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Short Communication

Verification of the geographical origin of European butters using PTR-MS

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ABSTRACT

In the present study, proton transfer reaction-mass spectrometry (PTR-MS) in combination with partial least square-discriminant analysis (PLS-DA) was evaluated as a method for the prediction of the origin of European butters. Eighty-three commercial butters from three European regions were subjected to headspace analysis using PTR-MS. Data were collected for the mass range *m/z* 20–150 using a dwell time of 0.2 s mass^{-1}, resulting in a cycle time just under 30 s. The log transformed headspace concentrations of the masses were subjected to PLS-DA in order to estimate classification models for the butter samples. One model predicted the region of origin; a second set of models predicted dichotomously whether or not a butter originated from a particular EU country. The performance of each model was evaluated by means of a 10-fold double cross validation procedure. For 76% of the butters the region of origin was predicted correctly in the cross validation. The success rate of the countries, averaged over all dichotomous models, was 88% but large differences between countries were observed. Additional work is required to study the underlying factors that determine the geographical differences in butter volatile compositions.

1. Introduction

Production, manufacture and distribution of agricultural products play an important role in the EC economy. A growing number of consumers attach great importance to the origin of food products as an indicator and component of quality. Many consumers now seek high quality products with a clear regional identity for (1) specific culinary or sensory qualities associated with regional products, (2) health, (3) identification with and support of particular (rural) areas, (4) decreased confidence in the quality and safety of products from outside the region, country or the EU (Gilg and Battershill, 1998; Kelly, 2003). Thus there is a demand for agricultural products with specific characteristics and identifiable geographical origin. It is central to the interest of producers, multiple retailers, and consumers that fair trade and thus authenticity is guaranteed. In 1992 EU legislation came into force which provided for a system for the protection of food names on a geographical or traditional recipe basis–similar to the familiar *appellation controllée* system in wine. The scheme highlights regional and traditional foods, which origin and authenticity are guaranteed. A key outcome is quality standard protection and the benefit of quality marks. The branding can enhance awareness of product strengths in home and export markets throughout Europe. This may in turn help producers take advantage of the consumers' increasing awareness of the importance of regional and speciality foods and demonstrate product strengths to premium multiple retailers. Key designations are Protected Designation of Origin (PDO), Protected Geographical Indication (PGI) and Traditional Speciality Guaranteed (TSG). Butter is a product that can be registered in the PDO/PGI/TSG schemes.

The definitive authentication of food products requires the use of highly sophisticated analytical techniques. Isotopic analysis, spectroscopy (UV, NIR, MIR, visible, Raman), chromatography, volatile analysis, polymerase chain reaction, enzyme-linked immunosorbent assay and thermal analysis are the principal techniques that have been successfully applied to food authentication in general since 2001 (Reid et al., 2006). The geographical origin of products is most often assessed by such strategies as

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mass spectrometry, spectroscopy, separation techniques, amongst others. Analysis of multi food components, as opposed to a single marker, seems a promising approach to establish geographical origin of food products as multivariate statistical analyses have become routine through software developments (Luykx and van Ruth, 2008). Statistical discrimination methods have proved good classification tools for multivariate instrumental data (Granitto et al., 2007).

Butter is a water-in-oil emulsion and essentially the fat of the milk. The main constituents of a normal salted butter are fat (80–82%), water (16–18%), salt (ca. 1%) and protein (ca. 1%) (www.wisdairy.com). In addition, butter contains fat-soluble vitamins A, D, and E. Consumers can be very loyal to specific PDO products and anticipate specific sensory characters. These sensory properties can be linked to volatile compounds that contribute to aroma. For verification of the geographical origin of food products, rapid volatile analysis would seem a promising approach. In 1996, 287 volatile compounds had been identified in butter and butter oil (Maarse and Visscher, 1996).

Proton transfer reaction mass spectrometry (PTR-MS) was developed in Innsbruck, Austria, for on-line analysis of volatile organic compounds (Lindinger et al., 1998). Proton transfer reactions induce chemical ionization of the vapours to be analysed. The mass spectral analysis yields a mass resolved fingerprint of the total volatile profile of a sample. Headspace PTR-MS analysis requires no pre-treatment of the sample, it is extremely sensitive (ppt level), and it allows rapid measurements (typically <1 min for a complete mass spectrum). Fingerprint mass spectra can be correlated with sensory properties (Biasioli et al., 2003, 2006). This technique has been used successfully for milk fat classification (van Ruth et al., 2007).

