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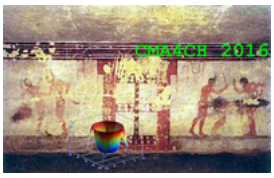

Coupling of NIR Spectroscopy and Chemometrics for the Authentication of Dried Fruits

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Abstract

A fast, effective and cheap identification method has been implemented for two types of dried fruits: almond and hazelnut.

Specifically, the almond of Avola was characterized through different analytical techniques (thermogravimetry, MIR and NIR spectroscopy), for its traceability and authentication. In order to recognize the type "Avola" from "not Avola" it was chosen both a discriminating approach (PLS-DA[1]) and a modeling classification (SIMCA[2]) obtaining good results. In addition it has chosen a data fusion strategy, which integrates the various instrumental signals collected in a single model, allowing to improve the percentage of correct classifications both on samples of the category of interest (ie almond Avola), and on the other products.

The same type of approach has been used for hazelnuts, for which, however, has been used only one of the signal acquisition technique: NIR spectroscopy. Were then acquired the spectra of 120 samples of hazelnuts and the results obtained, showed how one can obtain a reliable classification in the case of differentiation of Italian origin hazelnuts, than others from different countries, with both the discriminating technical PLS- DA that, above all, by the SIMCA modeling approach, with which they were unknown samples correctly classified 24 of 25 (15 Italian of 15).

Introduction

Dried fruits are complex matrices, rich in nutrients, fatty acids and other bioactive compounds, so that, by virtue of their particular composition, in recent years the attention paid to the possible benefits associated with consumption of these products has significantly increased[3]. On the basis of consumer demand and to strengthen the economic competitiveness of the products (in particular of almonds and hazelnuts), the European Union, which is one of the leading producers and consumers of almonds and hazelnuts, has put in place strategies to enhance the quality and characteristics linked to geographical origin of some dried fruits, through the awarding of PGI and PDO marks for specific products.

In this framework, it is clear that there is the need to develop an analytical approach that allows authentication and traceability of products of designated origin, to protect producers, traders and consumers from possible frauds that may occur when the product in question is partially or totally replaced with dried fruit of inferior quality.

Based on these considerations, the present study addresses the possibility of to developing an integrated analytical approach for the geographical traceability of samples of almonds or hazelnuts.

Materials & Methods

Almonds samples. 28 lots of almonds of which 10 Avola almonds and 18 from Italy and other countries were analyzed by NIR and MIR spectroscopy and thermogravimetry.

Experimentally almonds were analysed as its is and ground with NIR, grounded with MIR and thermogravimetry.

Hazelnut Samples. 120 batches of hazelnuts of different origin. For each package, we were analyzed 5 hazelnuts. Experimentally, each sample was cut in half and on each section, were performed 4 scans.

NIR analysis. The samples were analyzed in the same state just cutting in half the nuts (acquiring four spectra for each half) and after grinding (only almond). NIR analysis was carried out on a

Thermo Nicolet FT-NIR 6700 spectrometer, equipped with an integrating sphere and an InGaAs detector (Thermo Scientific, Walton, MA). The spectra were acquired at a nominal resolution of 4 cm^{-1} in the range 4000-10000 cm^{-1}, averaging 82 scans

Almonds MIR analysis. Recording of spectra MIR was carried out on samples ground with electric grinder, which were then layered on top of the ATR crystal and then by placing on a glass slide to even the flour obtained. MIR analysis was carried out on a PerkinElmer 1600 series FT-IR spectrometer equipped with a Globar source, a DTGS detector and a ZnSe ATR cell (10 reflections at 45° angles), operating between 400 and 4000 cm-1 at a nominal resolution of 4 cm-1. The spectra were acquired at a nominal resolution of 4 cm-1 in the range 4000-650 cm^{-1}.

Almonds Thermogravimetric analysis: 56 spectra were total acquired, 2 almonds for each lot. The termogravmetric analysis was performed using a PerkinElmer Sistem 7/4 thermobalance with vertical plate interfaced to a data station equipped with the TADS software. For the thermogravimetric analysis, a temperature gradient was used, providing a linear scan between 30 ° C and 850 ° C at a rate of 10 ° C per minute, maintaining the sample under O_2 flow.

Results

The pre-processed data of almonds from NIR and MIR spectral data and thermogravimetry were analyzed by a discriminating approach PLS-DA and modelling approach SIMCA. All models have achieved good results in calibration and prediction. To improve classification, it was decided to use a strategy of LOW and MID LEVEL data fusion. In the LOW level data fusion the arrays from different techniques have been concatenated and subsequently pretreated with blockscaling. In Mid Level Data Fusion instead, melting takes place using the significant variables extracted from models calculated on each of the individual blocks separately, in this case the matrix were built concatenating the scores of the PLS – DA models calculated on the data of the individual techniques.
In this case all types of pre-treatment (autoscaling and blockscaling) have led to comparable results. In fact, in the case of the mid-level you can get the 100% correct classification of all of the training samples, while the test set sample to a class is predicted incorrectly. As can be seen in the figure, the mid-level approach allows to obtain well-separated classes in the space of the latent variables.

The hazelnuts have led to a reliable classification in the case of differentiation of Italian origin hazelnuts, with respect to the other from different nations, with both the discriminating technique PLS-DA and, above all, by the SIMCA modeling approach, with which they have been classified correctly 24 unknown samples on 25 (15 Italian of 15).

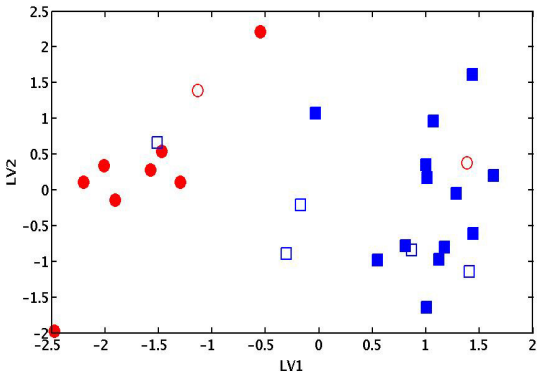

Figure 1: Mid level data fusion. Projection of the training samples (filled symbols) and the test set (empty symbols) on the two latent variables of PLS-DA model

Conclusions

The results of these studies have confirmed the versatility and reliability of fingerprint coupling instruments and chemometric methods for the investigation of complex matrices such as dried fruits.

References

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