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Spectroscopic Technique: Mid-infrared (MIR) and Fourier Transform Mid-infrared (FT-MIR) Spectroscopies

Romdhane Karoui, Juan Antonio Fernández Pierna and Eric Dufour

Introduction

Mid-infrared, like the other vibrational spectroscopies, represents an attractive option for quality control and screening because it is rapid, inexpensive and non-invasive. It has shown tremendous growth as an analytical tool in quality control and process monitoring. This growth is mainly due to instrumental developments and advances in chemometrics (Bertrand and Dufour, 2000).

The *chemical bonds* in the molecules have specific frequencies at which they vibrate, corresponding to *energy levels*. These vibrational frequencies are determined by the mass of the atoms, the shape (geometry) of the molecule, the stiffness of the bonds and the periods of the associated vibrational coupling. A specific vibrational mode has to be associated with changes in the permanent dipole in order to be active in the infrared area. Diatomic molecules have only one bond, which may stretch

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(i.e. the distance between two atoms increases or decreases). More complex molecules may have many bonds, and vibrations can be conjugated leading to two possible modes of vibration: stretching and bending (i.e. the position of the atom changes relative to the original bond axis). In such cases the vibrations lead to infrared absorptions at characteristic frequencies that may be related to chemical groups.

In practice, to measure a sample, a beam of infrared light passes through the sample and the absorbed energy at each wavelength is recorded. This can be done in two different ways; by scanning through the spectrum with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform system to measure all the wavelengths at the same time. As a result, taking into account the effects of all the different functional groups, an *absorbance* (or *transmittance*) spectrum is obtained showing at which wavelengths the sample absorbs the infrared light, thus allowing interpretation of the chemical bonds. A unique molecular fingerprint that can be used to confirm the identity of the sample is obtained.

Three types of vibrational spectroscopy are generally distinguished: near-infrared (NIR), mid-infrared (MIR), and Raman spectroscopy.

Theory and principles

The *NIR* region lies between 12 500 and 4000 cm^{-1} (0.8–2.5 μm), and NIR spectroscopy operates with a light source from which the sample absorbs specific frequencies corresponding to overtones and combination bands of vibrational transitions of the molecule primarily of OH, CH, NH and CO groups (for more information, see Chapters 3 and 4). The *MIR* region of the electromagnetic spectrum lies between 4000 and 400 cm^{-1} (2.5–50 mm) and is associated mainly with fundamental molecular stretching and bending vibrational frequency – i.e. the frequencies of the fundamental vibration modes of the molecules (from the stable vibrational state to the first excited vibrational state in the electronic ground state). *Raman* also lies in a region similar to MIR; in contrast with the other two techniques, it involves a scattering process that arises when the incident light excites molecules in the sample, which subsequently scatter the light. Most of this scattered light is at the same wavelength as the incident light, but some is scattered at a different wavelength. The process leading to this "inelastic" scatter is called the Raman effect (for more information, see Chapters 5 and 6).

MIR spectroscopy rapidly provides information on a very large number of analytes, and the absorption bands are sensitive to the physical and chemical states of individual constituents. MIR and NIR spectroscopy have a good signal intensity compared with Raman spectroscopy, but MIR has the advantage over NIR that trace elements can be identified. It can be thought of as a molecular fingerprinting method (Hvozdara *et al*., 2002; Steiner *et al*., 2003; Mazarevica *et al.*, 2004). Table 2.1 illustrated some advantages and drawbacks of MIR.

The high spectral signal-to-noise ratio obtained from modern instrumental analysis, as when using the Fourier transform infrared (FT-MIR) spectroscopy, allows the detection of constituents present in low concentrations, as well as subtle compositional and structural differences between and among multi-constituent specimens.

Table 2.1 Some advantages and drawbacks of MIR

Advantages	Drawbacks
• Relies on part of the spectrum that contains fundamental vibrations • Useful for qualitative and quantitative identification of functional groups • Characteristic and well-defined bands for organic functional groups • Unknown species can be identified	• The available energy decreases with wavelength • Expensive transmitting materials • Cells need to have short effective path lengths because most of the materials absorb in this region

MIR spectroscopic methods, and particularly FT-MIR spectroscopy, can be considered routine applications among standard laboratory techniques (Baeten *et al.*, 2000; Baeten and Dardenne, 2002). Such methods have been shown to be useful for a range of identification/authentication problems in different sectors.

Instrumentation

The first MIR instruments used a high-resolution diffraction *monochromator*, which has generally been replaced by *interferometry* technology, leading to the FT-MIR spectrometer. The main component in this spectrometer is the interferometer, the Michelson interferometer being most commonly used. An interferometer consists of two perpendicular mirrors, one moving at a constant velocity and the other being stationary (Figure 2.1). Between the mirrors there is a beam-splitter, normally made up of KBr coated with germanium (for the MIR region).

The beam-splitter splits a beam of light that enters (incident beam) into two new beams, one reflected onto the moving mirror and the other onto the fixed (stationary) mirror. The two beams are then reflected back and recombined at the beam-splitter. Owing to path differences between the mirrors, both beams undergo constructive and destructive interferences. The recombined beam is then passed on towards the sampling area, where it interacts with the sample. The transmitted, diffused or reflected light reaches the detector, where the energy is digitized, resulting in an output signal consisting of the sum of cosine waves. This is the interferogram. This interferogram consists of the intensity of energy measured versus the position of the moving mirror (function of time domain), and contains basic information about frequencies and intensities, but is not directly interpretable. The interferogram is then converted into a conventional infrared spectrum (function of frequency domain) by the mathematical function known as the Fourier transform.

Sample presentation

The development of FT-MIR instruments has been followed by the development of adequate sampling presentation techniques. Initially, the sample presentation techniques included fixed path-length transmission cells, coated or smeared films or windows, as well as hot pressed films and alkali halide pellets (KBr).

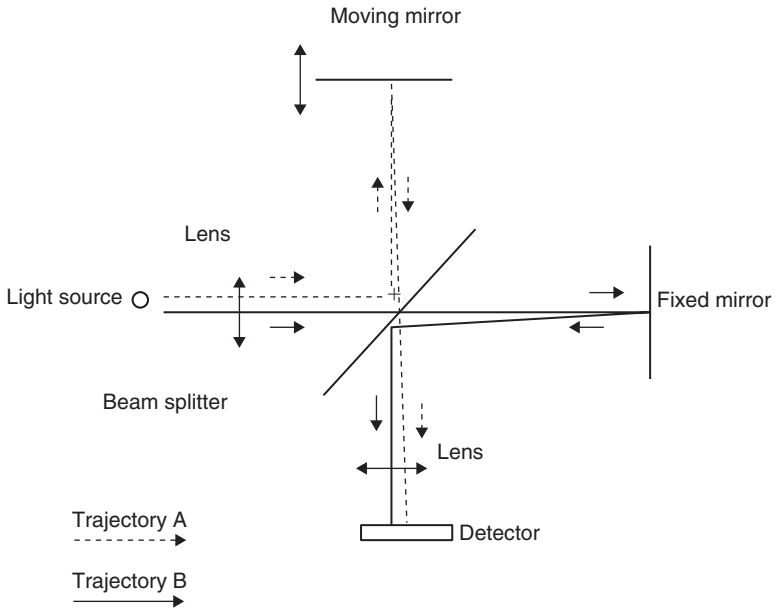

Figure 2.1 Schematic configuration of an interferometer.

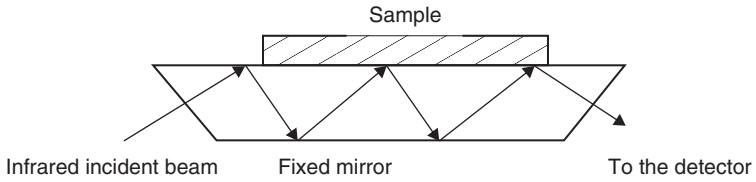

Figure 2.2 Horizontal attenuated total reflection (ATR) sampling device.

Maybe one of the most interesting developments has been the introduction of simple reflectance techniques as the *attenuated total reflectance* (*ATR*) system (Fahrenfort, 1961; Harrick, 1967) (Figure 2.2). With the ATR, the sample is in contact with a crystal of a high refraction index. This crystal is mainly made of ZnSe, Ge, ZnS, Si or diamond. The ATR system measures the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with the sample. For this, the radiation coming from the *beam-splitter* reflects off the inner surface of the crystal one or more times. A standing wave, called the *evanescence wave*, is generated for each reflection. Evanescence waves are penetrating electromagnetic fields that have decreasing intensity when moving away from their source. The evanescence waves penetrate the sample and interact with it, producing a spectrum. The penetration depth depends on the incident angle, the crystal and sample refraction indexes, and the infrared ray wavenumber.

ATR is a versatile and powerful technique for infrared sampling. It is useful for sampling the surface of smooth materials that are either too thick or too opaque for transmission IR measurement. The ATR is non-destructive, little or no sample preparation is needed, and it allows fast and simple sampling. However, the ATR crystal absorbs energy at lower energy levels, and most of the used crystals have pH limitations.

There must also be good contact between the sample and the crystal to be sure that the data obtained is accurate. ATR is a good technique for measuring solids such as paper, glass, cheese, meat, soft powders and dark-colored materials, as well as liquids including non-aqueous solutions such as oils, dyes and pastes, polymers and many other organic materials.

New ATR systems are based on a diamond interface for the analysis of liquids. In most cases, this is technically realized by a diamond substrate or a sandwich layer on a common ATR-substrate (ZnSe, Ge, BaF2, …).

Other sampling accessories include thermostatized flow cells and ATR cells coupled with an appropriate pump as well as IR-cards in polyethylene that can be used successfully for the analysis of fats and oils.

New developments

More recent improvements in MIR instruments include the development of on-line spectrometers, already available for gas or exhaust monitoring. The main innovation in this area is the use of fiber-optics for the connection between the spectrometer and the sensing device. However, there are several disadvantages, including losses in coupling and transmission, moisture sensitivity and mechanical sensitivity. Current applications include the monitoring and control of cultivations of *Gluconacetobacter xylinus* and production of gluconacetan, a food-grade exopolysaccharide (Kornmann *et al*., 2004), and the evaluation of quality traits in apricot fruits (Bureau *et al*., 2006).

These developments are also used in FT-MIR spectrometers attached to microscopes (FT-MIR microscopy) in order to measure infrared spectra from a tiny part of a sample. This combination has the dual advantages of clear chemical identification of the sample components by MIR spectroscopy, and high lateral resolution as obtained by microscopy. It thus allows direct access to spatially resolved molecular and structural information regarding the analyzed area. MIR microscopy has a wide range of applications, including, among others, in pharmaceuticals, forensic trace evidence, drug contamination, catalysts, minerals, plant leaves, animal tissue, cells, and industrial products defects.

Recently MIR imaging has been of considerable interest, owing to a number of new developments – mainly in the area of astronomy, where MIR cameras enable a wide range of observations. Among these are studies of the temperature characteristics of the atmospheres of different planets, as the MIR region is where the planets emit most of their radiation. Also, owing to the dust around them, still-forming stars glow brightly in the MIR, providing information about complex molecules which then leads to investigations of how stars and planetary systems form and evolve. MIR imaging has also been applied to several problematic areas in the agricultural and food industries (Elmore *et al*., 2005).

