Mid-Infrared Spectroscopy Coupled with Chemometrics: A Tool for the Analysis of Intact Food Systems and the Exploration of Their Molecular Structure−Quality Relationships − A Review

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1. Introduction

Public interest in food quality and methods of production has increased significantly in recent decades, due in part to changes in eating habits, consumer behavior, and the increased industrialization and globalization of food supply chains.[1] Demand for high levels of quality and safety in food production obviously requires high standards in quality assurance and process control; satisfying this demand in turn requires appropriate analytical tools for food analysis both during and after production. Desirable features of such tools include speed, ease-of-use, minimal or no sample preparation, and the avoidance of sample destruction. These features are characteristic of a range of spectroscopic methods including the mid-infrared (MIR). While it is true that near-infrared (NIR) spectroscopy has achieved greater uptake by the food industry,[2] reported applications of MIR in this sector have increased over the past decade or more.

Foods represent significant analytical challenges. They are highly complex, variable and can be found in a number of different physical states: these include solids, dilute solutions, emulsions, foams, highly visco-elastic forms, and glassy states. This has obvious consequences for the analytical tools and strategies that must be developed for analysis of these

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complicated, heterogeneous systems. Food systems are mainly composed of water, carbohydrates, proteins, fats, and other constituents that are present at low (mg/100 g) concentrations such as vitamins, minerals, etc. All of these components may contribute to the shape of the absorbance spectrum obtained in the mid-infrared region, although, in practice, the major components (water, carbohydrates, proteins, fats) dominate because constituents present at concentrations below approximately 0.1% w/w are difficult to detect in water-rich systems. Food heterogeneity results in considerable spectral complexity and conventional approaches to the use of spectra for, for example, quantitative predictions of major compounds may not be applied. A major advance in the application of MIR techniques to food analysis and other commodities has been in the application of powerful mathematical techniques known collectively as chemometrics. Such data analysis methods allow the extraction of valuable information from large and complex data sets and now underpin the application of MIR spectroscopy in many analytical fields.

Despite the growth in application reports, we are unaware of any review of the use of FT-IR spectroscopy for the analysis of foods in the past 5 years; therefore, a summary of work in this area is now warranted. The application of FT-IR spectroscopy to the monitoring of some specific biological processes such as fermentation has recently been reviewed[3] and will not, therefore, be covered in this Review. Rather, following a brief discussion of the principles and practice of MIR spectroscopy, this Review will provide a comprehensive overview of its application to the determination of the quality of several ingredients and food products. Actual examples illustrating the use of the technique in both laboratory and industrial environments will be discussed.

2. Infrared Spectroscopy − Overview of Theory and Principles

Chemical bonds vibrate at specific frequencies, which are determined by the mass of the constituent atoms, the shape of the molecule, the stiffness of the bonds, and the periods of the associated vibrational coupling. A specific vibrational mode must be associated with a molecule's dipole moment to absorb in the infrared spectral region. Diatomic molecules have only one bond that may stretch (i.e., the distance between two atoms may increase or decrease). More complex molecules have many bonds; vibrations can also be conjugated leading to two possible modes of vibration: stretching and bending. Phenomena that can further complicate the interpretation of MIR spectra include the presence of overtone and combination bands and Fermi resonances. Despite these potential problems, absorption frequencies may be used to identify specific chemical groups, and this capability has traditionally been the main role of FT-IR spectroscopy.[4]

The MIR region of the electromagnetic spectrum lies between 4000 and 400 cm^{-1} and can be segmented[5] into four broad regions: the X−H stretching region (4000−2500 cm^{-1}), the triple bond region (2500−2000 cm^{-1}), the double bond region (2000−1500 cm^{-1}), and the fingerprint region (1500−400 cm^{-1}).

Characteristic absorption bands are associated with major components of food. Water is a significant absorber in the MIR spectral region and can interfere with the determination of other components present in food systems.[6] Major bands are present at 3920, 3490, 3280, and 1645 cm^{-1}, although the exact location and shape of these bands may be affected by the presence of solutes,[7,8] hydrogen-bonding, and temperature.[9,10] The triglyceride ester linkage C−O at ∼1175 cm^{-1}, the C═O group (∼1750 cm^{-1}), and the acyl chain C−H (3000−2800 cm^{-1}) frequencies are commonly used to determine fat,[11−14] while the amide I (∼1653 cm^{-1}) and II bands (∼1567 cm^{-1}) have been used for the estimation of protein[15,16] and changes in protein secondary structure.[17−19] Vibrations arising from C−O and C−H stretch in the region between 1100 and 1000 cm^{-1} may be used to identify aqueous sugar molecules,[3,20] while more complex carbohydrate structures found in plants have major absorption bands at higher wavenumbers, for example, hemicellulose (1732, 1240 cm^{-1}), cellulose (1170−1150, 1050, 1030 cm^{-1}), lignan (1590, 1510 cm^{-1}), and pectin (1680−1600, 1260, 955 cm^{-1}).[21,22]

Absorptions in the fingerprint region are mainly caused by bending and skeletal vibrations, which are particularly sensitive to large wavenumber shifts, thereby mitigating against unambiguous identification of specific functional groups.[5] Even in this region, however, the spectrum may be used as a fingerprint of a sample such as a food product or food ingredient. Analysis of such fingerprints forms the basis of many applications of MIR spectroscopy in food analysis. Broad fields of application include constituent quantification and qualification issues for food and food ingredients; substance identification and authentication are included in the latter field.[23−26]

For further information on band assignment in the MIR region, the reader may refer to other texts.[4,5,20,27−29] For a fuller review of the fundamentals of MIR spectroscopy, the reader is referred to other publications.[20,30−32] Descriptions of MIR instrumentation are beyond the scope of this Review; the interested reader is directed to other sources.[5,33,34]

2.1. Sample Presentation

A critical development in MIR instrumentation regarding its application to complex biological structures and compounds has been the emergence of innovative sample presentation techniques.[35] Historically, these were restricted to fixed path length transmission cells in the case of liquid

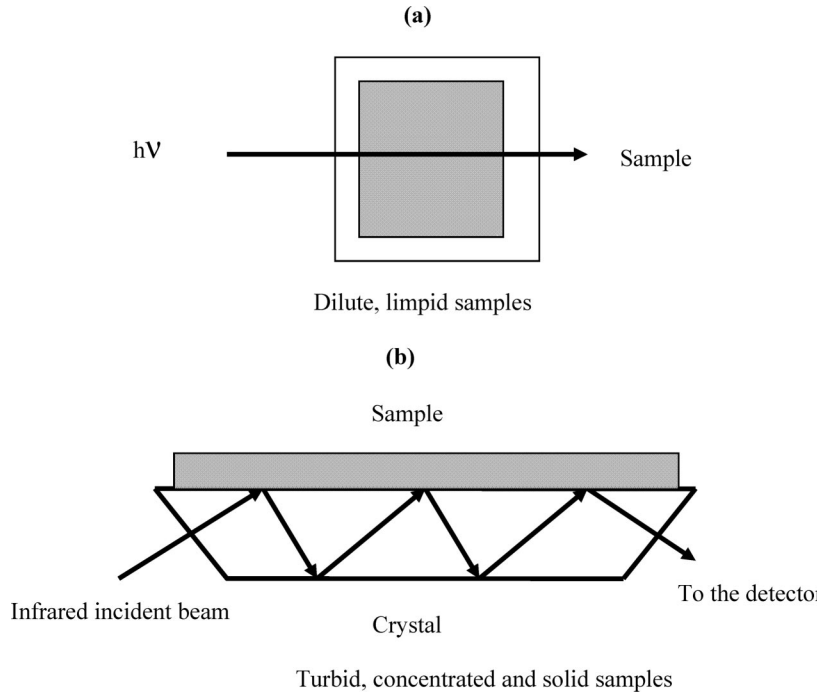

Figure 1. (a) Fourier transform infrared (FTIR) and (b) attenuated total reflection Fourier transform infrared (FTIR-ATR) for the analysis of dilute and intact food samples.

samples; for solids, alkali halide discs, mulls, and films were the standard options.[5] However, all of these required considerable sample processing and generally destroyed the material under investigation. Some examples of their use with foods have been reported,[36] but they require very small sample quantities, of the order of milligrams, and, while this may be an advantage for identification of synthesized molecules, it can pose problems for heterogeneous materials such as food in relation to representativity of such a small sample.

Sample presentation developments have included photoacoustic spectroscopy (PAS) and diffuse reflectance (DRIFT).[37−39] PAS is based on the energy released into a system as a result of sample relaxation after infrared absorption. If such energy is released in a closed cell containing the sample and a gas (e.g., helium), the gas expands, thereby producing sounds that can be detected via sensitive microphones. While relatively straightforward in principle and suited to powder samples in particular, the extraction of high-quality information from PAS systems is difficult in practice, and it is not a common analytical procedure; applications in food analysis are very rare, although PAS analysis of flour[40] and chocolate[41] has been reported. DRIFT involves the collection and measurement of diffusely reflected radiation emerging from crystalline or particulate sample materials; it is therefore appropriate for the analysis of powders, but the unavoidable presence of specularly reflected radiation (which contains no compositional information about the sample) degrades the spectral information and presents an analytical challenge.[35] Applications of DRIFT to food analysis are limited in number, although reports do exist of its use in determining the degree of esterification of pectic substances,[42,43] the characterization of rice,[44,45] a study of beans,[46] determination of fruit type in jams,[47] coffee varietal discrimination,[48,49] and, more recently, classification of Italian honeys.[50] Specular reflection measurements are also appropriate for powdered samples, although the sample surface needs to be smooth, necessitating the use of a surface film in some applications. This approach is mainly deployed for polymer analysis,[51] and the authors are unaware of any reported application in food.

Probably the most useful development has been the introduction of a simple reflectance technique called attenuated total reflectance (ATR; Figure 1).[52,53] With ATR, a sample (liquid or solid) is simply placed in intimate contact with the top horizontal surface of a crystal of high refractive index; typically, such crystals are made of zinc selenide (ZnSe), germanium (Ge), diamond, or thallium iodide (KRS-5). The ATR system measures changes in intensity that occur in a totally internally reflected infrared beam when the beam comes into contact with the sample. This interaction occurs when radiation entering the crystal undergoes total internal reflection at the top inner surface of the crystal one or more times; values of 9 or 11 are common depending on the exact geometry of the crystal. A standing wave called an evanescent wave is generated at the point of each reflection, penetrates the sample, interacts with it, and reduces its intensity at certain wavenumbers, thereby producing a spectrum. The penetration depth of this evanescent wave depends on the incident angle of the radiation, the crystal and sample refractive indices, and the infrared frequency. In general, it is only of the order of several (0.1−5) micrometers; this has an advantage, however, in that it makes sampling in aqueous solutions possible.[35]

ATR is a versatile and powerful technique for easy infrared sampling. It is useful for sampling the surface of smooth materials that are either too thick or too opaque for transmission measurements. ATR is a nondestructive method; in addition, little or no sample preparation is needed, and it allows fast and simple sampling regardless of the state of the food system (liquid, gel, solid, etc.). There must be a very good contact between the sample and the crystal surface to ensure the collection of high-quality, representative spectral data. Performance with solids is generally poorer than with liquids or gels given the difficulty in obtaining uniform and intimate contact between such samples and the

crystal surface. With solids, the use of a clamp accessory by means of which a standard pressure may be exerted on the material being analyzed may be useful. It should also be noted that most of the ATR crystals available have pH limitations. A caveat with ATR is that, because the measurement is taken essentially at a contact surface, high surface homogeneity is required for representative and accurate measurements.

3. Multivariate Statistical Analysis of IR Spectral Data

Chemical information contained in MIR spectra resides in the band positions, intensities, and shapes. Whereas band positions give information about the molecular structure of chemical compounds in a mixture, the intensities of the bands are related to the concentration of these compounds as described by the Beer−Lambert law. The easiest way to determine the content of a chemical compound is to measure the change in the intensity of a well-resolved band that has been unambiguously attributed to this compound. This is possible for a pure component system, but foods contain numerous components giving rise to complex spectra with overlapping bands. The most successful approach to extracting quantitative, qualitative, or structural information from such spectra is to use multivariate mathematical analysis. These powerful methods and the computer technology necessary to use them have only become readily available in recent years, but their use has become a significant feature of IR spectroscopy. A broad range of techniques is now available including data reduction tools, regression techniques, and classification methods.

