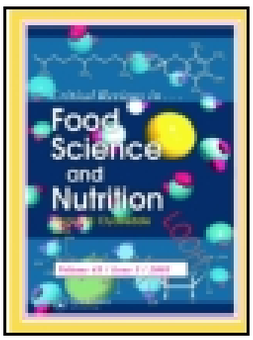

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REVIEW

Spectroscopic techniques for monitoring changes in the quality of milk and other dairy products during processing and storage

Mohammed Loudiyi[a], Havva Tümay Temiz[b], Amna Sahar[c], Muhammad Haseeb Ahmad[d], Oumayma Boukria[e], Abdo Hassoun[f], and Abderrahmane Aït-Kaddour[a]

[a]Université Clermont Auvergne, INRAE, UMRF, Aurillac, France; [b]Department of Food Engineering, Bingol University, Bingol, Turkey; [c]Department of Food Engineering/National Institute of Food Science and Technology, University of Agriculture Faisalabad, Faisalabad, Pakistan; [d]Department of Food Science, Govt. College University, Faisalabad, Pakistan; [e]Applied Organic Chemistry Laboratory, Sciences and Techniques Faculty, Sidi Mohamed Ben Abedallah University, Fez, Morocco; [f]Nofima, Norwegian Institute of Food, Norway Tromsø

ABSTRACT

The application of spectroscopic techniques can help in alleviating problems encountered during the processing of milk and dairy products. Indeed, traditional analytical methods (e.g., physico-chemical measurements, sensory, chromatography) are relatively expensive, time-consuming, and require chemicals and sophisticated analytical equipment, and skilled operators. Hence, there is a need to develop faster and less costly methods for accurately monitoring changes in the quality of milk and other dairy products during processing and storage.

Many nondestructive and noninvasive instrumental techniques are available for inline and online monitoring of food. These include fluorescence spectroscopy, mid-infrared (MIR), near-infrared (NIR), nuclear magnetic resonance (NMR), etc. These techniques are usually used in combination with chemometric tools a to explore the information present in spectral data.

This review article will discuss the potential of the above-mentioned spectroscopic techniques for monitoring chemical modifications of dairy products and the prediction of their functional properties during processing. The advantages and disadvantages of each technique are also discussed in this review. Finally, some conclusions are drawn, and the future trends of these methods are presented.

KEYWORDS

Spectrocopy; infrared; fluorescence; dairy products

Introduction

The popularity of milk can be attributed mainly to its numerous end-use applications (e.g., cheese, butter, milk powder). Recent changes in consumer lifestyles have led to innovative and less costly models of dairy products, especially regarding cheese consumption, e.g., in many types of fondue, pizza, French bread pizzas, or different sauces. In addition to the importance of flavor, the texture of the cheese and its functional attributes, such as free oil, viscoelasticity, stretching properties, color, etc (Guinee et al. 2015) are considered as an essential factor. Researchers are now focusing on developing numerous empirical and instrumental techniques to quantify and evaluate the functional properties of cheese, milk, and other dairy products (Rodriguez-Saona et al. 2006). In this context, chromatography, enzymatic techniques, atomic absorption spectroscopy, immunochemical assays, and mass spectrometry, among others, have been widely used. However, almost all of the analytical methodologies based on these techniques require a number of manipulations to make sample properties suitable for measurements. These manipulations often consist of multiple steps, including treatment with chemical enzymes, isolation, thermal treatment, homogenization, filtration, among others (Zöllner and Mayer-Helm 2006). All quantifications and characterizations are sample-destructive and most are often performed offline. Consequently, there remains a need for accurate, rapid, nondestructive, and cost-effective techniques that measure the functional properties of dairy products during processing in order to optimize the process and obtain the targeted food quality.

The modern dairy industry requires online and inline testing methods that measure the functional properties of dairy processing, so the measurements can be used to make real-time adjustments to the formulation or manufacturing procedure. The development of new, simple, and rapid methods that can be applied to monitor dairy processing has been the focus of research over the last few decades. Among them, spectroscopic techniques based on electromagnetic waves (Figure 1), such as ultraviolet-visible (UV-VIS: 100–750 nm), fluorescence (250–550 nm), near-infrared (NIR: 700–2500 nm), mid-infrared (MIR: 2500 nm–25 μm), and nuclear magnetic resonance (NMR:

CONTACT Abderrahmane Aït-Kaddour abderrahmane.aitkaddour@vetagro-sup.fr Université Clermont Auvergne, INRAE, UMRF, F-15000 Aurillac, France; A. Sahar amnasahar@uaf.edu.pk Department of Food Engineering/National Institute of Food Science and Technology, University of Agriculture Faisalabad, Faisalabad, Pakistan

This article has been corrected with minor changes. These changes do not impact the academic content of the article.

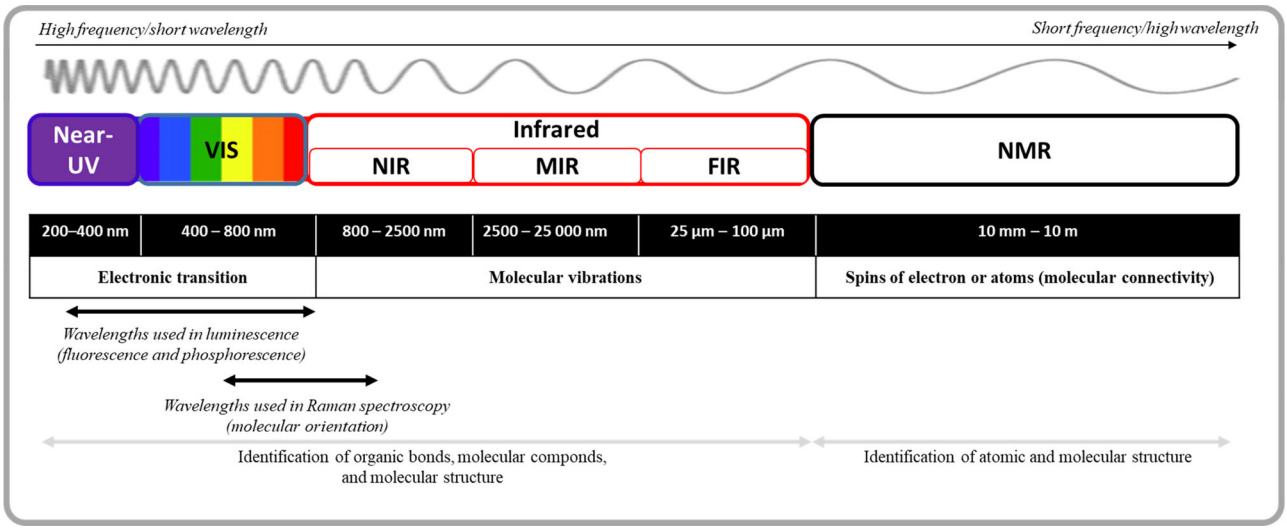

Figure 1. Principle of different electromagnetic techniques used to analyze milk and dairy products.

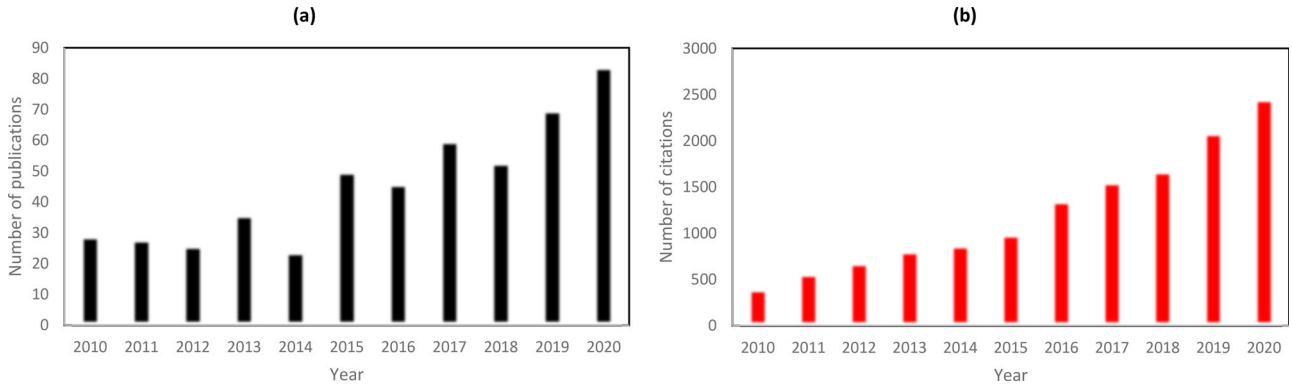

Figure 2. Number of publications (a) and citations (b) dealing with the use of spectroscopic techniques for monitoring changes in quality of milk or other dairy products. Data were obtained using Scopus (November 2020). Research criteria: TITLE-ABS-KEY (milk) OR (dairy product) AND (spectroscopy) AND (quality).

100 cm–10 m) spectroscopies, have been proposed. Some of these techniques (e.g., NIR, MIR, and fluorescence spectroscopy) have been widely used in the dairy industry for the evaluation of the gross composition of milk and dairy product (Müller and Steinhart 2007; Wold, Jørgensen, and Lundby 2002; Tsenkova et al. 1999). Due to the high potential of spectroscopic techniques, a vast number of papers about the use of these techniques for the evaluation of dairy products have been published continually in the literature. As can be seen in Figure 2, this number of publications for monitoring of quality characteristics of milk and its various products has increased from 30 to more than 80 from last ten years (2010 to 2020). However, until now, there has been no review in the literature focusing on a description of the use of these methods to delineate modification at the molecular structure and changes in composition of dairy products during processing and/or storage. Therefore, this review paper aims to provide a complete summary of the most relevant spectroscopic techniques, especially NIR, MIR, fluorescence, and NMR spectroscopies for both monitoring the chemical modification of dairy products, especially cheeses during processing and predicting their sensory and meltability properties. Specific examples exemplifying the application of these electromagnetic wave techniques will be presented, and their advantages and disadvantages will be discussed.

Fluorescence spectroscopy

General features

The phenomenon of fluorescence was previously described in detail in different scientific papers and books (Jakob Christensen et al. 2006; Sádecká and Tóthová 2007; Lackowicz 1999; Wolfbeis 2012). Briefly, fluorescence is the emission of lower energy light by a fluorescent molecule or fluorophore following the absorption of UV or VIS light. These molecules can be hydrophilic, hydrophobic, or even amphiphilic.

Fluorescence spectra can be recorded using the right angle mode or the front-face mode. The first mode can be used only with a low concentrated solution because, when the absorbance of the sample is higher than 0.05, the screening effect (or inner filter effect) induces a decrease in fluorescence intensity and a distortion of both excitation and emission spectra (Lackowicz 1999; Lakhal, Acha, and Aussenac 2012; Kamal and Karoui 2015). This limitation can be easily overcome by simple dilution of the sample until it reaches the appropriate absorbance value. Nonetheless, the results obtained on diluted solutions, for

example, a food product, cannot be extrapolated to its raw materials, in particular when the information sought concerns changes in conformations due to proximity or interactions between molecules. The second one, Front Face Fluorescence Spectroscopy (FFFS), was proposed to analyze concentrated samples (absorbance $>$ 0.05) directly (without dilution). In this case, analysis is performed at the surface and over a few micrometers in thickness. The emitted photons are collected, in theory, at an angle of 30°-60° with respect to the sample to minimize the collection of reflected photons. In both right angle and front face modes, excitation and emission spectra are recorded at a fixed wavelength, which is determined based on a prior knowledge of the fluorophores (e.g., tryptophan, vitamin A, riboflavin, lipid oxidation products, NADH, etc.) present in the food product being analyzed. Since the early 2000s, numerous research studies have been carried out on the potential of this method to characterize several food products such as milk, cheese, meat, fish, eggs, honey, etc. (Dufour, Frencia, and Kane 2003; Karoui and Blecker 2011; Sahar et al. 2009).

Without knowledge of the sample characteristics, the acquisition of a fluorescence emission excitation matrix (EEM) can be performed. The emission and excitation monochromators are used successively to measure the emission spectra for different excitations. The obtained EEM is a matrix containing excitation wavelengths, emission wavelengths, and fluorescence intensity. The EEM is a fluorescence map of all the fluorophores present in the system, providing a complete picture of the sample. However, the acquisition of the EEM spectra is time-consuming (about 30 to 40 minutes as compared to a few seconds in the case of FFFS at fixed excitation or emission wavelength). A good compromise between the acquisition of excitation spectra, emission spectra, and EEM is the Synchronous Fluorescence Spectroscopy (SFS). As with EEM, SFS has the advantage of being able to characterize several fluorophores from a single spectrum but in a shorter time. The use of this screening mode is advantageous when the manipulator is not familiar with the sample to be analyzed or the fluorophores contained in the sample. SFS has recently been introduced for food product analysis and has proved to be very useful in many applications. Indeed, several recent investigations have demonstrated the potential of SFS for studying various quality parameters (Aït-Kaddour et al. 2018; Liu et al. 2012; Sahar et al. 2016). Depending on the scan mode (i.e., constant rate, constant frequency, variable rate), three basic types of SFS can be performed (Patra and Mishra, 2002). However, to date, the most popular one in food analysis is known as constant-wavelength SFS, which consists of keeping a fixed wavelength interval, noted $\Delta\lambda$ ($= \lambda$em - λ ex) between excitation and emission monochromators.

