30744/brjac.2179-3425.point-of-view-hcgoicoechea

BrJAC

POINT OF VIEW

Past, Present and Future of Multivariate Calibration in Analytical Chemistry

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Booksh and Kowalski, in their outstanding report, stressed that analytical chemistry has its own theory, which we all know as chemometrics. The authors indicated that chemometrics "can be used to specify exactly what information can be extracted from the data produced by any analytical instrument or method" [1]. In accordance with this argument, it can be stated that multivariate calibration (MVC) has historically been applied to analytical chemistry, becoming one of the most important tools of chemometrics [2].

Table I comprehensively shows the classification of the data according to their structures, as well as the corresponding type of calibration that can be built with them. As can be observed, calibration performed with spectra (first-order data), matrices (second-order), and beyond is known as "multivariate calibration". In addition, if the calibration is built with second-order data or higher, it is called "multiway" calibration [3-6].

Table I. Hierarchy of data considering the nomenclature based on the concept of order (for data) and ways (for calibration)

Data order	Zero-order	First-order	Second-order	Third-order	Fourth-order
Structure for one sample	Scalar	Vector	Matrix	Three-dimensional array	Four-dimensional array
Structure for a sample set	Vector	Matrix	Three-dimensional array	Four-dimensional array	Five-dimensional array
Calibration	- One-way - Univariate	- Two-way - Multivariate	- Three-way - Multivariate - Multiway	- Four-way - Multivariate - Multiway	- Five-way - Multivariate - Multiway

Along these lines, we should first ask when the multivariate calibration was started to be implemented. Calibration methods, such as principal component regression (PCR) or partial-least squares regression (PLS), were introduced during the 1970s [7]. From that point onwards, numerous commercial and free software packages have been introduced to the analytical world to perform MVC with focus on PLS calibration. This MVC method has become the routine application of near infrared spectroscopy (NIR)-based analysis, primarily in the food industry and the process of analytical chemistry [2].

Cite: Goicoechea, H. C. Past, Present and Future of Multivariate Calibration in Analytical Chemistry. *Braz. J. Anal. Chem.,* 2021, *8* (32), pp 13-15. doi: http://dx.doi.org/10.30744/brjac.2179-3425.point-of-view-hcgoicoechea

The very first paper concerning MVC that reports the modeling of second-order data exploiting the second-order advantage was published in 1978 [8]. The second-order advantage represents the ability to selectively quantitate an analyte that is immersed in a multi-component system, with potential interferents, by only calibrating the pure analyte. This property was first observed in the field of second-order data, but has been extended by multiway data analysis [1]. Hence, it could be said that this is a revolutionary fact in analytical chemistry.

The second question that could be asked is what is the present state of MVC? A quick document search of "multivariate calibration" in *Scopus,* within the article title, abstract and keywords field, reveals that 3,878 documents were reported from 1978 to the present day, of which 1,040 documents were published in the last five years. The numbers indicate growing interest in this topic. Interestingly, few works have reported the modeling of third-order data or higher, meaning that, nowadays, researchers are mainly focusing on second-order data applications.

The final question to formulate is what can be expected from the MVC for the near future? The analyzed literature reveals that current researches are focused on the generation, exploration and modeling of third order-data. It is possible to observe that the concern lies in the generation of data with a high number of sensors in all three modes. Therefore, it can be envisaged that the future of MVC is aiming to consolidate second-order data applications to a wide window of fields and to investigate and optimize new ways to generate more and better higher-order data. On the other hand, this will be associated with the improvement of chemometric models and will deepen the study of the figures of merit, which is necessary to validate the models [9].

As a final thought, I would like to recall the good moments shared with the late Ronei Poppi, in 2006, at UNICAMP, making our first steps in the modeling of second-order data [10]. The objective was the development of a method for the determination of pesticides and their metabolites in wine by second-order high performance liquid chromatography data. By fortune, that goal allowed me to meet a great researcher and an exceptional person.

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