Principal component analysis (PCA) is a commonly used data compression and visualization tool, reducing a spectral data set into a small (generally less than 20) number of new, orthogonal (i.e., noncorrelated) variables on each of which a score (or value) for each sample is calculated. Graphical display of these scores can often reveal patterns or clustering within a data set because similar samples are expected to locate close to each other; unexpected sample locations in this hyperspace may alert the analyst to unusual or outlying samples, which may be reanalyzed or, as a final resort, deleted from the data set prior to further data processing. Principal component scores may be used in further mathematical operations to classify samples into different, naturally occurring groups. Similar data reduction approaches include canonical correlation analysis (CCA) and common components and specific weights analysis (CCSWA). A number of procedures are available for sample classification or discrimination; soft independent modeling of class analogy (SIMCA) is an example of a popular class-modeling method, while linear discriminant analysis (LDA), hierarchical cluster analysis (HCA), factorial discriminant analysis (FDA), artificial neural networks (ANN), and discriminant partial least-squares (PLS) are examples of much-used discriminant methods. Class-modeling methods focus on characterizing each of the classes of sample being analyzed and involve calculation of a model and boundaries within which samples of each particular type may be expected to be found. Discriminant methods focus on characterizing the boundaries between samples of different classes and do not involve the calculation of statistically robust confidence limits for each class. The use of IR spectra for quantification purposes may be achieved by regression techniques such as principal component regression (PCR) or PLS regression. As for PCA, PLS regression is based on the construction of new, uncorrelated factors from the original spectral data. A major difference between PCA and PLS regression is that, while PCA reduces the quantity of spectral data independently of any associated chemical information, PLS calculates new variables by selecting those dimensions that explain the maximum variance in both the spectral and the associated reference data sets. Therefore, PLS regression incorporates variables in the data that are relevant for describing the variation in associated chemical data. For fuller coverage of chemometric tools and procedures, the interested reader is referred to other sources.[54−63]

4. Application of IR Spectroscopy to Food Analyses

The number of reports of the application of FT-MIR and chemometric tools to food analysis has increased significantly in the last two decades. In the following sections, a range of such applications will be described grouped into sections on the basis of the nature of the food product.

4.1. Dairy Products

Curd formation is the essential step in cheese manufacture because it determines both the composition and the structure of the final cheese. Although considerable changes in curd structure occur during pressing, salting, and ripening processes,[64] all of these steps require excellent control of the coagulation process to obtain an optimum product. Although MIR spectroscopy has been widely used for the determination of several milk properties (e.g., milk composition), only limited studies describing the use of this method for monitoring the milk coagulation process have been published. Cecchinato et al.[65] and De Marchi et al.[66] assessed the potential of FT-MIR for the determination of milk coagulation properties, titratable acidity, and pH in Brown Swiss milk samples. Using 1200 individual cows in 30 herds located in northern Italy, MIR spectra (4000−900 cm^{-1}) and PLS regression were utilized to predict rennet coagulation time and curd firmness.[65] The outcome was poor because the best model developed for rennet coagulation time only provided an approximate prediction with a squared correlation coefficient (R^2) varying in the 0.61−0.69 range and a root-mean-square error of calibration (RMSEC) of 2.3−2.5 min (Table 1). The authors concluded that such models only allowed differentiation between low and high values. Predicted curd firmness did not permit even this differentiation. A study of the effect of lactation period and feed type on the quality of ewe's milk was reported by Maâmouri et al.[67] Using 12, 5-year-old lactating Sicilo-Sarde ewes, two groups (6 animals in each) were fed ad libitum iso-energetic diets based on either soybean or scotch bean meal. Differences in milk from the two groups of animals throughout the lactation period resulted in changes in the MIR spectra of milk, which reflected variations in its physicochemical composition (reduction in fat and increase in lactose content).[67] By applying PCA to the 3000−2800 and 1500−900 cm^{-1} spectral ranges, a good visual discrimination of milk samples on the basis of the feed was possible.

Determination of cheese quality throughout the ripening period is an important requirement for cheese producers. Several studies[55,57] have focused on this topic, and three spectral regions have been used: (i) 3000−2800 cm^{-1}, characteristic of fat; (ii) 1700−1500 cm^{-1}, characteristic of

Table 1. Application of MIR Spectroscopy to Dairy Products[a]

Milk Coagulation

constituent	data pretreatment	measurement mode	wavenumber range	measured range	R^2	calibration/prediction error	reference
rennet coagulation time (RCP)	none	reflectance	4000−900 cm^{-1}	3.2−29.6 (min)	0.61−0.69	RMSEC = 2.3−2.5 min	Cecchinato et al.[65]
curd firmness (a_{30})				6−59 (min)	0.49−0.52	RMSEC = 5.7−6.6 min	

Cheese Authenticity

parameter	data pretreatment	measurement mode	wavenumber range	% correctly classified	reference
differentiation between surface and center of soft cheeses	normalization	reflectance	3000−900 cm^{-1}	64.8% and 33.3% for calibration and validation data sets, respectively	Karoui et al.[77]
Emmental cheeses originating from different European countries−summer manufacture	normalization	reflectance	3000−2800 cm^{-1}	57.4% and 29.7% for calibration and validation data sets, respectively	Karoui et al.[79]
			1700−1500 cm^{-1}	84.5% and 48.6% for calibration and validation data sets, respectively	
			1500−900 cm^{-1}	83.7% and 77% for calibration and validation data sets, respectively	
Emmental cheeses originating from different European countries manufactured during winter	normalization	reflectance	3000−2800 cm^{-1}	84.1% and 85.7% for calibration and validation data sets, respectively	Karoui et al.[80]
			1700−1500 cm^{-1}	88.5% and 96.7% for calibration and validation data sets, respectively	
			1500−900 cm^{-1}	96.7% for both calibration and validation data sets	
Gruyère and l'Etivaz PDO cheeses	normalization	reflectance	3000−2800 cm^{-1}	90.5% for validation data set	Karoui et al.[82]
			1700−1500 cm^{-1}	80% for validation data set	
			1500−900 cm^{-1}	90.7% for validation data set	

Prediction of Physicochemical Parameters in Milk and Cheese

constituent	data pretreatment	measurement mode	wavenumber range	measured range	R^2	calibration/prediction error	reference
casein	not mentioned	reflectance	3000−1000 cm^{-1}	2.1−4%	n.a.	RMSEP = 0.035%	Sørensen et al.[15]
protein	water subtraction procedure with pure deionised water	reflectance	4000−1000 cm^{-1}	2.3−3.9 (% w/v)	n.a.	PE = 0.22%	Etzion et al.[84]
	2200 cm^{-1} absorbance of each spectrum was subtracted from all values of the spectrum and then the blank subtracted; the average of absorbance values between 2000 and 2200 cm^{-1} was used for final correction	reflectance	4000−600 cm^{-1}	0.4−4.3 (% w/v)	n.a.	RMSECV = 0.14	Iñón et al.[85]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	4.2−4.8 (% w/w)	0.33	RMSECV = 0.11	Karoui et al.[88]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	4−4.7 (% w/w)	0.62	RMSEP = 0.05	Karoui et al.[89]
	maximum normalization + first derivative + smoothing	reflectance	3000−900 cm^{-1}	2.3−3.5 (% w/w)	0.76	RMSEP = 0.18	Karoui et al.[92]

Table 1. Continued

Prediction of Physicochemical Parameters in Milk and Cheese							
constituent	data pretreatment	measurement mode	wavenumber range	measured range	R^2	calibration/prediction error	reference
fat	2200 cm^{-1} absorbance of each spectrum was subtracted from all values of the spectrum and then the blank subtracted; the average of absorbance values between 2000 and 2200 cm^{-1} was used for final correction	reflectance	4000−600 cm^{-1}	0.1−3.6 (% w/v)	n.a.	RMSECV = 0.24	Iñón et al.[85]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	28−38 (% w/w)	0.57	RMSEP = 0.8	Karoui et al.[89]
	maximum normalization + first derivative + smoothing	reflectance	3000−900 cm^{-1}	22.3−36.5 (% w/w)	0.83	RMSEP = 2.14	Karoui et al.[92]
pH	baseline correction of spectra at six points (3000, 2850, 1800, 1700, 1490, and 950 cm^{-1})	reflectance	4000−650 cm^{-1}	4.6−7.9	0.94	RMSECV = 0.38	Martin-del-Campo et al.[87]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	5.5−5.9	0.56	RMSECV = 0.005	Karoui et al.[88]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	5.5−6.0	0.84	RMSEP = 0.03	Karoui et al.[89]
	maximum normalization + first derivative + smoothing	reflectance	3000−900 cm^{-1}	6.1−7.5	0.84	RMSEP = 0.16	Karoui et al.[92]
dry matter	baseline correction of spectra at six points (3000, 2850, 1800, 1700, 1490, and 950 cm^{-1})	reflectance	4000−650 cm^{-1}	32.6−46.7 (g/100 g)	0.99	RMSECV = 1.07	Martin-del-Campo et al.[87]
	maximum normalization + first derivative + smoothing	reflectance	3000−900 cm^{-1}	43.6−50.9 (% w/w)	0.87	RMSEP = 0.83	Karoui et al.[92]
nonprotein nitrogen	baseline correction of spectra at six points (3000, 2850, 1800, 1700, 1490, and 950 cm^{-1})	reflectance	4000−650 cm^{-1}	3.1−50 (g/100 g)	0.98	RMSECV = 6	Martin-del-Campo et al.[87]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	0.3−1.2 (% w/w)	0.71	RMSECV = 0.08	Karoui et al.[88]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	0.2−1.0 (% w/w)	0.83	RMSEP = 0.05	Karoui et al.[89]
water-soluble nitrogen	baseline correction of spectra at six points (3000, 2850, 1800, 1700, 1490, and 950 cm^{-1})	reflectance	4000−650 cm^{-1}	15.8−104.1 (g/100 g)	0.73	RMSECV = 13.3	Martin-del-Campo et al.[87]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	0.5−1.4 (% w/w)	0.80	RMSECV = 0.07	Karoui et al.[88]
	normalization + first derivative + smoothing	reflectance	4000−400 cm^{-1}	0.4−1.3 (% w/w)	0.88	RMSEP = 0.08	Karoui et al.[89]
	maximum normalization + first derivative + smoothing	reflectance	3000−900 cm^{-1}	2.2−3.3 (% w/w)	0.79	RMSEP = 0.17	Karoui et al.[92]
Prediction of Sensory Attributes in Cheddar Cheese							
constituent	data pretreatment	measurement mode	wavenumber range	measured range	R^2	prediction error	reference
rubbery	absorbance of each spectrum was none or first derivative or scatter-corrected	reflectance	1767−930 and 4000−2839 cm^{-1}	2.9−44.6	0.90	RMSECV = 4.6	Fagan et al.[93]
creamy				10.7−70.7	0.90	RMSECV = 7.1	
melting				13.2−82.5	0.90	RMSECV = 7.4	
firmness				5.6−70.9	0.88	RMSECV = 7.4	
chewy				2.8−46.1	0.88	RMSECV = 7.4	

[a] n.a.: not applicable. RMSEC: root mean square error of calibration. RMSEP: root mean square error of prediction. RMSECV: root mean square error of cross-validation. PE: prediction error. R^2: squared correlation coefficient.

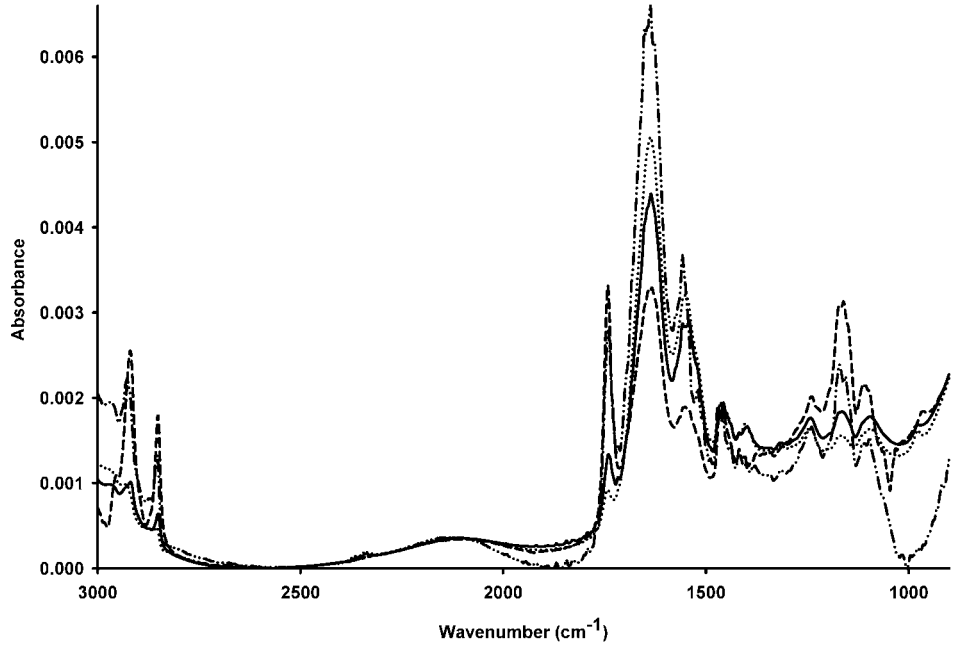

Figure 2. Example of MIR spectra recorded on traditional soft cheese at the central (−) and external (• • •) zones and stabilized soft cheese at the central (− − −) and external (− •• − •• −) zones.

protein; and (iii) 1500−900 cm^{-1}, the fingerprint region, in which many chemical compounds absorb. In several research studies, the normalized 3000−2800 cm^{-1} spectral region has been used as an indicator of the physical state of triglycerides.[55,57,68] Major shifts in spectral profile determined by the application of multivariate statistical analyses have been ascribed to changes (crystallization) in the physical state of fat.[68−70] Using 16 semihard cheeses varying in their protein (20.2−24.1%), fat (23.7−31.1%), and dry matter (50.2−57.9%) contents, one group sampled on a number of occasions during the ripening period, that is, after 1, 21, 51, and 81 days. To extract information from the spectral data sets, PCA was applied to the 1700−1500 cm^{-1} spectral region, and the sample scores on PCs 1 and 2 showed some incomplete separation of cheeses on the basis of their ripening time. In addition, the protein network characteristics of the ripened cheeses were found to be related to the initial composition of young (1 day old) cheeses. The best discrimination of cheese ripening time was obtained by these authors by applying CCA to data sets containing combined FT-IR and fluorescence spectra for these cheese samples. Additionally, they reported that the molecular changes that occurred in the secondary and tertiary molecular structures of major cheese components could be identified and monitored over time by CCA analysis of (i) the 1700−1500 cm^{-1} MIR spectral region plus tryptophan fluorescence spectra; and (ii) the 3000−2800 cm^{-1} spectral region and vitamin A spectra.[69,70] The authors suggested that FT-MIR and fluorescence spectroscopies provided a common description of cheese samples throughout ripening, allowing their potential use as tools for providing useful information related to protein structure in cheese.