These different advantages of fluorescence spectroscopy (i.e., sensitivity, specificity) and the commoditization of the chemometric methods convinced researchers to use this technique to investigate the quality of several dairy products, such as milk (Karoui, Martin, and Dufour, 2005; Mungkarndee et al. 2016), cheese (Christensen, Povlsen, and Sørensen 2003; Karoui et al. 2004; Loudiyi et al. 2017a,b), and yogurt (Christensen, Becker, and Frederiksen 2005) (Table 1). Indeed, dairy products contain different natural fluorescent molecules (e.g., vitamin A, tryptophan, riboflavin) and fluorescent compounds such as FMRP (Fluorescence Maillard Reaction Products) and lactulose, which can appear after processing (e.g., heat treatment). Their fluorophores have a unique signature (excitation and emission spectra) that can be used wisely to monitor changes in the quality of dairy products during processing and to predict their functional properties.

Monitoring thermal treatments

Technological treatments of milk, such as thermal processing, impact the sensory properties of milk which ultimately affects dairy products quality, like cheese. For example, it is well-known that thermal treatment results in the Maillard reaction between lactose and proteins (Gliguem et al. 2005; Martins, Jongen, and Van-Boekel 2001), and also cause changes in the structure of the components. Thus, it is of the utmost importance to monitor the effect of heat treatment on milk and milk products in order to control the quality of the final dairy product. In this context, FFFS was used by Kulmyrzaev, Levieux, and Dufour (2005) to evaluate changes in cow's milk following thermal treatments (57–72 °C for 0.5 up to 30 minute). The results of PCA (Principal Components Analysis) calibration model, when applied to the normalized spectra (aromatic amino acids, NADH, and FADH), showed good differentiation of milk samples when subjected to different temperatures and lengths of thermal treatment. By using the same chemometric tool and similar heating conditions (55 and 75 °C from 0.5 up to 30 minutes), Karoui and Kamal (2017) confirmed this investigation on camel's milk by analyzing its vitamin A fluorescence spectra. Moreover, the analysis of NADH, FMRP, and vitamin A by CCSWA (Common Components and Specific Weight Analysis) showed a better differentiation between milk samples heated at high temperatures (70 °C and 75 °C) compared to other heating conditions. The comparison between the accuracy of the fluorescent probes revealed that the FMRP probe was the most sensitive at detecting changes in milk as a function of heat treatment and holding time. Similarly, FFFS was applied to infant milk formula prepared by spray drying at different temperatures (72 °C, 95 °C and 115 °C). The infant milk formula was stored for one year at two storage temperatures (15 °C and 37 °C) before the spectra were taken in the tryptophan and vitamin A region. The results of the PLSR (Partial Least Squares Regression) model applied to tryptophan spectra were able to predict the pre-drying heat treatment temperature, soluble protein content, and storage time accurately with lower root mean square error of cross-validation (RMSECV). The results of PLS-DA (Partial Least Squares Discriminant Analyisis) can also discriminate between liquid and powder infant milk formula with respect to storage time. Given results were for cross-validated PLSR and PLS-DA models in the study (Henihan et al. 2018).

The quality of the cheese is highly dependent on the quality of the milk (e.g., animal breed, fat content, and

Table 1. Some examples of studies which applied fluorescence spectroscopy to monitor chemical modification of dairy products during processing and for predicting their functional properties (sensory and meltability).

Dairy product	Aim of the study	Fluophore	Chemometric tools	Reference
Cow milk	- Discrimination of milk samples subjected to heat treatment and homogenization	Vitamin A, tryptophan	PCA	(Dufour and Riaublanc 1997)
	- Evaluate changes in milk following thermal treatments	AAA, NADH, FADH	PCA	(Kulmyrzaev, Levieux, and Dufour 2005)
	- Investigate, at a molecular level, structure evolution during different milk coagulation process	Tryptophan	PCA	(Herbert et al. 1999)
	- Investigate the potential of SFS in the characterization of milk during mild heating and acidification	Offsets: from 20 to 240 nm with ($\Delta\lambda = 20$)	PCA, PARAFAC	(Boubellouta and Dufour 2008)
	- Investigate the potential of SFS in the characterization of milk after mineral addition (citrate, phosphate and citrate)	Offsets: 80 nm	PCA	(Boubellouta, Galtier, and Dufour 2009)
Camel milk	- Characterize changes occurring in milk by the application of mild heat treatment (55-77 °C)	Vitamin A, NADH, FMRP	PCA, CCSWA	(Karoui and Kamal 2017)
Yoghurt	- Monitoring of the oxidative stability and quality of yoghurt during storage by FFFS	Excitation: 270 to 550 nm Emission: 310 to 590 nm	PARAFAC	(Christensen, Becker, and Frederiksen 2005)
	- Evaluate the potential of FFFS to evaluate the effect of packaging (polylactate and polystyrene) and light on the oxidation of yoghurt during storage		PCA, PLSR	(Miquel Becker et al. 2003)
Cheese	- Evaluation of maillard browning and oxidative stability of process cheese during storage by FFFS	Excitation: 270 to 550 nm Emission: 310 to 590 nm	PARAFAC	(Christensen, Povlsen, and Sørensen 2003)
	- Monitoring the modification affecting proteins during cheese ripening	Tryptophan	CCSWA, CCA	(Mazerolles et al. 2002)
	- Discrimination of Emmental cheeses according to their origin		PCA, FDA	(Karoui et al. 2005)
	- Investigate the changes of tryptophan fluorescence spectra during cheese ripening		PCA, CCA	(Mazerolles et al. 2001)
	- Discrimination of the different soft cheese according to their manufacturing process	Vitamin A, tryptophan	PCA, FDA	(Herbert et al. 2000)
	- Investigate the potential of FFFS to monitor structural changes and meltability of cheese in correlation with rheological parameters		PCA, FDA, CCA	(Karoui, Laguet, and Dufour 2003)
	- Delineate texture characteristics of Salers cheese by sensory analysis, rheological measurements and FFFS		PCA, CCA, PCR	(Lebecque et al. 2001)
	- Investigate changes at molecular and macroscopic levels of young and ripened soft-cheeses using rheology, MIR and FFFS		CCSWA	(Kulmyrzaev et al. 2005)
	- Investigate the potential of SFS to monitor gentle heating of cheeses varying in their salt contents and type	Offsets: from 20 to 80 nm with ($\Delta\lambda = 120$)	ICA	(Loudiyi et al. 2017b)
	- Investigate the potential of SFS to monitor gentle heating and cooling of cheeses varying in their salt contents and type			(Loudiyi et al. 2017a)
	- Investigate the reliability of dynamic testing rheology, MIR and SFS to evaluate the meltability and the viscoelastic behavior of a semi-hard cheese	Offset: 80 nm	PCA, CCSWA	(Boubellouta and Dufour 2012)

protein content) and heat treatment (e.g., thermization, pasteurization) applied during manufacturing. In this context, the discrimination of cheeses according to the heating process applied to milk (i.e., raw and thermised), has been investigated by Karoui et al. (2004) and Karoui et al. (2005) who analyzed Emmental cheeses via the tryptophan fluorescence spectra (ex: 290 nm; em: 340 nm). The authors reported that this fluorescence probe spectra coupled with PCA could discriminate Emmental cheeses produced from raw and thermized milk. In this study, the tryptophan probe was the only fluorophore considered. Nonetheless, it would be of interest to compare these results with changes in the shape and intensity of the vitamin A fluorescence spectra, which also were found to be a valuable probe characterization of cheeses. Developed models were externally validated for all three studies. (Herbert et al. 2000).

Monitoring milk coagulation and syneresis

Milk coagulation is the most significant step in the development of the texture of most dairy products (e.g., cheeses, yogurts); it also governs their quality. The first study conducted on the monitoring of milk coagulation via fluorescence spectroscopy was investigated by Herbert et al. (1999). In this study, it was demonstrated that FFFS coupled with PCA was capable of detecting specific structural changes in casein micelles. The results were dependent on the three coagulation processes studied (i.e., glucono-δ-lactone-GDL-, rennet, and a mixed system containing both glucono-δ-lactone and rennet). In another study, Boubellouta and Dufour (2008) also reported the ability of fluorescence spectroscopy using SFS mode to monitor chemical modifications

occurring during milk coagulation at two different temperatures (30 °C and 40 °C), which confirmed previous investigations. The SFS spectra were collected in the 250–550 nm excitation wavelength range using 11 offsets (i.e., 20, 40, 80, 100, 120, 140, 160, 180, 200 and 240 nm) to obtain a more in-depth overview of the chemical phenomenon occurring during milk coagulation via GDL. Due to the 3 D structure of the data, PARAFAC (Parallel Factor Analysis) was applied and permitted to extract three fluorophores assigned to tryptophan (ex: 292; em: 342 nm), vitamin A (ex: 323; em: 423 nm), and riboflavin (ex: 460; em: 520 nm). During the acidification experiment, the authors observed drastic changes in the concentration modes of the three components for the sample with a pH below 5.6, in accordance with structural changes occurring in casein micelles. In a recent study (Boukria et al. 2020), SFS coupled with 2DCOS (two-dimensional correlation spectroscopy) was proposed to determine differences between five milk mixtures containing camel's milk (CaM) and cow's milk (CM) (i.e., 100% CaM, 75% CaM:25% CM, 50% CaM:50% CM, 25% CaM:75% CM, and 100% CM) at the molecular level. The 2DCOS-SFS method highlighted dissimilarities among the different formulations on both synchronous and asynchronous maps. In addition, according to Noda's rule, the rate of molecular structure modification in fluorescence probes (riboflavin, tryptophan, and vitamin A) matches with common coagulation phenomena, which are generally reported during enzymatic coagulation of milk. This study demonstrated that 2DCOS-SFS is a successful strategy to discriminate between milk mixtures and to monitor molecular structure modifications during the coagulation process. After the study of milk coagulation via a decrease in pH and an enzymatic procedure, Boubellouta, Galtier, and Dufour (2009) studied the chemical modifications of skim milk after mineral addition (0, 3, 6 and 9 mM of calcium (Ca), phosphate or citrate) at 30 °C and 4 °C. After applying PCA to the spectral collection, the authors reported that the phenomena induced by the addition of phosphate were different from those observed following the addition of Ca, citrate, or a Ca-chelating agent. In the last two studies, only the 80 nm offset was used to study the chemical modification of milk during processing. This offset was proposed because the spectra obtained exhibited a higher number of fluorescence bands compared to the previously studied offset, and it can be considered a strong candidate for monitoring the manufacturing process in the dairy industry.

Monitoring dairy products during storage and ripening

Monitoring oxidative stability

The oxidative stability of dairy products is of interest to the dairy industry. The oxidation processes in milk can lead to strong off-flavors and in deterioration of the nutritional quality of milk, making the oxidized milk unacceptable to consumers. Christensen, Becker, and Frederiksen (2005) used PARAFAC analysis and FFFS (i.e., excitation range: 270–550 nm and emission range: 310–590 nm) for monitoring the oxidative stability and quality of yogurt during storage. PARAFAC analysis of the fluorescence landscapes exhibited three fluorophores, all strongly related to the storage conditions of the yogurt. The loading profiles of the 1st, 2nd, and 3rd components were assigned respectively to riboflavin, tryptophan, and lumichrom (the oxidative product of riboflavin). Regression models between fluorescence landscapes and riboflavin content, determined by traditional chemical analysis, were performed, yielding a RMSECV of 0.09 ppm of riboflavin. This corresponded to 7% of the mean riboflavin content in the yogurt sample. The researchers concluded that fluorescence spectroscopy, in combination with chemometric tools, has potential as a rapid method for monitoring the oxidative stability and quality of yogurt. This finding was in accordance with Miquel Becker et al. (2003) who studied the effect of packaging (polylactate and polystyrene) and light on the oxidation of yogurt during storage from 0 to 35 days via FFFS (excitation range: 270–550 nm; emission range: 310 to 590 nm). Regarding yogurt samples stored for 35 days in light, tryptophan seemed to be present, while the riboflavin signal decreased considerably.