Applications of MIR and FT-MIR in foods, drinks, cotton and wood

The application of MIR spectroscopy in combination with multidimensional statistical techniques for the evaluation of *food quality* has increased. The development of

FT-MIR in recent years affords the possibility of obtaining unique information about protein yield, protein structure and protein–protein and proteilipid interactions without introducing perturbing probe molecules. Thus, most papers have used FT-MIR to determine the quality of food products. Analyses have focused on measurements in the 4000–900 cm^{-1} spectral region, within which three spectral regions have been used; 3000–2800 cm^{-1}; 1700–1500 cm^{-1} and 1500–900 cm^{-1}. These were selected because they are rich in information, while the inclusion of the other spectral data (i.e. 4000–3000 cm^{-1} and 2800–1700 cm^{-1}) might interfere with the extraction of useful information. Water exhibits a strong absorption band in most of the considered food products, overlapping amide I and II protein bands. Owing to the high absorbance at about 1640 cm^{-1} in the amide I and II regions, and in order to comply with the Beer-Lambert law, the path length of the cuvette has to be in the 10 μm range.

Dairy products

Monitoring the quality of cheese throughout ripening

Rapid screening techniques to determine quality characteristics of *cheeses* throughout ripening are of great interest for both industry and consumers. In common with the processed food industry at large, the dairy industry has come under increasing pressure to deliver products of high and constant quality to the marketplace.

The *ripening* process implies several complex modifications, which take place simultaneously or successively. Indeed, the biochemical transformations impart new characteristics: the paste of the cheese is modified in its composition and structure, and consequently in its appearance, consistency and color. At the same time, flavor and typical taste develop. Such processes ensure a constant excellent quality of the product, and control can be achieved by examining the phases of the production process and/or the finished products.

Proteolysis is the principal and most complex biochemical event occurring during the ripening of cheese. Indeed, during cheese ripening part of the casein is converted into water-soluble nitrogenous compounds, such as peptides and amino acids (Fox, 1989). These peptides have different solubilities in water and other solvents. Therefore, extractions with different solvents and subsequent quantification of nitrogenous compounds in the cheese extract are used to study the extent of proteolysis in cheese.

The determination of the chemical composition of cheese is a very important task which has classically been undertaken by different physicochemical methods to determine the pH-value, fat, nitrogen fractions, volatile fatty acids, organic acids content, etc. However, such methods are cumbersome, require a great deal of time and are expensive, and in some cases the results are not very accurate. Taking this into account, the development of new methods for the determination of chemical parameters is of great importance.

Nowadays, there is a need in the cheese-processing industry for tools that can be used for real-time control of production lines to check whether in-process material, during a given processing step, meets the necessary compositional or functional specifications to reach a predetermined quality standard in the final product. In this context, spectroscopic techniques such as MIR are fast, relatively low-cost, and provide

a great deal of information with only one test. They are considered to be sensitive, non-destructive, rapid, environmentally friendly and non-invasive, making them suitable for on-line or at-line process control and appropriate for process control.

The potential of FT-MIR in monitoring the ripening time of 16 experimental semi-hard cheeses at four different times of ripening (1, 21, 51 and 81 days) has been investigated by several researchers (Dufour *et al*., 2000; Mazerolles *et al*., 2001, 2002).

In the first step, *principal component analysis* (PCA) was applied to the 1700–1500 cm^{-1} spectral region recorded in the investigated cheeses at different ripening times, and the pattern of each component was examined. The authors clearly demonstrated the potential of PCA to facilitate discrimination between cheeses as a function of their ripening times. In addition, the rational molecular basis for the observed discrimination of the spectral patterns and their relation to known absorptions due to amide I and II was indicated by the same researchers, who stated that one or several continuous phenomena that occurred during the ripening stage were detected at the level of amide I and II absorption bands.

In the second step, and in order to determine the link between FT-MIR and fluorescence spectra, Mazerolles *et al*. (2001) applied canonical correlation analysis (CCA); on one hand to the 1700–1500 cm^{-1} spectral region and tryptophan fluorescence spectra, and on the other to the 3000–2800 cm^{-1} spectral region and vitamin A spectra. A relatively high correlation was found, since the first two canonical varieties with squared canonical correlation coefficient were higher than 0.58. The researchers concluded that FT-MIR and fluorescence spectra provide a common description of cheese samples throughout ripening.

In a similar approach, Martín-del-Campo *et al*. (2007a) used FT-MIR to monitor the ripening stage of Camembert-type cheese produced at a pilot scale. Cheeses samples were analyzed at two different zones (core and under-rind) during the first 10 days of ripening, as well as after 13, 15, 17, 20 and 27 days of ripening. From the results obtained, it was reported that throughout the ripening stage the under-rind spectra showed some modification in the spectra, while only a weak difference was observed between the recorded core spectra. The authors attributed the bands observed on the FT-MIR to molecules that are present in cheeses during ripening. Indeed, carbohydrate- and organic acid-associated bands were found in the 1490–950 cm^{-1} spectral region. Other bands located around 1096 cm^{-1} (secondary alcohol ν C–O and δ O–H), 1082 cm^{-1} (δ O–H) and 1045 cm^{-1} (primary alcohol ν C–O) have been associated with lactose by the same research group, which corroborates with the findings of others (Lanher, 1991; Picque *et al*., 1993; Cadet *et al*., 2000; Coates, 2000; Grappin *et al*., 2000). For the under-rind cheese samples, an increase in the absorbance at 1160 cm^{-1} during the first 6 days followed by a decrease until the end of the ripening stage was observed. This evolution has been ascribed to the presence of monosaccharides like glucose and galactose, which come from the lactose degradation throughout the ripening stage.

Regarding the region located between 1700 and 1500 cm^{-1}, two important peaks – *amide I* at 1640 cm^{-1} (ν C=O, ν C–N) and *amide II* at 1550 cm^{-1} (δ N–H and ν C–N) – characteristic of and associated with protein response were observed, in agreement with previous findings (Dufour and Robert, 2000; Grappin *et al*., 2000; Robert and Dufour, 2000). Significant changes were recorded for amide I and II bands

for the under-rind cheese samples, but only amide II bands for the core. In addition, the ratio of absorbance amide I to absorbance amide II showed a significant change throughout the ripening stage for both cheese sections. Modifications in the intensity and position of different bands in the amide I peak have been associated with changes in casein secondary structure, protein aggregation and protein–water interaction, as reported by others (Guerzoni *et al*., 1999; Mazerolles *et al*., 2001; Vannini *et al*., 2001; Kulmyrzaev *et al*., 2005). A continuous decrease in the band located at 1652 cm^{-1} and a continuous increase in that located at 1550 cm^{-1} during the ripening of semi-hard cheeses and cheeses inoculated with different strains of *Y. lipolytica* was pointed out by Mazerolles *et al*. (2001) and Lanciotti *et al*. (2005), and Vannini *et al*. (2001), respectively. However, Guerzoni *et al*. (1999) reported a continuous increase for both amide bands in goat cheeses produced by different processes.

Considering the 3000–2800 cm^{-1} spectral region characteristic of fat, the authors noted that neither methylene (bands around 2920 and 2851 cm^{-1}) nor methyl (bands around 2954 and 2871 cm^{-1}) signal changes were significant for the core, while they were significant in the spectra recorded on the under-rind zone, confirming the findings of Dufour *et al*. (2000), and Kulmyrzaev *et al*. (2005) regarding semi-hard cheeses and soft cheeses, respectively. Regarding semi-hard cheeses, Dufour *et al*. (2000) reported an increase in the $A\nu_{as}\ CH_2/A\nu_{as}\ CH_3$ ratio throughout ripening.

Finally, and in order to extract information from the data sets, Martín-del-Campo *et al*. (2007a) applied PCA to the spectral data set and the similarity map showed good discrimination of cheese samples presenting a ripening time of 15 days or less from the others. In order to achieve interpretation at the molecular level, the researchers studied the eigenvectors corresponding to PC1 and PC2. The eigenvector 2 showed two important regions related to amide I and II, and another assigned to carbohydrates (1500–950 cm^{-1}). The former showed an opposition between a positive band located 1632 cm^{-1} (amide I) and a negative one observed around 1543 cm^{-1} (amide II) peaks. The obtained results confirmed those found previously by Mazerolles *et al*. (2001) with semi-hard cheeses and Kulmyrzaev *et al*. (2005) with soft cheeses; while the latter have pointed out that changes in the 1700–1500 cm^{-1} spectral region could classify cheeses according to their ripening times. The opposition between amide I and II was also observed. The lactate bands located at 1589 cm^{-1} and 1743 cm^{-1} have been observed in different varieties of cheeses (Guerzoni *et al*., 1999; Kulmyrzaev *et al*., 2005; Lanciotti *et al*., 2005). Martín-del-Campo *et al*. (2007a) reported that the band at 1589 cm^{-1} was found to correlate with the spectral evolution of cheese from day 1 to day 8 – the period during which the concentration of lactic acid increases from days 1–5 before decreasing after day 5 (Leclercq-Perlat *et al*., 2004).

Prediction of some chemical parameters in dairy products

FT-MIR milk analyzers are widely used in the dairy industry to determine major components such as fat, protein, lactose, solid contents, etc. Lynch and Barbano (1995) used FT-MIR to determine how well the calibration equations generated by using reconstituted *milk powders* could be used to predict the chemistry of raw milk samples. In their studies, 12 reconstituted powders and 7 raw milk samples were analyzed in 7 laboratories using FT-MIR. For each laboratory, corrected and uncorrected data were recorded.

The authors considered that corrected data reflected current calibration. The reconstituted powders were found not to provide an accurate fat calibration for testing raw milk samples, as can be obtained with raw milk calibration samples. This has been attributed primarily to differences in the characteristics of the fat in the reconstituted powders and in raw milk. Regarding protein, the analytical precision for both types of calibration were found to be comparable. In another study, the accuracy of FT-MIR to determine casein content in dairy cows' milk was investigated (Sørensen *et al*., 2003). By applying *partial least squares* (*PLS*) regression to the FT-MIR spectra and casein amount determined by reference method, *standard errors of prediction (SEP)* of 0.033% and 0.89% for casein concentrations in the range of 2.1–4.0% and 70.7–81.0% were found, respectively. The main conclusion of this study was that FT-MIR was found to be less sensitive to heat denaturation of whey proteins than was the reference method. The obtained results were recently confirmed by the investigations of Etzion *et al*. (2004), who succeeded in predicting protein concentrations of 26 milk standards produced at the laboratory scale for which the amount of proteins varied from 2.27 to 3.90 g $100\,g^{-1}$. However, in their study the authors observed significant interference when the water subtraction procedure was applied, which they considered to be the primary obstacle to the determination of protein level. Another problem stated by the authors has been attributed to the fact that milk spectra were influenced by other constituents, such as fat and lactose, forming a potential buffer layer between the ATR crystal and the protein cells. Using the same approach, Iňón *et al*. (2003a) utilized the same technique to predict the nutritional parameters of 83 commercially available bottles of milk covering the whole range of available brand names and types of milk in Spain – i.e. whole (25), semi-skilled (35), skimmed (23), and with (45) and without (38) additives, including nutritional modified milks for babies (5) and a milkshake with tropical fruits (1). The researchers applied PLS regression for the determination of total fat, total protein, total carbohydrates, calories and calcium, and relative precisions of 0.062 g $100\,g^{-1}$, 0.04 g $100\,g^{-1}$, 0.039 g $100\,g^{-1}$, 0.66 kcal $100\,ml^{-1}$, and 2.1 mg Ca.$100\,ml^{-1}$ were obtained, respectively. One of the main conclusions of this study is that FT-MIR-ATR could be used as a suitable technique for the classification of milk samples.