In a similar approach, Martín-del-Campo et al.[71] used FT-MIR to monitor the ripening process of soft cheeses, in this case, Camembert. Samples of cheese were taken from two sites (the core and just under the rind) at different aging times (i.e., after 10, 13, 15, 17, 20, and 27 days) and scanned using FT-MIR. No changes were observed in the case of core samples, although those collected from under the rind did show some spectral modification throughout the ripening period studied. These authors attributed bands located around 1096 cm^{-1} to secondary alcohol ν C−O and δ O−H, while a band located around 1082 cm^{-1} was ascribed to δ O−H; an absorption at 1045 cm^{-1} was attributed to primary alcohol ν C−O, which was associated with the lactose grouping, in agreement with the findings of Grappin et al.[72] and Lanher.[73] Martín-del-Campo et al.[71] observed two intense peaks corresponding to amide I absorption around 1640 cm^{-1} (ν C═O, ν C−N) and amide II at 1550 cm^{-1} (δ N−H and ν C−N). Significant changes were recorded for both amide bands in the case of the under-rind cheese samples, while only amide II showed significant changes in the case of core samples. Changes in both the intensity and the position of amide I bands were ascribed to the modification that occurred in casein secondary structure, protein aggregation, and protein−water interactions, corroborating investigations of others.[69,74−76] Regardless of the sampling zone, absorptions in the 3000−2800 cm^{-1} region were characteristic of methylene (around 2920 and 2851 cm^{-1}) and methyl bands (2954 and 2871 cm^{-1}).

FT-MIR has been applied to determination of both the quality and the geographic origin of different varieties of ripened cheeses. With regard to soft cheeses, Karoui et al.[77] reported that the ratio of ν_{as} CH_2/ν_{as} CH_3 absorbance bands was higher for (i) stabilized cheese samples than for traditional cheese samples, and (ii) for the central zone of a cheese when compared to an outer zone irrespective of cheese variety (Figure 2). This difference in the ν_{as} CH_2/ν_{as} CH_3 ratio has been ascribed to a difference in the inoculated bacterial strain used for each cheese variety as reported by Lanciotti et al.[78] Determination of the geographic origin of Emmental cheeses produced in different European countries was also investigated by FT-MIR. Best results were obtained using the 1500−900 cm^{-1} spectral region in combination with vitamin A spectra recorded on cheeses produced during winter and summer periods, respectively. For Emmental cheeses produced during summer, correct classification rates of 83.7% and 77% were obtained for the calibration and validation data sets, respectively, suggesting the potential of this spectral region as a valuable tool for the determination of the geographical origin of cheeses.[79] This result was

confirmed on cheeses produced during the winter period, with correct classification rates of 96.7% for both the calibration and the validation spectra when considering the 1500−900 cm^{-1} spectral region.[80] These findings were later confirmed by Karoui et al.[81,82] who reported that FT-MIR provided relevant information for confirmation of the geographical origin of experimental Jura hard cheeses and Swiss Gruyère and l'Etivaz PDO cheeses. The potential of FT-MIR and fluorescence spectroscopies to determine the geographic origin of cheeses independently of their production times (winter or summer) was determined by concatenating spectra obtained from the two techniques on a sample basis; correct classification percentages of 89% and 77% were obtained for calibration and validation spectra, respectively.[83] The relatively low correct classification percentages were attributed to a significant effect of the production season on the characteristics of the cheeses studied.

Using a different approach, the potential of FT-MIR to predict some chemical parameters in dairy products has been investigated by many research groups. For example, the predictive ability of FT-MIR in determination of the casein content of cow's milk was investigated by Sørensen et al.[15] By applying PLS regression to FT-MIR spectra and casein content determined by reference methods, standard errors of prediction (SEP) of 0.033% and 0.89% for casein concentrations in the range of 2.1−4% and 70.7−81% were reported, respectively. Recently, Etzion et al.[84] successfully predicted protein concentration in 26 milk standards produced on a laboratory scale in which such concentration varied from 2.27% to 3.90%. However, in their study, these authors[84] observed (i) a significant interference when a water subtraction procedure was applied; this interference was considered as the primary obstacle to the accurate determination of protein content; and (ii) milk spectra were influenced by other constituents (e.g., fat and lactose), which formed a buffer layer between the ATR crystal and the protein. Nutritional parameters (i.e., fat, protein, carbohydrate, calories, calcium) of 83 commercially bottled Spanish milks covering the entire range of available brand names and types of milk were successfully determined by FT-MIR.[85] The prediction of nutritional parameters[80,86] in yogurt was confirmed separately by the same research group.

In cheese products, Martín-del-Campo et al.[87] utilized FT-MIR to determine pH, acid-soluble nitrogen, nonprotein nitrogen, ammonia (NH_4^+), lactose, and lactic acid at different ripening times by the application of PLS regression. With the exception of pH, good prediction (Table 1) of all of the parameters studied was reported; difficulty in prediction of pH was also encountered by Karoui et al.[88] who stated that FT-MIR could be used only for differentiating between cheeses with low and high pH values. Karoui and co-workers were unable to accurately predict total nitrogen in Emmental cheeses produced during summer and winter periods,[88,89] although they were able to accurately quantify water-soluble nitrogen. In a comparison of FT-MIR and NIR in this application, Karoui and co-workers[90−92] suggested the use of FT-MIR for the determination of water-soluble nitrogen and NIR for the prediction of both fat and total nitrogen. The combination of both NIR and FT-MIR spectra did not improve the results obtained on this data set.[91]

Organoleptic quality of cheeses, the most important attribute for the consumer, can be measured directly by sensory analyses. However, while the use of a trained sensory panel is the most effective method for assessing cheese quality characteristics, it is time-consuming, expensive, and not suitable for practical use when many samples need to be analyzed online or at-line in the food industry. In this context, FT-MIR was suggested as a rapid tool for screening the instrumental texture and meltability attributes of process cheese.[93] Application of PLS regression in this study revealed good prediction of, for example, meltability ($R^2 = 0.9$; root-mean-square error of cross-validation (RMSECV), 7.4; measured range, 13.2−82.5).

To extract information from FT-MIR spectra, all of the studies described above for dairy products used descriptive (PCA, CCA) or predictive techniques (FDA, PLS). In several studies, FT-MIR was coupled with other spectroscopic methods such as NIR and/or fluorescence spectroscopy and reference methods (e.g., rheology and physicochemical methods). To effectively utilize all of the information contained in such data sets, the use of chemometric tools allowing the simultaneous analysis of all data sets is required. A recently developed strategy (CCSWA) has been applied to simultaneously interrogate the physicochemical, FT-MIR, and fluorescence data sets recorded on cheese samples throughout ripening.[59,81] Results obtained showed the effectiveness of CCSWA for monitoring modifications in triglycerides and the protein network that take place during ripening. Indeed, spectral characteristics of ripened cheeses were found to be linked to the initial chemical composition and to the protein network and fat structure determined in the early stage of ripening. These results obtained were later confirmed[94] following the application of CCSWA to the tryptophan, vitamin A, and riboflavin spectra recorded on 15 soft cheeses produced by three different cheese making procedures. According to the similarity map defined by the common components 1 and 3, stabilized soft cheeses named M3 were differentiated from traditional cheeses named M1 and M2. In addition, for a considered cheese, a good discrimination according to the sampling zone (external and central zones) was found. The authors[94] reported that the results obtained were not found with the PCA applied separately to the tryptophan, vitamin A, and riboflavin, suggesting that the CCSWA methodology allowed one to use simultaneously all of the spectroscopic information given by the three intrinsic probes in a very efficient way.

4.2. Meat and Meat Products

Spoilage in meat and meat products is a major potential health hazard and the cause of significant economic loss to the industry sector. Organoleptic characteristics associated with spoilage can include changes in appearance (i.e., discoloration), the development of off-odors, slime formation, or any other characteristic that makes the food undesirable for human consumption.[95] It is widely accepted that detectable organoleptic spoilage is a result of decomposition and the formation of metabolites caused by the growth of microorganisms. More than 50 methods (e.g., organoleptic, microbiological, and physicochemical) have been used for the detection of microbiologically spoiled or contaminated meat products.[95] Because of the limitations of these methods (e.g., they are time-consuming, labor-intensive, and require highly trained panellists), Ellis et al.[96] explored the potential of FT-MIR for the measurement of biochemical changes within a chicken or meat substrate so as to improve both the accuracy and the speed of detection of microbial spoilage. Their study involved comminuted chicken breasts, which were left to spoil at room temperature for 24 h. FT-MIR

measurements were collected at hourly intervals directly from the meat surface using an ATR accessory with total viable counts being measured by classical plating methods. PLS regression was used to predict surface bacterial loads and produced root-mean-square error (RMSE) values of 0.15, 0.23, and 0.27 log units for the calibration, cross-validation, and independent test sample sets, respectively. These authors reported that absorbance peaks in the 1500−700 cm^{-1} region were positively correlated with spoilage, although no single, unique peak was obvious. Using a value of 10^7 bacteria·g^{-1} as a threshold for fresh versus spoiled poultry meat, a genetic programming approach was used to discriminate between fresh and spoiled chicken and quantify the level of spoilage, respectively. Using FT-MIR, these authors claimed to be able to acquire a metabolic snapshot and quantify, noninvasively, the microbial loads of food samples accurately and rapidly in 60 s, directly from the sample surface. One of the main conclusions of these studies was that FT-MIR could aid in the Hazard Analysis Critical Control Point process for assessment of the microbiological safety of food at the production, processing, manufacturing, packaging, and storage levels. Later, Ellis and coauthors[97] explored the potential of FT-MIR for the analysis of comminuted beef meat (rump steak) contaminated at low spoilage levels; useful information was again found in the 1500−700 cm^{-1} spectral region (i.e., 1413−1405 and 1374−1104 cm^{-1}). However, the models developed in this application were not as accurate as that used to predict bacterial spoilage in poultry[96] by the same authors. It was proposed that this was due to the spoilage processes in beef being different from those in poultry; additionally, and perhaps significantly however, the bacterial contamination load in beef was significantly lower than that observed in chicken and ranged from 5×10^4 to 4×10^7 cfu cm^{-2} as compared to 2×10^6 to 2×10^9 cfu cm^{-2} (chicken). The genetic programming approach applied in this beef study selected absorbances at wavenumbers in the region 1420−1400 cm^{-1}, specifically a vibration at 1413 cm^{-1} from C−N attributable to amides; other vibrations selected were from free amines (e.g., 1112 and 1374 cm^{-1}). This was interpreted by the authors as suggesting that the most significant functional groups selected that can be correlated to bacterial spoilage are those arising from amides and amines; it was reported as likely that this arises from the onset of proteolysis. In a similar approach, Ammor et al.[98] monitored the spoilage of minced beef stored in conventional and active packaging at four different temperatures (i.e., 0, 5, 10, and 15 °C) until the spoilage was very pronounced (i.e., 554 h, approximately 23 days). By applying PLS regression to centered and standardized (1/standard deviation) FT-MIR ATR spectra, the prediction accuracy for pH (R^2 = 0.92; slope = 0.93; range = 5−6; offset = 0.39; RMSE = 0.12) and total variable counts (R^2 = 0.80; slope = 0.8; range = 6.5−9.4 cfu/g; offset = 1.49; RMSE = 0.58) were found to be excellent and approximate, respectively (Table 2). In a second step, FDA based on three defined sensory groups (fresh, semifresh, and spoiled) was applied to the FT-MIR spectral data sets. The authors claimed 100% correct classification in the training sample set and 76.3% correct classification when a cross-validation technique was used; no information on the type of cross-validation was included in the report. This level of difference may perhaps be explained by the use of 39 principal components as an input into the factorial discriminant approach. Nonetheless, no fresh beef sample was classified as spoiled or vice versa. These authors also reported successful (92.5% correct classification with cross-validation) discrimination between the three types of packaging in which the meat was stored, that is, air, modified atmosphere, and active packaging.

