Potential of near infrared spectroscopy for the analysis of volatile components in cheeses

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ARTICLE INFO

ABSTRACT

Near Infrared Spectroscopy (NIRS) was used for the determination of volatile compounds in cheeses allowed to ripen for different times using a remote fibre-optic reflectance probe. To do so, cheeses with known and varying percentages of cow's, ewe's, and goat's milk were elaborated and used as reference material. The volatile compounds determined were: acetaldehyde, ethanol, 1-propanol, 2-butanol, 2-pentanol, 3-methyl-1-butanol, 2-butanone, 2-pentanone, 2-heptanone and 2-nonanone. The regression method employed was the modified partial least squares (MPLS). The calibration results using 67–72 samples of cheese had a correlation coefficients (RSQ) between 0.600 for the 3-methyl-1-butanol and 0.903 for the 2-nonanone. The robustness of the method was confirmed by applying it to twenty new samples of different compositions and ripening times which did not belong to the calibration group. Likewise, the correlations between the factors of influence studied and the volatile compounds were carried out. The results of the NIRS method are comparable with those of the purge-and-trap-gas chromatography-mass spectrometry.

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1. Introduction

The volatile compounds found in cheese are the result of a complex combination of microbial and biochemical activities throughout manufacture and ripening process (Pillonel, Ampuero, Tabacchi, & Bosset, 2003). Among these, proteolysis, lipolysis and lactose fermentation are major biochemical events (Fox & Wallace, 1997). Degradation of amino acids leads to amines, aldehydes, alcohols, acids and sulphur compounds. Breakdown of fatty acids produces esters, methyl ketones and secondary alcohols.

The importance of volatile compound determinations is due to their correlation with the flavour, which depends on the ripening, time, cheese-technology, seasonality, etc. The volatile fractions of some Iberian Peninsula cheeses such as Manchego (Gómez-Ruiz, Ballesteros, González, Cabezas, & Martínez-Castro, 2002), Roncal (Izco & Torre, 2000), Zamorano (Fernández-García, Carbonell, Gaya, & Nuñez, 2004) and Serra da Estrela (Dahl, Tavaria, & Malcata, 2000; Tavaria, Dahl, Carballo, & Malcata, 2002; Tavaria, Tavares, Silva-Ferreira, & Malcata, 2006; Villaseñor, Valero, Sanz, & Martínez-Castro, 2000) have been studied as a response to the growing interest in the characterisation of traditional products protected by a Denomination of Origin.

Volatile compound analysis is usually carried out by gas chromatography, but it is necessary to use several techniques for

* This important reference establishes correlations between the sensory attributes of cheese and different volatiles. The *n*-Butanoic acid and branched chain acids contributed to higher scores for sharp, rennet and brine odours, and rancid and rennet flavours in Idiazabal cheese than in Zamorano, Roncal and Manchego cheeses. On the other hand, acetic acid, methyl ketones and their reduction products contributed to the higher scores for buttery and toasty odours.

** Work on the fundamentals of the near-infrared spectroscopy (NIR) and how to develop quantitative models applicable from the spectral information and chemometrics.

† Relates how the evolution experienced during ripening and the seasonal variation of the volatile fraction of Zamorano cheese were studied by using purge and trap extraction and GC-MS analysis. It states that the concentrations of acetaldehyde, propanal and branched chain aldehydes, 2-methyl ketones, higher molecular weight alcohols, and most esters increased significantly with ripening.

‡ This reference exemplifies the use of the NIR (near infrared spectroscopy) methodology in the establishment of the origin of milk used in making cheeses.

§ This work establishes the ranges that are taken as reference in the prediction capability (RPD) of the equations obtained by near infrared spectroscopy. From these RPD values it can be inferred if the models developed using NIR are applicable to unknown samples.

extraction and concentration, such as static and dynamic headspace, steam distillation, high-vacuum distillation, molecular distillation, direct extraction (liquid/liquid or liquid/solid), supercritical fluid extraction (SFE), simultaneous (steam) distillation extraction (SDE), dialysis, solid-phase extraction (SFE), solid-phase microextraction (SPME) or headspace sortive extraction (HSSE) previous to the chromatography and mass spectrometry detection (MSD) (Mariaca & Bosset, 1997; Panseri et al., 2008; Tavaria, Silva Ferreira, & Malcata, 2004). Although they are normally less sensitive than human noses, electronic noses offer some significant advantages in the analysis of volatile compounds (Ampuero & Bosset, 2003).

Although the physical-chemical analyses are promising techniques, they are time consuming and need a lot of pollutant reagents. Nevertheless, in contrast, Near Infrared Spectroscopy (NIRS) has the advantage of being a rapid, cheap, non-destructive, non-contaminating, and multiparametric method (Rodriguez-Otero, Hermida, & Centeno, 1997). NIR spectroscopy has been extensively used to determine the physical-chemical parameters of cheeses such as moisture, fat or total solids (Adamopoulos, Goula, & Petropakis, 2001; Da Costa Filho & Volery, 2005; Mazerolles, Duboz, & Hugot, 2000). In a similar approach, NIR reflectance spectroscopy has been used to predict moisture, fat and inorganic salts in processed cheeses (Blazquez, Downey, O'Donnell, O'Callaghan, & Howard, 2004).