Picque and colleagues (Martín-del-Campo *et al*., 2007b) used the FT-MIR to *predict* some chemical parameters (pH, acid-soluble nitrogen, non-protein nitrogen, ammonia (NH_4^+), lactose and lactic acid) by applying PLS regression. The obtained results showed good prediction of these parameters, except for that of pH. Indeed, the accuracy obtained for dry matter and pH was in agreement with those of Karoui *et al*. (2006a) for commercial soft cheese. The authors concluded that, although the physicochemical parameters were determined at different ripening time, they were comparable to previous findings obtained on ripened cheeses.

Karoui *et al*. (2006b–2000d) have also used FT-MIR to determine chemical parameters in Emmental cheeses produced in the summer and winter seasons, and originating from different geographic origins. For Emmental cheeses produced during the summer period, Karoui *et al*. (2006c) pointed out that the best results for water-soluble nitrogen (WSN) ($R^2 = 0.91$; ratio of standard deviation to root mean square error of prediction (RPD) = 3.34) (Figure 2.3a), non-protein nitrogen (NPN) ($R^2 = 0.77$; RPD = 2.08) (Figure 2.3b), pH ($R^2 = 0.57$; RPD = 1.41), NaCl ($R^2 = 0.45$;

RPD = 1.33) and total nitrogen (TN) (R^2 = 0.43; RPD = 1.34) were obtained when the spectra were subjected to the first derivation and smoothing after being subjected to maximum normalization. The researchers concluded that FT-MIR transmission spectroscopy could be considered as an alternative technique for the determination of

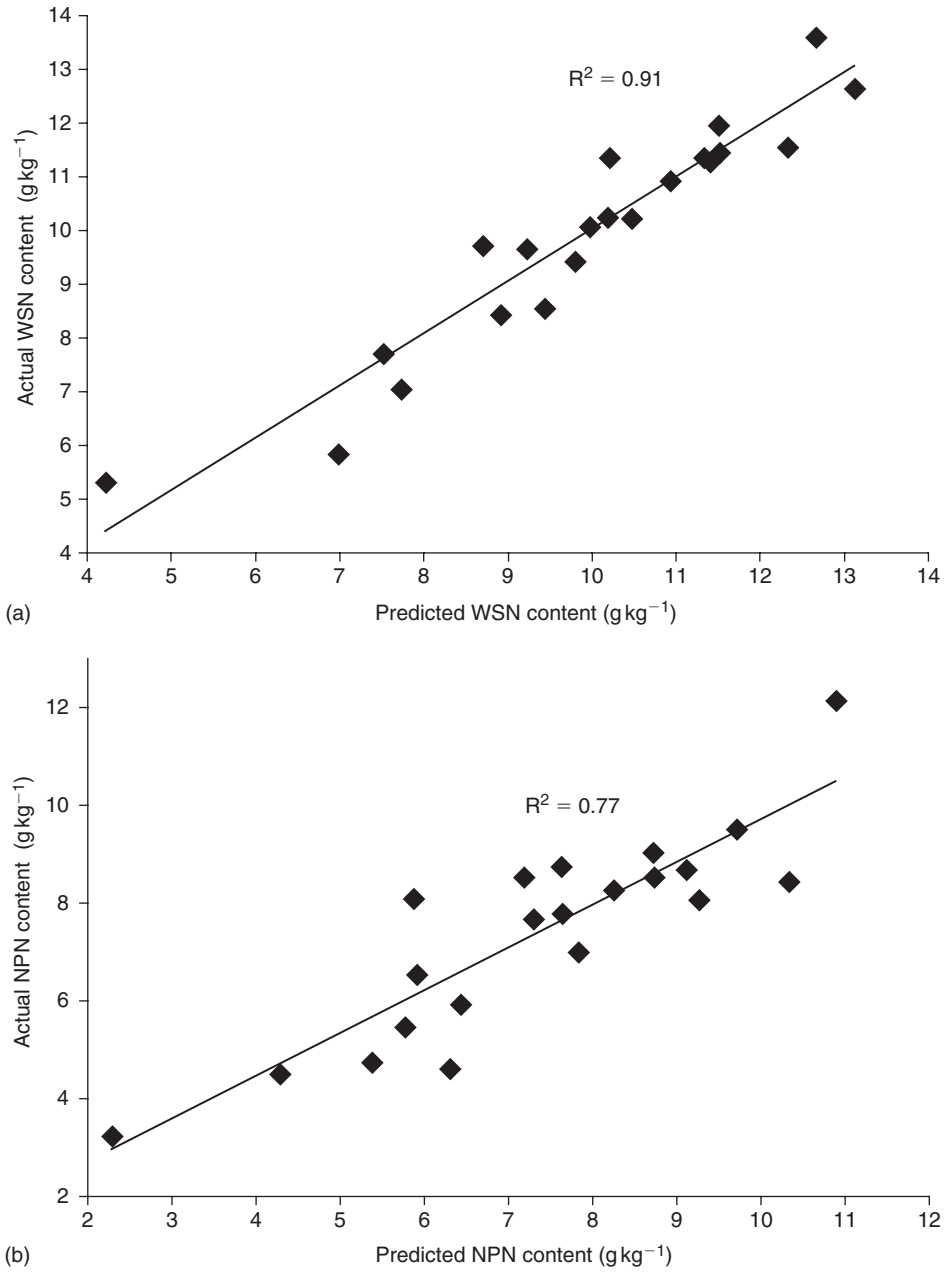

Figure 2.3 Linear regression plot of actual versus predicted (a) water soluble nitrogen (WSN) and (b) non-protein nitrogen (NPN) content of the validation data set for the Fourier transform infrared spectroscopy (FT-MIR) on recorded on European Emmental cheeses produced during summer period.

NPN and WSN of Emmental cheeses produced during summer and originating from different European countries. The obtained results were in agreement with the findings of Martín-del-Campo (2007b), who found an R^2 of 0.92 and an RPD of 3.27 for NPN on soft cheese samples presenting different ripening time. In order to achieve

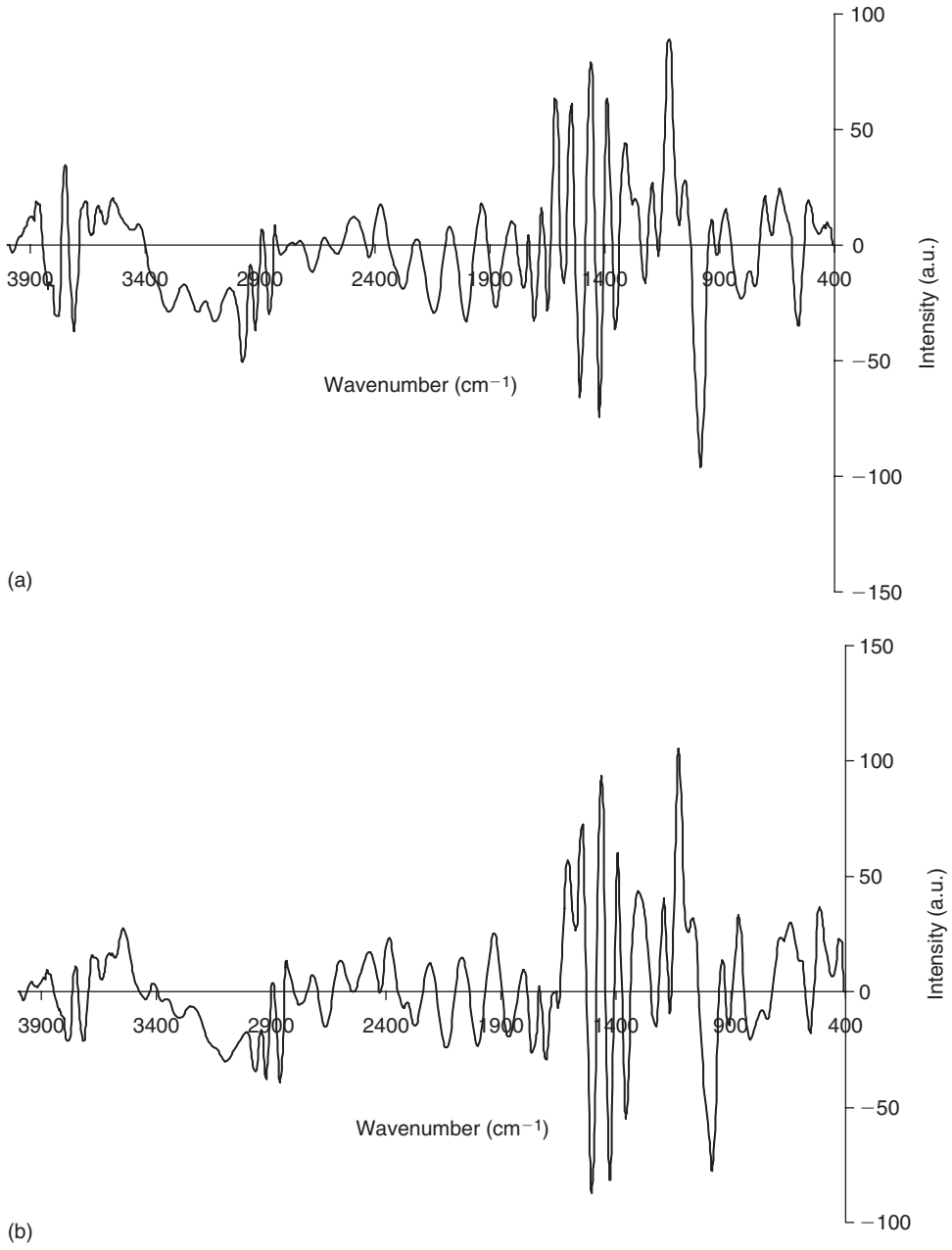

Figure 2.4 Correlation coefficient over the entire wavelength range of (a) non-protein nitrogen (NPN) and (b) water-soluble nitrogen (WSN) for the Fourier transform infrared spectroscopy (FT-MIR) recorded on European Emmental cheeses produced during the summer period.

interpretation at the molecular level, Karoui and colleagues (2006c) studied the *correlation coefficient distribution* of WSN and NPN over the entire wavelength range. They observed that the 1620–979 cm^{-1} spectral region was the most important spectral region, owing to the presence of several correlation peaks (Figures 2.4a, 2.4b). When the wavelength range of 1620–979 cm^{-1} was considered only during the PLS cross-validation stage, the resultant model for NPN and WSN provided very similar results to the model developed for the entire wavelength range.