Wold, Jørgensen, and Lundby (2002) demonstrated the potential of FFFS to assess the oxidation of different dairy products such as Swiss cheese, cream cheese, and sour cream stored under different conditions (at 4 °C, in light with exposure to air, in light with no exposure to air, in darkness with exposure to air, and in darkness without exposure to air). The results showed a significant decrease in the fluorescence intensity at approximately 525 nm and a corresponding increase in the 415 – 490 nm spectral regions. This effect was ascribed to photo-degradation of riboflavin as a result of illumination. Moreover, variations observed in two small peaks located around 620 and 630 nm were related to the interaction between light exposure to light and exposure air. Christensen, Povlsen, and Sørensen (2003) reported an equivalent study on cheese during storage in darkness and light up to 259 days, at 5, 20, and 37 °C, respectively. Fluorescence landscapes with excitation from 240–360 nm and emissions in the range of 275–475 nm were analyzed by PARAFAC. The results of the fluorescence landscapes exhibited four fluorophores associated to tryptophan (ex: 300 nm; em: 347 nm; ex: 280 nm; em: 339 nm), vitamin A (ex: 320 nm; em: 411 nm), and a compound derived from oxidation products (ex: 360 nm; em: 431 nm). All fluorophores showed a change in the fluorescence signal corresponding to the storage time and the grade of oxidation, suggesting that fluorescence spectroscopy in combination with chemometrics has potential as a fast method for monitoring the stability of processed cheese.

Monitoring structural and textural modifications

The texture of cheese, at both the molecular and macroscopic levels, is influenced by many factors including milk origin, milk treatment (e.g., homogenization, heat treatment), type of starter, amount of starter added (Baer, Ryba, and Casey 1997), ripening time (Pillonel et al. 2002), and manufacturing and storage conditions (e.g., temperature, salt content) (Loudiyi et al. 2017a,b). Fluorescence spectroscopy

has been reported by different authors as a promising tool for exploring the development of texture during ripening (Dufour et al. 2000; Dufour et al. 2001; Garimella, Prow, and Metzger 2005) (Table 1). Herbert et al. (2000) used the tryptophan (ex: 290 nm) and vitamin A (em: 410 nm) spectra to discriminate between eight groups of soft cheeses as a function of their cheese-making procedure and ripening time. The authors reported that the environment of tryptophan residues was relatively more hydrophilic for the old cheeses than for those analyzed at an earlier stage. This phenomenon was assigned to both the partial proteolysis of caseins resulting in an increase of tryptophan exposure to the solvent and an increase of pH during ripening, which modified the tertiary and quaternary structure of casein micelles. Thus, FDA (Factorial Discriminant Analysis) was applied to the most relevant PCs to test the accuracy of FFFS for differentiating between the soft cheeses. The authors obtained a slightly better classification with vitamin A spectra (96 and 93% for the calibration and validation samples, respectively) compared to tryptophan spectra (95 and 92% for the calibration and validation samples, respectively). However, in their investigations, the authors used only samples from the center of the cheeses, which limited interpretation in the case of soft cheeses and restricted the possibility of utilizing this technique for real-time control of cheese ripening. These results were confirmed by Karoui and Dufour (2003), who identified differences between spectral features of the surface and the center of the cheeses. The authors reported that the tryptophan fluorescence spectra were larger for the external zone than for those of the central zone. The environment of tryptophan residues at the molecular level was found to be more heterogeneous in the surface samples than in the center. These differences were attributed to an increase in the capacity of water sorption by caseins.

Prediction of cheese functional properties

Changes in cheese during ripening were also described with fluorescence spectra (Table 1), with traditional methods such as sensory, chemical, and rheological measurements, used for reference. For example, Dufour et al. (2001) applied Principal Component Regression (PCR) to predict sensory variables from the tryptophan fluorescence spectra in soft cheese and found squared correlations between fluorescence spectra and sensory texture attributes of 0.13–0.69. This observation corresponds well with the findings of Lebecque et al. (2001), who obtained an R^2 below 0.5 in the prediction of sensory attributes from fluorescence tryptophan spectra. Better results were achieved using fluorescence vitamin A spectra on Salers cheese with an R^2 of 0.78, 0.61, 0.52, and 0.52 for deformability, friability, adhesivity, and microstructure, respectively. Nonetheless, no cross-validation or validation of the models were performed during this study. However, these findings confirm the work of Herbert (1999), who found a high correlation ($R^2 > 0.5$) between sensory attributes and vitamin A spectra in the study of soft cheeses. This suggests that measurements conducted at a molecular level by fluorescence spectroscopy can be related to macroscopic measurements determined via sensory analysis.

The previous conclusion was confirmed by the same team (Karoui, Laguet, and Dufour 2003), which investigated the potential of FFFS to monitor structural changes and the meltability of Comté, Emmental, and Raclette cheeses in correlation with their rheological parameters measured from 5 to 60 °C. PCA applied to the emission and to the excitation spectra of tryptophan and vitamin A provided good differentiation between cheese samples as a function of temperature. Canonical Correlation Analysis (CCA) applied to dynamic oscillatory rheology measurements and fluorescence spectra (tryptophan and vitamin A) showed high correlations as the squared canonical coefficients for canonical variables 1 and 2 were of 0.94 and 0.49, respectively. Similar results regarding the melting temperatures of fat (i.e., 30, 32, and 31 °C for Emmental, Comté, and Raclette respectively) were obtained from dynamic oscillatory rheology data (i.e., considering the complex viscosity-*-parameter) and the analysis of variation of the intensities of the vitamin A emission fluorescence spectra (ratio of the 322 and 295 nm peaks) during heating. This finding was later confirmed by Karoui, De-Baerdemaeker, and Dufour (2008).

In another study, Karoui and Dufour (2006), used PLSR in conjunction with tryptophan and riboflavin fluorescence spectra recorded at 20, 35, and 80 °C to predict the storage modulus (G′), loss modulus (G″), strain, loss tangent (tan δ), and complex viscosity (η^*) of 20 semi-hard cheeses ripened for 2, 30 and 60 days. The results from their study showed that using PLSR, tryptophan fluorescence spectra recorded at 20 °C on 2-day-old cheeses predicted G′, G″, strain, tan δ, and η^* measured at 80 °C on the 60-day-old cheeses with R^2 of 0.96, 0.94, 0.96, 0.96 and 0.94, respectively. However, riboflavin fluorescence spectra gave slightly lower R^2 values of 0.77, 0.77, 0.85, 0.76, and 0.77 for G′, G″, strain, tan δ, and η^* respectively. Centered data was used for the calibration whereas internal validation was performed through leverage corrections to determine the authenticity of all these predicted models. The potential of FFFS to predict the meltability of processed cheese spreads and products was also investigated by Garimella, Prow, and Metzger (2005) on twenty-seven commercial samples from three manufacturers. Fluorescence spectra of tryptophan (ex: 290 nm; em: 305 to 400 nm) were collected on each sample at 20 °C. Additionally, dynamic oscillatory rheometry was applied to each sample in order to calculate the meltability index (the temperature at tan $\delta = 1$). A prediction model using PLSR and cross-validation method gave a high correlation coefficient of 0.93 between fluorescence spectra and cheese meltability. Also, a negative correlation ($R \approx -0.8$) between the peak of tryptophan (335−350 nm) and the cheese meltability index was observed. The authors noted that this correlation may be due to the presence of tryptophan residues in the more hydrophobic environment of stronger emulsions as compared to the more polar environment of weaker emulsions. These results indicated that the melting properties of processed cheese spreads and products are related to a molecular structure that can be measured

using FFFS. Hence, FFFS can be used as a technique to predict the meltability of processed cheese. Recently, Ozbekova and Kulmyrzaev (2017) investigated the potential of fluorescence spectroscopy to predict rheological characteristics (yield stress and flow stress, G′, and G″ measured at the linear-viscoelastic region - LVE), melting temperatures using temperature sweep tests (from 20 to 70 °C) and chemical composition of Tilsit (semi-hard) cheeses. Emission spectra of tryptophan residues (305–480 nm, ex: 290 nm) and vitamin A (340–620 nm, ex: 322 nm), and excitation spectra of vitamin A (250–350 nm, em: 410 nm) were recorded from 20 to 70 °C. PCA and PLSR were applied to the fluorescence spectra to extract information on the rheological properties, chemical composition, and melting temperatures. The results of PCA applied to the spectra (tryptophan emission, vitamin A emission, and excitation) obtained at 25 °C showed that discrimination between cheeses was dependent on their chemical composition. Considering the LVE region of the oscillation tests, the best regression model ($R^2 = 0.82$) to predict G′ and G″ was obtained by applying PLSR to the tryptophan emission spectra of the cheeses. Yield stress and flow stress were predicted with $R^2 = 0.90$ from the vitamin A emission and excitation spectra, respectively. Melting temperatures, moisture, protein, and fat contents were also predicted from the vitamin A emission spectra with $R^2 = 0.98$.

In a similar approach, Boubellouta and Dufour (2012) studied the structure at the molecular level and rheology characteristics of Comté (hard cheese) and Raclette (semi-hard cheese) cheeses as a function of temperature via dynamic oscillatory rheology and SFS. The results of SFS provided relevant information related to the cheese protein and fat structures during melting, allowing the study of their structural changes. In addition, the authors confirmed that the temperatures of fat and cheese melting could be derived from analysis of the variation in the fluorescence intensity of the 322 and 295 nm bands, respectively. More recently, Loudiyi et al. (2017a) demonstrated that direct analysis of the proportions of the independent components associated with vitamin A after Independent Components Analysis (ICA) could be used for the evaluation of fat melting in Cantal-type cheeses (i.e., Cheddar like cheese) with varying in their salt contents (0.5% NaCl, 1% NaCl, 2% NaCl, 1.5/0.5% NaCl/KCl, 1/1% NaCl/KCl). However, in a similar study, Loudiyi et al. (2017b) failed to predict cheese matrix melting using this method. They clearly reported that chemical modification due to levels of salt and ripening time could be monitored by tryptophan, vitamin A, riboflavin, and FMRP bands after applying ICA (Loudiyi et al. 2017a,b). Recently the sensory evaluation index of Cheddar cheese was predicted using the PLS model applied to fluorescence data. The authors found a higher coefficient of determination for calibration ($R = 0.8$) and the predicted value showed comparable accuracy with other conventional methods (Chiba et al. 2019).

Advantages and disadvantages

The detailed overview presented above clearly suggests that fluorescence spectroscopy coupled with chemometric tools is a valuable method for both monitoring chemical changes during processing offering a potential for process control of dairy products and for predicting their sensory, rheology, and melting properties. In comparison with light absorption measurements, fluorescence spectroscopy is more sensitive (i.e., 1000 times more sensitive and specific than infrared techniques), because the measured signal has, in principle, zero background. In addition, fluorescent compounds are susceptible to their environment and offer the possibility of characterizing molecular interactions and reactions.

Despite the exciting potential of this technique and its high sensitivity for the characterization of milk and dairy products during processing, the interpretation of fluorescence spectra is still challenging, likely due to the complexity of the food products (composition and anisotropy) being studied. Indeed, the use of single-pair emission-excitation wavelengths can be severely limited by the overlap of spectra and inner filter effects (in which non-fluorescence compounds absorb the excitation radiation or that emitted by target fluorophore). Moreover, when fluorescence spectroscopy is used for the analysis of complex matrices, emission from one fluorophore can excite one of the compounds, quenching the fluorescence from the target compounds (Lourenço et al. 2012). These phenomena create difficulty in associating a clear and specific physicochemical phenomenon to the variation of the bands, especially when using classical FFFS. This has been depicted by the different studies published to date that used endogenous fluorophores for food analysis. Using the SFS and EEM as multidimensional fluorescence can provide a better overview of the biochemical phenomenon occurring during processing. In the future, efforts need to be made by the spectrometer designers in terms of the spectral acquisition time in order to make this technique more compatible with the requirement of the industry. Fluorescence imaging using a multispectral device can also be a powerful strategy to give a clearer picture of the undergoing chemical modification during food processing due to its ability to gather both spectral and spatial information.

To date, only the Amaltheys® device developed by Spectralys Innovation has been proposed to the dairy industry for predicting quality parameters of dairy products. In contrast, a higher industrial application can be found in the other wavelength regions that imply absorption phenomena, such as infrared spectroscopy (NIR and MIR).

Infrared spectroscopy

General features

Infrared (IR) spectroscopy is a technique used to monitor the absorption and reflection of light (Luykx and van Ruth 2008). IR spectroscopy is a quicker, cheaper, and more sensitive technique for monitoring and characterizing the food matrix that demands no skillful analyst. The IR wavelength range is generally classified into three spectral regions: the near-infrared, mid-infrared, and far-infrared. The near-infrared (NIR) ranges from 14,000 to 4000 cm^{-1}, the mid-infrared (MIR) ranges 4000–400 cm^{-1}, and the far-infrared falls

between 400 and 10 cm^{-1}. NIR spectroscopy is the most frequently used method in many branches of industry, while MIR spectroscopy has proved to be very useful for the analysis of milk and dairy products.

Milk analysis using MIR equipment is generally more accurate for chemical interpretation of vibrational bands than the corresponding NIR method. This is because MIR contains more specific information (i.e., fundamental absorptions) and stronger signals than NIR due to overtones and combination bands observed in this wavelength range. In addition, the spectrum of dairy products that can be observed with instruments based on Fourier transform infrared (FTIR) spectroscopy showed promising results with regard to the number of components (e.g., specific sugars, casein, and urea) that can be measured (Hewavitharana and van Brakel 1997).