Several research studies have been performed to assess the potential of FT-MIR for authentication of meat samples. In a study conducted by Al Jowder et al.,[99] differentiation between raw minced chicken, pork, and turkey meats was reported following the use of PCA. Additionally, for each meat species, discrimination between fresh and frozen-then-thawed raw meat was reported, a finding later confirmed in a feasibility study by Rannou and Downey[100] who stated that better classification of meat samples was obtained with vis−NIR than with FT-MIR (91.9% and 86.5% of overall correct classification was obtained from the two methods, respectively). Interestingly, when combined vis−NIR−MIR spectra were analyzed together, an improved, overall correct classification rate of 94.6% was achieved.[100] In a larger study, Downey et al.[101] attempted discrimination between minced chicken, turkey, pork, beef, and lamb based on MIR and vis−NIR data using a series of chemometric tools, FDA, SIMCA, *k*-nearest neighbors (KNN), and PLS regression. Using the five meat types, correct classification values of 94.8% (FDA), 83.5% (KNN), 85.1−93.9% (SIMCA), and 98.7−88.3% (PLS) were obtained, respectively. As for the feasibility study, the main classification problem encountered in this study was the separation of chicken and turkey meat samples. Al Jowder et al.[102,103] later succeeded in differentiating between muscle and offal tissue types (i.e., liver, kidney) and in detecting adulteration of raw and cooked beef containing 20% adulterants (i.e., heart, tripe, kidney, and liver). In fact, a cross-validated correct classification rate of approximately 97% was obtained by use of the 1895−990 cm^{-1} spectral region; no explanation for the use of this particular spectral region was given by the authors. Moreover, the authors used a relatively high number of PLS loadings (n = 15) in their models, which carries with it the danger of apparently increasing correct classification rates through model overfitting, that is, the fitting of the model to noise. Recently, differentiation between carcasses of suckling lambs according to their rearing systems (i.e., reared on ewes' milk or milk replacer) was described by Osorio et al.[104] following the use of discriminant-PLS regression on MIR spectra (4000−750 cm^{-1}). Complete (100%) correct classification was reported for perirenal and omental samples on the basis of the rearing system (Table 2).

McElhinney et al.[105] executed a feasibility study on the use of MIR and vis−NIR spectroscopy for the quantification of lamb in minced lamb-in-beef mixtures. Using 32 minced beef, 33 minced lamb, and 5%, 10%, and 20% lamb-in-beef samples (33 of each), PLS models were developed using the MIR fingerprint range (2000−800 cm^{-1}) for samples, which included the entire sample set or excluded the 100% lamb material. SEP for these sample sets were 10.6% and 4.3%, respectively; high numbers of PLS loadings were necessary for these models, 16 and 10, respectively.

Reported studies on the use of FT-MIR as a method for determining chemical parameters in meat products are limited. Qiao et al.[106] assessed the potential of three spectroscopic methods (i.e., Raman, NIR, and FT-MIR) to predict amino-acid contents in animal meals. Best results were obtained using fingerprint FT-MIR (2000−650 cm^{-1}

Table 2. Application of MIR Spectroscopy to Meat Products[a]

Physicochemical and Microbiological Parameters							
constituent	data pretreatment	measurement mode	wavenumber range	measured range	R^2	calibration/prediction error	reference
total viable count (log_{10}) in beef meat	none	reflectance	4000−600 cm^{-1}	5.5−7.4 organisms/g	n.a.	RMSE = 0.4, 0.6, and 0.4 logs for calibration, cross-validation, and independent test sets	Ellis et al.[97]
total viable count (log_{10}) in chicken	none	reflectance	4000−600 cm^{-1}	5.5−7.4 organisms/g	n.a.	RMSE are 0.2, 0.2, and 0.3 log units for the calibration, cross validation, and independent test sets, respectively	Ellis et al.[96]
total viable count (log_{10}) of beef meat	none	reflectance	4000−400 cm^{-1}	6.5−9.4 cfu/g	0.80	slope = 0.8	Ammor et al.[98]
pH	none	reflectance	4000−400 cm^{-1}	5−6	0.92	slope = 0.93	Ammor et al.[98]
turkey content in chicken meat	baseline correction + area normalization	reflectance	1800−1000 cm^{-1}	10−90% (w/w)	0.64	SDR = 14.8% (w/w)	Al-Jowder et al.[99]
pork content in chicken meat	baseline correction + area normalization	reflectance	1800−1000 cm^{-1}	10−90% (w/w)	0.71	SDR = 13.8% (w/w)	Al-Jowder et al.[99]
prediction of amino acids (9)	reduced to a data spacing of 8 cm^{-1} + first-order derivative	reflectance	4000−650 cm^{-1}	0.2−3.0%	0.68	RMSEP = 0.14%	Qiao et al.[106]

Meat Authenticity					
parameter	data pretreatment	measurement mode	wavenumber range	% correctly classified	reference
beef stored under air, modified atmosphere packaging and active packaging	none	reflectance	4000−400 cm^{-1}	100% correct classification and 76.3% correct classification when cross-validated	Ammor et al.[98]
differentiation between raw pork, chicken, and turkey meat homogenates	normalization	reflectance	4000−640 cm^{-1}	100% and 86.5% for calibration and validation data sets, respectively	Rannou and Downey[100]
differentiation between raw beef and beef containing 20% (w/w) of a range of a potential adulterants (heart, tripe, kidney, and liver)	none	reflectance	4000−800 cm^{-1}	97% of cross-validated classification	Al-Jowder et al.[103]
discrimination of fat samples (perirenal and omental) from carcasses of suckling lambs reared on ewes' milk or milk replacer	not mentioned	reflectance	4000−750 cm^{-1}	100% correct classification of perirenal and omental samples according to the rearing system 100% correct classification of perirenal fat samples 90% correct classification of omental fat samples	Osorio et al.[104]

[a] n.a.: not applicable. RMSE: root mean square error. SDR: standard deviation of the residual. R^2: squared correlation coefficient.

spectral range), although preparation for MIR analysis was more time-consuming than NIR due to the grinding step required.

Some proteolytic enzymes from plants and animals have been utilized as meat tenderizers in either home cooking or industrial treatment. In this context, research studies using FT-MIR have been performed to detect the presence of hexanal and methyl sulfide in thermally processed products and to monitor the oxidation process of meals stored in modified atmosphere packaging.[107] Results obtained showed the ability of FT-MIR to detect lipid oxidation and the formation of sulfur compounds at an early stage (e.g., during the first 6 weeks of storage). However, no physicochemical validation with traditional methods (e.g., peroxide values) was performed by the authors; this shortcoming was also present in a paper of Lizuka and Aishima,[108] which reported a clear differentiation between reference beef and beef treated with pineapple juice.

4.3. Fish

Research studies involving the use of FT-MIR for characterization of the quality of fish and fish products are limited, although the first publication appeared in 1989.[109] A protocol for the conversion of fish tissue into a milk-like emulsion for analysis by the Multispec MK I infrared milk analyzer was developed, and the results obtained showed that transmission infrared spectroscopy could be used for fish quality control purposes. However, the application required a relatively long experimental time due to the procedure required for preparation of the sample emulsion. To address this problem, Pink et al.[110] used FT-MIR with an ATR cell together with FT-NIR (in transmission mode) for studying frozen, minced hake samples. PLS regression applied separately to both spectral data sets for the prediction of dimethylamine revealed that (i) the 1600−890 cm^{-1} range for FT-MIR and (ii) the 1530−1866 nm range for FT-NIR were the spectral regions of choice for best predictions. An R^2 value of 0.96 and standard error of performance of 4.36 were observed following the use of FT-MIR (Table 3). More recently, Bocker et al.[111] applied FT-MIR microscopy and reported that the amide I spectral region was sensitive to changes occurring during brine salting of Atlantic salmon, confirming previous findings reporting that this technique could distinguish between salted and unsalted farmed salmon.[112] Indeed, significant changes in the 3600 and 3200 cm^{-1} region of MIR spectra of unsalted and salted salmon fillets after different storage times (days) and under oxidative conditions have been observed. No change was apparent in the shape of the spectra of unsalted fish fillet until 17 days storage had elapsed, while salted fish showed changes after 2 days storage. These changes in the shape of spectra have been ascribed to the appearance of newly formed components; broadening of the absorption band at 3470 cm^{-1} and a reduced frequency value for bands at 3012 and 1746 cm^{-1} have been related to the formation of hydroperoxides during oxidation of fish lipids. Given that such hydroperoxides are more reactive and unstable than those produced following the oxidation of edible vegetable oils, they evolve more quickly to produce secondary products. FT-MIR was also advanced as a possible tool for determination of fish freshness.[113] By applying FDA to normalized spectral data, correct classification rates of samples (fresh and frozen−thawed fish) of 75% and 87.5% for validation sample sets were reported using a model that included information from

Table 3. Application of MIR Spectroscopy to Fish Products[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% correct classification	reference
prediction of dimethylamine	path length correction based on the area measurements and mean centering	reflectance	4000−800 cm^{-1}	1−83 mg/100 g of fish	0.96	standard error of performance = 4.4	Pink et al.[110]
differentiation between fresh and frozen fish	normalization	reflectance	3000−900 cm^{-1}	n.a	n.a.	1500−900 cm^{-1}: 75% for validation data set 1700−1500 cm^{-1}: 37.5% for validation data set 3000−2800 cm^{-1}: 87.5% for validation data set concatenation of the three spectral regions: 87.5% for validation data set	Karoui et al.[113]

[a] n.a.: not applicable. R^2: squared correlation coefficient.

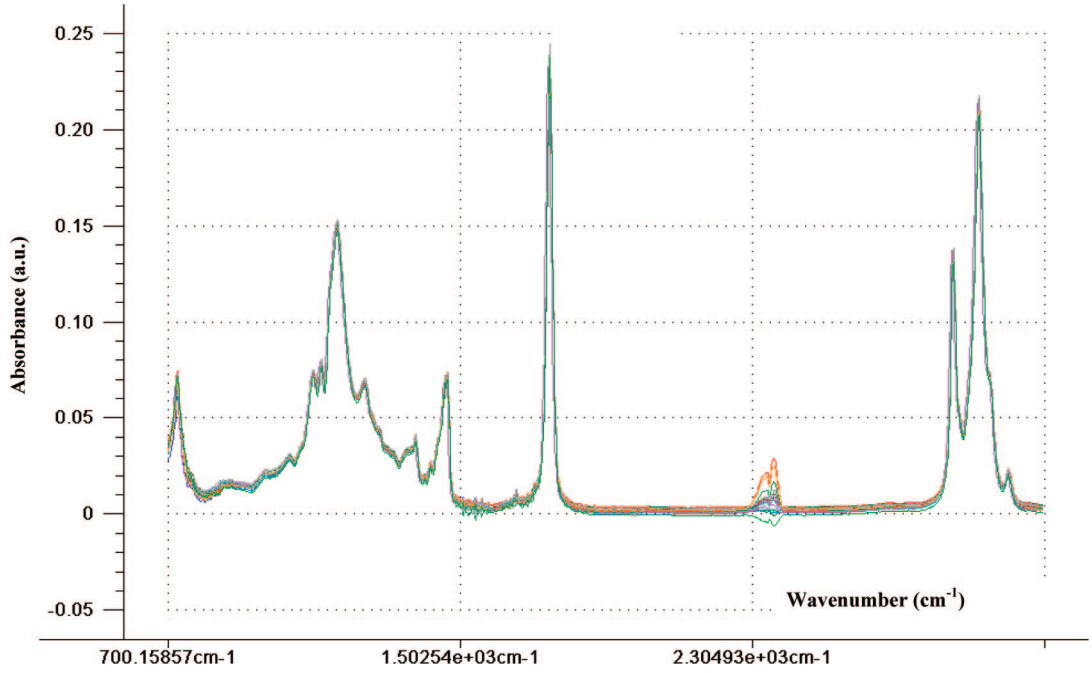

Figure 3. Representative olive oil ATR spectra.

the 1500−900 and 3000−2800 cm^{-1} spectral regions.[113] Only 37.5% correct classification was obtained using the 1700−1500 cm^{-1} region. However, these results were not obtained using intact fish samples; spectra were acquired from juice exudates, diluted 1:1 in ultrapure water.