Unsuccessful measurement of TN was achieved for Emmental cheeses produced during the summer period using the FT-MIR-PLS measurement method. The researchers reported that the obtained results confirmed their previous findings reporting that the FT-MIR cannot be used with success to predict TN in Emmental cheeses produced during winter (Karoui *et al*., 2006d). The correlation coefficients and the root mean square error of prediction (RMSEP) values reported in their study were in the same range as reported in previous investigations (Pierce and Wehling, 1994; Wittrup and Nørgaard, 1998). However, in the investigations by Karoui *et al*. (2006d) the Emmental cheeses were from variable sources – they came from different European countries, and were manufactured with raw or thermized milk, using different cheese-making procedures and ranging in age.

Karoui *et al*. (2006c) reported that quantitative measurement of pH indicates that FT-MIR can discriminate only between high and low values, while the results obtained for NaCl were not supported by the methodology since the R^2 values of the calibration and validation data sets were 0.47 and 0.45, respectively (Tables 2.2, 2.3). These values have been reported to be relatively smaller than those obtained by Karoui *et al*. (2006d) on Emmental cheeses produced during the winter. The researchers attributed these differences to the fact that a smaller range in NaCl content was considered (0.24–0.97 g 100 g^{-1}) for the summer-produced cheeses than for the winter-produced cheeses (0.19 and 1.36 g 100 g^{-1}). However, they stated that further investigation was needed to confirm this hypothesis.

In a similar approach, Karoui and colleagues (2006b) compared FT-MIR and NIR for predicting the same physicochemical parameters on Emmental cheeses produced during the winter season. The researchers suggested the use of NIR for the determination of fat and TN contents, and of FT-MIR for NaCl and NPN contents as well as for pH. Similar results were obtained for WSN using the two techniques together. The main conclusion of their study is that the combination of both NIR and FT-MIR spectra did not improve the results, since comparable results to those obtained from either the NIR or FT-MIR were obtained.

Determination of the quality and the geographic origin of dairy products at the retailed stage

Today, the European market is saturated with food products. The new challenge is not to produce a standard product which is only differentiated by price, but to produce products that have unique characteristics and meet consumer expectations. Two approaches can be used to reach these goals. On one hand, fulfilling consumer demands can be achieved through the creation of commercial brand products with unique texture, flavor or usage appeal characteristics; on the other, *Protected*

Table 2.2 Validation results of PLS cross-validation regression on calibration sample set of Emmental cheeses produced during summer period

Compositional parameter	LV	R^2	RMSECV ($g\,100\,g^{-1}$)	RPD
NaCl	11	0.47	0.127	1.37
pH*	11	0.56	0.005	1.50
NPN	12	0.71	0.085	1.85
TN	8	0.33	0.112	1.11
WSN	12	0.80	0.068	2.22

NPN, non protein nitrogen; TN, total nitrogen; WSN, water-soluble nitrogen; LV, latent variables; R^2, determination coefficient; RMSECV, root mean square error of cross-validation; RPD, ratio of prediction deviation (Standard deviation/RMSECV)
*pH is expressed without units.

Table 2.3 Validation of PLS cross-validation regression on validation set of Emmental cheeses produced during summer period

Compositional parameter	R^2	RMSEP ($g\,100\,g^{-1}$)	RPD
NaCl	0.45	1.54	1.32
pH*	0.57	0.07	1.41
NPN	0.77	0.99	2.08
TN	0.43	1.24	1.34
WSN	0.91	0.65	3.34

NPN, non protein nitrogen; TN, total nitrogen; WSN, water-soluble nitrogen; LV, latent variables; R^2, determination coefficient; RMSEP, root mean square error of prediction; RPD, ratio of prediction deviation (Standard deviation/RMSEP)
*pH is expressed without unit.

Designation of Origin (PDO) indicates brands of a particular quality because they can be made only from raw milk possessing specific features, which also fulfils consumer demands. A PDO cheese is defined according to its geographical area of production, and also according to the description of the materials and of the technology used (Bertoni *et al*., 2001).

Several techniques for assessing the *authenticity* of PDO food products have been used, and these can be classified into two categories. *Traditional techniques*, such as gas chromatography, capillary gas chromatography of lipid fractions and electrophoretic separation of proteins, focus on the existence or absence of certain chemical compounds in the authentic product (Pillonel *et al*., 2002). Although these methods provide valuable information regarding the composition and biochemistry of cheeses, they are time-consuming and expensive processes which require highly skilled operators and are not easily adapted to online monitoring. Hence, an urgent demand exists for rapid, inexpensive and efficient techniques for quality control. A great number of non-invasive and non-destructive instrumental techniques, such as infrared and fluorescence spectroscopic techniques, have been developed for the authentication of food products. These new analytical tools require limited sample preparation and appear promising. Recently, the potential of FT-MIR for determining the *geographic*

origin of Emmental cheeses manufactured during the winter and summer seasons has also been investigated (Karoui *et al*., 2004a, 2004b, 2005a, 2005b). The application of FT-MIR to determine the shelf-life of Pasta Filata and Crescenza cheeses was investigated by Cattaneo *et al*. (2005) and Giardina *et al*. (2003), respectively. These authors reported that FT-MIR allowed the evaluation of the shelf-life period in which cheese was maintained and suggested the use of this technique for the classification of cheeses in real time on the basis of their shelf-life.

In order to obtain a more detailed description regarding the variation in the spectra recorded for cheese, Karoui *et al*. (2005b) applied the first derivative to the spectra of Emmental collected from different European regions (Figure 2.5). Contribution to the lipids can be observed in the 3000–2800 cm^{-1} spectral region, which is dominated by two strong bands at 2915 and 2846 cm^{-1} associated with methylene anti-symmetric and symmetric stretching (Dufour *et al*., 2000), respectively. Two other bands resulting from the asymmetric and symmetric stretching modes of the terminal methyl groups were also present at 2954 and 2860 cm^{-1}, respectively. Contributions to the amide I band can be observed around 1684 and 1622 cm^{-1}. This part of FT-MIR was used by other researchers (Mazerolles *et al*., 2001) to investigate the secondary structure of several proteins. The absorption bands at 1578, 1526 and 1512 cm^{-1} are generally assigned to the amide II vibrations, while that around 1578 cm^{-1} has been attributed to soluble carboxylic acids, such as lactate (which has a characteristic wavelength at 1575 cm^{-1}, as shown by Picque *et al*., 1993). The region located between 1500 and 900 cm^{-1}, called the fingerprint region, refers to C–O and C–C stretching modes (1153–900 cm^{-1}) as well as other numerous bonds (amide III) and P–O.

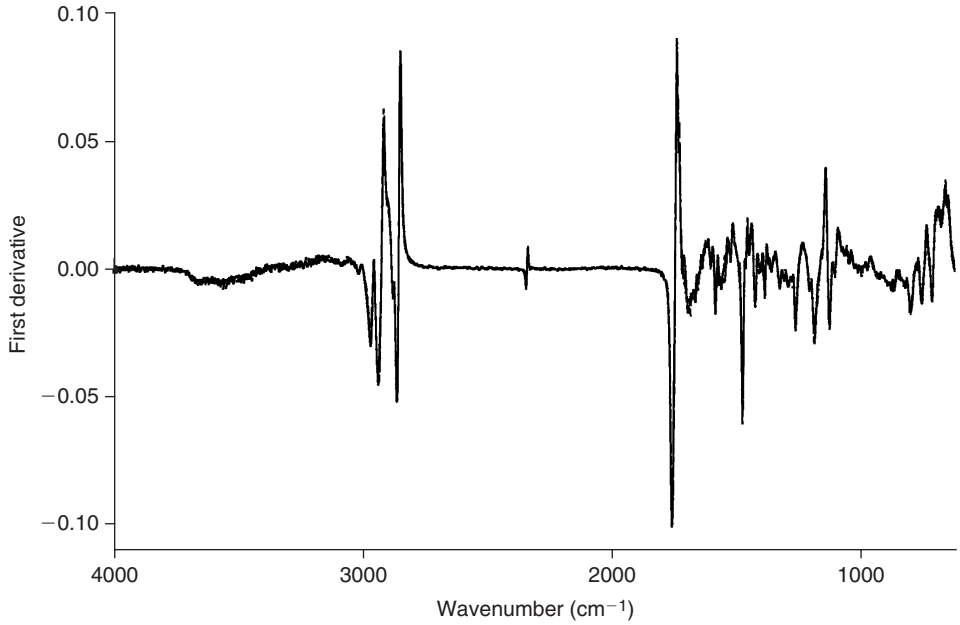

Figure 2.5 Averaged first derivative of the Fourier transform infrared spectroscopy (FT-MIR) spectra for Emmental cheeses from Austria (——), Germany (.....), Switzerland (------), France (-·-·-·-) and Finland (— —).

In order to extract information from the data set and to assess the potential of FT-MIR to authenticate cheeses according to their geographic origin, Karoui and colleagues (2005b) applied PCA to the three normalized data sets corresponding to the three spectral regions (3000–2800 cm^{-1}, 1700–1500 cm^{-1} and 1500–900 cm^{-1}). For these three spectral regions, the plots of the scores for PC1 versus PC2 did not reveal any outlying samples or any obvious spatial pattern in the sample score distribution.

The authors then applied *factorial discriminant analysis (FDA)* to the first 20 principal components (PCs) of PCA performed on the three data sets corresponding to 3000–2800 cm^{-1}, 1700–1500 cm^{-1} and 1500–900 cm^{-1} spectral regions for the different cheeses. Before applying FDA, five groups were created, for cheeses from Austria, Finland, Germany, Switzerland and France. Regarding the 3000–2800 cm^{-1} spectral region, the authors pointed out good discrimination of Finnish cheeses from the other cheeses. In addition, correct classifications of 84.1% and 85.7% were observed for the calibration and validation data sets, respectively (Table 2.4). Analysis of this table illustrates that cheeses from Austria and Finland were well classified, while some misclassification occurred for cheeses from Switzerland, France and Germany.

Table 2.4 Classification table for Emmental cheeses produced during winter period and originating from different countries based on mid-infrared (MIR) (3000–2800 cm^{-1}, 1700–1500 cm^{-1} and 1500–900 cm^{-1}) validation data sets

Predicted[a]	Observed[b]				
	Austria	**Finland**	**Germany**	**France**	**Switzerland**
	MIR: 3000–2800 cm^{-1} spectral region				
Austria	**4**	–	–	1	–
Finland	–	**6**	–	–	–
Germany	–	–	**11**	1	1
France	–	–	1	**25**	5
Switzerland	–	–	1	3	**32**
% Correct classification	**100**	**100**	**84.6**	**83.3**	**84.2**
	MIR: 1700–1500 cm^{-1} spectral region				
Austria	**2**	–	–	–	–
Finland	–	**6**	–	–	–
Germany	1	–	**12**	–	–
France	1	–	1	**28**	2
Switzerland	–	–	–	2	**36**
% Correct classification	**50**	**100**	**92.3**	**93.3**	**94.7**
	MIR: 1500–900 cm^{-1} spectral region				
Austria	**2**	–	–	–	–
Finland	–	**6**	–	–	–
Germany	2	–	**13**	–	–
France	–	–	–	**30**	1
Switzerland	–	–	–	–	**37**
% Correct classification	50	**100**	**100**	**100**	**97.4**

[a]The number of predicted cheese samples
[b]The number of observed cheese samples.