MIR spectroscopy

MIR spectroscopy is a rapid and reliable technique that makes it possible to simultaneously obtain specific information about different chemical and structural parameters, mainly in the 4000–400 cm^{-1} region, because these bands are associated with vibrations of functional groups of molecules. These bands are associated with different components of milk and cheese such as proteins, fats, lactose, and lactic acid (Dufour et al. 2000; Karoui and Debaerdemaeker 2007; Kishor and Thakur 2015; Santos et al. 2013). MIR spectroscopy has been widely used for measuring cheese composition (Rodriguez-Saona et al. 2006), sensory, meltability attributes, and instrumental texture parameters (Fagan et al. 2007a,b). This technique can be also used for different authenticity issues such as the determination of the geographic origin of cheese (Karoui et al. 2004; Karoui et al. 2005) in the last decade as shown in Table 2.

Typically, the MIR region can be classified into three spectral sub-regions: 3000–2800 cm^{-1}, 1700–1500 cm^{-1} and 1500–900 cm^{-1}. There are two strong bands in the range of 3000–2800 cm^{-1}, which are associated with methylene antisymmetric (2920 cm^{-1}) and symmetric stretching (2845 cm^{-1}) modes (Casal and Mantsch 1984). Weaker bands resulting from the asymmetric and symmetric stretching modes at 2955 and 2870 cm^{-1} are due to the terminal methyl groups (CH_3). The variation in bands taken for methyl and methylene groups clearly differentiate between the semi-hard (Dufour et al. 2000), soft (Kulmyrzaev et al. 2005), and experimental bovine (Lanciotti et al. 2005) cheeses. Dufour et al. (2000) used this region to identify fatty acids and to determine the polymorphic behavior of membrane phospholipids and cheese triglycerides. These authors also described changes in the peaks of methyl and methylene and the ratio of Aνas CH_2/Aνas CH_3 during ripening.

The second region (1700–1500 cm^{-1}) is dominated by an amide I band around 1655 cm^{-1} and an amide II band at about 1550 cm^{-1}, related to peptide bonds of proteins. The amide I band is mainly due to the stretching of the C = O group, while the amide II band is primarily characterized by a combination of the swing phase in the N–H group and the C–N stretching. This part of the MIR spectra is generally used to investigate the secondary structures of proteins (Boubellouta and Dufour 2012). An absorption band around 1615 cm^{-1} has been assigned to the side chains of protein (Abbott et al. 1991), while protein aggregation was linked to the variations around 1620 cm^{-1} (Dufour et al. 1994). The water band has very strong absorption around 1640 cm^{-1} (O–H band), which could overlap with other fundamental vibrations such as amide I (C–N stretch and C=O stretch, 1655 cm^{-1}) (Yang and Irudayaraj 2001). Furthermore, some information related to soluble carboxylic acids, such as lactates, can be obtained by the absorption band around 1575 cm^{-1} (Picque et al. 1993). The evolution of amide bands was also described for different varieties of cheeses. Modifications in the intensity and position of various peaks in the Amide I band have been associated with changes in casein secondary structure (e.g., α-helix, ß-sheet and unordered), protein aggregation, and protein/water interaction (Cadesky et al. 2017; Grewal, Huppertz, and Vasiljevic 2018; Kulmyrzaev et al. 2005).

Monitoring of cheese ripening

The characterization of the chemical parameters of cheeses during ripening and the impact of the season have been investigated in different studies. One of the earliest studies that identified the potential of MIR spectroscopy to determine the age of Cheddar cheese undergoing ripening was performed by Chen, Irudayaraj, and McMahon (1998). Based on this analysis, Dufour et al. (2000) used MIR spectral data to study structural variations of 16 semi-hard cheeses during ripening. PCA was applied to spectral data and showed a clear contrast among the cheese samples at various stages of the ripening process. Moreover, a shift of the methylene bands during ripening was observed and attributed to the changes in the structure of triglycerides acyl chains in fat globules. In 2001, Mazerolles et al. (2001) demonstrated that MIR spectroscopy could be used to monitor the ripening process of cheese by analyzing only modifications to the secondary protein structure (i.e., amide I band at 1675, 1652, 1640 and 1627 cm^{-1}) of the cheese. In another investigation, Mazerolles et al. (2002) used the MIR spectroscopic technique to study the behavior of protein during cheese ripening by using different chemometric methods (PCA, CCSWA, and CCA) and found that MIR was an efficient tool for monitoring the modifications of proteins that were observed during the ripening process. Similarly, Wang et al. (2011) applied different chemometric tools, self-deconvolution, second derivative analysis, and band curve fitting of the amide I band to study the proteins secondary structure modifications of cheddar cheese during ripening (i.e., 10, 60, 120 and 180 days). The authors found a series of changes in the secondary structure (i.e., a decrease in α-helix content and an increase in the ß-sheet content) with the progression of ripening time. Based on their results, the authors determined that casein hydrolysis strengthened the

Table 2. Some examples of studies which applied MIR spectroscopy to monitor chemical modification of dairy products during processing and for predicting their functional properties (sensory and meltability).

Dairy product	Aim of the study	Wavelength range	Chemometric tools	Reference
Cow milk	- Evaluate the feasibility to apply MIR-microspectroscopy to detect and quantify milk adulteration	4000-700 cm^{-1}	SIMCA, PLSR	(Santos, Pereira-Filho, and Rodriguez-Saona 2013)
	- Examine the effectiveness of MIR spectroscopy in predicting milk fat globule size	5000-900 cm^{-1}	PLSR	(Fleming et al. 2017)
Milk	- Investigate the potential of PLS method coupled with FT-MIR for discovery and measurement of milk corruption	4000-600 cm^{-1}	PLSR	(Kishor and Thakur 2015)
Yoghurt	- Evaluate the potential of MIR for quantitative detection of whey in samples of milk powder via the measurement of the presence of glycomacropeptide	4000-600 cm^{-1}	PCA, PLSR, DA	(De Carvalho et al. 2015)
Cheese	- Use of MIR spectroscopy to follow texture development in full-fat and reduced-fat Cheddar cheese during ripening	4000-400 cm^{-1}	MLR	(Irudayaraj, Chen, and McMahon 1999)
	- Flavor quality analysis of cheese using FT-IR spectroscopy		SIMCA, PCA	(Subramanian, Harper, and Rodriguez-Saona 2009)
	- Investigate the use of FTIR: ATR spectroscopy for measurement of fat, protein, and moisture content in Swiss cheese		PLSR	(Rodriguez-Saona et al. 2006)
	- Investigate the changes of FTIR spectra in the methylene region and of vitamin A fluorescence spectra during ripening of semi-hard cheese	3000-2780 cm^{-1}	PCA, CCA	(Dufour et al. 2000)
	- Monitoring the modifications affecting proteins during cheese ripening	3000-900 cm^{-1}	CCSWA, CCA	(Mazerolles et al. 2002)
	- Study the reliability and accuracy of MIR and FFF spectroscopies coupled with chemometric methods for identifying Saint-Nectaire cheeses manufactured under different conditions		PCA, FDA	(Boubellouta et al. 2010)
	- Assess the potential of the VIS-NIR and MIR spectroscopies to determine differences between the sampling zones and manufacturing process of ripened soft cheese			(Karoui et al. 2006)
	- Investigate the changes of FTIR spectra in the Amide I and II regions and of tryptophan fluorescence spectra from semi-hard cheeses during ripening		PCA, CCA	(Mazerolles et al. 2001)
	- Changes at molecular and macroscopic levels of young and ripened soft-cheeses using rheology, MIR and FFFS	3000-2800 cm^{-1} 1700-1500 cm^{-1} 1500-900 cm^{-1}	CCSWA	(Kulmyrzaev et al. 2005)
	- Investigate the reliability and accuracy of dynamic testing rheology, MIR and SFS to evaluate the meltability and the viscoelastic behavior of a semi-hard cheese		PCA, CCSWA	(Boubellouta and Dufour 2012)
	- Assess the potential of NIR, MIR, and FF spectroscopies using multivariate statistical methods to discriminate Emmental cheeses originating from different European countries		PCA, FDA, CCSWA	(Karoui et al. 2005)
	- Determination of the geographic origin of Gruyere PDO and L'Etivaz PDO Swiss cheeses		PCA, FDA	(Karoui et al. 2007)
	- Prediction of instrumental texture and meltability attributes of processed cheese using MIR spectroscopy and chemometric tools	4000-640 cm^{-1}	PCA, PLSR	(Fagan et al. 2007a)
	- The potential of MIR spectroscopy for determination of selected sensory attributes in processed cheese samples			(Fagan et al. 2007b)
	- Determining the geographic origin of Emmental cheeses produced during winter and summer using MIR and FS data	4000-900 cm^{-1}	PCA, FDA	(Karoui et al. 2004)
	- Examine the feasibility of using the NIR and MIR spectroscopic techniques for the determination of chemical parameters (pH, WSN, NPN, NaCl and fat) of European Emmental cheeses with different origin		PLS	(Karoui et al. 2006)
	- Evaluate the suitability of FTIR to follow the evolution of physicochemical parameters throughout ripening of Camembert-type cheeses	4000-650 cm^{-1}	PCA, PLSR	(Martín-del-Campo et al. 2007)

hydrogen bonds, which is responsible for such a shift in the structure.

Although monitoring the ripening process is a challenging task, the studies reported above demonstrated that MIR spectroscopy can be a powerful tool for performing this task. The characteristics of cheeses during ripening is another essential parameter that can be predicted by MIR spectroscopy. The spectral fingerprints of ATR-FTIR were used to predict the ripening date of Camembert cheese, with a precision of ±1 day via the PLSR method. Following the same logic, Lerma-Garcia et al. (2010) used FTIR spectral information for the classification of Pecorino cheese with

respect to ripening time in hard and semi-hard cheeses. Production techniques (for fossa and non-fossa cheeses) were also identified using the same approach. Similarly, Crescenza cheese was ripened for 20 days and the critical day (i.e., the sixth day) was determined using FTIR spectroscopic approach (Cattaneo et al. 2005)

Most of the studies reported above focused on the spectral signature of proteins; nonetheless, the signature of carbonyl groups can also be considered, as reported by Rodriguez-Saona et al. (2006). The authors developed a fast, simple, and reliable screening tool to predict the composition of Swiss cheese by using FTIR-attenuated total reflection (FTIR-ATR) spectroscopy coupled with PLSR. The authors reported that the FTIR-ATR could classify the cheese based on their manufacturer and aging time by extracting useful information from the spectral fingerprints related to carbonyl groups, likely due to their distinctive lipid composition.

Monitoring functionality of cheese

The potential ability of MIR spectroscopy for predicting chemical groups and its sensitivity to structural changes in different food products led various researchers to evaluate the properties of MIR spectroscopy coupled with multivariate data analysis to predict functional properties of cheeses, such as sensory and meltability attributes. Fagan et al. (2007b) used multidimensional statistical analysis (i.e., PLSR) on MIR spectral data for the prediction of instrumental texture (i.e., texture profile analysis) and meltability attributes. The authors reported that cohesiveness (R^2 = 0.81) and Olson and Price meltability (R^2 = 0.81) could be predicted, whereas hardness and springiness models showed relatively poor predictions (R^2 = 0.77) after full cross-validation. For the computer vision meltability, the model after full cross-validation was able to discriminate between high and low melt values (R^2 = 0.64). Furthermore, the same authors (Fagan et al. 2007a) reported in another study that MIR spectroscopy, in conjunction with PLSR, could predict several sensory characteristics of cheese. Indeed, the range of error ratio (RER) values of the calculated models varied between 7.2 and 9.6, after cross-validation confirming previous results reported by Irudayaraj, Chen, and McMahon (1999) on full-fat Cheddar cheese (FFCC) and reduced-fat (RFCC) Cheddar cheese during ripening. The authors demonstrated that springiness had a better correlation, compared to hardness and adhesiveness, with the bands at 1741, 1167 and 2850 cm^{-1} (R(CO)X, C–C, and C–N stretch) for FFCC and at 1116 and 1744 cm^{-1} (R(CO)X and C–O in fat and protein) for RFCC. The correlation coefficients corresponding to the respective wavenumbers were 0.7, 0.62, and 0.53 for FFCC and 0.33 and 0.33 for RFCC.

The flavor of the cheese is also an important parameter and was predicted to determine the quality of cheese via MIR spectroscopy (Table 2). In this regard, Kocaoglu-Vurma et al. (2009) used simple solvent extraction technique along with attenuated total reflectance infrared spectroscopy for the classification of Swiss cheese with respect to flavor quality. The authors applied soft independent modeling of class analogy (SIMCA) for classification and PLSR models for prediction of sensory attributes of swiss cheese produced by different manufacturers in various regions from spectral information taken with attenuated total reflectance infrared spectroscopy. Based on SIMCA classification models, cheese samples can be easily placed in different classes according to the region and manufacturer as they differ from each other with respect to flavor profile such as fermented, unclean, low flavor, sour, and good Cheddar. Similarly, the PLSR models shows high values (0.69–0.96) of correlation coeffient for validation that indicates the authenticity of predictive models. In the same year, these results were confirmed by Subramanian, Harper, and Rodriguez-Saona (2009), who applied the same approach on Cheddar cheese and found a clear separation between the different cheese clusters based on the flavor of the cheese. The authors reported that the MIR spectra could be correlated to specific flavor notes such as fermented, sour, and unclean, and could be classified using chemometric models. Moreover, they reported that after using the SIMCA model the discrimination between the samples was mainly attributable to organic acids, fatty acids and their esters, and amino acids (1450 to 1350 and 1200 to 990 cm^{-1}), which are known to contribute significantly to cheese flavor.