4.4. Edible Oils

Olive oil is probably the most popular vegetable oil consumed as a food. Olive oils are classified into a specific number of legally defined categories according to the method of their extraction and, therefore, purity. Categories vary from extra-virgin olive oil (EVOO) to lampante with the latter not being used for human consumption. EVOO represents the highest quality and most expensive oil, which is much sought after by consumers. Therefore, EVOO is often the subject of economic fraud through blending with cheaper oils or oil grades. Such a practice represents a commercial fraud but may also have potential health implications depending on the adulterant oil.[114] The most common adulterants found in EVOO are refined olive oil, residue oil, synthetic olive oil, and nut oil.[115−118] In this context, FT-MIR and Raman spectroscopies have been investigated[119] to assess their potential for (i) discriminating between seven different groups of oils, that is, EVOO, refined olive oil, sunflower oil, rapeseed oil, soybean oil, peanut oil, and corn oil; and (ii) differentiating EVOO samples from those adulterated with certain seed oils at different levels varying from 5% to 45% v/v. Correct classification rates for a validation sample collection of 100% and 93.1% were obtained with FT-MIR and Raman spectroscopies, respectively. The results obtained above by different authors confirmed the findings of other investigations reporting the ability of FT-MIR to discriminate between (i) EVOO and EVOO adulterated with sunflower oil[120] or with a corn−sunflower oil binary mixture;[121] (ii) EVOO and EVOO adulterated with hazelnut oil present at a concentration ≥8%;[116] and (iii) pure camellia oil adulterated with soybean oil in the 5.5−22.4% range.[122] Most of the valuable information contained in the FT-MIR spectra was found in the 1500−900 cm^{-1} (the fingerprint region) and was tentatively ascribed to C−H bending and deformation in fatty acids. Representative spectra of oils are shown in Figure 3 (unpublished results).

Bombarda et al.[123] succeeded in determining the geographic origin and composition of the essential oil lavandin (var. Grosso) by FT-MIR and gas chromatography using a flame ionization detector; the two techniques gave similar results, suggesting that FT-MIR could be used as a potential tool for authentication of this and other essential oils. In an earlier report, Caetano et al.[124] applied classification and regression trees (CART) and support vector machines (SVM) in an attempt to classify olive oils on the basis of their geographic origin, that is, Italian versus non-Italian and Ligurian versus non-Ligurian. CART was chosen because of its simplicity, while the SVM approach allowed for the mapping of complex, nonlinear relationships. In the discrimination of Italian versus non-Italian oils, both approaches produced models with relatively high sensitivity but low selectivity; this means that the probability of accepting a non-Italian oil as Italian was considerable. In the discrimination of Ligurian oils, the opposite behavior was obtained, meaning that the probability of wrongly classifying a Ligurian oil was high. The investigation of Sinelli et al.[125] allowed differentiation of fresh from aged edible oils and was recently supported by Le Dréau et al.[126] who observed differences between fresh, aged, and heated oils from six different vegetable sources. In addition, good correlation between analytical parameters describing oil deterioration arising from both heating time and changes in the 1500−900 cm^{-1} spectral region was highlighted by Moros et al.[127]

Fats used in food product formulations induce some physicochemical, rheological, and sensory changes in the finished products. In this context, Bellorini et al.[128] assessed the abilities of various analytical methods for differentiating between the nature of fats utilized in food products; specifically, these authors targeted the identification of tallow (ruminant fat) and its differentiation from nonruminant fats. Four different techniques were compared in terms of their

suitability for enforcing existing and emerging legislation on animal byproducts (i.e., FT-MIR, gas chromatography coupled with mass spectrometry, immunoassays, and polymerase chain reaction methods). Samples of different, individual fats and oils as well as mixtures of the fats were studied using this range of analytical methods. Results obtained showed that FT-MIR and GC−MS differentiated between pure fat samples quite well but showed only limited ability to identify the animal species or even the animal class to which fat(s) belonged. The other two techniques (immunoassays and polymerase chain reaction) were able to identify the origin species of the fats; they were also the only techniques able to identify low concentrations of tallow in a mixture of fats prepared by the rendering industry.[128] This was the case even when the samples were sterilized at temperatures above 133 °C. One of the main conclusions of this study was that, while the combination of FT-MIR and multivariate data analysis techniques permitted the classification of pure lipid samples according to their origin (ruminant vs nonruminant), they proved not to be suitable for detecting a specific fat, tallow, at concentrations of less than 10% in a mixture of fats.

FT-MIR in transmission mode has been used for the quantification of peroxide values of vegetable oils, and the results obtained showed that reproducibility of the FT-MIR was better than that of the traditional technique (determined by the American Oil Chemists' Society iodometric method).[129] These results were later confirmed by Guillen and Cabo[130] reporting that FT-MIR could be used for the determination of oxidative stability and antioxidant activity of different edible oils, which were submitted to oxidation in a convection oven with air circulating at 70 °C. In another approach, Van de Voort et al.[131] succeeded in determining the level of peroxide values of edible fats and oils by FT-MIR transmission spectroscopy. A PLS calibration model for the prediction of peroxide value was developed using data in the spectral range 3750−3150 cm^{-1}. Validation of the method was carried out by comparing the PLS-predicted peroxide values of a series of vegetable oils to values obtained by the American Oil Chemists' Society iodometric method. Reproducibility of the FTIR 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 latter. This capability was later discussed by Guillén and Cabo[132] who reviewed the capability of FT-MIR to characterize edible oils and fats. Included in that review were determination of the degree of unsaturation or iodine value, trans-double bond content, average chain length or saponification number, solid fat content, peroxide and anisidine values, and free fatty acid quantification. Regarding the latter, Inón et al.[133] reported an R^2 value of 0.99 and an RMSECV equal to 0.036 in the estimation of free fatty acids in commercial olive oils over a range of 0.23−6.39% (w/w) (Table 4). These authors investigated a wide selection of mathematical approaches for choosing the calibration sample set, attenuation of the spectral range, preprocessing methods (mean centering, multiplicative scatter correction, standard normal variate), and PLS regression. However, the number of samples analyzed was small: a calibration and validation set of 16 and 28 samples, respectively.

4.5. Cereals and Cereal Products

The formation of a flour:water dough represents a key technological step in the production of bread and other baked goods. Many complex interactions occur during this process, which induce changes in structure at both the molecular and the macroscopic levels. Dough must be mixed for a specific time and using particular energy inputs to ensure optimal volume and texture in any subsequent baked product. In this context, FT-MIR has been studied by several groups to monitor changes occurring in bread dough.[134−137] One study[135] aimed to evaluate the correlation between FT-MIR and FT-NIR spectroscopy to give a better understanding of the spectral modifications recorded during bread dough mixing using a 2D cross-correlation (2D CORR) method. While the specific focus of this study was on the NIR region, the authors reported the involvement of MIR bands centered at 3300 (O−H), 1650 (amide I), 1546 (amide II), 1245 (amide III), and 980 cm^{-1} (C−H) in dough structure development. ATR-FTIR was used[136] in a study of changes in protein secondary structure in high water absorption systems (90%) used in gluten−starch separation processes. Success in the monitoring of relative structural changes in protein secondary structures was reported, and it was noted that formation of β-sheet structures at the expense of all others took place during mixing. A similar sampling approach was used in an investigation of factors responsible for dough stickiness.[137] Infrared spectra indicated that fat and gluten appear to be located on the surface of sticky dough rather than water or starch. Significant differences in amide I and amide II band intensities were noted for kneaded and stretched gluten in comparison to untreated, wet gluten. In agreement with the previous report, these authors concluded that a major decrease in α-helix and increase in β-sheet structures was apparent as a result of kneading and stretching of dough. Sinelli et al.[138] reported the application of NIR and MIR spectroscopy to the study of dough proofing, the resting period after mixing during which fermentation commences. Strong baker's flour, retail flour, and gluten-free flour formulations were investigated over a 1 h period in each case; the aim was to investigate macromolecular changes occurring during this phase of bread production and to determine optimum proofing times based on objective spectral measurements. Changes with time were studied by plotting PC1 and PC2 scores for each flour type against time (Figure 4); reproducible and different curves were obtained for each flour type. On the basis of these studies, the authors concluded that FT-IR spectroscopy revealed information about the relative importance of protein and starch moieties during proofing, although a note of caution was sounded regarding the representativity of the ATR sample which was actually measured, that is, a surface measurement essentially.

Midinfrared spectroscopy has also been applied to the classification of modified starches according to the type of chemical modification involved.[139] These authors deployed a large array of chemometric procedures including LDA, quadratic discriminant analysis (QDA), kNN, SIMCA, PLS-DA, ANN, and SVM to identify a range of chemically modified starches. Two hundred and thirty two (232) starch samples of four different classes were studied: the class "native" consisted of 38 samples, the class "E1412" consisted of 25 samples, the class "E1422" consisted of 57 samples, and the class "E1422" consisted of 112 samples. Results demonstrated that the various discrimination methods were effective tools for the classification of starches according to

Table 4. Application of MIR Spectroscopy to Oil Products[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% of correct classification	reference
differentiation between olive oil and hazelnut oil	absorbance [($D1$ log $1/R$) at 1438 cm^{-1}) − absorbance ($D1$ log $1/R$) at 1461 cm^{-1})]/ absorbance ($D1$ log $1/R$) at 1481 cm^{-1}). $D1$ and R correspond to first derivative and reflectance, respectively	reflectance	4000−900 cm^{-1}	n.a.	n.a.	90.5% and 94.4% of correct classification for olive and hazelnut oils, respectively	Baeten et al.[116]
authenticity of edible oils of different botanical origin and detection of adulteration	normalization and baseline correction	reflectance	3000−600 cm^{-1}	5−45% (w/w)	n.a.	correct classification rate of 100%	Marigheto et al.[119]
authentication of olive oils adulterated with sunflower oils	none	reflectance	4000−800 cm^{-1}	20−100 mL of vegetable oil/L of olive oil	0.97 for the cross validation		Tay et al.[120]
detection of corn−sunflower binary mixture, cottonseed, and rapeseed oils, in olive oil	mean centered	reflectance	4000−650 cm^{-1}	2−20% (v/v)	0.93−0.98	corn−sunflower binary mixture cottonseed and rapeseed oils in olive oil with SEPs of 1.04, 1.4, and 1.32, respectively	Gurdeniz et al.[121]
discriminating and quantifying soybean oil adulteration in camellia oils	first derivative: standard normal variate + variance scaling + mean centering + Norris derivative	reflectance	4000−650 cm^{-1}	5.5−22.4% (v/v)	0.99	RMSECV = 0.85	Wang et al.[122]
evaluation of virgin olive oil freshness	none	reflectance	4000−550 cm^{-1}	n.a.	n.a.	100%, 75%, 92%, and 100% of validated correct classification obtained for fresh oils, oil stored during 1 year in the dark, 2 years in the dark, and 1 year in the light	Sinelli et al.[125]
heating time estimation of sunflower and seed oils	second derivative (Savitzky−Golay method, number of smoothing points = 10)	reflectance	4000−500 cm^{-1}	147−189 °C	0.55	RMSECV = 19 °C	Moros et al.[127]
heating temperature estimation of sunflower and seed oils	second derivative (Savitzky−Golay method, number of smoothing points = 10)	reflectance	4000−500 cm^{-1}	0−1920 min	0.98	RMSECV = 166 min	Moros et al.[127]
prediction of free fatty acid concentration	subtraction from all centered spectra of the average absorbance between 1904 and 1976 cm^{-1} + standard normal variate	absorbance	4000−635 cm^{-1}	0.23−6.39% (w/w)	0.99	RMSECV = 0.036	Inón et al.[133]

[a] n.a.: not applicable. RMSECV: root mean square error of cross-validation. R^2: squared correlation coefficient.