Considering the amide I and II regions, similar results to those obtained with the 3000–2800 cm^{-1} spectral region, i.e. 88.5 and 96.7% (Table 2.4) of correct classifications, were observed for the *calibration and validation* data sets, respectively. The researchers claimed that the best results were obtained with the 1500–900 cm^{-1} region, since the map of the FDA defined by the discriminant factors 1 and 3 allowed good discrimination between Emmental cheeses from the different countries (Figure 2.6). Indeed, cheeses from Switzerland and Finland were located on the left according to discriminant factor 1, whereas those from France, Austria and Germany were located on the right. Correct classifications amounting to 96.7% (Table 2.4) were observed for the calibration and validation sets. Table 2.4 shows that cheeses from Germany, France and Finland were totally discriminated. However, Swiss and Austrian cheeses showed less than 100% correct classification (97.4% and 50%, respectively). One of the main conclusions of this study was that the 1500–900 cm^{-1} spectral region is considered by the researchers to be a promising tool for reliable determination of the origin of Emmental cheeses. The obtained results confirmed those obtained by the same research group on Emmental cheeses produced during the summer period, since the best results were obtained by using the 1500–900 cm^{-1} spectral region (Karoui *et al*., 2004b). The obtained results were confirmed recently by Giardina *et al*. (2003) on a typical Pasta Filata cheese. These latter authors analyzed 112 cheese samples coated with biodegradable wax or paraffin at 90 and 120 days of shelf-life and found that the 1100–1035 cm^{-1} and 1720–1690 cm^{-1} spectral regions could be used to classify cheese samples according to the days of shelf-life and the type of coating.

Finally, Karoui and colleagues (2004a) assessed the potential of FT-MIR to determine the region in which Emmental cheeses were produced independently of the

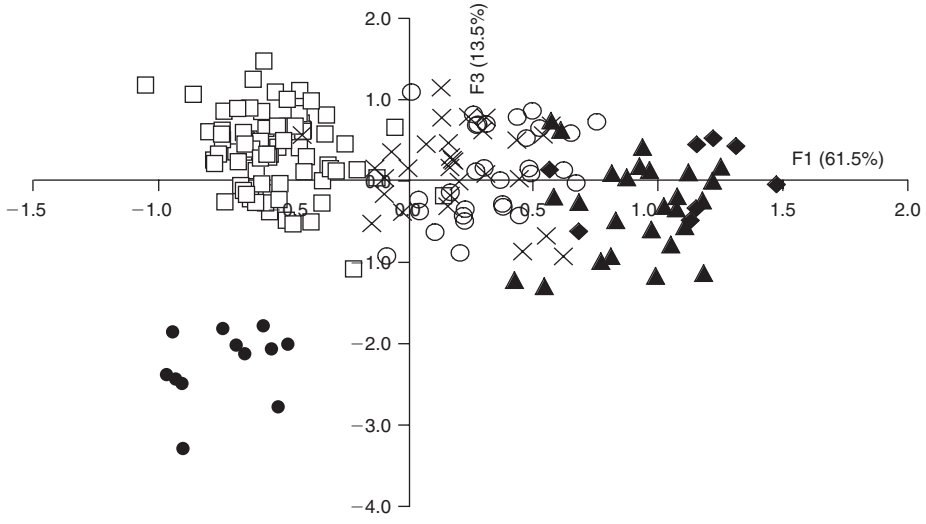

Figure 2.6 Discriminant analysis similarity map determined by discriminant factors 1 (F1) and 3 (F3) for 1500–900 cm^{-1} spectral region of Emmental cheeses produced during the winter period and originating from Austria (◆), Switzerland (□), Germany (▲), France (from thermized milk, ×; from raw milk, ○) and Finland (●).

production season by using the concatenation technique, which was analyzed by FDA. Although, the results obtained did not allow 100% correct classification of cheeses, the authors concluded that the obtained findings could be considered promising considering the significant effect of the season on the characteristics of investigated cheeses. The findings were later confirmed by the investigation of Karoui *et al*. (2005a) reporting that the FT-MIR provided relevant information on the geographical origin of both experimental Jura hard cheeses and Swiss Gruyère and l'Etivaz PDO cheeses. The researchers pointed out that the calibration stage and development of the calibration equations are the limiting steps for adopting FT-MIR as a technique for the authentication of dairy products, as these are time-consuming and costly. However, when the calibration stage is accomplished successfully, the determination of a chemical property or geographical origin can be carried out very rapidly with a single analysis for minimal cost.

Meat and meat products

The nature of some meat products (pies, sausages, burgers) offers many possibilities for adulteration. Cheaper cuts or offal may be substituted for expensive cuts, and water or vegetable matter may be added. The potential of FT-MIR to differentiate between three meats – turkey, chicken and pork – was shown by Al-Jowder *et al*. (1997). Indeed, by applying PCA to the spectral data sets, good discrimination was observed between fresh and frozen-then-thawed turkey, chicken or pork samples. The same research group also showed that FT-MIR could discriminate fresh meat from that which had previously been frozen. In another study, Al-Jowder and colleagues (1999) indicated the potential of FT-MIR to detect adulteration of raw, ground beef with certain types of offal obtained from the same species – specifically, kidney and liver. Comparing the 1000–1200 cm^{-1} spectral region, clear differentiation between the spectra of the investigated meat samples was observed. The researchers ascribed these variations to the high level of collagen in liver samples. PLS regression was then applied in order to quantify the amount of added offal. The prediction errors obtained in the calibration data sets were found to be 4.8% and 4%, respectively, for the kidney and liver samples. The same research group (Al-Jowder *et al*., 2002) has recently assessed the potential of FT-MIR to discriminate between pure beef and beef containing 20% of a range of potential adulterants, such as heart, tripe, kidney and liver. FT-MIR spectra were recorded on raw samples as well as samples cooked using two different cooking regimes. By applying chemometric tools to the collection spectra, good discrimination of pure meat samples from adulterated samples irrespective of cooking regime was found, with a correct classification of 97% was obtained. The authors pointed out the possibility of discriminating between pure beef and the other samples adulterated with heart, tripe, kidney and liver, but this became more difficult as the cooking level increased.

Some proteolytic enzymes from plants or animals have been widely used as meat tenderizers for food processing in home cooking and industrial treatment. Lizuka and Aishima (1999) assessed the potential of FT-MIR to differentiate between reference beef and beef treated with pineapple juice. The obtained results showed good

discrimination between the two meat samples. In another study, Adhikari *et al*. (2003) used FT-MIR for detecting the presence of hexanal and methyl sulfide in a meal ready-to-eat (MRE) omelet with ham, as well as to monitor changes in the levels of hexanal and methyl sulfide in selected thermally-processed MRE products held under modified-atmosphere packaging and at elevated storage temperatures. The researchers concluded that FT-MIR method could be used as a tool for routine quality analysis of stored MRE and other food products.

Cereals and cereal products

The potential of FT-MIR use in cereals and cereal products has increased over the past few years with the propagated application of chemometric tools. Cocchi *et al*. (2004) used FT-MIR to discriminate among flour samples of different cereals and pseudo-cereals, namely wheat, oats and buckwheat, subjected to different technological treatments – dehulling, toasting and puffing. The use of oats and buckwheat is currently limited to the production of low-diffusion or niche foods. When compared with major cereals, such as wheat, maize and rice, these minor cereals are interesting because of their content of natural nutrients and biologically active components. The obtained results highlighted the usefulness of FT-MIR to characterize and better understand the flour matrices. One of the main conclusions of this study was that the obtained results were considered to be encouraging in view of studying mixtures of the flours, to predict their performances in dough- and bread-making processes. In another study, Kim *et al*. (2007) used FT-MIR to determine trans fatty acids in ground cereal products without oil extraction. PLS models were developed for the prediction of trans fatty acids in ground samples using several wavelength selections on the basis of bands related to lipids. The models developed with a number of samples of 79 predicted trans fatty acids in ground samples with a *standard error of cross-validation* (*SECV*) of 1.10–1.25 (range 0–12.4%) and R^2 of 0.85–0.88, and in validation samples (n = 26) with a SEP of 0.96–1.12 (range 0–12.2%) and R^2 of 0.89–0.92, indicating sufficient accuracy for screening. Sample trans fatty acid percentages were predicted as accurately within the fingerprint region (1500–900 cm^{-1}) as within the entire range (4000–650 cm^{-1}), indicating, in concert with the regression coefficients, the importance of the isolated trans double bonds at 966 cm^{-1} in development of the model.

Lizuka and Aishima (1999) investigated the ability of FT-MIR and NIR to differentiate between 27 soy sauces produced from whole soybeans and 30 from defatted soybeans. The researchers applied factor analysis applied separately to MIR and NIR, and indicated the existence of some difference between the two sauces. By applying *linear discriminant analysis* (*LDA*), 94.7% and 100% correct classification were obtained for MIR and NIR spectra, respectively.

In the food industry, starch is used to modulate product characteristics such as texture, appearance and stability in a wide range of applications. In the unmodified or native form starches have limited use in the food industry, and therefore starches undergo a process of modification to modulate their properties to provide the expected thickening, water-binding, stabilizing, gelling effect or to improve the

mouth feel and shininess of the product. Fernández Pierna *et al*. (2005) evaluated the potential of FT-MIR spectroscopy to identify modified starches in a food industry environment. To do this, MIR spectra were collected with a spectral resolution of 4 cm^{-1} using a Perkin-Elmer Spectrum 2000 FTIR spectrometer (Perkin Elmer Corporation, Norwalk, CT, USA) equipped with an ATR system Specac MKII GoldenGate (Specac Inc., Smyrna, GA, USA) positioned to give an incident angle of 45°. This spectrophotometer is fitted with a wire coil operated at 1350 K as an IR light source, a potassium bromide beam-splitter and a DTGS detector. Starch samples (232) were collected from various factories located in the USA and Europe of four different classes: one unmodified and three modified. The performance of different classification methods was compared by the researchers, who applied methods such as LDA, quadratic discriminant analysis (QDA), k-nearest neighbors (k-NN), soft independent modeling of class analogies (SIMCA), PLS-DA, ANN and support vector machines (SVM). The results showed that the different discrimination methods based on FT-MIR data can be effective tools for the classification of starches according to the type of chemical modification undergone, but the best results were obtained using the SVM technique, with more than 85% of the samples correctly classified when validating the model.

Edible oils

Olive oil is classified according to purity, and can vary from *extra-virgin olive oil* (*EVOO*) to lampante, which is not fit for consumption. According to the International Olive Oil Council, *virgin olive oil* (*VOO*) is the oil obtained from the fruit of the olive tree solely by mechanical or other physical means under conditions (particularly thermal) that do not lead to adulteration in the oil, and which has not undergone any treatment other than washing, decantation, centrifugation and filtration. The high-quality EVOO may thus be mislabeled or adulterated with cheaper oil. This is not only a commercial problem but also has health implication (Kochhar and Rossell, 1984). Adulteration involves the addition of cheaper oils; the most common adulterants found in VOO are refined olive oil, residue oil, synthetic olive oil–glycerol products, seed oils (such as sunflower, soy, maize and rapeseed) and nut oils (such as hazelnut and peanut oil) (Baeten *et al*., 1996, 2005; Downey *et al*., 2002; Sayago *et al*., 2004). The low price of olive–pomace oil means that it is sometimes used for adulterating EVOO. For this reason, a rapid method to detect such a practice is important for quality control and labeling purposes.