In addition to this, Cantal cheese was heated at different temperatures (20 –70 °C) to determine the behavior of heat treatment using ATR-MIR spectroscopy. The ATR-MIR spectra were taken in different regions as shown in Figure 3. It was observed that the absorbance of light shows a clear demarcation at various temperature treatments which is due to the changes in the functional properties of the cheese that ultimately conclude the potentional of this ATR-MIR spectroscopy. Such results can be utilized to develop authentic chemometric models that can serve the current need to develop rapid and non invasive methologies for monitoring of various parameterts of dairy products.

Advantages and disadvantages

The dairy related research work presented above demonstrates that MIR spectroscopy is a widely used method presumably due to its simplicity of use, high repeatability, and high sensitivity, while offering high-quality spectra. In addition, when an ATR crystal is available, the technique can be used even for samples containing high levels of water. Moreover, MIR absorption bands are highly specific, which generally makes the interpretation of the variation in the spectral bands easy, especially when coupled with accurate chemometric tools.

These characteristics encouraged researchers and manufacturers to explore this technique to monitor chemical modifications occurring during dairy product processing for process control and to predict the sensory and melting properties of dairy products. Nonetheless, this method is highly sensitive to water vibration, which can lead to a problematic interpretation of chemical bands (i.e., the secondary structure of the protein in the amide I and II regions) and its inline implementation appears complicated. This technique is also unable to determine substances that are present in very low

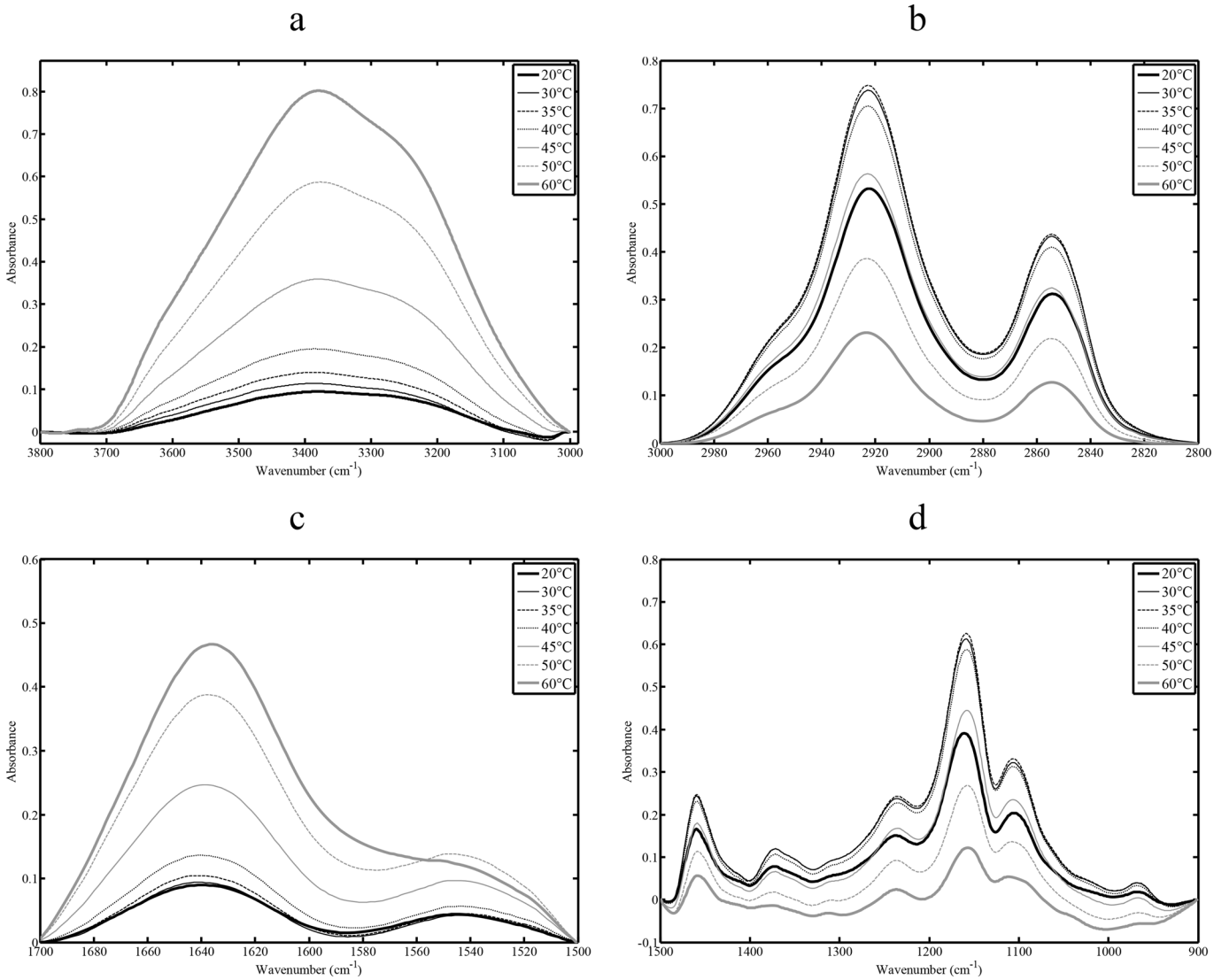

Figure 3. ATR-MIR spectra ([a] 3800–3000 cm^{-1}; [b] 3000–2800 cm^{-1}, [c] 1700–1500 cm^{-1} and [d] 1500–900 cm^{-1}) recorded during heating (20–60 °C) of Cantal type cheese (Loudiyi and Ait-Kaddour 2018).

concentrations in milk and dairy products. Likewise, the noise level of this method may be a hurdle for achieving accurate measurements (Table 2) (Boubellouta et al. 2010; Karoui et al. 2006a,b; Kishor and Thakur 2015; Santos et al. 2013; Hansen and Holroyad 2019; Yaman 2020).

NIR spectroscopy

NIR spectroscopy is being applied to the monitoring and characterization of various parameters of pharmaceutical products, related materials, agricultural and food commodities with little or no sample preparation. This technique has proven its ability for at-line, in-line, and on-line process control due to its rapid, nondestructive, and low running costs. It can simultaneously identify several components of food in a sample within a short time (Rodriguez-Otero, Hermida, and Centeno, 1997). This technique can also use longer path lengths as compared to the MIR (i.e., optical fibers made from quartz glass). NIR signals are associated with molecular vibrations, specifically the overtones and combinations of fundamental vibrations. Chemical bonds present in the light atoms (i.e., C–H, O–H, and N–H) show high vibrational frequencies and result in overtone and combination bands that can be detected in the NIR region (14000–4000 cm^{-1}) (Osborne, Fearn, and Hindle, 1993). NIR spectroscopy is a valuable tool to measure the four key components, including lipids, carbohydrates, proteins, and water. The region for water absorptions is present between 1471 and 1923 nm (6800 and 5200 cm^{-1}), whereas, the methyl group of proteins and lipids can be found at 2174 and 2380 nm (4600–4200 cm^{-1}). Furthermore, the terminal methyl groups can be detected at approximately 1220 and 1724 nm (8200 and 5800 cm^{-1}).

Over the last decades, NIR spectroscopy has shown its potential in various applications of the dairy industry, especially in cheese and milk processing. The rennet coagulation of milk was defined using the NIR spectroscopic approach (Cipolat-Gotet, et al. 2012; Klandar, Lagaude, and Chevalier-Lucia 2007; Laporte, Martel, and Paquin 1998; Lyndgaard, Engelsen, and Van Den Berg 2012; O'Callaghan, O'Donnell, and Payne 2000). This technique was also employed to characterize reconstituted skim milk powder (Giardina et al.

2004) and to investigate lactose-free milk during storage (Giardina, Cattaneo, and Barzaghi 2003). Similarly, NIR spectroscopy has also been extensively used i) to determine the physicochemical parameters of milk and cheeses, such as moisture, fat, protein, dry matter, and total solids (Adamopoulos, Goula, and Petropakis 2001; Da Costa Filho and Volery 2005; González-Martín et al. 2014; Lucas et al. 2008; Mazerolles, Duboz, and Hugot 2000; Purnomoadi et al. 1999) as well as the physicochemical parameters of butter (Hermida et al. 2001; Heussen et al. 2007), ii) to predict moisture, fat and inorganic salts in processed cheeses (Blazquez et al. 2004) and to anticipate sensory properties in a large variety of cheeses (Blazquez et al. 2006; Downey et al. 2005), and iii) for the determination of peptides (González-Martín et al. 2009), texture (Blazquez et al. 2006; Revilla et al. 2009), and the degree of ripening (Burns and Ciurczak 1992; Cattaneo et al. 2005) in cheese (Table 3).

Monitoring milk coagulation

Cipolat-Gotet et al. (2012) compared milk coagulation properties measured via a traditional mechanical device (i.e., the Formagraph) and a NIR optical device, the Optigraph. Individual milk samples of 913 Brown Swiss cows from 63 herds located in Trento Province (Italy) were analyzed for rennet coagulation time, curd-firming time, and two measures of curd firmness using the two instruments mentioned above under identical conditions. The authors reported that optical instruments that record NIR signals are promising tools for identifying rennet coagulation time (RCT, min), curd-firming time (k20, min), and the two measures of curd firmness. In another study, Giardina et al. (2004) used 2 D-NIR-COSS to study the rearrangement of water molecules during the process of milk rennet coagulation. They analyzed the water combination band at 1930 nm via a two-dimensional analysis of NIR/NIR spectra. Absorptions above 1924 nm suggested that the process involves H-bonded water molecules rather than free molecules and more specific molecules with one-H-bond.

Monitoring quality of cheese and milk during storage

NIR spectroscopy was used to study the effects of temperature and the number of days of storage on the final quality of 122 delactosated milk samples (Giardina, Cattaneo, and Barzaghi 2003). The authors compared spectral data with colorimetric results obtained from Tristimulus Colorimetry. They found that it is possible to identify samples based on the number of days of storage, demonstrating the feasibility of NIR spectroscopy to show the structural modifications of milk components that occur during storage.

Da Costa Filho and Volery (2005) used NIR spectroscopy to quantify the total solid contents of fresh cheeses, manufactured with low, medium, and high solid contents. The spectra were recorded between 400 and 1700 nm. Various calibrations were built using different spectral ranges, and the best model was obtained using the range between 960 and 1700 nm. The selection of this spectral range is reasonable because the second overtone of the OH stretching band at 970 nm, the combination of the first overtone of the OH stretching and the OH bending band at 1190 nm, and the first overtone of the OH stretching band at 1450 nm emerge in this range. Good discrimination of cheeses according to their solid contents was noted, highlighting the possibility of using NIR spectroscopy to monitor the solid content of cheese products during processings.

Online monitoring of critical control points (e.g., before pressing, after pressing, and after salting) is important for determining the quality of cheese. Eskildsen and his coworkers (2019) used these three critical points to predict dry matter and fat contents in Swiss cheese blocks using the PLSR model built on NIR data with the following specification of scanning reflection (908–1676 nm), scanning interaction (760–1040 nm), and imaging interaction measurements (760–1040 nm). The authors used different approaches for the validation of PLSR models. However, the best results were found using cross validation method where RMSECV for dry matter (0.64%) and fat contents (0.44%) were recorded. In contrast, fat and protein contents were determined with greater accuracy in goat cheese whey from NIR spectral data using the PLS model (Galdino et al. 2020).

In another study performed by Skeie et al. (2006), free amino acids generated during the ripening of rindless Norvegia and Präst cheeses were predicted via NIR spectral fingerprints in the region between 780-2500 nm using univariate and PLSR models. Overlapping signals were observed due to the presence of different components such as water, amino acids, and lipids. However, some peaks were allocated to different bands. The peaks at 940–970 nm were assigned to the second overtone O–H and C–H stretches, whereas the peaks at 1154 nm peak were allocated to the second overtone C–H stretch. Similarly, the peaks in the 1330–1600 nm region were associated with the first overtone O–H and N–H in amino and amide groups. The 1654 nm peak was related to amino and amide groups. The peaks at 1724–1762 nm were assigned to first overtone C–H stretches. The 1940 nm region matched with the first overtone O–H stretches, and the 2124 nm band was related to amide groups. The authors reported good prediction of free amino acids (e.g. aspartate, serine, methionine, threonine, glutamate, valine) and the total amount of free amino acids in grated cheese during the ripening process using NIR spectral data. Similarly, various parameters of processed cheese (e.g. moisture, fat, and inorganic salts) were predicted from NIR reflectance spectroscopy (Blazquez et al. 2004). Moreover, this technique was also employed to monitor the cheese-making process as discussed by Adamopoulos, Goula, and Petropakis (2001). The author recorded the NIR spectra during the manufacturing of traditional Feta cheese. The bands at 1940, 2180 and 2310 nm were allocated to moisture, protein, and fat, respectively. A computer program (i.e., Instalab 600-Dickey-John) was used to calibrate the models, which were further validated using an independent set of analyzed samples. The authors concluded that this technique as precise and rapid information for process control of cheese production.

