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Feasibility study of discriminating the manufacturing process and sampling zone in ripened soft cheeses using attenuated total reflectance MIR and fiber optic diffuse reflectance VIS–NIR spectroscopy

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Abstract

The use of visible–near infrared (VIS–NIR) and mid infrared (MIR) spectroscopies for rapid characterisation of 15 traditional and stabilised retail soft cheeses, manufactured with different cheese making procedures was described. A fiber-type, VIS–NIR spectrophotometer (Zeiss Corona 45 VIS–NIR) in a measurement range of 315–1700 nm and a Fourier transform spectrometer (IFS 66V/S, Bruker, Belgium) in a measurement range between 3000 and 900 cm^{-1} were used to scan spectra in reflectance mode at the external (E) and central (C) zones of the investigated cheeses. The principal component analysis (PCA) applied to the normalised spectral data set (VIS–NIR and MIR) did not provide a good discrimination of cheeses. Therefore, the factorial discriminant analysis (FDA) was applied separately to the first 5 principal components (PCs) of the PCA performed on the VIS–NIR and MIR data sets. Regarding the MIR spectra, the percentage of samples correctly classified into six groups (three for the E and three for the C zones) by the FDA was 64.8% and 33.3% for the calibration and validation samples, respectively. Better classification was obtained from the VIS–NIR spectra since the percentage of samples correctly classified was 85.2% and 63.2% for the calibration and validation samples, respectively. Finally, a concatenation technique was applied on the first 5 PCs of the PCA performed on the VIS–NIR and MIR data sets. This technique allowed a quite satisfactory classification of the investigated cheeses according to their manufacturing process and their sampling zone. In this case, correct classifications (CC) of 90.7% and 80.6% were obtained for the calibration and the validation samples, respectively.

Keywords: Soft cheese; Visible–near infrared; Mid infrared; Chemometry; Concatenation

1. Introduction

In the production and marketing of foods, constancy of both quality and composition is important and considerable time and effort is devoted during the manufacturing process for achieving this aim. Processed cheese is one such product the attributes of which are expected by the consumer to be stable, independently of the source of raw materials, milk origin, milk treatment, season, type and amount of starter added, manufacture conditions and ripening time and temperature. There is a large variety of soft cheeses according to manufacturing conditions. The major production of cheese around the world is based on soft cheeses, with Camembert being the one of the most popular varieties. During cheese ripening, the casein is converted by proteolysis into breakdown products. The extent of this degradation plays an important role in determining cheese texture and depends on the activities of enzymes and microorganisms (Law, 1987). Proteolysis can vary with

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cheese variety. Therefore, each type of cheese has its own characteristic proteolytic pattern, resulting from the enzymatic degradation of peptides and also from amino acid catabolism (Polo, Ramos, & Sanchez, 1985).

The increase in quality control of agricultural products requires the development of instruments for a rapid determination of the quality defining parameters. Using conventional methods such as oven drying, Gerber or standard micro/macro-Kjeldahl procedures for the determination of moisture, fat and protein content, respectively, is laborious and time consuming. In the recent years, spectroscopic techniques have been used quite often in the agricultural and food industries. These analytical techniques are relatively of low cost and can be utilised in both fundamental research and in the factory as on-line sensors for monitoring dairy processes (Rodriguez-Otero, Hermida, & Centeno, 1997).