The aim of the present study was to evaluate the usefulness of PTR-MS data in combination with appropriate statistical techniques for prediction of the origin of European butter samples.

2. Materials and methods

2.1. Materials

Eighty-three market butters of European origin (18 European countries), with the same production and collection period, were provided by the EU-JRC IRMM (Geel, Belgium) and stored in the freezer. The samples originated from the following regions in Europe: East, North/West, and South (Table 1). The countries were arbitrarily assigned to regions in this market-orientated supply study. This type of study monitors the situation of the consumer, the samples were collected from shops around Europe. The advantage is that it represents the market situation for the consumer, on the other hand the disadvantage is that the origin and the specifications of the samples cannot be identified. In studies developing authentication methods, a market-orientated supply study is often the starting point.

Table 1
Distribution of 83 butter samples over countries and European regions.

Country	Region		
	East	North/West	South
Estonia	2		
Lithuania	3		
Slovakia	3		
Latvia	4		
Poland	5		
Slovenia	5		
Czech Republic	7		
Hungary	9		
Denmark		1	
Germany		2	
Sweden		3	
Ireland		5	
Belgium		6	
Spain			2
Portugal			6
Switzerland			6
France			7
Italy			7
Total	38	17	28

2.2. PTR-MS analysis

PTR-MS is a technique for analysis of volatile compounds. Proton transfer reactions are used to induce chemical ionization of the vapors to be analyzed. The sample gas is continuously introduced into a drift tube, where it is mixed with H_3O^+ ions formed in a hollow cathode ion source. Volatile compounds that have proton affinities higher than water (>166.5 kcal/mol) are ionized by proton transfer from H_3O^+, mass analyzed in a quadrupole mass spectrometer and eventually detected as ion counts/s (cps) by a secondary electron multiplier. The outcome is a mass resolved fingerprint of the total volatile profile of a samples. PTR-MS is interesting for this fingerprinting approach as (1) it requires no pre-treatment of the sample, (2) it allows rapid

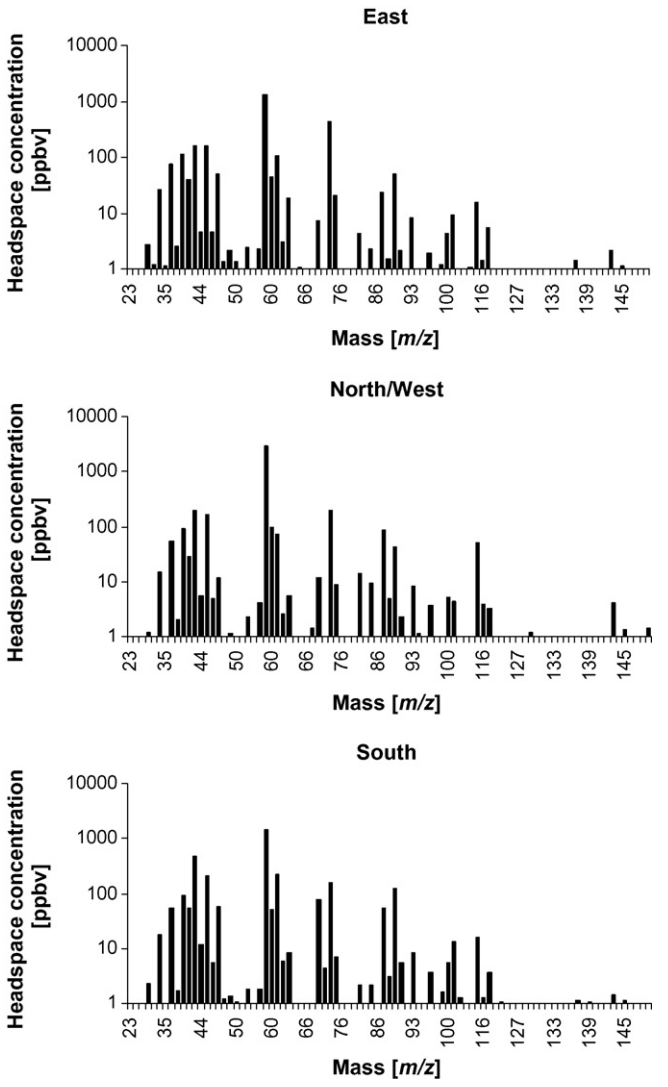

Fig. 1. Mean fingerprint mass spectra of the headspace of butters originating from the East, North/West, and South of Europe.