Table 3. Some examples of studies which applied NIR spectroscopy to monitor chemical modification of dairy products during processing.

Dairy product	Aim of the study	Wavelength range	Chemometric tools	Reference
Camel milk	- Assess the potential of NIR for the detection of adulteration in camel milk with goat milk	1000-2500 nm	PLS-DA, PCA, PLSR	(Mabood et al. 2017)
Milk powder	- Provide information related to milk coagulation using NIR		PCA	(Lyndgaard, Engelsen, and Van Den Berg 2012)
Cow milk	- Develop a NIR reflectance optic monitoring rennet coagulation of milk		MPLS	(Laporte, Martel, and Paquin 1998)
	- investigate whether different feed sources affect the accuracy of NIR spectroscopy for the prediction of milk fat and protein contents	Fat: 1720 and 2300-2350 nm Protein: 1,51,82,17,22,226 and 1748 nm	MLR	(Purnomoadi et al. 1999)
Butters	- Assess the feasibility of using NIR for butter authentication	714-2500 nm	PCA, PLS-DA, PLSR	(Heussen et al. 2007)
	- Analysis moisture, solid-non-fat and fat, without any previous sample treatment using NIR spectroscopy	400-2500 nm	PCA, MLR, PCR, MPLS	(Hermida et al. 2001)
Cheese	- Determination of moisture and fat contents in hard and semi-hard cheeses by NIR spectroscopy	800-1100 nm	PLSR	(Mazerolles, Duboz, and Hugot 2000)
	- Use of NIR spectroscopy to the measurement of texture (sensory and instrumental) in experimental processed cheeses	750-2498 nm	PLSR	(Blazquez et al. 2006)
	- Use of NIR spectroscopy as a quality control tool during the production process of feta cheese	Moisture: 1,94 μm Protein: 2,18 μm Fat: 2,13 and 2,33 μm	LR	(Adamopoulos, Goula, and Petropakis 2001)
	- Compare the performance of broad-based versus specific NIRS calibration in their ability to accurately predict the total solids content of the five types of fresh cheeses	400-1700 nm (visible/NIR)	PCA, PLSR	(Da Costa Filho and Volery 2005)
	- Use of the VIS-NIR reflectance spectroscopy for the prediction of dry matter, fat, pH, vitamins, minerals, carotenoids, total antioxidant capacity, and color in fresh and freeze-dried cheeses	400-2500 nm (visible/NIR)	MPLS	(Lucas et al. 2008)
	- Use of NIR spectroscopy for the prediction of consistency and flavor properties of semi-hard cheese	1100-2500 nm	PCA, PLSR	(Sørensen and Jepsen 1998)
	- Investigate the utility of NIR reflectance spectroscopy for the determination of maturation and selected sensory parameters in Cheddar cheese	400-2498 nm	PCA, PLSR	(Downey et al. 2005)
	- Use of FT-NIR spectroscopy to evaluate the self-life period in Crescenza cheeses	1200-4000 nm	PCA	(Cattaneo et al. 2005)
	- Use of NIR spectroscopy to predict the development of selected free amino acids during cheese ripening	780-2500 nm	PLSR	(Skeie et al. 2006)
	- Prediction of mineral content of fresh cheeses using NIR spectroscopy	Reflectance mode: 866-2530 nm Transmittance mode: 850-1050 nm	PLSR	(Manuelian et al. 2017)
	- Examine the feasibility of using the NIR and MIR techniques for the determination of chemical parameters of European Emmental cheeses with different origin	1000-2500 nm	PLSR	(Karoui et al. 2006)
	- Assess the potential of NIR, MIR and FF spectroscopies using multivariate statistical methods to discriminate Emmental cheeses originating from different European countries		PCA, FDA, CCSWA	(Karoui et al. 2005)
	- Use of NIR spectroscopy for the identification of cheeses made with different milks	1100-2000 nm	MPLS	(Revilla et al. 2009)
	- Use of NIR spectroscopy for the analysis of volatile compounds in cheeses		MPLS	(González-Martín et al. 2014)

Furthermore, Manuelian et al. (2017a) predicted the minerals and fatty acid profile of cheese using NIR transmittance (NIT) spectroscopy in the region 850–1050 nm. The authors applied this technique to cheese samples prepared from different milk species and ripened the samples for varying lengths of time. The spectral data correlated with the mineral and fatty acid profile required using a modified partial least squares regression (MPLS). The researchers noted that minerals (e.g., Ca, P, S, Mg, and Zn), the major fatty acids (FAs) like myristic, palmitic, and oleic acids as well as, some minor FAs can also be predicted using spectral data. These results proved that NIT spectroscopy can be

utilized as an appropriate method for predicting the most abundant minerals and FAs found in cheese during process control and optimization in the production of cheese. Conversely, in another study, the authors (Manuelian et al., 2017b) demonstrated that mineral (e.g., Ca, K, Mg, P, and Na) content was difficult to predict using NIR (reflectance mod: 866–2530 nm or transmittance mode: 850–1050 nm) for 130 samples of Mozzarella and 118 samples of Stracchino cheeses; likely due to the indirect sensitivity of NIR spectroscopy on these components.

In addition, the freshness of Crescenza (an Italian fresh cheese) was identified by Cattaneo et al. (2005) using NIR-Fourier transform infrared (FT-NIR) (from 12,000 to 4000 cm^{-1}). The authors determined various absorption bands for milk components such as water (7270, 7070, 5420, 5290 and 5030 cm^{-1}) and fat (8250, 5990 and 5770 cm^{-1}) in the spectral fingerprints. A clear classification of three groups of cheeses according to their freshness was also observed. Hence the authors concluded that this technique could be applied as a suitable method for the evaluation and characterization of the freshness of Crescenza cheese.

Monitoring functional properties of dairy products

NIR spectroscopy was also used for the monitoring of sensory attributes. Sørensen and Jepsen (1998) applied this technology to study the sensory characteristics of semi-hard cheese using NIR spectroscopy in transmittance mode (850–1050 nm) and reflectance mode (1110–2490 nm). In this study, cheese from thirty-two batches, prepared with modification of undesired bacteria that variated in the pH and moisture content, were measured during ripening at 5, 7, 9, and 11 weeks The use of PLSR demonstrated that the previous wavelength regions were suitable for monitoring and predicting the consistency and flavor attributes ($0.7 < R^2 < 0.8$) of cheeses. These results were confirmed by Karoui et al. (2006), who reported that NIR spectroscopy could be suited to predict the sensory attributes of Emmental cheeses. The authenticity of predictive models were confirmed by RER which has been calculated by dividing the constituent's range by its error of prediction. The RER was between 5 and 7 for most of the characteristics (with one of 10 and one of 3.5), while the ratio performance deviation (RPD = Standard deviation/RMSECV) was largely between 1.5 and 2. The results confirmed the findings of Downey et al. (2005) who predicted the ripening time and sensory attributes of twenty-four Cheddar cheeses produced with five renneting enzymes and stored at 4 °C for up to nine months. Researchers constructed a PLSR model applied to the spectral ranges 750–1098 nm and 1100–2498 nm. The former spectral range produced more accurate results, demonstrating its suitability in predicting the maturity and sensory attributes (i.e., crumbly, rubbery, chewy, etc.) of cheese samples.

So far, a limited number of research articles pertaining to the prediction of textural characteristics of cheese using NIR spectroscopy have been published. In this regard, the sensory and textural parameters of experimental processed cheeses stored for 2 and 4 weeks at 4 °C were predicted with the help of PLSR that was developed with NIR reflectance data obtained in the range of 750–2498 nm (Blazquez et al. 2006). The authors reported that firmness, meltability, rubberiness, and creaminess can be projected using this technique. In the same context, Revilla et al. (2009) developed models for the prediction of the instrumental texture of 96 hard ewe's cheeses using NIR spectroscopy in combination with chemometric tools. The MPLS regression method was used to obtain the NIR equations. The calibration, with multiple correlation coefficients (RSQ) of 0.961 and standard error of prediction (SEP) of 2.1 N, allowed determining texture in the range 0.0–49.0 N. The RPD (the ratio of the standard deviation of reference data in validation set samples to SEP) value obtained was 5.4, indicating that the NIR equation was applicable to unknown samples.

Advantages and disadvantages

NIR spectroscopy is gaining popularity in the monitoring of different industrial process operations due to its low running costs. It is considered to be a rapid, reliable, and environmentally friendly technique that can be used for real-time measurements in various online applications. However, the online monitoring of the process is challenging due to factors such as variation in temperature and moving samples. In addition, NIR cannot determine the low concentration (concentrations below 0.1% (w/w)) of components present in a food sample. The low structural selectivity of NIR is due to the overlap of different overtone and combination bands as compared to MIR radiation, through which many fundamentals can be observed at discrete positions. Such overlapping of signals makes the interpretation more difficult than in the conventional MIR spectrum. This problem in NIR makes it difficult to study the secondary structure of proteins in dairy products. The higher amount of moisture in the food sample also poses a problem for the interpretation of NIR signals, as NIR signals scatter the light and water absorption bands, which interferes with the signals at which important chemical characteristics can be observed (Williams and Norris 1987).

Furthermore, the complex matrix of food and the heterogeneity of the intact sample makes it challenging to obtain accurate results. Therefore, different preprocessing methods are being used to remove the abnormalities induced in the spectra for obtaining the accurate and precise chemometric models for classification and prediction. Light scattering is the physical phenomenon in NIR spectra that can be eliminated by multiplicatve scatter effect, standardard normal variate and normalization whereas spectra derivatives can be done by using Savitzky-Golay and Norris-william that remove the multiplicative as well as additive effects in the spectral data for getting accurate subsequent chemometric models. The main aim of numerous studies was to develop real-time online measurements but not to perform them, a fact that is often not explicitly stated in the research. Therefore, there is a need to classify the semi-industrial and industrial applications that may assist with the discovery of practically relevant applications of NIR spectroscopy.

Nuclear magnetic resonance spectroscopy

General features

NMR is used to study opaque, heterogeneous samples and has proved its worth in various useful applications in dairy research (Duce et al. 1995). The basic principle of NMR is the absorption and emission of energy in the radio frequency range of the electromagnetic spectrum. The nuclei having odd numbers of protons or neutrons, like ^{1}H and ^{13}C are the most studied, but nuclei from the isotopes of many other elements (e.g., ^{23}Na, ^{31}P, etc.) can also be observed.Hence, NMR spectroscopy can be utilized to study the complete molecular structure of a food sample by showing the interactions of an individual atomic nucleus that is dependent upon the atoms surrounding it. For the various types of food and food products, high-resolution NMR (HR-NMR) (which utilizes frequencies above 100 MHz) is usually preferable compared to low-resolution NMR (LR-NMR) (which uses frequencies of 10–40 MHz), as HR-NMR provides more detailed information regarding the molecular structure of a food sample. However, HR-NMR is the most expensive analytical techniques to employ. Therefore, LR-NMR has proved to be very useful in the food industry (Tellier and Mariette 1995; Nordon, McGill, and Littlejohn 2001). The potential of NMR to track changes in major and minor components occurring upon the application of different process conditions has been reported in the literature (Belloque, De La Fuente, and Ramos 2000; Hubbard et al. 2002; Huppertz et al. 2006; Kamatari et al. 2004; Sørensen et al. 2014; Sørensen et al. 2015).

Monitoring high-pressure milk processing

One of the first studies on NMR characterization was conducted in 1972 by Chandan, Cullen, and Chapman, who used ^{1}H NMR to study the molecular structure of the freeze-dried milk fat globule membrane (MFGM). In this study, the authors identified the resonance pattern of different protons in lipids and proteins for the purpose of differentiating MFGM from other biological membranes and concluded that the MFGM is structurally and functionally distinct from the others (Chandan, Cullen, and Chapman 1972). Based on these results, NMR was identified as a potential technique for monitoring the homogenization procedure of milk. Homogenization is a step that prevents the creaming of milk during storage by applying high pressure, which breaks larger fat globules into smaller ones. One-dimensional (^{1}H, ^{13}C) and two-dimensional (^{1}H-^{13}C, ^{1}H-^{15}N, ^{1}H-^{31}P) NMR were used to study this phenomenon (Hu et al. 2004). The authors observed a significant variation between homogenized milk and non-homogenized milk in both signal-to-noise and resolution on the NMR spectra. Moreover, they reported that non-homogenized milk showed broad resonances due to very large milk fat globules, which were ultimately reduced to smaller-sized globules in the homogenized milk. This study proved the potential of NMR to assess the size of milk fat globules and, therefore, its suitability for monitoring this step during milk processing.