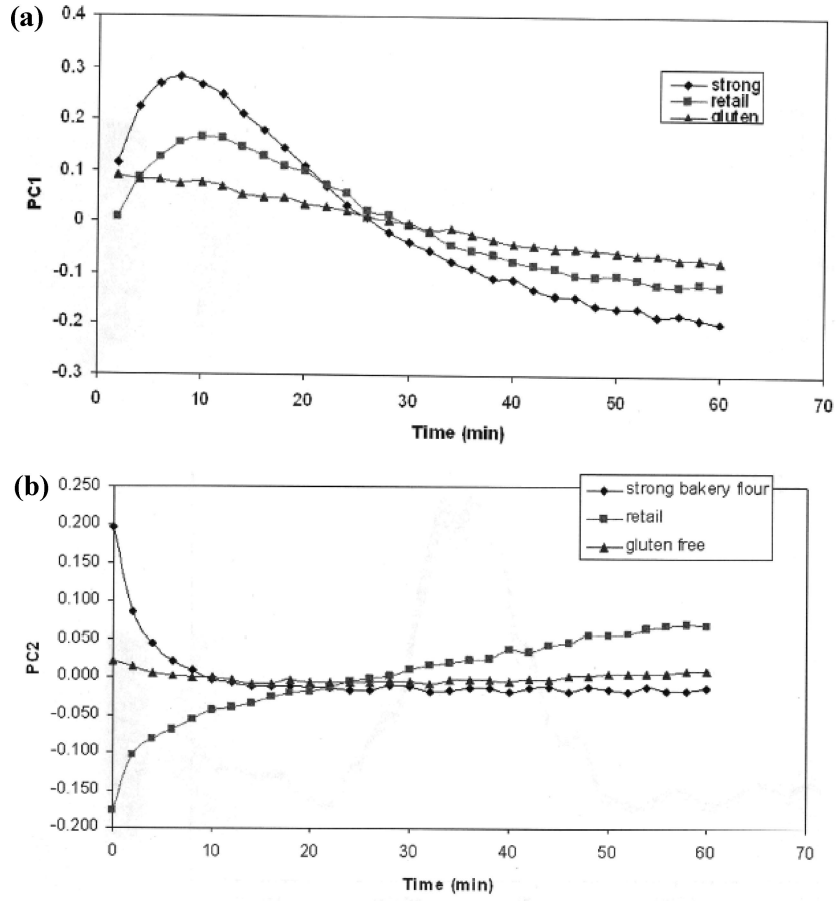

Figure 4. Principal components 1 (a) and 2 (b) scores versus time for strong bakers', retail, and gluten-free flour during proofing (Sinelli et al.[138]).

their chemical modification. Best results were obtained using the SVM technique. Another study of carboxymethylated nonstarch polysaccharides was reported by Yuen et al.[140] These authors compared Raman and FT-IR spectroscopy for predicting the degree of substitution in cellulose, guar, locust bean, and xanthan gums. IR marker bands at 1315 and 1605 cm^{-1} were identified, and predictive models with high correlation ($r > 0.96$) between the spectroscopic and wet chemistry data were reported. No prediction error values were, however, included in that paper.

FT-IR spectroscopy has been used in investigations of the rubbery and glassy states of starch,[141] retrogradation of natural cross-linked starch,[142] gelatinized and retrograded wheat starch,[143] gelatinization changes in rice starch as a function of pressure and temperature,[144] temperature effects on sorghum starch,[145] and retrogradation of potato starch.[146] Reports have also been published on the differentiation of cheese sauces according to starch type,[147] cassava starch edible film properties,[148] sweet potato starch hydrolysis,[149] starch granule organization in wheat, potato, maize, waxy maize, and amylomaize,[150] and cell wall polysaccharides with emphasis on arabinoxylans.[151]

Findings reported by Fernández Pierna et al.[139] showed that FT-MIR could be used for (i) monitoring changes in protein secondary structure during batter mixing, (ii) demonstrating that hydrated gluten is one of the major contributors to dough stickiness, and (iii) ascribing absorbances to chemical changes taking place in bread dough development during mixing. Additionally, FT-MIR has recently demonstrated its ability to determine optimum dough mixing time by focusing on changes occurring in the secondary structure of gluten.[152] Indeed, the ratio of 1336 cm^{-1}/1242 cm^{-1} absorbance bands, corresponding to α-helix and β-sheet conformations of protein, respectively, was found to be a valuable indicator of optimum mixing time. Cocchi et al.[36] separated different flour samples that were submitted to different technological treatments by FT-MIR, highlighting the utility of the technique to the characterization of flour matrices.

Regarding the ability of FT-MIR to predict chemical parameters in cereals and cereal products, Kim et al.[153] successfully determined the quantity of trans fatty acids ($R^2 = 0.92$, SEP = 0.96; Table 5) present in ground cereal products without an oil extraction step using PLS regression of data collected in the 1500−900 cm^{-1} spectral region. These results confirmed previous findings reporting that FT-MIR could be used for the quantification of ash and protein in commercial wheat flour[154] (Table 5) and protein in rice samples treated with different amounts of radiation doses, that is, varying from 250 to 3000 Gray (Gy).[155] However, NIR was found to be the better technique for prediction of amylose content in wheat flour.[155]

Classification of cereal flours on the basis of MIR spectra of puffed products has been reported by one group.[156] Six pure flours from wheat, oats, and buckwheat were subjected to different technological treatments (dehulling, toasting, and puffing), and 10 binary mixtures were produced by blending the wheat flour with each of the others in varying proportions. Spectra were collected in transmission (KBr discs). Following the application of wavelet pretreatment, PCA revealed clustering of the flours types into separate groups, although no discriminant models were developed in this study. In

Table 5. Application of MIR Spectroscopy to Cereal Products[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% correct classification/ assignment bands	reference
chemical assignment of MIR bands during dough mixing	standard variate correction + second derivative	reflectance	4000−800 cm^{-1}	n.a.	n.a.	starch: 1153, 1088, and 1011 cm^{-1} water: 3383, 3269, 3209, and 3068 cm^{-1} protein: 1647, 1545, and 1246 cm^{-1} lipid: 2968, 2927, 1454, 1408, and 1327 cm^{-1}	Aït Kaddour et al.[134]
classification of modified starches	no information	reflectance	4000−800 cm^{-1}	n.a.	n.a.	78% correct classification	Fernández Pierna et al.[139]
				Determination of Physicochemical Parameters			
mixogram midline point	baseline correction of spectra at six points (4000, 3990, 2500, 1880, and 700 cm^{-1}) + advanced ATR correction algorithm + second derivative band area at 1242 cm^{-1} (β-sheet)	reflectance	4000−700 cm^{-1}	6.4−2.3 min	0.97	SE: 0.0004 (min)	Seabourn et al.[152]
trans-fatty acid in ground cereal	second derivative	reflectance	4000−650 cm^{-1}	0−12.2% (total fat in the product)	0.89−0.92	standard error of performance = 0.96	Kim et al.[153]
protein content	multiplicative signal correction + mean centering	reflectance	4000−650 cm^{-1}	8.9−13.2% (w/w)	0.98−0.99	RMSECV = 0.18−0.18	Ferrão et al.[154]
	Savitzky−Golay smoothing + multiplicative scatter correction	reflectance	4000−350 cm^{-1}	7.4−8.4% (w/w)	0.72	RMSECV = 0.22	Shao et al.[155]
ash content	multiplicative signal correction + mean centering	reflectance	4000−650 cm^{-1}	0.3−1.3% (w/w)	0.97−0.98	RMSECV = 0.038−0.039	Ferrão et al.[154]
amylose content	Savitzky−Golay smoothing + multiplicative scatter correction	reflectance	4000−350 cm^{-1}	20.0−24.6% (w/w)	0.66	RMSECV = 0.17	Shao et al.[155]

[a] RMSECV: root mean square error of cross-validation. SE: standard error. n.a.: not applicable.

another study of extruded cereal products, Cremer and Kaletunc[157] investigated the spatial distribution of starch, protein, and lipid in corn and oat flour-based material using FT-IR microspectroscopy. Results revealed an even starch distribution as a continuous phase in cereal-based extrudates, while protein was located in small, discrete regions. Lipids in oat flour extrudates were less evenly distributed than starch but more so than protein.

One study has been reported,[158] which described the use of FT-IR spectroscopy for studying protein structure in legumes (*Phaseolus vulgaris* L. and *Lens culinaris* L.). Attention was paid to the amide I absorption band in whole seed flours before and after dry heating and autoclaving. Dry heating was reported not to appreciably affect secondary protein structure in lentil while causing a reduction in β-sheets, an increase in aggregates, and the appearance of random coil structures in common bean flour. Overall, heat-induced complexes of legume proteins have a high stability because of the high content of β-sheet structures, which may affect protein utilization from flours thus treated.

4.6. Sugar and Honey

FT-MIR has been utilized as a rapid tool for the determination of both the geographical and the botanical origins of honey. Tewari and Irudayaraj[159] analyzed honey from seven floral sources and obtained 100% correct classification using both FT-MIR and electronic-nose data. Results obtained were confirmed by Ruoff et al.[25] who studied 422 honey samples (11 unifloral and 411 polyfloral) originating from different European countries, that is, Switzerland, Germany, Italy, Spain, France, and Denmark. Ruoff et al.[25] and Karoui et al.[160] reported good discrimination of honey samples according to floral origin: percentage of correct classification for the validation data sets varied in the range of 71−100% (Table 6). This finding was recently confirmed by Bertelli et al.[50] (2007) on Italian honey samples: 100% and 93% of samples in the calibration and validation data sets, respectively, were correctly classified.

Routine analysis of sugar cane juice samples for sugar content is performed by polarimetric or refractometric methods. Recently, FT-MIR was used to determine glucose, fructose, and sucrose amounts in aqueous mixture solutions.[161] These authors prepared aqueous mixtures containing 10%, 20%, and 40% w/v total sugars with different combinations of glucose, fructose, and sucrose. By applying PLS regression to FT-MIR reflectance spectra, excellent predictions were found with R^2 values $\geq$0.99 (standard error of calibration varied between 0.33−0.38, 0.26−0.32, and 0.36−0.38 for glucose, fructose, and sucrose, respectively, Table 6), confirming recent and earlier findings of Ruoff et al.,[162] Maalouly et al.,[163] and Cadet and Offmann.[164] Investigations of these latter authors reported that FT-MIR was more convenient than HPLC. In another study, FT-MIR was deployed to measure physicochemical properties of honeys.[165] Good predictions of fructose, glucose, and sucrose in honey samples (R^2 values of 0.88, 0.92, and 0.98 and standard deviation values of 2.55%, 4.44%, and 3.61% (w/v), respectively) were reported by the authors (Table 6).[165]

Hennessy et al.[26] reported success in the use of FT-MIR spectroscopy for confirming claimed geographic origin in a selection of honeys from Ireland (n = 25), Mexico (n = 25), Argentina (n = 25), Czech Republic (n = 50), and Hungary (n = 25). This sample collection contained filtered and nonfiltered material. Spectra were collected using an ATR accessory and a germanium crystal (11 internal reflections). First- and second-derivative and standard normal variate (SNV) pretreatments were separately applied to the spectral data, which were processed using PLS-DA, FDA, and SIMCA. An overall correct classification rate of 93.3% was obtained by PLS-DA, while FDA correctly identified 94.7% of honey samples. Correct classifications of up to 100% were achieved using SIMCA, but some classes had very high associated false positive classification.[26] While these reported correct classification rates may not be high enough for a definitive confirmation of geographic origin, they suggest the possibility of deploying the technique as a screening tool in such an application. In earlier work, Kelly et al.[166] described the use of FT-MIR ATR spectroscopy for discrimination of Irish honey and such honey adulterated with various sugar syrups. A total of 580 authentic Irish honeys were studied together with a random selection of some of these honeys adulterated by inverted beet syrup (n = 280), high-fructose corn syrup (n = 160), partial invert cane syrup (n = 120), inverted beet syrup (n = 280), dextrose syrup (n = 160), and beet sucrose (n = 120). For each adulterant, a range of concentrations was used from approximately 10% to 70% w/w. On the basis of the spectra collected, the authors reported discrimination between authentic honeys and honeys in this sample set using a decision tree approach with levels of accuracy that may have commercial value. Discrimination between authentic honeys and those adulterated by high-fructose corn syrup or inverted beet syrup met with low success rates, and it was stated that FT-MIR spectroscopy would be unlikely to be the method of choice for their detection.

Adulteration detection of Irish honey samples by glucose−fructose mixtures has been investigated by Kelly et al.[51] Samples studied were authentic honey (n = 320) and adulterated honeys (n = 221); adulterants used were solutions of both D-fructose and D-glucose in the weight ratios 0.7:1.0, 1.2:1.0 (typical of honey composition), and 2.3:1.0. Each adulterant solution was added to individual honeys at levels of 7%, 14%, and 21% w/w. Examples of FT-IR spectra of authentic Irish honeys and those adulterated with sugar solutions are shown in Figure 5. Both PLS-DA and k-nearest neighbors techniques were studied; best classification models were obtained by PLS-DA on first derivative spectra with overall correct classification rates of 93%; 99% of samples adulterated at levels of 14% w/w or higher were correctly identified. These results were claimed by the authors to reveal the potential of this spectral technique for use as a screening technique to detect this type of adulteration.