Several techniques can be used to detect olive oil adulteration. Among them are colorimetric reactions, and determination of iodine and saponification values, density, viscosity, refractive index, and ultraviolet absorbance (Gracian, 1968). However, these methods may be time-consuming and require sample manipulation. To overcome these handicaps, other techniques have been applied. The most noteworthy are spectroscopic techniques such as NIR, FT-MIR, nuclear magnetic resonance and fluorescence spectroscopy.

Van de Voort *et al*. (1994) used FT-MIR for the quantitative determination of peroxide values (PV) of vegetable oils in transmission mode. Calibration standards were

prepared by the addition of *t*-butyl hydroperoxide to a series of vegetable oils, along with random amounts of oleic acid and water. Additional standards were derived through the addition of mono- and diglyceride spectral contributions, as well as zero PV spectra obtained from deuterated oils. The researchers applied PLS regression to the 3750–3150 cm^{-1} region and compared the obtained values with those determined by the reference method (AOCS – American Oil Chemists Society). The reproducibility of the FT-MIR method (coefficient of variation CV = 5%) was found to be better than that of the chemical method (CV = 9%), although its accuracy was limited by the reproducibility of the chemical method. Later, the same research group (Van de Voort *et al*., 1995) used the FT-MIR to determine simultaneously the percentage *cis* and *trans* content of edible fats and oils. The system was calibrated to predict the *cis* and *trans* content of edible oils by using pure triglycerides as standards and the PLS regression method. The efficacy of the calibration was assessed by triglyceride standard addition, by mixing of oils with varying *cis/trans* contents, and by analyzing fats and oils of known iodine value. Each of the approaches verified that the FT-MIR method measured the *cis* and *trans* content in a reproducible (±0.7%) manner, with the measured accuracies being 1.5% for standard addition and 2.5% for the chemically analyzed samples. Comparisons also were made using the conventional AOCS method for the determination of *trans* isomers by FT-MIR spectroscopy, and the obtained results showed that the FT-MIR–PLS approach worked well for a wide range of *trans* contents, including those between 0 and 15%. The researchers concluded that FT-MIR could be implemented in place of a variety of AOCS wet chemical methods.

Marigheto *et al*. (1998) used FT-MIR and Raman spectroscopies to assess their ability to discriminate between oils originating from different botanical sources, and to detect added adulterants. In their studies, several oil samples were used – EVOO, refined oil, sunflower, rapeseed, soybean, sesame, hazelnut, swe*et* almond, grapeseed, safflower, peanut, walnut, mustard, corn, palm, coconut and palm kernel oils. In total, 140 spectra were collected to form a data base called "pure oils", in which seven different groups were present: EVOO (n = 36), refined oil (n = 10), sunflower oil (n = 28), rapeseed oil (n = 18), soybean oil (n = 21), peanut oil (n = 9) and corn oil (n = 18). These samples were further divided into a calibration set of 84 spectra, a validation set of 27 spectra and a test set of 29 spectra. After that, 11 of the EVOO group were chosen to be adulterated with 5 seed oils and 5 EVOO were adulterated with 5 olive oils, at different levels of adulteration (5, 15, 25, 35 and 45%). The researchers then applied LDA and an *artificial neural network* (*ANN*). For FT-MIR, 100% of the samples were correctly classified by using 15 PC scores and by using an ANN with 12 PC scores. However, for Raman spectra, the best prediction was only 93.1% for 10 PC scores with LDA, which did not improve with the use of more PC. The authors concluded that FT-MIR is better than Raman for classifying oil samples and detecting adulteration. The obtained results were confirmed later by Tay *et al*. (2002), who pointed out that FT-MIR was able to discriminate EVOO from those adulterated with sunflower oil at different concentrations. This could be due to the difference in the content of free fatty acids in olive oil, as has been demonstrated by Inón *et al*. (2003b), who indicated the ability of FT-MIR to determine the

content of free fatty acids with an R^2 of 0.996. Recently, Baeten *et al*. (2005) used FT-Raman and FT-MIR spectroscopy for the detection of the presence of hazelnut oil in olive oil at low percentages. Their study was performed on the entire oil and on its unsaponifiable matter. Different mixtures were prepared using VOO and hazelnut oils from several geographical origins in different percentages. For the univariate analysis, the Fisher coefficient was used to detect MIR spectral zones that distinguish olive from hazelnut oils. The most important differences were found in the fingerprint region characteristic of the stretching and bending vibrations of C–C and C–O groups of the molecules. Regarding multivariate analysis, stepwise LDA was applied to extract, interpret and exploit the information from the spectra. Complete discrimination between olive and hazelnut oils was observed, and it was found that adulteration can also be detected if the presence of hazelnut oil in olive oil is higher than 8%. The limit of detection is higher when the blends are of edibles oils from diverse geographical origins.

Recently, Wang *et al*. (2006) examined two spectroscopic techniques, ATR-FT-MIR and fiber-optic diffuse reflectance NIR spectroscopy, for the identification of camellia oil adulteration. Camellia and soybean oil were mixed together in accurately weighed proportions to obtain calibration and validation sets of 50 adulterated samples. The amount of soybean oil as the adulterate in camellia oil ranged from 5% to 25%. By examining the 1132–885 cm^{-1} spectral region, minor differences between adulterated and pure camellia oil samples were observed, particularly at 912, 1097 and 1120 cm^{-1}, corresponding to C–H bending and C–H deformation of fatty acid. In order to extract information from the spectral data sets the authors applied PLS regression, and promising results were obtained. Indeed, the R-value of the model was around 0.99; while the values corresponding to RMSEP and the *root mean standard error of cross-validation* (*RMSECV*) were 0.67 and 0.85, respectively. The authors concluded that FT-MIR spectroscopy could be considered a powerful tool for the identification of pure camellia oil.

In another study, Guillén and Cabo (1997) reviewed the use of MIR in the study of fats and oils. Differences between dispersive and FT-MIR techniques were indicated by the researchers. The review stated the usefulness of FT-MIR for determining the degree of unsaturation or iodine value, *trans*-double bonds content, free fatty acid content, average chain length or saponification number, solid fat content, and peroxide and anisidine values.

Bellorini *et al*. (2005) assessed the abilities of various methods to differentiate the sources of fats used in feedstuff formulations. The main target was the identification of tallow (ruminant fat) and its differentiation from non-ruminant fats. Four different techniques were compared in terms of their suitability for enforcing existing and upcoming legislation on animal by-products: (1) FT-MIR applied to fat samples, (2) *gas chromatography coupled with mass spectrometry* (*GC-MS*) to determine fatty acid profiles, (3) immunoassays focusing on the protein fraction included in the fat, and (4) *polymerase chain reaction* (*PCR*) for the detection of bovine-specific DNA. Samples of the different fats and oils, as well as mixtures of these, were probed using these analytical methods. The obtained results showed that FT-MIR and GC-MS differentiated pure fat samples quite well but showed limited ability to identify the

animal species or even the animal class the fat(s) belonged to; there was no single compound or spectral signal that permitted species identification. However, immunoassays and PCR were both able to identify the species or groups of species that the fats originated from, and they were the only techniques able to identify low concentrations of tallow in a mixture of fats prepared by the rendering industry, even when the samples had been sterilized at temperatures above 133°C. The authors concluded that the combination of FT-MIR and multivariate techniques allows classification of pure samples according to their origin, but that it is not possible to use any single compound for reliable species identification.

In a similar approach, Gasperini *et al*. (2007) used FT-MIR for the classification of different food oil co- and by-products of potential use for feed preparation. Using this technique, a sure classification of fatty acid calcium soaps, fully hydrogenated fatty acids, lecithins, acid oils from chemical refining, acid oils from physical refining, and fish oils was observed. The remaining categories of animal fats, fried oils and oils recovered from exhausted bleaching earth could be differentiated by using one or two additional chemical tests.

Wine

Wine is routinely transported to bottling and packaging facilities, and between wineries for blending purposes. At present, there is no recognized method available to monitor easily the wine authenticity before and after transportation. The refractive index is commonly used as an indicator of wine dilution; however, it is not recognized as a technique to authenticate wine samples (Somers and Evans, 1974). Analytical control methods in an industrial environment, whether qualitative or quantitative, are essential in order to assess raw materials, products and by-products, as well as to optimize the manufacturing process itself. Conventional chemical methods of wine analysis involve time-consuming, laborious and costly procedures (Francis *et al*., 2005; Munck *et al*., 1998; Otto, 1999). Therefore, a robust, rapid and inexpensive method for quality assurance purposes is needed in the wine industry to ensure that wine parameters conform to specification, in order to guarantee the quality of the final product delivered to the consumer. FT-MIR could be an alternative technique to authenticate wine products. Visual examination of the infrared spectra is subjective, and often cannot discriminate between authentic and adulterated product, but the application of multivariate data analysis techniques presents the possibility of unraveling and interpreting the spectral properties of the sample and allowing classification without the use of direct chemical compositional information. One of the advantages of spectroscopic technology is that it allows the assessment of chemical structures through analysis of the molecular bonds in FT-MIR and also builds a characteristic spectrum that represents a "fingerprint" of the sample. This leads to the possibility of using spectra to determine complex attributes of organic structures in the sample, which are related to molecular chromophores, organoleptic scores and sensory characteristics.

Bevin and colleagues (2006) assessed the potential of FT-MIR to discriminate between 161 Australian wine samples originating from three grape varieties, namely

Shiraz, Cabernet Sauvignon and Merlot, and which were collected from six commercial wineries. When a wine was being dispatched for transportation to another processing site, a sample was taken and a FT-MIR spectrum obtained; when the wine arrived at its final destination, a second sample from the same wine was taken and a new spectrum acquired using an instrument of spectral similarity to the first. The two obtained spectra recorded with the same sample were then compared to confirm the authenticity of wine, or to observe changes that may have occurred during transportation.

From the FT-MIR spectra produced by the wine samples using the two instruments, the authors noticed that water and ethanol absorption peaks dominated the spectra, with the C–O stretch for primary alcohols at 1050 cm^{-1}, while the C–H stretch was observed in the 2850–2960 cm^{-1} spectral region. Regarding the 1690–1760 cm^{-1} region, it contained information relating to C=O stretching for aldehydes, carboxylic acids and esters. In order to extract information from the data sets, and to assess the variation in the wine spectra of the same wine measured using the two instruments, the authors applied chemometric tools. PCA confirmed that differences between wine samples were small. The authors concluded that discrimination between wine samples by a rapid analytical technique such as FT-MIR would be difficult (Bevin *et al*., 2006). The authors suggested the elimination of bands relating to water, since these account for approximately 85–90% of the wine sample matrix. By applying PLS regression, a good prediction of the similarity index from the FT-MIR was obtained.

