CMA4CH 2012, Mediterraneum Meeting
Use of Multivariate Analysis and Chemometrics in Cultural Heritage and Environment
4th ed., Rome, Italy, Europe, 27-30 May 2012
lecture

Coupling Chemometrics and NIR Spectroscopy for Food and Drug Authentication

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Abstract

Different examples of successive coupling of Near Infrared Spectroscopy and chemometric for solving problems of authentication and quality control of food and drug samples will be presented.

In particular, topics as the traceability of PDO products, the determination of nutritional value of cereals and the quantification of enantiopurity of pharmaceutical API will be discussed.

Introduction

The methods of vibrational spectroscopy, such as NIR and FT-IR, are fast and easy to use fingerprinting techniques, that can be used without (or with minimum) sample preparation, are not destructive, and have shown great effectiveness for the solution of many different kind of problems. However, it must be stressed that these techniques, in order to provide accurate and reliable answers, need to be coupled to a proper chemometric data treatment.

In this communication, the successful coupling of chemometric regression and classification techniques to experimental data collection in the near infrared region of the electromagnetic spectrum for the solution of problems related to the authentication of the quality of food and drugs will be presented.

In all these frameworks, the importance of selecting the relevant spectral features on the quality of the final results will be stressed by means of representative examples.

Traceability of foodstuff

Near-infrared spectroscopy coupled to chemometrics is used to build an analytical protocol to authenticate the origin of two high value-added food products: extra virgin olive oil and pistachios.

As far as olive oil is concerned, attention was focused on the possibility of authenticating PDO oils from Sabina (Italy) so a set of certified samples was collected from local producers, together with oils from other geographical origins. All samples were analyzed by NIR (in transflection mode) and the results were processed by chemometric discriminant (PLS-DA) and class-modeling (SIMCA) techniques. Both approaches allowed an accurate traceability of Sabina oils with respect to oils from a different origin. In particular, SIMCA models resulted in high sensitivity and specificity and PLS-DA provided a high classification rate (>93%) as evaluated on an external validation set. As the data set comprised samples from different harvest years, the impact of this variable on the accuracy of classification models was also investigated [1].

In the case of pistachio, 483 samples from six different origins (Sicily, India, Iran, Syria, Turkey and U.S.A.) were analyzed by NIR spectroscopy. Spectra were recorded on half seeds cut longitudinally in reflectance mode. Spectral data were then analyzed by chemometrics to build classification models by SIMCA and PLS-DA. The discriminant approach resulted in classification accuracies higher than 90% for most of the classes. On the other hand, SIMCA built in class-models with high sensitivity and specificities, with the only exception of the two categories Turkey and Iran, whose heterogeneity resulted in a poorer (anyway higher than 80%) specificity. In particular, the results obtained for the samples coming from Bronte (Sicily), the only PDO pistachio production in Europe [2]– 100% non error rate in PLS-DA, 90% sensitivity and 97% specificity in SIMCA, as

evaluated on the external test set – are very promising from the viewpoint of the authentication of this product.

Determination of nutrient content in naked oat samples

A rapid accurate and precise method for simultaneous determination of β−glucan and protein content in naked oat samples, based on the coupling of near infrared spectroscopy and chemometrics will be presented [3]. In particular, three different spectroscopic approaches (NIR and NIT on flour and NIT on whole grains) and various spectral pretreatments were considered. To account for the possibility of outlying samples, a robust version of the PLS algorithm (namely Partial robust M-regression [4]) was used. All the models resulted as accurate as the reference methods, reflectance spectroscopy being the technique providing the best outcomes. Variable reduction by inclusion of the most relevant predictors only (as evaluated by VIP scores [5]) resulted in simpler and, in a case more parsimonious models, without loss in accuracy.

Quantification of enantiomeric excess in pharmaceutical formulations

The results of a study on the possibility of predicting the enantiometric excess of APIs in different formulations and commercial drugs in a fast and accurate way will be discussed. This approach relies on the fact that, in the solid phase, the different interactions in the crystals result in the racemic mixture and the enantiomers having different infrared spectra [6]. This diversity can then be used to build calibration model, which allows the accurate quantification of the enantiomeric excess of an API in the solid state in a non-destructive/non-invasive fashion (Figure 1).
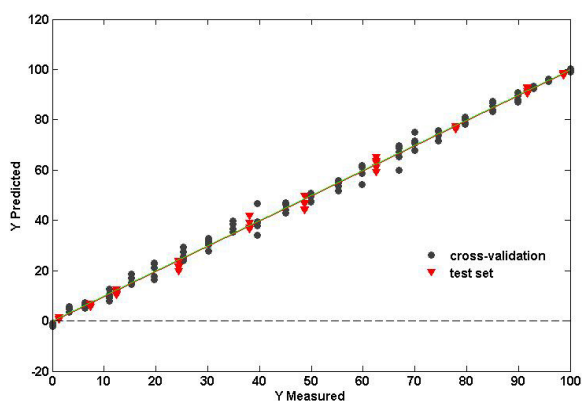

Figure 1 Predictions of the enantiometic excess of ibuprofen for training (circle) and test (triangle) sets

Conclusions

All the reported examples show how coupling chemometrics to NIR analysis of food and pharmaceutical samples can be a successful approach for solving many real world problems.

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