In a recent study (Yang et al. 2020), the effect of cycled high-pressure processing on the structural changes in macromolecules and the level of small molecules in whole and skimmed milk samples were investigated using high-field liquid state ^{1}H NMR. The signal differences for the two different milk samples were observed in terms of resonance intensities ascribed to fatty acyl chains and lactose. The applied process resulted in a slight reduction in the amide N-H region of NMR resonances, which was explained by changes in protein conformations.

Monitoring milk coagulation process

Maintaining the correct amount of water in or out of milk gel is essential for obtaining the desired quality in dairy products (i.e., cheese, yogurt, quark, etc). van Vliet and Walstra (1994) used rheometry, permeametry, and NMR spectroscopy to investigate this phenomenon. The authors concluded that because the structure of the casein aggregates is strongly dependent on the temperature and pH of milk rather than the presence of bound water, casein aggregates are also responsible for the ease of water removal from the gel. Within this context, they utilized an inverse correlation between spin-spin relaxation time constants, T_2, and the mobility of the hydrogen nuclei, which may be reduced by several orders of magnitude through the interactions of water and a macromolecule. Hansen et al. (2010) collected Time Domain Low Field NMR (TD LF-NMR) data during milk coagulation, cutting, and syneresis without any interruption. At the same time, in a parallel experiment, gel firmness was monitored rheologically. Three different components of water protons (i.e., $T_{2,1}$, $T_{2,2}$, $T_{2,3}$) characterized the gel formation and syneresis, while only one of them ($T_{2,3}$) was ascribed to syneresis. The presence of $T_{2,1}$ and $T_{2,3}$ was explained by the water protons of casein and whey, respectively. A meaningful correlation between syneresis rate, pH (6.3–6.5), and temperature (32–35 °C) was noted (Hansen et al. 2010). In a recent study, ^{1}H TD-NMR has been employed for noninvasive monitoring of water mobility during curd evolution in raw and heat-treated cow's milk and goat's milk. T_2 values were recorded for 70 minutes, which encompassed the duration from initial rennet addition, to complete curd coagulation, to syneresis. Two different T_2 values (i.e., $T_{2,P}$, and $T_{2,F}$), were observed and assigned to the protons affected by the exchange phenomena in the protein gel network and fat-related protons, respectively. The mobile protons of whey explained the $T_{2,S}$ values recorded during syneresis. A complementary behavior, the compensation of a $T_{2,P}$ decrease with an increase in $T_{2,S}$ was found. The raw and heat-treated cow's milk and curds were also differentiated by their T_2 values. This differentiation was explained by heat-induced protein modifications, such as the denaturation of whey proteins, the interactions between β-lactoglobulins and κ-casein, and the alteration of the syneresis process (Curti et al. 2019).

NMR based metabolomics is another approach to the study of the relationship between milk and its physical or technological properties. ^{1}H NMR and ^{13}C NMR metabolite spectroscopy were employed to correlate the metabolite profiles of milk samples from two dairy cow breeds (Sortbroget Dansk Malkekvaeg and Jersey) to their technological quality (i.e., coagulation profile). The PCA loadings plot of ^{1}H NMR data revealed that a high concentration of choline and lower concentrations of citrate and carnitine were responsible for good coagulation. Similarly, the PCA loadings plot of ^{13}C NMR data determined the highest contribution of lactose resonated to the discrimination of milk samples according to their coagulation properties. All PCA models were validated using segmented cross-validation in the study (Sundekilde et al. 2011). The same authors extended the context of their study to a considerable number of milk samples (n = 407). A significant difference between non-coagulating and well-coagulating milk samples was observed in terms of several metabolites. Similar to the previous study, all developed PLS and OPLS-DA (orthogonal partial least square - discriminant analysis) models were cross-validated. It has been found that relative concentrations of lactate, acetate, creatinine, and choline were higher, and glutamate, carnitine, and glycerophosphocholine were lower in the well-coagulating milk samples (Sundekilde et al. 2014).

Monitoring the behavior of water in dairy products

Kuo et al. (2001) used LR-NMR to monitor the changes in the molecular mobility of water in Mozzarella cheeses (i.e., Pasta filata and non-Pasta filata) over ten days of ripening. Using two NMR parameters (i.e., spin-lattice or longitudinal relaxation time constant (T_1) and spin-spin or transverse relaxation time constant time (T_2) of protons), it was reported that changes in physicochemical parameters, proteolysis, and modification of the protein matrix resulted in higher water mobility and increased hydration (Kuo et al. 2001). Low-field (LF) ^{1}H NMR was employed to monitor water mobility in acidified milk drinks. The effects of pectin concentrations and protein types on water protons were noted. A relation between high pectin concentrations, the lower mobility of the water protons, and hence lower T_2 values was established. This correlation was also observed in most of the samples lacking whey protein concentrate. The heating and cooling of the acidified milk drink samples that had low pectin addition or no pectin addition resulted in a new T_2 value, which was ascribed to whey separation (Salomonsen et al. 2007). The findings of Salomonsen et al. (2007) followed the results of several previous research articles that employed NMR-based methods to characterize gel structures of model systems in terms of viscosity, water holding capacity, denaturation, and microstructure (Hinrichs, Götz, and Weisser 2003; Ruth Hinrichs, Bulca, and Kulozik 2007; Ruth Hinrichs et al. 2004; Le Dean, Mariette, and Marin 2004).

The mobility and composition of phosphates and Na^{+} ions in two semi-hard cheese was monitored via ^{31}P and ^{23}Na NMR spectroscopy. Regarding the signals obtained by cross-polarization ^{31}P NMR measurements, the immobile phosphate population was attributed to the interaction between colloidal forms of phosphate groups from phosphoserine residues (PSer) and colloidal calcium phosphates (CCP). Conversely, the phosphate molecules in the soluble phase, which arise mainly from the presence of relatively mobile phosphoserine residues was described as the mobile population. ^{23}Na NMR results revealed that the ratio of bound Na ions was higher in the samples that contained a greater amount of NaCl in its formulation. This study proved the previously reported (Wahlgren, Dejmek, and Drakenberg 1990) exchange between Ca^{2+} and Na^{+} that results in: first, the weakening of the cross-linkage between phosphoserine residues of caseins and inorganic colloidal phosphates; and second the increase in the proportion of mobile phosphates (Gobet et al. 2010). In a recent study, Hindmarsh et al. (2019) employed ^{31}P NMR to perform proton to phosphorus cross-polarization (CP) kinetic experiments (^{1}H-^{31}P CP-MAS) and extended the study of Gobet et al. (2010). The authors monitored the state of CCP and PSer separately in the casein micelles and investigated the hypothetical relationship between the state of the ^{31}P and the textural properties, namely compression force and meltability. They also conducted an aging study that lasted 40 days through which proteolysis, combined with the dynamics of the free water and immobile calcium phosphate, was determined to be the primary factor responsible for the texture. A decline in free water content was observed during the first 20 days, and the possible migration of water from the cheese serum into the proteins was shown as the cause of increased CCP mobilization, especially in the first 20 days. A strongly probable positive correlation (R = 0.98) between free water content and compression force and a weakly probable negative correlation (R = −0.93) between free water content and meltability was noted. T_2 relaxation values were recorded during aging, and the changes were found to be similar to those reported by Kuo et al. (2001) and Hindmarsh et al. (2019).

Salt uptake and water loss during the brining of Feta cheese, an essential step in the ripening process, was studied using MRI (magnetic resonance imaging) and NMR relaxometry. A high linear correlation between the average signal intensity and the water content was obtained (R^2 = 0.984). The results showed that the T_1 remained constant at lower brine concentrations, whereas a decrease in T_1 value was observed at higher concentrations (Altan et al. 2011). Boisard et al. (2013) utilized ^{23}Na NMR spectroscopy to monitor the mobility of sodium ions in model cheese samples. Na mobility was discussed for total and bound sodium populations. Higher protein content resulted in lower T_1 values in comparison to higher lipid content, which indicates that higher protein and lower lipid contents have a limiting effect on the mobility of Na ions. This result was explained by the greater resistance and less elasticity in the cheese samples containing high levels of protein and low levels of lipids. The addition of salt to the model cheese formulations resulted in the enhanced mobility of Na ions. The

previous rheological relation, which demonstrated lower resistance in salt-added samples, confirmed again this result. T_2 values representing the mobility of bound Na ions showed the same behavior with that of T_1 (Boisard et al. 2013). In the same context, Silva et al. (2017) employed TD-NMR to investigate the effect of partial substitution of NaCl with KCl and the addition of flavor enhancers (i.e., arginine, yeast extract, and oregano extract) on the water mobility of Probiotic Prato cheese during processing. The results showed that Na reduction was responsible for lower T_2 in treatments with a 50% reduction of NaCl compared to a formulation containing 100% NaCl. However, all treatments resulted in firmer cheeses as higher percentages of water could be linked to protein or protein/fat network. The authors ascribed this finding to the high hydrophilicity of NaCl. Regarding cheese with added arginine, a significant alteration in the molecular dynamics of the system was noted. Due to the presence of hydroxyl and amine groups in its structure, strong hydrogen bonds of the water molecules in the cheese matrix were presumably favoured. Purportedly, arginine interacted largely with the bound water and confined water in the cheese. The authors suggested that yeasts had a pertinent interactions with free water and did not affect the fraction of bound water or fat. Additionally, they concluded that the presence of oregano extract in treatment with a 50% NaCl composition had little influence on matrix relaxation (Silva et al. 2018).

In a recent study, Smith et al. (2017) emphasized the dependence of Mozzarella cheese functionality (i.e., hardness and meltability) on the mobility of its components during ripening. The relaxation times determined by ^{1}H NMR measurements throughout the repening process showed an increase in the interaction between water and proteins, allowing the binding of more free water. They also revealed a decrease in free water due to the presence of carboxyl and amino free groups which are resulted from casein proteolysis.Similarly, the mobility of phosphorus was followed by the utilization of its inverse correlation with regard to line width in the ^{31}P magic-angle spinning NMR (MAS NMR) spectra. During the 40-days of storage, the immobile phosphorus ratio declined, while mobile phosphorus increased. Regarding the relationship between calcium ions and phosphorus, increased solubilization of colloidal calcium phosphate nanoclusters, a change in water distribution within the cheese structure, and improved hydration of the protein matrix was associated with an enhanced percentage of mobile phosphorus (Smith et al. 2017). Cais-Sokolinska et al. (2018) employed NMR to monitor the molecular dynamics of water within the matrix of the goat cheese Pasta-filata. A strong correlation was established between moisture content and T_1 and between fat content and T_2 (Cais-Sokolińska et al. 2018). Mozzarella cheese is different from other Pasta filata cheeses due to the thermomechanical process applied during production, namely stretching in hot water. Heating during the stretching enhances protein interactions and promotes calcium insolubilization and free serum separation. Molecular interactions that occur during stretching and during refrigerated storage are two essential factors that affect the final structure of Mozzarella cheese. Furthermore, NMR was used to monitor the effect of the water temperature on the water mobility in Mozzarella cheeses as they are stretched. T_1 and T_2 values were recorded at time zero and then once a week for the 28-day duration of storage. NMR images of cheese samples were also obtained. In the conclusion of the study, increased protein hydration and structural rearrangements in the protein matrix which were potentially the result of proteolysis were credited for the significant changes in T_1. These results were in accordance with those of Smith et al. (2017). Four different hydrogen populations, namely $T_{2,\ 1}$ $T_{2,\ 2}$, $T_{2,\ 3}$, and $T_{2,\ 4}$ were identified and attributed to bound water ($T_{2,\ 1}$), immobilized water ($T_{2,\ 2}$, $T_{2,\ 3}$) , and free water ($T_{2,\ 4}$), respectively. A clear explanation relating to the changes of $T_{2,\ 1}$ during storage was not provided. However, a significant increase in $T_{2,\ 3,}$ which represents the water interacting with the protein structure of the cheese was observed. In contrast, $T_{2,\ 4}$ decreased during an increasing period of storage. Additionally, NMR images showed a more homogenized distribution of water and an increase in the particle size of fat throughout storage. These findings were independent of the water temperature utilized for Mozzarella stretching (Gonçalves and Cardarelli 2019).

Tomaszewska-Gras et al. (2019) employed LF-NMR relaxometry and differential scanning calorimetry (DSC) to analyze semi-hard, hard, and extra-hard goat's cheese samples for water mobility and thermal properties. The percentage of moisture in a fat-free sample was between 49–56%, 54–69%, and $<$ 51% for semi-hard (SHG), hard (HG), and extra-hard (EHG) goats cheese, respectively. The ratio of fat: protein (1.2) and the percentage of fat in dry matter (50.7%) were kept constant for all three groups. The percentage of water-soluble extracts (WSE) and free amino groups were in the order of SHG $<$ HG $<$ EHG. A decrease was observed in T_1 values with increased fat and protein content, which was attributed to the binding of water due to an increase in the amount of water-soluble extracts that resulted from enhanced proteolysis and the entrapment of water in the proteolipidic network. T_2 values were analyzed as $T_{2,1}$ and $T_{2,2}$ that arise from bound water fraction and bulk water fractions, respectively. Since no significant changes were observed for $T_{2,2}$ (the value of any cheese type), this parameter was referred to major bulk water fraction of water-in-fat emulsions. In addition, $T_{2,1}$ values decreased with increasing pH, and the limiting effect of increased H^{+} ion concentration on the mobility of bound water protons was noted. An essential outcome of this study was the establishment of a significant correlation ($R = 0.96$) between NMR parameter T_1 and an increased amount of freezable water content (e.g., an increased ratio of bulk water to bound water determined by DSC (Tomaszewska-Gras et al. 2019).