In a similar approach, Edelmann *et al*. (2001) examined the potential of FT-MIR and UV-Vis for their ability to discriminate Austrian red wines of different cultivars (Cabernet Sauvignon, Merlot, Pinot Noir, Blaufränkisch (Lemberger), St Laurent and Zweiget). The authors used *cluster analysis*, a descriptive technique, to classify samples. The results obtained from the UV-VIS (250–600 nm) showed that the Pinot Noir variety was clearly separated from the other cultivars. Five of seven St Laurents were classified as belonging to the Zweiget cultivar. The Blaufränkisch, Cabernet Sauvignon and Merlot wines overlapped and could not be separated. The authors concluded that although UV-Vis spectroscopy appeared to be a promising technique, this technique was not capable of clearly separating all cultivars. Regarding the results obtained in the FT-MIR spectral region (1640–950 cm^{-1}), the best results in terms of separation of the different cultivars were achieved after applying the first derivative, since all the wine cultivars were well separated. The authors concluded that UV-Vis spectroscopy is a limited technique for the authentication of wine samples, but with FT-MIR almost complete discrimination of the investigated cultivars was achieved.

Recently, the ability of FT-MIR to discriminate between Cognac and other distilled drinks such as whiskies, rums, brandies, Armagnacs, bourbons and counterfeit products has been investigated (Picque *et al*., 2006). The spectra of raw products, dry extracts and phenolic extracts were recorded. The authors applied PCA to the 151 spectra scanned from the distilled drinks. Cognac samples were found to form a homogenous group after examining the similarity map defined by the first two PCs. Whiskies, bourbons and rums were completely separated from the Cognac group,

and displayed considerable dispersion in the factorial space. Subsequently, the authors applied PLS-DA to the three sets of spectra (dry extract spectra, phenolic dry extract spectra and concatenated spectra from the two previous sets). Whatever the spectral data, the models correctly predicted between 94 and 99% of the calibration samples. Regarding validation sets in comparison with the calibration set, the percentage of correct classification remained similar for phenolic dry extract spectra and associated spectra, but decreased by 10% for dry extract spectra. The authors concluded that FT-MIR differentiates Cognac from other distilled drinks. The infrared spectra of dry extracts and polyphenolic dry extracts provided additional information and allowed good discrimination between Cognac and non-Cognac drinks. Picque *et al*. (2006) suggested that the combination of FT-MIR with other analytical determination, such as UV-Vis spectra and/or other data analysis such as neural network, might also enhance the discrimination of counterfeit products from Cognac and other products. In a similar approach, the same research group (Picque *et al*., 2005) used FT-MIR to discriminate red wines according to their geographical origin and vintage. The dry extract of 338 wines of the same variety (Gamay), collected in three areas (Gaillac, Beaujolais and Touraine) over 4 years (1998, 1999, 2000 and 2002) were analyzed at 1800–800 cm^{-1}. The authors applied PCA to the spectral data sets, and good discrimination of wine samples according to their year of production was achieved. However, no clear separation according to the geographical origin of wines was highlighted. The authors then applied PLS regression, and 92% of the samples were correctly classified in the validation data sets (100% for the samples of 2000 and 2002, 90% for those of 1999, and 55% for the group belonging to 1998). Regarding PLS regression applied to the wine samples to determine their geographical origin, 85% of the validation samples were correctly classified. The main confusion was reported to be the classification of Gaillac and Beaujolais wines into the group of Touraine wines. The authors concluded that phenolic compounds are significant in the discrimination of red wines according to the geographic origin and year of production.

Within the framework of the TYPIC project (QLK1-CT-2002-02225; http://www.typic.org/), the Walloon Agricultural Research Centre (CRA-W) in Belgium decided to study the potential of FT-MIR to authenticate wines, the primary aim of this work being to match consumers' buying behavior and perception of typical food products with the most relevant objective attributes that define the typicality of those products. The project plans to develop suitable analytical methods to enable skilled producers of such products to characterize and guarantee taste qualities and assure the traceability of these attributes in the EU.

The samples for the study were initially selected on the basis of their main attributes related to the typicality of the wines. The study concerned a collection of 120 red wines from Germany and France. For each wine, two different vintages were studied. The French wines consisted of 20 typical Beaujolais wines (from the Beaujolais region) and 10 wines from other regions. The typical wines were divided into two groups: Beaujolais Village and Beaujolais Crus wines (Brouilly, Chénas, Chiroubles, Côte-de-Brouilly, Fleurie, Juliénas, Morgon, Moulin à Vent, Régnié and Saint-Amour). The German wine group contained 24 typical Dornfelder wines from

the Pfalz region and 6 from other regions (Dornfelder being the name of the grape variety and not a geographical designation like Beaujolais). The other wines were either Dornfelder wines cultivated in other regions (Rheinhessen, Wurtemberg) or other cultivars (Pinot Noir, Cabernet Sauvignon) harvested in the Pfalz region.

PCA was applied to the collection data sets in order to classify wines according to their origin; a certain tendency to separate them was observed. The researchers concluded that the combination of FT-MIR and chemometric methods have a great potential for the classification of wines according to typical attributes of country of origin and vintage.

Sugar and honey

In combination with multivariate statistical analyses, FT-MIR has proved to be a promising screening method with respect to predict glucose, fructose and sucrose in aqueous mixtures (Sivakesava and Irudayaraj, 2000). Spectra of different aqueous mixtures of 10, 20 and 40% total sugars with different combinations of glucose, fructose and sucrose were used for calibration and validation data sets. The best results for predicting each type of sugar content were obtained after applying the first derivative to the FT-MIR spectra. The R^2 values for the calibration models for glucose, fructose and sucrose were 0.997, 0.998 and 0.997, respectively, between the predicted values and actual values. The authors concluded that the calibration set samples were accurate in predicting sugar contents in complex mixtures and commercial beverages. One of the main conclusions of this study was that FT-MIR could be used for rapid detection of sugars in complex mixtures. These results were in agreement with previous investigations reporting that FT-MIR could be utilized to detect adulteration of maple syrup with additives such as cane and beet sugar solutions (Paradkar *et al*., 2003). The results obtained from this study showed that FT-MIR and also NIR could be used for detecting the type and level of adulterants such as pure beet and cane sugar solutions in maple syrup. However, the best results were obtained with FT-MIR rather than with NIR, since the R^2 values were more than 0.98 and 0.93 for FT-MIR and NIR, respectively. The authors suggested that the carbohydrate region (1200–800 cm^{-1}) which was assigned to C–O and C–C stretching vibration of sugars (Cocciardi *et al*., 2006), as well as the organic and amino acid (1800–1200 cm^{-1} and 3200–2800 cm^{-1}) regions, could be identified in the FT-MIR spectra and used as markers for detecting adulterants in maple syrup with a high degree of accuracy. The obtained results were in agreement with the findings of Maalouly *et al*. (2004), who used NIR and MIR to determine sugar contents in beets. In another study, Cadet and Offmann (1997) used FT-MIR combined with PCA and *principal component regression* (*PCR*) and reported that FT-MIR could be used for analysis of sugar-cane juice. Indeed, this technique was found to be more accurate than the commonly used polarimetric technique, and more convenient than HPLC. The authors claimed that FT-MIR could be easily adopted for online measurement in industry.

Recently, FT-MIR was used to determine both the geographical and botanical origin of honeys. Tewari and Irudayaraj (2005) analyzed seven floral sources of honey. The calibration data set comprised 350 samples. Classification accuracy of nearly

100% for the seven different floral honeys was obtained by using FT-MIR and z-nose methods. The main conclusion of this study was that FT-MIR technique is able to detect floral origin with 2–3 minutes based on the developed calibration. The obtained results were recently confirmed by Ruoff and colleagues (2006), who analyzed 11 unifloral and 411 polyfloral samples. The honey samples originated from Switzerland, Germany, Italy, Spain, France and Denmark. The authors applied PCA and LDA and found that the error rates ranged from 0.1% to 8.3% in both Jackknife classification and validation, depending on the honey type considered. The authors concluded that FT-MIR spectroscopy is a valuable tool for the authentication of the botanical origin and quality control of honey, and may also be useful for the determination of its geographic origin. Using a similar approach, the ability of FT-MIR to determine some chemical parameters of honey samples was investigated (Lichtenberg-Kraag *et al*., 2002). In their study more than 1600 honey samples were analyzed by FT-MIR and reference methods to develop a PLS regression-based calibration model for the major contents and properties of honey (sugars, praline, moisture, hydroxyproline, pH and electrical conductivity). For the calibration model, the R^2 was found to vary from 0.84 to 0.98, indicating acceptable calibration for most of the parameters. The authors then tested the validation spectral collection and found high correlation, since the R^2 ranged from 0.81 to 0.99; good repeatability (0.84–0.99); and no statistical difference in the reference methods. The authors concluded that not only the chemical composition but also the physical properties of honey can be determined by FT-MIR.

Fruits and vegetables

As mentioned previously, adulteration of food has occurred for a long time and has ranged from the simple addition of natural components to much more serious cases of contamination with harmful substances (Collins, 1993). As fruit is the most costly ingredient in jam, adulteration with cheaper ingredients, such as sugar or vegetable matter, may take place. In order to protect consumers from adulteration, as well as to avoid unfair competition, it is important to use analytical techniques that can assess the composition of food with a high degree of accuracy. In this context, FT-MIR has been used to differentiate between strawberry- and non-strawberry-containing jams (Defernez and Wilson, 1995). The authors used two techniques, diffuse reflectance infrared and ATR, and found that the former led to a classification success rage of almost 100%, while the latter allowed only 91% correct classification; they attributed this to the fact that ATR was strongly influenced by the spectral difference between normal and reduced total sugar content jams. Subsequently, Holland *et al*. (1998) used FT-MIR to detect adulteration of strawberry purées. In their study, 983 fruit purées (both strawberry and non-strawberry) were used for the establishment of the PLS model, and 94.3% correct classification was obtained. The long-term potential of the model was established with the years 1993 and 1994, and illustrated by analyzing fruit which were harvested in 1995, and a correct classification rate of 96.6% was observed. Finally, a blind test of the model was performed using a set of 23 fruit purée samples produced by a company and a correct classification rate of 96%

was observed, with 22 of 23 samples correctly classified. The authors concluded that the building model could be used for the analysis of fruit of subsequent years, which makes FT-MIR a potential technique for the routine screening of fruit over an extended period of time.

Recently, the ability of FT-MIR to predict nutritional parameters such as carbohydrate content and energetic value in commercially available juice fruit has been investigated by Moros *et al*. (2005). The authors analyzed 63 highly heterogeneous samples covering fruit juices and milk-added fruit juices, among others. By applying PLS regression, the authors found that the RMSEP of 18.4 kJ $100\,ml^{-1}$ and 0.72 g $100\,ml^{-1}$ for the energetic value and total carbohydrates, respectively.