4.7. Fruit and Vegetables

As fruit is the most costly ingredient in jams, adulteration with cheaper ingredients, such as sugar and vegetable matter, may occur. To protect the consumer from adulteration and avoid unfair competition, the use of MIR as a screening tool was investigated by several groups. Diffuse reflectance and ATR were used to differentiate between strawberry jam and such jam containing nonstrawberry constituents; correct classification rates of 100% and 91%, respectively, were observed (Table 7).[47] These findings were confirmed later by Holland et al.[167] who analyzed 983 fruit purées, which were prepared in the laboratory using fruit collected over 2 years (1993 and 1994); different adulterants such as apple, plum, sugar solutions (glucose and sucrose), red grape juice, and rhubarb compôte were mixed with the strawberry

Table 6. Application of MIR Spectroscopy to Sugar Products[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% correct classification/ assignment bands	reference
authentication of the botanical and/or geographical origin of honey	baseline correction and area normalization	reflectance	4000−600 cm^{-1}	n.a.	n.a.	100% and 97.3% of validation data sets obtained using 1500−950 cm^{-1} and 3200−2200 cm^{-1}	Tewari et al.[159]
	not mentioned	reflectance	4000−550 cm^{-1}	n.a.	n.a.	71−100% of correct classification for the validation data sets for unifloral honey 83% and 86% of correct classification of honey according to their geographical origin (Switzerland and Germany)	Ruoff et al.[25]
	first and second derivative + normalization	reflectance	4000−600 cm^{-1}	n.a.	n.a.	100% and 93% correct classification obtained for the calibration and validation sets, respectively	Bertelli et al.[50]
	mean normalization + standard normal variate + first and second derivatives	reflectance	4000−800 cm^{-1}	n.a.	n.a.	correct classification varied between 93.3% and 100%	Hennessy et al.[26]
	first derivative + second derivative	reflectance		n.a.	n.a.	correct classification rates of 96.2%, 97.5%, 95.8%, and 91.7%, respectively, obtained for authentic honey and honey adulterated by beet sucrose, dextrose syrups, and partial invert corn syrup	Kelly et al.[166]
	normalization + first and second derivative	reflectance		7−21% (w/w) of adulterant in honey		93% correct classification with 99% of samples adulterated at 14% or greater correctly identified	Kelly et al.[51]
prediction of sugar content in pure aqueous solution and honey	PLS2-first derivative	reflectance	4000−750 cm^{-1}	glucose: 1−32% (w/v)	0.99	SEC = 0.33−0.38%	Sivakesava and Irudayaraj[161]
	PLS1-first derivative			fructose: 2−32.5% (w/v)	0.98	SEC = 0.26−0.32%	
	PLS1-first derivative			sucrose: 2−32.5% (w/v)	0.99	SEC = 0.36−0.38%	
	not mentioned	reflectance	4000−550 cm^{-1}	fructose: 20.9−45.7 g/100 g	0.84	SEP = 1.2 g/100 g	Ruoff et al.[162]
				glucose: 21.5−38.2 g/100 g	0.94	SEP = 0.9 g/100 g	
				sucrose: 0−9.7 g/100 g	0.91	SEP = 0.3 g/100 g	
				turanose: 0−5.5 g/100 g	0.77	SEP = 0.2 g/100 g	
	centered data	transmission	5012−926 cm^{-1}	fructose (mean: 37.3% (w/v)	0.88	SD = 2.6%	Lichtenberg et al.[165]
				glucose (mean: 28.9% (w/v)	0.92	SD = 4.4%	
				sucrose (mean: 3.02% (w/v)	0.98	SD = 3.61%	
prediction of total sugar in beverage samples	PLS1-first derivative	reflectance	4000−750 cm^{-1}	0−53.85% (w/v)	n.a.	PE: 0−15.6% (w/v)	Lichtenberg et al.[165]
prediction of sucrose content	centered data	reflectance	5000−700 cm^{-1}	7.25−24.31 g/100 mL	n.a.	SD: 0.29	Cadet and Offmann[164]
prediction of physicochemical parameters in honey	centered data	transmission	5012−926 cm^{-1}	pH (mean: 4.08)	0.66		Lichtenberg et al.[165]
				moisture (mean: 16.1%)	0.53		
				free acidity (mean: 14.7 mVal/cm)	0.85		
	not mentioned	reflectance	4000−550 cm^{-1}	water: 13.4−24.6 g/100 g	0.99	SEP = 0.24 g/100 g	
				free acidity: 6−34 mequiv/kg	0.96	SEP = 2 mequiv/kg	
				pH: 3.8−6	0.87	SEP = 0.16	

[a] n.a.: not applicable. SEC: standard error of calibration. SEP: standard error of prediction. SD: standard deviation. PE: prediction error.

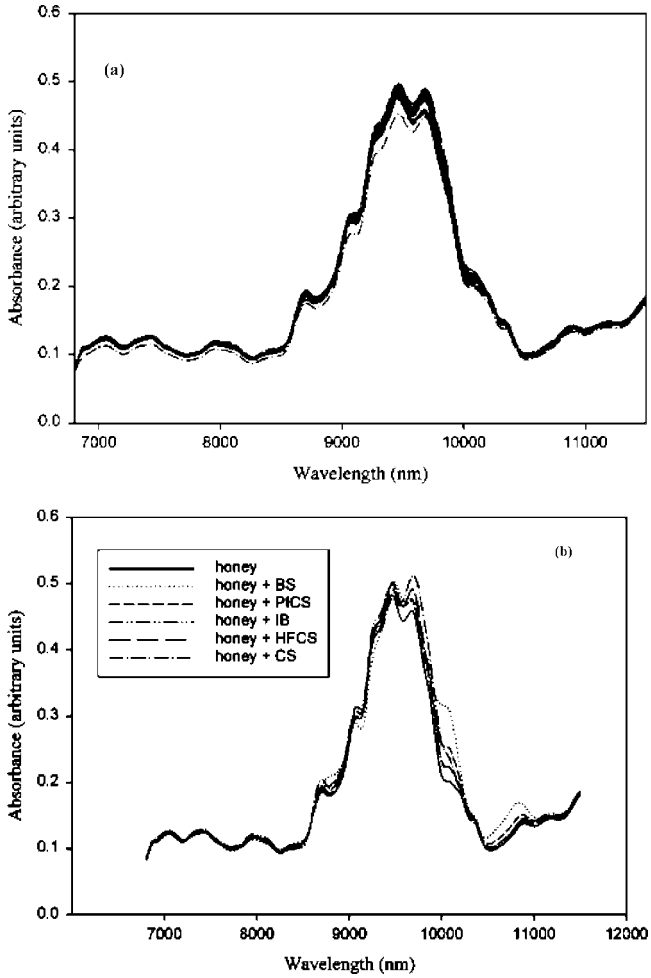

Figure 5. Mid-infrared ATR spectra of a random selection of (a) authentic Irish honeys and (b) adulterated Irish honey with beet sucrose (BS), partial invert cane syrup (PICS), inverted beet syrup (IB), high fructose corn syrup (HFCS), and dextrose syrup (CS) (Kelly et al.[51]).

samples. Purées of strawberry only and others (pure nonstrawberry or adulterated strawberry) were used for the establishment of a discriminant PLS model (on a test set comprising 317 samples), and 94.3% correct classification (strawberry or nonstrawberry) was obtained. The authors tested the robustness of the model with fruits harvested in 1995, and 96.6% of samples were found to be correctly classified. One of the main conclusions of this study was that the model could be used for the analysis of fruit of subsequent years; this hypothesis was advanced because 22 of 23 commercially produced fruit purées were correctly classified. In another study involving apple juice, Kelly and Downey[168] used FT-MIR for the detection of single strength apple juice adulterated by sugars, partially inverted cane syrup (PICS), beet sucrose (BS), high fructose corn syrup (HFCS), and synthetic solutions of fructose:glucose:sucrose (FGS). The sample set comprised 224 authentic and 480 adulterated samples with adulterants being added to individual juices at levels of 10%, 20%, 30%, and 40% w/w. Best classification models achieved overall correct classification rates of 96.5% (PICS), 93.9% (BS), 92.2% (HFCS), and 82.4% (FGS), respectively. In addition, PLS models were reported able to predict adulterant content to within ±10% w/w approximately in the case of PICS, BS, and HFCS adulterants; no success with quantification of FGS mixtures was found. These results were confirmed recently by others who succeeded in detecting both the type and the inclusion percentage of adulterants (cane and beet sugar solutions) in maple syrup,[169] using 1800−800 and 3200−2800 cm^{-1} spectral ranges. Recently, FT-MIR was used to determine the geographic origin of saffron samples from four different countries [Greece (n = 40), Iran (n = 87), Italy (n = 60), and Spain (n = 63)].[170] The authors used discriminant analysis on the first 24 principal components obtained from the spectral collection, and the best classification was found (2000−700 cm^{-1}) with an overall correct classification rate of 93.6%; Greek, Iranian, Italian, and Spanish saffron were 90%, 89.5%, 96.7%, and 98.4% correctly classified, respectively (Table 7). These results agreed with those of Kim et al.[171] who reported the ability of FT-MIR to discriminate between strawberry samples of different geographical origins (Japan and Korea) and cultivars (Table 7).

In another approach, Reid et al.[172] compared the ability of FT-MIR and NIR to determine the effect of heat treatment on the quality of apple juice samples produced from four varieties, that is, Bramley, Elstar, Golden Delicious, and Jonagold. Chemometric procedures applied were PLS1 (for differentiation on the basis of heat-treatment), PLS2 (for varietal differentiation), and LDA applied to PC scores. PLS1 produced correct classification rates of 77.2% for heat-treatment by both NIR and MIR, and PLS2 gave correct classification rates between 78.3−100% for MIR spectral data. Although differentiation due to variety achieved higher correct-classification rates than that for heat-treatment, the authors stated that there was much scope for research into the use of FT-MIR for separation of samples according to the heat-treatment, particularly as this is an important food safety issue. Using the same approach, FT-MIR was used to determine changes in the chemical composition of carrot cell walls during treatment with auxin, which causes significant cell elongation.[173] In situ FT-MIR was applied to study the heat stability of proteins and properties of the glassy matrix in slowly dried, desiccation-tolerant and rapidly dried, desiccation-sensitive carrot somatic embryos. Slight but significant differences were observed in the amide I spectral region. Indeed, the amide I band of slowly dried embryos was observed at ∼1654 cm^{-1}, while a shift to lower wavenumbers (∼1632 cm^{-1}) was found in rapidly dried carrots. Another preliminary study pointed out the usefulness of FT-MIR for monitoring the fermentation process of pineapple.[174]

FT-MIR has also demonstrated its ability to determine nutritional parameters and antioxidant capacity of fruits and vegetables.[175,176] Moros et al.[175] analyzed 63 highly heterogeneous samples covering fruit juices and fruit juices with added milk by FT-MIR and reference methods; promising results were obtained. Considering the calibration data collection of 40 samples, an R^2 value of 0.97 and an RMSEP of 0.65% (w/v) were observed. These results were confirmed recently by Bureau et al.[177] who analyzed 757 apricots harvested at different maturation times and belonging to eight different cultivars. The most suitable spectral region lay between 1500 and 900 cm^{-1}, and excellent predictions were observed for the following parameters in apricot slurries: citric acid, malic acid, soluble solids content, and titratable acidity. This confirmed previous findings of the same research group which reported the usefulness of FT-MIR for prediction of sucrose, glucose, fructose, malic, and citric acid contents in apricot.[178] In another study, Lam et al.[179] determined with success the antioxidant capacity in three

Table 7. Application of MIR Spectroscopy to Fruit and Vegetables[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% of correct classification/ assignment bands	reference
differentiation between strawberry and non strawberry jams	not mentioned	diffuse reflectance	4000−800 cm^{-1}	n.a.	n.a.	100% and 91% of the insoluble materials of the jams and jams, respectively	Defernez and Wilson[47]
	baseline correction at 1802 cm^{-1} + normalization of the spectra at the integrated spectral area over the range 1802−899 cm^{-1}	reflectance	1802−899 cm^{-1}	n.a.	n.a.	94.3% of correct classification for strawberry and non strawberry was obtained	Holland et al.[167]
differentiation of apple juice samples on the basis of heat treatment and variety	normalization + first derivative	reflectance	4000−800 cm^{-1}	n.a.	n.a.	heat treatment: 77.2% of correct classification. variety: 78.3−100% of correct classification	Reid et al.[172]
detection of sugar adulterants in apple juice	reduce each spectrum to 16 score values + raw data or first derivative	reflectance	4000−800 cm^{-1}	10−40% w/w of adulterants in apple juice	0.76−0.94	RMSECV: 4.6−9.5 correct classification 82.4−96.5%	Kelly and Downey[168]
discrimination and classification of adulterants in maple syrup	none or first derivative	reflectance	4000−400 cm^{-1}	0−27 g/kg in steps of 5 g/kg	0.91−0.99	SEP = 0.82−1.12	Paradkar et al.[169]
determination of sugar and organic acids in apricot fruits	SNV	reflectance	1500−900 cm^{-1}	glucose: 0.6−5.1% (w/w)	0.87	RMSEP = 0.26	Bureau et al.[177]
				fructose: 0.2−1.7% (w/w)	0.74	RMSEP = 0.15	
				sucrose: 0.3−11.7% (w/w)	0.85	RMSEP = 0.80	
				citric acid: 0.1−41.5 mequiv/100 g	0.96	RMSEP = 1.99	
				malic acid: 0–27.7 mequiv/100 g	0.97	RMSEP = 1.28	
				titratable acidity: 5.6−40.6 mequiv/100 g	0.96	RMSEP = 1.10	
				soluble solids content: 6.9−22.2% Brix	0.92	RMSEP = 0.49	
antioxidant capacity determination	second derivative + smoothing	reflectance	4000−400 cm^{-1}	36.5−142.8 oxygen radical absorbance capacity	0.93	RPD = 5.09	Lam et al.[179]
determination of the geographic origin of saffron	second derivative	diffuse reflectance	4000−400 cm^{-1}			93.6% of correct classification for all the saffron samples (n = 250); 90%, 89.5%, 96.7%, and 98.4% for saffron samples originating from Greece, Iran, Italy, and Spain, respectively	Anastasaki et al.[170]
discrimination of commercial strawberry cultivars	second derivative	reflectance	4000−400 cm^{-1}			100% of samples were correctly classified according to their cultivars and countries	Kim et al.[171]

[a] n.a.: not applicable. SEP: standard error of prediction. RMSEP: root mean square error of prediction. SNV: standard normal variate. RMSECV: root mean square error of cross-validation.

fruit varieties, that is, blueberry, grape, and blackberry. External validation of the model developed using 16 samples for prediction of oxygen radical absorbance capacity (varying between 38.5 and 139.6) was successful with R^2 equal to 0.93 and a RPD of 5.09. FT-MIR was also used for the determination of the degree of methyl esterification of papaya pectins during three ripening stages.[180] The methyl esterification degree was determined on the basis of the intensities at 1740 and 1630 cm^{-1} (which are characteristic of carbonyl groups of galacturonic acid and methyl ester, respectively) using the following formula: $[A_{1740}/(A_{1740} + A_{1630}\ cm^{-1})]$. Results obtained were in agreement with those achieved using an established method.