In a recent study, Gilbert et al. (2020) used ^{1}H-LF-NMR and Laplace's transformation to differentiate spontaneous syneresis from bulk water mobility in yogurt made from pasteurized milk and commercial stirred yogurts. As the ^{1}H-LF-NMR-based method is less destructive and allows researchers and dairy-product manufacturers to track a

sample throughout its storage, it has become an alternative to the classical centrifugation method. The potential of NMR to reveal the behavior of water in dairy systems was reported in the literature with an emphasis on the significance of fitting applied mathematical models to magnetic signal changes. Interpretation of water and fat NMR relaxation, water mobility, and applications in dairy systems were discussed in detail (Mariette 2018). Considering the potential of NMR in this regard, further studies demonstrating the potential of this method would be valuable. There is space in the literature for studies employing NMR-based approaches to monitor water and ion mobility that reveal changes caused by applied processes and that assess the final quality of dairy products such as ice-cream, butter, etc.

Monitoring cheese ripening

NMR spectroscopy has demonstrated its ability to monitor chemical changes (e.g., water, lactose, and free amino acid content) observed during cheese ripening. Rodrigues et al. (2011), reported the metabolic profiling of potential probiotic or symbiotic cheeses via classical biochemical analyses and ^{1}H NMR spectroscopy, allowing discrimination between different types of cheeses by maturation time and added probiotic and/or prebiotic bacteria. The ^{1}H NMR spectral signatures taken during the 60-day ripening process generated significant changes in lactose that converted to lactate and ketone bodies by the end of storage. Moreover, the authors also predicted the bacterial strain supplement (when comparing Bifidobacterium lactis vs. lactobacillus casei) using OPLS models based on NMR spectral data. However, developed models were not validated. They reported that these strains add different metabolites during the ripening process of cheese (Rodrigues et al. 2011). Piras et al. (2013) also used a ^{1}H NMR metabolomics approach to study the aging of the Fiore Sardo cheese, which were prepared with autochthonous adjunct lactic acid bacteria cultures. The authors developed cross-validated SIMCA and externally validated PLSR models to differentiate between the cheeses and to identify their maturation ages, and the types of added cultures from the ^{1}H NMR spectra (Piras et al. 2013). Similar results were exhibited by Consonni and Cagliani (2008), who used SIMCA, O-PLS, PLS-DA, and PCA, and ^{1}H NMR to develop a model to determine the geographic origin and ripening process of Italian Parmigiano Reggiano and Grana-type cheeses. During the ripening process, different cheese produced different levels of younger cheese samples (14 months of ripening) had higher leucine and isoleucine contents, whereas 30 month-old cheeses had a larger amount of threonine. These results are useful in monitoring cheese ripening by the NMR signal although any internal or external validation was performed within the study (Consonni and Cagliani 2008).

Furthermore, Mazzei and Piccolo (2012) used a similar approach to discern buffalo milk Mozzarella cheeses from different regions using high-resolution MAS-NMR (^{1}H HRMAS-NMR) to measure the effects of two-day aging on the cheese sample. Internally validated discriminant analysis (DA) models with 100% success were developed for group differentiation of Mozzarella cheeses from two different production sites in Campania. The authors reported significant NMR signals from isobutylic alcohol, lactic acid, and acetic acid, all of which are known by-products of Mozzarella biodegradation, and offered potential uses for these compounds in the characterization of Mozzarella di Bufala Campana during aging (Mazzei and Piccolo 2012).

Along a similar vein, Lamanna et al. (2008) studied the ripening process of soft Italian cheeses by using HR-MAS combined with liquid NMR and concluded that an observed increase in NMR signals was due to both glucose and lactose, which is co-resonant with glucose (Lamanna et al. 2008). Furthermore, De Angelis Curtis et al. (2000) applied HR-NMR and LR-NMR to measure changes in water localization and amino acid profile, respectively, of Italian cheeses undergoing ripening via 18 months of storage. Ripening time and sampling zone were used as the basis of their study. The authors noted that while free water increased, bound water decreased during ripening. The researchers also found an increase in amino acid contents during the ripening stage, generally associated with the metabolic processes and breakdown of protein (De Angelis Curtis et al. 2000), contrasting the results of Bordoni et al. (2011), who investigated the relations between cheese aging, protein digestibility, and nutritional quality in Parmigiano Reggiano cheese via LF- and HR-NMR. They determined that the content of free amino acids and small organic compounds were independent of the age of the cheese samples (Bordoni et al. 2011).

Monitoring quality changes during freezing

Kuo, Anderson, and Gunasekaran (2003) utilized online LF-NMR spectroscopy to examine the impact of freezing on Mozzarella, Pasta Filata, and non-Pasta Filata cheeses via two NMR parameters that measured the formation of ice during the freezing process: the spatial redistribution of water T_2 relaxation time and the changes in the water self-diffusion coefficient (D) within non-frozen and stored-frozen cheeses. Significant changes in both parameters were observed in frozen and non-frozen cheese samples, as well as during the thawing of the samples. It was concluded that these previously-described parameters for measuring the formation of ice during the freezing process could be used to characterize cheese during the freezing process (Kuo, Anderson, and Gunasekaran 2003). These investigations were recently confirmed by Zhu et al. (2020), who used a ^{1}H NMR-based untargeted method on freeze-dried milk samples stored at 20 °C, 4 °C, and −20 °C. There was a significant change in the metabolome of freeze-dried milk powder stored at 20 °C while the metabolome of samples stored at 4 °C and −20 °C remained stable. The researchers determined that there were reductions in orotic acid, riboflavin, and acetyl-carbohydrate concentrations, and increases in fatty acids, threonic acid, and uridine in the freeze-dried milk powder stored at 20 °C (Zhu et al. 2020).

Table 4. Some examples of studies which applied NMR spectroscopy to monitor chemical modification of dairy products during processing.

Dairy product	Aim of the study	Type NMR	Frequency (MHz)	Chemometric tools	Reference
Buffalo and cow milks	- Differentiate the milk samples by using a limited number of NMR parameters	^{13}C NMR	75.5	Fuzzy logic analysis	(Andreotti et al. 2002)
Cow milk: Cheese	- Effect of different types of dairy diet on milk fat composition	^{1}H NMR	600	Classification tress (CT), PCA	(Marseglia et al. 2013)
Milk	- Comparison between novel and standard methods for analysis of free fatty acids in milk	^{1}H NMR	600.13	SIMCA, PCA	(Wiking et al. 2017)
Ice cream	- Effects of different prebiotic dietary oligosaccharides on physical, thermal properties and micro-structure characteristics of sheep milk ice cream	^{1}H NMR	23.4	PCA, HCA	(Balthazar et al. 2017)
Cheese	- Combination of NMR and MRI to study water distribution and to understand salt uptake and moisture loss in feta cheese	^{1}H NMR, MRI	43.85	NNLS regression	(Altan et al. 2011)
	- A NMR metabolomics to classify cheese samples based on their maturation age and the type of added cultures	^{1}H NMR	399.95	PCA, PLSR	(Piras et al. 2013)
	- Ripening and geographical discrimination of cheeses	^{1}H NMR	500.13	SIMCA, O-PLS, PLS-DA, PCA	(Consonni and Cagliani 2008)
	- Evaluate the quality and origin of Mozzarella cheese	^{1}H NMR	400	PCA, DA, HCA	(Mazzei and Piccolo 2012)

Monitoring quality changes during storage

Haque and his coworkers (2010) investigated interactions between water and protein within Milk Protein Concentrate (MPC) powder to understand their effects on solubility. ^{1}H NMR was used to measure proton transverse relaxation time (T_2). Relative humidity (a_w 0.0–0.85), temperature (25 and 45 °C), and aging (a 12-week duration) resulted in variations in the T_2 values of proton fractions. As a result, the T_2 values were classified as short, intermediate, or long, based on: first, the distance between water molecules and the surface of protein; and second, the mobility of water. The study demonstrated that water moves through the surface of the protein, becoming less mobile at higher a_w values. The authors concluded that an increase in water content caused a corresponding increase in interactions between water molecules and protein surfaces (Haque et al. 2010). In further research by the same group, high-resolution solid-state NMR was used to monitor changes in the molecular structure and dynamics of proteins found in milk protein concentrate (MPC) powder during storage under different conditions. The study aimed to discover the relation between the molecular mechanism of protein aggregation and the loss of solubility. Chemical shift or relative intensity changes between aged and non-aged samples were determined to be insignificant for major bands, namely backbone carbonyl, backbone α carbon, and side-chain methyl and methylene carbons. The lack of correlation between NMR parameters and the solubility of MPC was explained by the fact that the loss of solubility is related to the surface of powder particles, while NMR responses are related to the properties of bulk proteins. In addition, it was suggested that long-term storage at high relative humidity may result in reduced rigidity of molecular domains due to their interaction with water. Plasticization by water during aging increases the molecular mobility of proteins, which may diminish protein denaturation and the interactions between proteins (Haque et al. 2015).

Advantages and disadvantages

NMR is a versatile spectroscopic technique for studying opaque heterogeneous samples, that can be considered a promising method for the classification of dairy product quality and monitoring their chemical modifications during processing (Table 4). As compared to other spectroscopic techniques, NMR is less sensitive, but it does not require extensive chemical manipulation of samples. It can easily differentiate the content of short-chain acyl groups in dairy products. However, this technique requires a complex series of optimization and time-dependent measurements. Indeed, the nature of the pulse sequence used in experimentation is critical, although it may generate negative results, as discovered in investigations in the dairy sector. For example, NMR based sensors used in industrial applications of dairy products has been effectively used for the analysis of several classes of compounds including meat (Damez and Clerjon 2013). Newer devices are in development, which will clear the way for TD-NMR experiments outside the laboratory.

Conclusion and future trends

This review provided an overview of electromagnetic wave techniques used for monitoring the chemical modification of dairy products as they undergo different processing technologies. These techniques showed great potential for predicting certain functional properties (sensory and meltability) and

monitoring modification at a molecular level of various dairy products, especially cheese, during processing and storage.

Over the last several decades, spectroscopic techniques, particularly NIR and MIR spectroscopy, have been utilized for many applications not only in the laboratory but also at industrial scale. Both MIR and NIR spectroscopy have demonstrated their potential for enhancing knowledge and understanding of dairy product parameters throughout production and product quality assessment. The main advantage of these assessment methods is that they are chemical-free techniques wherein sample preparation time is critically reduced or even eliminated. MIR spectroscopy can be considered as an efficient tool for describing molecular structures (including, protein secondary structure) and physical states, thus identifying functional properties of cheeses. By contrast, NIR spectroscopy has disadvantages when compared to MIR spectroscopy, such as its low sensibility and low structural selectivity due to the superposition of many different overtones and combination bands in the NIR region.

Fluorescence spectroscopy established its usefulness for in-line monitoring of physicochemical modifications during dairy product processing (e.g., storage, coagulation, heating) because it generates relevant in-line physico-chemical information without perturbing molecular changes that occur during product processing. Thus, it is a valuable method that can be used by the scientific community and the dairy industry to analyze, control, and interpret physical and chemical phenomena at the core of dairy product quality. Nonetheless, fluorescence spectroscopy is a physical method used specifically for studying intrinsic fluorophores in milk products which makes it difficult to obtain information about complex molecular modifications. An efficient way to obtain more data is to combine alternative detection techniques, such as NIR, MIR, or UV light spectroscopies, with fluorescence spectroscopy. As fluorescence is a complex phenomenon, more research is needed to extract the various factors that affect dairy processing.

The NMR technique has found specialized applications in the dairy sector and is actively being employed in laboratories. While measurement accessories and analytical methods based on NMR are still developing, this technique has demonstrated considerable potential for the assessment of milk fat globules, structural rearrangement of the protein matrix, and water mobility in dairy products by allowing researchers and dairy producers to monitor chemical modifications and metabolite changes during processing and ripening. NMR spectroscopy, although less sensitive than other techniques, does not require extensive chemical manipulation of samples and conveniently highlights distinctions between the contents of various dairy products. The main drawback of this technique remains in the high cost instrumentation for routine applications.

Despite the above-mentioned restrictions and constraints that currently limit the wider application of spectroscopic techniques for routine industrial use; the increasing need to monitor chemical modifications in dairy products and to predict the functional properties of these products, as along with the ongoing development of spectroscopic and chemometric methods will make these techniques more efficacious for application in the dairy sector.

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

Abderrahmane Aït-Kaddour http://orcid.org/0000-0003-4132-539X

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