Rapid characterization of dry-cured ham by Curie-point pyrolysis-mass spectrometry.

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Summary:
The aim of this work was to recognize dry-cured ham types by a rapid and automatic fingerprinting technique. A large number of products gathered from 3 Southern European countries were analyzed by Curie-point pyrolysis-mass spectrometry (CpPyMS). The resulting fingerprints allowed us to recognize the original product type of each dry-cured ham. We were also able to predict, for new samples, their most probable type with the associate risk of miss-classification.

Introduction:

Rapid characterization of food product quality is a major industrial goal. Accustomed consumers are often able to perceive subtile organoleptic product changes.

New techniques allowing fast fingerprinting of an important part of the product composition are emerging. Curie-point pyrolysis is one of the focused techniques for extraction of a gaseous mixture representative of the product macro-molecular fraction. Mass spectrometry is an appropriate method for the analysis of the extracted compounds in order to obtain a product fingerprint.

In this study, results of classification of 6 types of dry-cured ham by Curie-point pyrolysis mass-spectrometry will be presented.

Material and methods:

Analyzed products:

Local manufacturers from the 3 countries involved (Italy, France and Spain) produced 2 types of typical country hams, for a total of 6 different types : Parma hams (PA) and Low-weight Italian homestyle hams (IL) in Italy, Bayonne hams (BA) and Corsican hams (CO) in France, Iberian hams (IB) and Serrano hams (SE) in Spain. Thirty hams of each type were used for the experiment. The analyses were performed on a longitudinal slice from the middle of the *Biceps femoris*.

Instrumentation-sampling :

Pyrolysis is the thermal degradation of complex molecules in a vaccum, causing their reproducible cleavage to a mixture of smaller volatile fragments called pyrolysate (TSUGE, 1994). Curie-point pyrolysis is a particularly reproducible version of this technique. It offers a means of rapidly temperature raising to a precisely controlled equilibrium temperature (OERTLI and al., 1973). The source of heat in this pyrolysis system is the interaction of a high-frequency oscillator with a ferromagnetic metal (V-shape foil). An alternating magnetic flux is induced in the conductor causing the rapid increase of temperature. At a temperature specific for the material (the Curie-point temperature), a transition from ferro- to paramagnetism occurs. The energy intaken by the metal falls and the temperature is held at the Curie-point. Recording of pyrolysate compounds based on their mass-to-charge ratio by mass spectrometry leads to a pyrolysis spectrum.

A RAPyD 400 designed by Horizon instrument was used. This is a fully automatic and compact system perfectly adapted to CpPyMS routine analysis, allowing up to 150 samples per round. The V-shape foil is a thin 1 cm-0.6 cm alloy film (Fe(50%)-Ni(50%)) with a 530°C specific Curie-point. Foils were purchased from Horizon instrument. The aim in preparing a sample is to obtain a thin coating of material over the inside of the foil.

Due to the foil characteristics, a special sampling technique for food products was designed. Using a specific puncher, a spur was made within the fold of the V-shape foil at about 3/4 of the length from the end of the foil. Sampling was performed by sticking the foil into the sample. Taking the foil out of the dry-cured ham allowed extraction of a few muscle fibres (1-2 mm^3). The foil was then inserted into the mouth of a small rimless glass tube ; the prepared tubes were fitted with O-rings and held in the magazine, ready for CpPyMS analysis.

Data processing:

The whole range of mass fragments (12-400 m/z) recorded by mass spectrometry was used. Each mass fragment is seen as a variable. The total abundance of the specific fragment was used as the value for the corresponding variable. Related to previous unpublished results, the products were only analyzed once (180 analyses) in random order. The spectrum abundances were normalized according to the total abundance of the spectrum in order to get rid of the product size variance.

Due to the large number of variables (389 fragments), the appropriate selection of relevant variables was necessary in order to provide robust discriminant models. The set of selected variables was then used to recognize the 6 types of dry-cured ham. Cross-validation was performed in order to confirm the generalization ability of the model.

We used neural-networks, also known as multi-layer perceptrons (BISHOP, 1995), for the 3 parts of the data processing : selection of variables, model computation and cross-validation.

Momentum Backpropagation algorithm was used for the learning part of the data processing. Magnitude weight pruning was used in order to select the relevant variables by gradually removing useless links. The use of magnitude pruning allows an overlarge network (over designed in terms of number of units and links) to be reduced by pruning, after a first learning step, reaching a suitable network architecture of the classification network whilst increasing its generalization performance.

The network had 6 outputs, one per product type (class). If the product was well assigned to a product class only one out of the 6 outputs had the value 1, the other ones had 0. This allows computation of an assessment of the miss-classification risk or trust in the classification result.

Results and discussion :

Sample preparation took 10 seconds. The analysis lasted 90 seconds. All the products were then analyzed in less than 5 hours.