Recently, the use of NIRS technology employing a remote reflectance fibre-optic probe has been studied for the analysis of the percentage of milk (cow's, ewe's and goat's) used in the elaboration of cheeses (Gonzalez-Martiin et al., 2007) and also for the determination of peptides (González-Martín, Hernández-Hierro, Vivar-Quintana, Revilla, & González-Pérez, 2009) and texture (Revilla et al., 2009) of cheeses with different ripening times.

In this work the use of NIRS technology employing a remote reflectance fibre-optic probe has been studied for the analysis of volatile compounds in cheeses allowed to ripen for different times. To do so, cheeses with known and varying percentages of cow's, ewe's and goat's milk were elaborated and used as reference material where the ripening control was carried out over 6 months.

2. Material and methods

2.1. Samples and cheese-making procedure

To perform the present study a total of 100 cheeses of known composition were elaborated and controlled. Cheeses were prepared in the laboratory because cow, ewe and goat's traditional cheese-making procedures are very different and the manufacture process can strongly affect the flavour profile depending on the chosen starter, the type of rennet and on the various changes that can be introduced in the technological process. The cheese-making procedure was as follows: raw milk (40 L), not standardised, was incubated with 15 mg L^{-1} direct-vat-set starters made of *Streptococcus lactis, cremoris* and *diacetilactis,* (MA400, Arroyo Laboratories, Santander, Spain) at 30 °C. After 10 min at 32 °C, 12.5 mg L^{-1} of calf rennet (90% chymosin, 10% trypsin, 1:150,000 strength) was added to each vat. Coagulation was allowed to take place over 20–70 min. When the curds had developed the desired firmness, evaluated subjectively, they were cut with a cheese harp until pieces similar in size to a grain of rice were obtained. The curd was then stirred for 30 min and heated for 10–20 min at 37 °C until it had reached the desired consistency to improve its drainage with sieves. The curd was packed in round hoops (1 kg) and pressed for 6 h at 1.5 kg cm^{-2} at 20 °C. After pressing, the cheeses were salted by soaking them

in sodium chloride brine (18 g/100 ml) at 18 °C for 6 h. The cheeses were then moved to a drying chamber, where temperature (15 °C) and relative humidity (70%) were controlled. Bovine, ovine and caprine raw milk were obtained directly from the producers in Zamora (Spain). Cheeses with different compositions were elaborated, prepared with known, varying amounts of milk, from cows, ewes and goats, with percentages ranging between 0 and 100% (Gonzalez-Martiin et al., 2007). These were cylindrical, with an initial diameter of 10 cm and a thickness of 5 cm and they were monitored over 6 months (at 0.2, 1, 2, 3, 4, 5 and 6 months), using one of the pieces at each time. Table 1 shows the number of samples, the composition of the analysed cheeses, the ripening time and the season (summer or winter) when the milk was collected.

2.2. NIR spectroscopy

A Foss NIRSystem 5000 with a standard 1.5 m 210/7210 bundle fibre-optic probe, Ref n° R6539-A, was used. The probe employs a remote reflectance system and uses a ceramic plate as reference. The window is of quartz with a 5 × 5 cm surface area, measuring reflectance in the IR zone close to 1100–2000 nm. The measurement of the spectra was carried out using NIRS technology and a remote reflectance fibre-optic probe that was applied directly to the cheese samples with no prior treatment or manipulation. The spectra were recorded at intervals of 2 nm, performing 32 scans for both the reference and samples. To minimise sampling error, all the samples were analysed in triplicate. The software used was Win ISI 1.50 installed on a Hewlett–Packard Pentium III computer.

Table 1
Composition and number of samples of cheeses analysed.

Composition	No of samples	Month of ripening	Winter	Summer
100% Cow	12	2,3,4 (3 samples)	7	
		5 (1 sample)		
		6 (2 samples)		5
100% Ewe	14	1,5 (1 sample)	9	
		2, 3 (3 samples)		
		4 (4 samples)		
		6 (2 samples)		5
100% Goat	13	1 (1 sample)	8	
		2,3,4 (3 samples)		
		5 (1 sample)		
		6 (2 samples)		5
25% Cow 75% Ewe	11	0,1,2,5 (1 sample)	7	
		3,6 (2 samples)		
		4 (3 samples)		4
25% Cow 75% Goat	12	0,1,5 (1 sample)	7	
		3,4,6 (2 samples)		
		2 (3 samples)		5
25% Ewe 75% Goat	8	0,5,6 (1 sample)	4	
		3 (2 samples)		
		4 (3 samples)		4
75% Cow 25% Goat	5	5 (1 sample)	2	
		3,6 (2 samples)		3
75% Ewe 25% Goat	6	5 (1 sample)	3	
		6 (2 samples)		
		4 (3 samples)		3
33% Cow 33% Ewe 33% Goat	6	5 (1 sample)	3	
		6 (2 samples)		
		4 (3 samples)		3
50% Cow 50% Ewe	6	1,4,5,6 (1 sample)	4	
		3 (2 samples)		2
50% Ewe 50% Goat	2	4,6 (1 sample)	2	
				0
50% Cow 50% Goat	2	6 (2 samples)	1	
				1
75% Cow 25% Ewe	3	5 (1 sample)	1	
		6 (2 samples)		2