Coffee

Coffee is a popular food product throughout the world. A huge amount of coffee is processed, and this has been going on for a very long time. However, the processing of coffee is empirically controlled based on information provided by cup tasters and manufacturing experts, and thus process control may generally be due to the expertise accumulated in each coffee manufacturing company. Additionally, the prepared coffee is produced through many complicated operations such as roasting, grinding, blending and extraction. Furthermore, the coffee beans, as the basis of the prepared coffee, are miscellaneous, as is highly reflected by the varieties and geographical origins. An objective and stable method of evaluating prepared coffee characteristics is therefore desirable for process control, because the prepared coffee is not only the final product but also the liquid food tasted by consumers. In order to have a good grasp of the prepared coffee characteristics for process control, it is very important that not only the contents of the main components but also their molecular structures are non-destructively and simultaneously monitored in real time. Subsequently, application of spectroscopy, especially in the MIR region, to the above measurement is desirable as a high potential implement. In this context, Suchánek *et al*. (1996) pointed out that the green coffee could be quantitatively analyzed by FT-MIR. In other studies, Briandet *et al*. (1996a, 1996b) and Kemsly *et al*. (1995) investigated the potential of diffuse reflection FT-MIR to discriminate between *Arabica* and *Robusta* varieties. Briandet *et al*. (1996b) applied LDA on the principal scores, and the obtained results allowed 100% correct classification for both calibration and validation samples. The researchers concluded that FT-MIR combined with chemometric tools could be used to identify and quantify *Arabica* and *Robusta* contents of freeze-dried instant coffees, and suggested the use of this technique for off-line quality control of freeze-dried coffees. In another study, the same research group (Briandet *et al*., 1996a) examined FT-MIR as a rapid alternative to wet chemistry methods for the detection of adulteration of freeze-dried instant coffees. The spectra of pure coffees and of samples adulterated with glucose, starch or chicory in the range 20–$100\,g\,kg^{-1}$ were collected. Two different FT-MIR sampling methods were employed; diffuse reflectance and ATR. The authors tested three different statistical treatments of the spectra. First, the spectra were compressed by PCA and LDA was then performed. With this approach, a 98% successful classification rate was achieved.

Secondly, a simultaneous PLS regression was carried out for the content of three added carbohydrates (xylose, glucose and fructose) in order to assess the potential of FT-MIR for determining the carbohydrate profile of instant coffee, and promising results were obtained. Lastly, the discrimination of pure from adulterated coffee was performed using an ANN. A perfect rate of assignment was obtained, since the generalization ability of the ANN was tested on an independent validation data set, and again 100% correct classification was achieved. The obtained results confirmed previously investigations reporting that FT-MIR could be used to discriminate between *Arabica* and *Robusta* lyophilized coffees (Downey *et al*., 1997). The bands located in the 5700–6450 nm (1754–1550 cm^{-1}) were attributed to caffeine, while those located in the region 7700–8700 nm (1298–1149 cm^{-1}) were assigned to chlorogenic acid.

Recently, the usefulness of FT-MIR in identifying specific compounds in coffee, such as volatile and non-volatile compounds that constitute the flavor of brewed coffee, was investigated by Lyman *et al*. (2003). The 1800–1680 cm^{-1} carbonyl region for vinyl esters/lactones, esters, aldehydes, ketones, and acids was found to provide a flavor-print of the brewed coffee. The researchers stated that the heating rates of green coffee beans to the onset of the first and second cracks are important determinants of the basic taste and aroma of brewed coffee. In another study, the influences of the coffee varieties and the roasting degree on the FT-MIR spectral characteristics of brewed coffee, as well as the useful of FT-MIR to determine the caffeine and chlorogenic acid contents in brewed coffee, were examined (unpublished results). Differences between the second derivatives of the FT-MIR spectra of the brewed *Arabica* and *Robusta* coffees were observed around several peaks. In addition, the brewed coffee from the Brazilian variety exhibited different spectral features from those of the other *Arabica* coffees. Moreover, the roasting conditions of the Indonesian beans were found to reflect the spectral features of the brewed coffee. Furthermore, the caffeine and chlorogenic acid contents in brewed coffee would be determined by the spectroscopic method, as well as those in the aqueous solutions. The obtained results confirmed those of Singh *et al*. (1998), who pointed out the ability of FT-MIR to predict the amount of caffeine located around 1655 cm^{-1} present in coffee, since the sensitivity of the technique was found to be less than 5 ppm.

Identification of bacteria of food interest

The identification of *microorganisms* of interest in food and food products by traditional microbiological methods is time-consuming. In addition, these methods require skilled operators and, in some cases, are unable to discriminate microorganisms at the strain level. In this context, the use of MIR to differentiate *bacteria* has been studied since the 1950s. Unfortunately, owing to the weak performance of dispersive spectrometers, these kinds of studies did not allow good discrimination. Since Naumann and coworkers (1991) published their pioneering work in the field of the identification and differentiation of microorganisms by FT-MIR, various research groups around the world have shown the validity of FT-MIR for giving sufficient information to distinguish microorganisms both at species and strain

levels. Indeed, Amiel *et al*. (2000, 2001) reported that FT-MIR provided good discrimination of bacteria between different genera, species and even strains. They first assessed the ability of FT-MIR to identify lactic acid bacteria (LAB) used in the dairy industry. Different strains were used in their study: *Lactobacillus* (12 species, 3 subspecies), *Lactococcus* (4 species, 3 subspecies), *Leuconostoc* (3 species, 3 subspecies), *Weissella* (1 species) and *Streptococcus* (2 species). The authors applied DA to the FT-MIR spectra, and 100% correct classification was obtained at the genus and species levels, while 86% was achieved at the subspecies level. Amiel *et al*. (2000) then tested 48 wild isolates which had been previously identified by biochemical testing and the RAPD method, and 100% and 69% correct classifications were obtained at the genus and species levels, respectively. The authors concluded that, although there was a relatively low number of isolates, FT-MIR could be considered as a useful technique for the discrimination and identification of LAB. Subsequently, the same research group (Amiel *et al*., 2001) used FT-MIR to point out that this technique could be used for taxonomical purposes. They illustrated this with two examples: the distinction between *Streptococcus thermophilus* and *Streptococcus salivarius*, and the taxonomic range of *Lactobacillus casei*, *paracasei*, *zeae* and *rhamnosus*. The authors reported that, concerning the taxonomic subject, their results partially confirmed those found with the reference method (Dellaglio *et al*., 1991). However, FT-MIR allowed good separation of *Lactobacillus zeae* from *Lactobacillus rhamnosus*, while API50CHL failed to differentiate between them. One of the most important conclusions of this study was that the information contained in FT-MIR spectra could be complementary to that found with genomic information, and consequently this technique could be introduced in a polyphasic taxonomic approach. The obtained results were confirmed recently by Yu and Irudayaraj (2005), who succeeded in differentiating between six microorganisms at the strain level. They reported that that FT-MIR spectroscopy can provide not only molecular fingerprints of the cell envelope, but also compositional and metabolic information about the cytoplasm under different physiological conditions. This approach could be an effective alternative to traditional nutritional and biochemical methods of monitoring and assessing the effects of inhibitors and other environmental factors on microbial cell growth.

In the same field of dairy products, Lucia *et al*. (2001) investigated the suitability of FT-MIR as a rapid technique to investigate the secondary structure of proteins in aqueous solutions and its changes as a consequence of microbial proteolytic activity, as well as to identify the contribution of different strains of *Yarrowia lipolytica* used in cheese ripening. The researchers observed that significant differences in the amide I and II bands of both curds and cheeses obtained from milk inoculated with *Lactococcus lactis* subsq. *Lactis* and different strains of *Yarrowia lipolytica* occurred during the ripening stage. They concluded that FT-MIR spectroscopy could be a promising tool to monitor changes that occurred during ripening in cheeses inoculated with different strains.

The German Federal Health Office has also developed a method based on FT-MIR for the rapid identification of microorganisms. Indeed, Fehrmann *et al*. (1995) used this spectroscopic technique to classify microorganisms in the dairy industry,

especially for *clostridium* spp. The best information was found in the 1500–1000 cm^{-1} region. However, no explanation regarding the chemical compounds involved in the identification of microorganisms was given. In other studies, Fayolle *et al*. (2000) and Picque *et al*. (1993) used FT-MIR and MIR, respectively, to monitor the fermentation processes by measuring sugars, ethanol and organic acid concentrations during alcoholic and lactic fermentations. By applying PLS regression, the SEP were found to vary between 1.4 gl^{-1} and 4.5 gl^{-1} for galactose and fructose, respectively (Fayolle *et al*., 2000).

To date, several methods have been proposed to measure and to detect bacterial spoilage in meat and meat products. These include enumeration methods based on microscopy, ATP bioluminescence and the measurement of electrical phenomena, as well as detection methods based on either immunological or nucleic acid based procedures. The major drawbacks are that they are time-consuming and labor-intensive, and give retrospective information. The ideal method for on-line microbiological analysis of meat would be rapid, non-invasive, reagentless and relatively inexpensive, and these requirements can be met via the application of a spectroscopic approach. Recently, Ellis *et al*. (2004) used FT-MIR to measure biochemical changes within the meat substrate, enhancing and accelerating the detection of microbial spoilage. The authors pointed out that FT-MIR could be considered as a novel method for the quantitative detection of food spoilage. Indeed, by applying PLS regression to the FT-MIR spectra, an accurate estimation of the bacterial loads obtained by classical plating methods was observed. The authors concluded that FT-MIR is able to acquire a metabolic snapshot and quantify, non-invasively, the microbial loads of food samples accurately and rapidly in 60 seconds, directly from the sample surface. The authors also pointed out that it was evident that the FT-MIR spectra contained biochemical information that allowed correlation with the spoilage status of chicken, but they did not mention which biochemical species measured by the FT-MIR could be related to such spoilage.

Cotton and wood

Rapid identification of the nature of the extraneous matter in cotton at each stage of cleaning and processing is necessary so that action can be taken to eliminate or reduce its presence and improve efficiency and quality. To respond to this need, FT-MIR spectra of retrieved foreign matter were collected and subsequently rapidly matched to an authentic spectrum in a spectral database (Himmelsbach *et al*., 2006). The database includes contaminants typically classified as "trash", cotton plant parts, and grass plant parts. The researchers pointed out that the FT-MIR method was able to provide specific identification of extraneous materials in cotton. In another study, Nuopponen *et al*. (2006) have used FT-MIR to estimate wood density and chemical composition (lignin, cellulose and wood resin contents and densities). Using the spectral ranges 4000–2800 cm^{-1} and 1800–700 cm^{-1}, these parameters were found to present an R^2 varying from 0.6 to 0.9 after applying PLS regression. The same research group reduced the number of wavelengths to five characteristic of lignin bands located at 1600, 1510, 1273, 1220 and 1077 cm^{-1}, and similar results were

obtained. They concluded that a hand-held device based on FT-MIR could be used to determine the quality of these parameters.

Recently, the effect of temperature on wood charcoal structure and chemical composition has been investigated (Labbé *et al*., 2006). Wood charcoal carbonized at various temperatures was analyzed by FT-MIR coupled with multivariate analysis and by thermogravimetric analysis to characterize the chemical composition during the carbonization process. The multivariate models of charcoal were able to distinguish between species and between wood thermal treatments, revealing that the characteristics of the wood charcoal depend not only on the wood species, but also on the carbonization temperature. One of the main conclusions of this study was that FT-MIR was able to classify wood species for the mellowing process.

Conclusions

Over the past 20 years, researchers and users of mid-infrared spectroscopy in the field of food sciences have mainly studied the determination of the amount of the main components in food products. This knowledge is mandatory, but is not sufficient to predict the technological and organoleptic properties of processed food. As described in this chapter, infrared spectra also provide information regarding the physical states and molecular structures of the main food components, such as lipids, proteins, carbohydrates, etc. It is therefore expected that, in the coming years, infrared spectroscopy combined with chemometric tools will provide a reliable tool for the understanding of the bases of food molecular structure and, as a consequence, their qualities.

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