Some attempts have been made to determine a number of parameters (i.e., carotenoids, sugars, and dry matter, etc.) in carrot roots using both NIR and MIR methods.[181,182] The prediction of dry matter and α- and β-carotene with the two techniques was successful, while the prediction of sugars in carrot roots (fructose, glucose, sucrose) was not satisfactory. Later, the same research group applied ATR-IR spectroscopy (2000−850 cm^{-1}) to develop precise calibration models for the prediction of sugar content. The results showed that, with the exception of sucrose, determination of fructose, glucose, and total sugar to be predicted with high accuracy.

4.8. Coffee

Coffee is one of the most popular beverages in the world. It is comprised of many hundreds of components such as metal ions, volatiles, chlorogenic acid, caffeine, fatty acids, sterols, diterpenic alcohols, tocopherols, and triglycerides. Kemsley et al.[48] successfully discriminated between Arabica and Robusta coffee beans by FT-MIR, reporting 100% correct classification. However, the study was performed on a limited number of samples (20 Arabica, 8 Robusta), and the model needs to be tested on a larger number of bean samples including other coffee varieties before universal application may be recommended. Discrimination between Robusta and Arabica in instant coffees was reported by the same research group when 52 instant coffee samples, 29 pure Arabica and 23 pure Robusta, were scanned by FT-MIR.[49] Using spectra collected in diffuse reflectance, these researchers observed 100% correct classification; the authors[49] attributed this discrimination to differences in the amount of chlorogenic acid and caffeine in Arabica and Robusta varieties. This assumption was later confirmed by Downey et al.[183] as illustrated in Table 8 who attributed absorption bands located in the 1754−1550 and 1298−1149 cm^{-1} regions to caffeine and chlorogenic acid, respectively. These results were confirmed recently by Wang et al.[184] who succeeded in differentiating between Kona and non-Kona coffee mixtures. In another study, Briandet et al.[185] assessed the potential of FT-MIR to discriminate between pure freeze-dried instant coffees and samples adulterated with glucose, starch, or chicory in the range 2−10% (w/w). Using ANN, 100% correct classification for pure and adulterated coffees was observed. The 1800−1680 cm^{-1} carbonyl region (characteristic of vinyl esters/lactones, esters, aldehydes, ketones, and acids) was stated to provide information related to the flavor of brewed coffee.[186] The intensity and duration of heat treatment of the green coffee beans largely contributed to the basic taste and aroma of this product. The same research group found differences in the FT-MIR spectra between brewed Arabica and Robusta coffees. Regarding determina-

Table 8. Application of MIR Spectroscopy to Coffee Products[a]

parameter	data pretreatment	measurement mode	wavenumber range	measured range	R^2	error/% of correct classification/assignment bands	reference
discrimination between coffee species	baseline correction at 1900 cm^{-1} + normalization none	diffuse reflectance	4000−800 cm^{-1}	n.a.	n.a	100% of correct classification	Kemsley et al.[48] and Briandet et al.[49] Downey et al.[183]
Kona coffee authentication	first derivative second derivative mean centering variance scaling	reflectance	4000−400 cm^{-1}	n.a	0.85−0.99	SEP: 0.74−20% 100% of correct classification of Kona coffee mixture and non-Kona coffee mixture	Wang et al.[184]
adulteration detection in instant coffee with glucose, starch, or chicory	baseline correction at 1900 cm^{-1} + normalization	diffuse reflectance or reflectance	4000−800 cm^{-1}	20−100 g/kg	n.a	100% of correct classification	Briandet et al.[185]
determination of caffeine content in coffee	band at 1655 cm^{-1} was used	transmission	3500−700 cm^{-1} not mentioned (deduced from the spectra)	5−40 ppm	n.a	sensitivity: 5 ppm	Singh et al.[187]

[a] n.a.: not applicable.

tion of chemical components in coffee, quantitative prediction of caffeine content with a sensitivity of less than 5 ppm was found on the basis of an absorption band located around 1655 cm^{-1}.[187] This result corroborated previous findings of Suchánek et al.[188] who reported that green coffee could be quantitatively analyzed by FT-MIR spectroscopy.

4.9. Identification of Bacteria in Different Food Systems

The relative advantages of MIR as an alternative to traditional methods for the identification and differentiation of bacteria were assessed in the 1950s as stated by Nelson et al.[189] Unfortunately, due to the poor performance of dispersive spectrometers at that time, the aforementioned studies did not permit accurate bacterial identification. Hardware developments in interferometers and advances in multivariate data analysis tools reawakened interest in utilizing FT-MIR for microbiological analysis. Studies conducted by Amiel et al.[190,191] on the identification of lactic acid bacteria in dairy products allowed discrimination of bacteria at the species level, although only a limited number of strains were investigated. These results corroborated earlier findings of Fehrmann et al.[192] To compare the results obtained by FT-MIR and traditional methods, Amiel et al.[190] analyzed 48 wild isolates of lactic acid bacteria, which were independently identified by biochemical tests and RAPD methods. By applying FDA to the spectral data sets, 100% and 69% correct classification rates were obtained at the genus and species levels, respectively, suggesting that the technique had limited capabilities, especially at the species levels (Table 9). Later, the same research group[191] explored the use of FT-MIR for taxonomical purposes, and their results partially confirmed those of Dellaglio et al.[193] One of the most important conclusions of these studies was that the information contained in FT-MIR spectra could be complementary to genomic information and consequently could be introduced in a polyphasic taxonomic approach. This assumption was confirmed by Lucia et al.[17] who observed changes in the secondary structure of proteins (1700−1500 cm^{-1} related to amide I and II absorbances) of both curds and cheeses inoculated with different strains of *Yarrowia lipolytica* and *Lactococcus lactis*. Recently, Lamprell et al.[194] succeeded in discriminating *Staphylococcus aureus* strains from different species of *Staphylococcus*; additionally, strains of *Staphylococcus aureus* isolated from raw milk and different varieties of French raw milk cheese were identified as such. The results obtained are in agreement with previous findings reporting that FT-MIR was able to discriminate between five species of *Candida*[195] and two strains of *Schizosaccharomyces* and *Saccharomyces cerevisiae*.[196]

Yu and Irudayaraj[197] pointed out that, under different physiological conditions, FT-MIR can provide information related to the bacterial cell wall and also compositional and metabolic information contained in the cytoplasm. This was supported recently by Al-Quadri et al.[198] who succeeded in monitoring biochemical changes in bacterial cells, that is, *Escherichia coli*, *Listeria innocua*, that occurred during bacterial growth. Following the application of PCA to the data sets, a clear discrimination between the four phases (i.e., lag, log, stationary, and death phase) was observed whatever the bacterial cell. To confirm this result, the authors later applied SIMCA, and the percentage of correct classification of the four phases was found to be satisfactory (Table 9). In addition, clear differentiation between bacterial cells was observed, a fact recently discussed by Mietke et al.[199] who succeeded in differentiating between probiotic and wild-type *Bacillus cereus* isolates using FT-MIR. Using the same approach, studies assessed the potential of FT-MIR to detect bacteria in fruit juices.[200−203] Yu et al.[201] applied FT-MIR ATR to apple juices contaminated with eight bacteria at different concentrations (103−108 cfu mL^{-1}). Results showed that FT-MIR can differentiate apple juice contaminated with bacteria at a concentration level of 103 cfu mL^{-1}, corroborating the findings of others[200] who succeeded in using FT-NIR to differentiate pathogenic strains and apple juices contaminated with *E. coli* strains. Recently,[202,203] FTIR was successfully applied to the differentiation of *E. coli* from other bacteria in apple juice. In another approach, Ellis et al.[204−206] quantified spoilage bacteria by FT-MIR and classical plating method, and similar results were obtained by both. These findings were fully supported by Ammor et al.,[98] reporting that FT-MIR spectroscopy could be used for the determination of bacterial loads on meat stored at temper-

Table 9. Application of MIR Spectroscopy to Bacteria Identification

parameter	data pretreatment	measurement mode	wavenumber range	error/% of correct classification/assignment bands	reference
identification of lactic acid bacteria in cheese	normalization to one absorbance unit at 1640 cm^{-1}	reflectance	4000−700 cm^{-1}	100% at the genus and the species level; 86% at the subspecies for collection strains 100% at the genus and 69% at the species level for wild isolate 100% at the genus and 41% at the species level for reference strains collected from other laboratories	Amiel et al.[190]
discrimination of *Staphylococcus aureus* strains from different species of *Staphylococcus*	normalization of the area between 1800 and 750 cm^{-1} to a value of 1	reflectance	3000−750 cm^{-1}	97% of *Staphylococcus aureus* spectra were correctly classified	Lamprell et al.[194]
monitoring bacterial growth of *E. coli* and *L. innocua*	binning + smoothing + second derivative + normalization	reflectance	4000−600 cm^{-1}	*E. coli*: 90%, 96.7%, 93.3%, and 83.3% of correct classification for respectively lag, log, stationary, and death phase *L. innocua*: 76.7%, 90%, 100%, and 76.7% of correct classification for, respectively, lag, log, stationary, and death phase	Al-Qadiri et al.[198]

atures ranging varying from 0−15 °C under both conventional and active packaging.

Although some studies used IR methods to directly determine microorganisms in a food matrix with favorable results, more work needs to be performed to validate this approach in a wide range of foods. FT-MIR may have practical limitations in the long term, unless the specific analysis needed for determining food safety in a particular food system is always tied to one or a few microorganisms.

5. Conclusions and Perspectives

During the past decade, a considerable effort has been made by researchers to explore the possibilities offered by FT-MIR spectroscopy in the field of food science and technology. Chief among the areas of research have been quantitative determination of the main components in food systems and the authentication of food products, particularly those produced using a specific and traditional technology in a limited production region. Quantitative knowledge concerning the main components in food and food products is necessary but not sufficient to predict the technological and organoleptic properties of processed food.

In the present Review, FT-MIR has been shown to demonstrate its ability to determine various properties of food products without the use of chemicals or time-consuming sample preparation. As described in this Review, the FT-MIR spectrum is rich in information on both physical states and molecular structures of the main food components (i.e., lipids, proteins, carbohydrates, etc.). Once the calibration stage is accomplished successfully, the determination of a chemical component of a food or confirmation of its provenance can be carried out very rapidly for minimal running costs. This was demonstrated by examples in which measurement of a given chemical parameter has been appropriately described and validated, as well as situations showing potential applications that require further research and validation. In this context, FT-MIR sensors may provide more specific information than NIR instruments because the information given by the latter is based on molecular overtone and combination vibrations, which are less sensitive and specific. The combination of FT-MIR with other rapid spectroscopic techniques such as fluorescence spectroscopies has, in some applications, provided valuable additional information related to the quality and/or authenticity of food products.

An increased research effort in the field of FT-MIR could address some of the challenges of FT-MIR measurements of food products and further explore the physicochemical changes that are (i) mostly not fully understood and (ii) responsible for the modification of the stability, organoleptic, and/or typicality of food products.

One application of in situ FT-MIR spectroscopy concerns the monitoring and control of cultivation of *Gluconacetobacter xylinus* and production of gluconacetan, a food grade exopolysaccharide.[207] The authors stated that MIR sensors could be considered as powerful tools allowing (i) control of bioprocesses without disturbing the fermentation and (ii) faster bioprocess development and strain characterization. The development of chemometric tools and sensors allows us to foresee the use of FT-MIR in the near future as a tool for online determination of the overall quality of complex food systems.

Even though the present Review focused on food industry products, the principles are broader and generally applicable to other fields (pharmaceutical, biotechnology, etc.). It is therefore expected that in the coming years, FT-MIR combined with chemometric tools will continue to grow as a reliable tool for understanding the molecular basis of food structure and, as a consequence, food quality.

6. References

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