For the selection of relevant variables 13 networks were built from different random starting points. Magnitude pruning was performed in order to iteratively disconnect the non-relevant weight for each of the networks. As a result, 34 variables were not completely disconnected at least 9 times out of the 13. Using these 34 inputs, magnitude pruning was used to reduce the topology of the initial overlarge network 34/18(720)/6 (34 inputs, 18 units in the hidden layer and 6 outputs for a total of 720 links). This lead to a reduced and more suitable classification network : 33/15(115)/6. All the products were well classified by the classification network.

The cross-validation of the whole set of dry-cured hams was above 95% (Figure 1). 100% of CO and IB, 83 % of BA and more than 90% of IL, PA and SE were cross-validated.

Despite a very small product varying greatly in size, this highly simple and rapid sampling technique in association with CpPyMS and appropriate data processing, Resulted in a nearly perfect classification of the dry-cured hams.

Conclusion:

The results presented clearly show the ability of CpPyMs for rapid classification of dry-cured ham. This instrumentation linked with the use of appropriate data processing techniques and a specific sampling is a very promising method for rapid quality control or objective certification of dry-cured hams.

Further work will validate the reproducibility of the signal provided by the instrumentation (VERNAT, 96) but will also work towards tuning the various instrumental parameters, regarding the analyzed product, in order to increase the number of relevant variables. This tuning will also allow prediction of other valuable characteristics of meat product in further studies.

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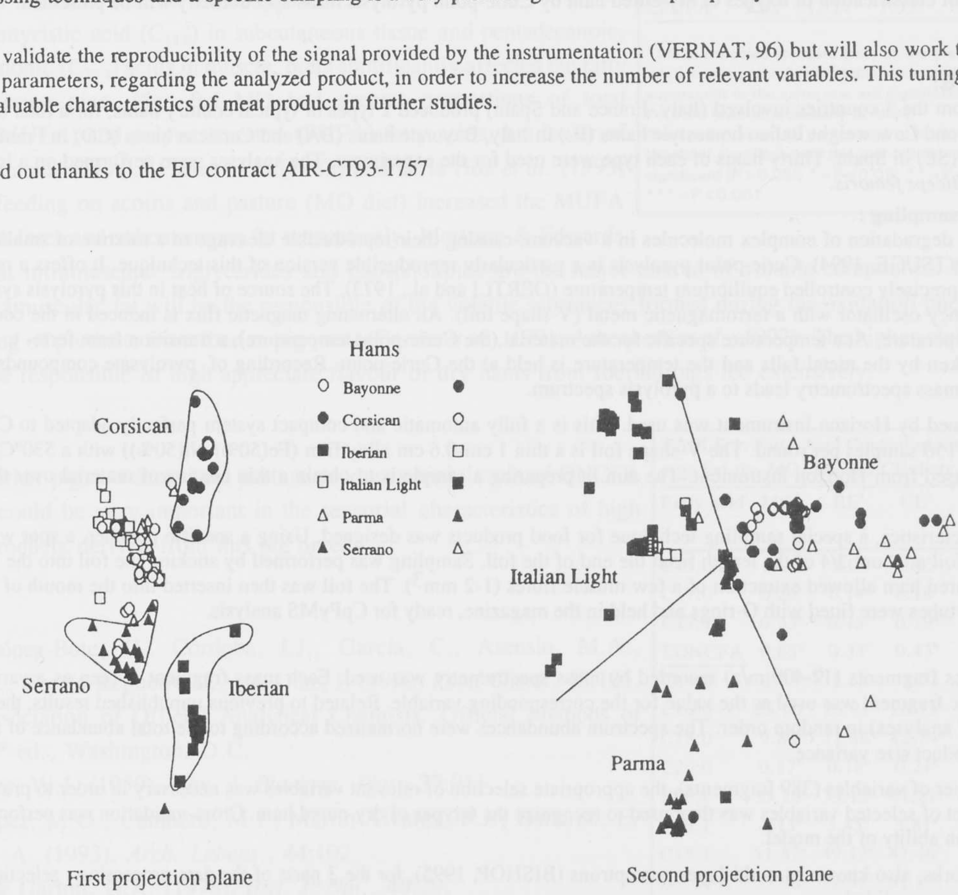

Fig1: Presentation of the cross-validation results. Each dot is plotted twice from the 6 dimensional outputs towards two more visually compliant 2 dimensional plane.

References

BISHOP C. M. (1995), Neural Networks for pattern recognition, *Clarenton Press, Oxford.*

OERTLI C.H., BUHLER Ch., SIMON W. (1973) Curie Point Pyrolysis Gas Chromatography Using Ferromagnetic Tubes as Samples Supports. *Chromatographia*, **Vol. 6, No. 12**, 499-502.

TSUGE S. (1994) Analytical pyrolysis - past, present and future. *Journal of Analytical and Applied Pyrolysis*, **32**, 1-6.

VERNAT G. (1996) Curie-point pyrolysis for rapid characterization of food product (in publication).