The near infrared (NIR) and mid infrared (MIR) spectroscopies are characterised as non-destructive techniques, fast and easy to be implemented where no reagents are required and no wastes are produced. They are well suited for determining the major components of cheese such as water, fat and protein (Adamopoulos, Goula, & Petropakis, 2001; Adams, Latham, Barnett, & Poynton, 1999; Cattaneo, Giardina, Riva, & Giangiacomo, 2005; Čurda & Kukacková, 2004; Hermida, Gonzalez, Sanchez, & Rodríguez-Otero, 2001; Laporte, Martel, & Paquin, 1998; Mazerolles, Duboz, & Hugot, 2000; O'Callaghan, O'Donnell, & Payne, 2000; Sørensen & Jepsen, 1998; Wittrup & Nørgaard, 1998). The NIR is based on the electromagnetic absorption of organic compounds, results from overtones, combinations and overtones and combinations of fundamental vibrations occur in the MIR region. The reason why NIR is well suited when assessing the presence of water or protein for instance is due to these overtones and combinations of OH and NH bonds. The minor effort to be put for sample preparation before measurement in the NIR case is advantage over the MIR, when a rapid measurement is needed. Furthermore, the existing MIR techniques are still far from being adopted as portable instruments for in situ or on-line applications, since they are sensitive to vibrations and a special effort is needed for sample preparation. Due to the short time needed for measurements performed with VIS–NIR and MIR spectroscopy these spectroscopic techniques may be considered as fast methods for assessing sampling zones and cheese varieties.

Although, significant differences of pH, moisture, fat and nitrogen contents between the external (E) and central (C) zones of soft cheeses have been reported, all the studies about the potential of using spectroscopic techniques to study the molecular changes in soft cheeses have been performed without considering the effect of the sampling zones (Dufour, Devaux, Fortier, & Herbert, 2001; Herbert, 1999; Herbert et al., 2000; Kulmyrzaev et al., 2005). Recently, Verdini and Rubiolo (2002) and Verdini et al. (2004) have investigated the effect of the sampling zones during the ripening of Port Salut Argentino cheese using destructive techniques such as compression test, stress relaxation test and Reversed Phase-High Performance Liquid Chromatography (RP-HPLC).

The objective of the present study was to assess the potential of the VIS–NIR and MIR spectroscopies to determine differences between the sampling zones and manufacturing processes of 15 ripened soft cheeses.

2. Materials and methods

2.1. Cheese samples

Among fifteen different soft cheeses, ten traditional (M1, $n = 5$ and M2, $n = 5$) and five stabilised (M3, $n = 5$) cheeses were purchased from a Belgian local supermarket. These cheeses were manufactured using different mesophilic starter cultures and they were of the white-mould acid-curd type (Herbert, 1999; Herbert et al., 2000). A classical cheese making procedure was used to manufacture soft cheeses. The composition of raw milks was adjusted with cream or skim milk in order to obtain the desired fat–protein ratio. M1 and M2 are traditional soft cheeses of circular shape, thin white coat with ivory ripples which develops a smooth and creamy texture. Both M1 and M2 cheeses were manufactured from raw milk. M1 differed from M2 in the starters used during the cheese making procedure. The M3 is a stabilised soft-white cheese manufactured from pasteurised milk, with oval shape and a smooth, velvety, pure penicillin rind. The M3 cheese differed from M1 and M2 cheeses in the cheese making procedure and the starter cultures used. Each cheese was cut into two symmetric parts according to its median line (Karoui & Dufour, 2003). One part was used for the MIR measurements, the other for VIS–NIR spectroscopic measurements. For the MIR measurements, slices of $8 \times 1 \times 0.5$ cm were cut at the surface and the centre of the cheese, with a cheese slicer. The cut at the surface was performed after removing the primary surface of mould growth, which formed a thin, gray-white and felt-like rind.

2.2. VIS–NIR measurement

The spectra were recorded in the range of 315–1700 nm using a mobile, fiber-type visible (VIS) and near (NIR) spectrophotometer developed by Zeiss Company (Zeiss Corona 45 VIS–NIR fiber, Germany). It is fast, precise and robust, without moving parts. The spectra resolution was 3.2 nm in the VIS and 6 nm in the NIR range. The light source was a 20 W tungsten halogen lamp illuminating the targeted cheese surface. The light illumination and reflectance fibers were gathered at a 45° angle position in a lens holder.

No specific preparation was performed before scanning with the VIS–NIR spectrophotometer. The sample was cut and the measurement surface was levelled carefully with a