Novel calibration design for multiple components.

Dmitry Kirsanov[1], Vitaly Panchuk[1], Andrey Legin[1]

[1]*Chemistry Department, St. Petersburg State University, St. Petersburg, Russia*
d.kirsanov@gmail.com

The multivariate calibration is a well-established technique in numerous fields of analytical chemistry. It is especially useful when dealing with multicomponent mixtures where classical least squares approach with a single variable fails because of e.g. a complex shape of analytical signal, lack of signal selectivity, etc. Usually to establish regression model one will require a set of reference data from another method/instrument, e.g. to calibrate NIR spectrometer for prediction of ash content in wheat grain one has to analyze all calibration samples with standard technique (burning in ash oven) first. This is the most straight-forward way of multivariate calibration and it allows for taking into account the influence of all the components in the real complex multicomponent mixtures since dealing with real samples. There are however certain cases when this direct approach cannot be used, e.g. when real samples are hardly available or very expensive. In this situation an obvious way for calibration is design of model mixtures simulating real samples. In case of only one component of interest an approach for design is quite obvious: the concentrations of the component must be evenly distributed along the concentration scale. When numerous components are of interest the situation is getting more tricky: e.g. to study all possible combinations of seven components with five particular concentration levels of each will require 5^7=78125 different mixtures to be studied. Definitely this is far from being doable in a common laboratory practice. The literature on experimental designs for calibration with multiple components is quite sparse. The works of Brereton [1,2] with cyclic permutation design are worth of mentioning, however the number of samples in these designs is strictly fixed to provide for the orthogonality of components. We suggest an approach to calibration design which is valid with any number of components and any number of mixtures. Thus, the experimentator can adopt the design to his/her particular needs taking into account the number of mixtures affordable from “time and money” considerations. This approach is based on the algorithm of even distribution of points in a hypercube. The details on the algorithm and comparison of its performance with cyclic permutation design will be provided in the presentation.

[1] R. Brereton, Analyst, 1997, Vol. 122, pp. 1521–1529
[2] J.A. Munoz, R. Brereton, Chemometrics and Intelligent Laboratory Systems, 1998, Vol. 43 pp. 89–105